Recovery of lakes and streams in the UK from the effects of acid rain

UK Acid Waters Monitoring Network 20 Year Interpretative Report

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UK Acid Waters Monitoring Network
20 Year Interpretative Report

Report to Defra

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Table of Contents

List of Tables

List of Figures

Executive Summary

The Network

"Acid rain" was recognised as a major environmental concern in the 1970s. In the 1980s it was conclusively established that the emission of sulphur and nitrogen gases from the combustion of fossil fuels was the principal cause of the acidification of upland waters in the UK and in many other European countries. In 1987 the UK Government began a national programme to reduce emissions and the UK Acid Waters Monitoring Network (AWMN) was established in 1988 to monitor the response of acidified surface waters to emission reductions.

This report is the 5th major interpretative analysis. It concludes that acidified lakes and streams are now showing clear signs of both chemical and biological recovery of acidification in all affected regions but that the recovery so far is limited and that other stresses in future, especially from atmospheric nitrogen (N) deposition and from climate change, may prevent a full recovery.

The AWMN has been and is the key provider of information on surface water acidification to UK Government and Devolved Administrations, and the sole UK provider of data and expertise to the UNECE International Cooperative Programme on the Assessment and Monitoring of Effects of Air Pollution on Rivers and Lakes (ICP Waters), set up under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP).

The Network consists of 22 mainly headwater lakes and streams. It includes both reference (or "control") sites situated in low acid deposition areas of the UK and acidified sites across the UK uplands in areas previously receiving high loads of acid deposition. There are paired lake and stream sites and paired afforested and moorland sites in the Network, and the sites span a range of sensitivities to acid deposition.

Trends in precipitation and surface water chemistry

Overall there have been significant improvements in water quality, and this is indicated most clearly by the increases in Acid Neutralising Capacity (ANC) that have occurred at all acidified sites.

The concentration of non-marine sulphate in AWMN surface waters has fallen substantially across the Network over the last 20 years, although most sites show little further decrease since 2000 AD, and, for the majority of sites, concentrations remain between three and six times higher than those observed in the reference sites in the north-west of Scotland.

Trends in the concentration of nitrate, the secondary acidifying pollutant, are much less clear showing substantial inter-annual variability and marked seasonality. However, seven sites now show slight, but statistically significant, long-term reductions in concentration while two show long-term increases in nitrate concentration.

Chloride concentration, dominated by sea-salt inputs, has declined significantly in many sites following very high levels in the first few years of monitoring. These changes primarily reflect a reduction in the intensity of Atlantic storms over the last 20 years. Some sites may also have experienced significant reductions in chloride from decreased industrial emissions of hydrochloric acid. Both sources of chloride exert acidifying effects and their reductions will have contributed to the observed improvement in surface water chemistry.

There has also been a significant decrease in acidity (increase in pH) at most acidified sites, a decrease in the strength of acid episodes in streams and decreases in toxic labile aluminium concentrations at the most severely acidified sites. However, concentrations of labile aluminium remain significantly above the safe "background" levels of 10 $\mu g\ l^{-1}$ at many sites.

Dissolved organic carbon (DOC) concentrations have increased at all sites across the Network. These increases are attributed principally to falling sulphate concentrations and indicate a return to higher DOC concentrations that are assumed to have occurred naturally in the past. The DOC trend is also linked to the general reduction in sea-salt inputs over the monitoring period.

Biological trends

Diatoms are a group of microalgae used as indicators of water quality. The AWMN data show that there has been a clear change in diatom species composition over the last 20 years at all acidified sites, consistent with the increase in pH described above.

New **aquatic plant** species have appeared in seven of the lake sites and four of the stream sites. In most cases these are acid-sensitive species e.g. *Myriophyllum alterniflorum* (alternate water milfoil) and *Subularia aquatica* (water awlwort). However, the appearance of *S. aquatica* in Lochnagar could also be linked to recent warming as winter ice-cover at this alpine site has decreased significantly in recent years. This may also in part be a response to an increase in the availability of nitrate acting as a fertiliser.

Benthic invertebrates include insect species, mostly at the larval stage, molluscs, leeches, and worms. Although the observed changes at most sites remain fairly modest, significant temporal trends are now apparent at about half of the sites in the Network. The shifts in assemblage composition that have taken place are those expected as a result of reduced acidity.

Acid deposition caused severe reductions and, in some cases, the complete elimination of **salmonid fish** (i.e. brown trout and Atlantic salmon) populations from many of the most sensitive lakes and streams in the UK. However, there are now some signs of recovery, with trout having re-established themselves at three of the most acidified sites in the Network (Old Lodge, Scoat Tarn and Blue Lough), reflecting improvements in water quality. However, there are many sites where fish densities remain low compared to less acidified sites.

Trends in toxic trace metals

Fossil fuel combustion releases toxic trace metals (e.g. lead, mercury, zinc) as well as acid gases to the atmosphere and their deposition to surface waters matches the temporal and geographical pattern of acid deposition in the UK, as shown by the analysis of trace metals in sediment cores and sediment traps from the AWMN lakes.

There is evidence from Lochnagar of a decrease in the deposition of lead and mercury since 1996, but data from the trace metal concentrations in sedimenting material, collected by sediment traps, at some sites in the Network have so far shown little or no decrease. This is attributed to the remobilisation of legacy pollutants from catchment soils by soil erosion.

Recovery progress

After twenty years there is consistent and compelling evidence for both chemical and biological improvement of the acidified sites across the Network. The central concern now is whether the improvement can be sustained and whether the targets for recovery can be achieved.

Recovery targets are defined by the UNECE Gothenburg Protocol of 1999, and the EU Water Framework Directive of 2000. The former is concerned with the reduction of emissions to a level where the "critical load" of acidity to lakes and streams is not exceeded. The latter requires the restoration of acidified waters to "good ecological status".

The extent to which critical load exceedances will decline is very unclear as it is dependent on the uncertain future behaviour of nitrate in catchment soils. The Steady-State Water Chemistry (SSWC) model, that treats nitrate behaviour conservatively, indicates that exceedances have already been eliminated at 12 of the 23 sites (using the most recent deposition data from 2004-06), whereas the First-order Acidity Balance (FAB) model, which allows for future soil nitrogen saturation, indicates that exceedance has been eliminated at only 4 sites.

In the context of the Water Framework Directive, results using the dynamic model MAGIC indicate that 20 of the 22 sites have Acid Neutralising Capacities below those expected under reference conditions and ten fall below the ANC 20 $\mu eq\ l^{-1}$ critical limit used as a target under the Gothenburg Protocol.

These results are consistent with data from palaeoecological analysis that also indicates that biological recovery to date, whilst positive, is so far very limited. Possible reasons for the limited chemical and biological recovery include:

- the continued influence of acid deposition (both sulphur and nitrogen) on water acidity;
- a delay in the recovery of the base cation status of catchment soils due to continued acid deposition inputs exceeding weathering rates at some sites;
- increased nitrate leaching from soils;
- a delay in the increase in pH at the most acidified sites;
- continuing high concentrations of toxic labile aluminium at the most acidified sites;
- the continued release of pollutant S from organic catchment soils;
- the counter effect of additional pressures associated with nitrogen enrichment, toxic substances and climate change.

Future trends and threats

Projections from the dynamic model MAGIC for the AWMN sites indicate that surface-water acidity will continue to decrease in the next decade but that reductions in acid deposition will be insufficient to raise ANC above the 20 $\mu eq\ l^{-1}$ critical limit for five sites by 2020. Best and worst-case steady-state critical load models predict that between five and 15 sites will continue to exceed critical loads by 2020.

The release of nitrate from soils to surface waters is predicted to confound the rate of chemical recovery at the AWMN sites. Future climate change will affect this process but the net effect is difficult to predict. Increased nitrate leaching may cause eutrophication not only at acidified sites but potentially at all sites. However, evidence for such an effect at present is limited.

Sites with partially afforested catchments are all showing evidence of recovery proportionate to the decrease in acid deposition. This trend should continue in future with changes in forest cover unlikely to significantly alter the path to recovery.

Although the deposition of toxic substances has declined significantly over recent decades their concentration in aquatic biota and in surface sediments of AWMN sites remains high. There is now strong evidence that this is related to the re-mobilisation of pollutants that have accumulated in soils over the industrial period and their transport to surface waters by soil erosion. Any future increase in storm frequency and intensity will accelerate soil erosion and potentially lead to an increase in the exposure of aquatic biota to toxic substances.

Future climate change also poses a threat to the recovery of acidified upland waters through the projected increase in the intensity and frequency of storm events, especially those with high sea-salt concentrations, which lead to highly acidic, ecologically damaging runoff. Analysis of the 20-year record from the Network shows a strong negative relationship between ANC and the state of the Arctic Oscillation (AO), a mode of climate variability in the Northern Hemisphere associated with wet, relatively warm winters in Western Europe, which has intensified over recent decades.

Recommendations

As acidified waters begin to recover a fuller understanding of the recovery process would be gained if the Network were to be restored to its original configuration of sites. In particular this would increase the value of the Network with respect to:

- the provision of scientific advice relevant to the demands of UNECE protocols and the EU WFD placed on Defra and other agencies;
- understanding the future influence of climate change and other potential stresses on upland waters that may confound the success of these policies; and
- the various needs of users including Environment Agencies (EA, SEPA, EANI), Conservation Authorities (Natural England, CCW, SNH), the Forestry Commission and Water Utilities charged with the protection and management of upland water ecosystems.

The installation of temperature and water level/water flow recorders at AWMN sites is especially important as future climate change, especially with respect to the predicted increase in precipitation and associated sea-salt deposition is seen as one of the principal threats to the recovery process.

Enhancement of the Network to measure chlorophyll *a* and algal standing crops would be beneficial in order to provide evidence for the potentially enriching effect of nitrogen deposition on upland waters. This is relevant especially to the eutrophication aspects of the Gothenburg Protocol.

Improved advice on the implementation of the Water Framework Priority Substance Directive could be provided if the monitoring protocols for metals was restored at Lochnagar and introduced at other selected sites across the Network.

Recent funding reductions threaten the continuity and integrity of the AWMN. As one of the UK's highest quality unbroken long-term monitoring programmes and the only one dedicated to the monitoring of water quality and freshwater biodiversity in the uplands the Network represents an invaluable resource for both UK science and policy.

Upland waters are important ecologically but they also provide vital information on how they and their catchments are responding to environmental change through the interacting effects of air pollution, land-use change and climate change. A strategic vision for the Network is required if it is to fulfil its potential as a system capable of tracking the ecological response of all types of upland waters and their catchments to future changes in pressures and if it is to be seen as a fundamental element of National Capability in the field of environmental monitoring. A meeting that includes the current, and potentially future, user community is recommended to develop a long-term strategy for the Network.

1. Introduction

Martin Kernan, Don Monteith, Rick Battarbee, Chris Curtis, Ewan Shilland and Gavin Simpson.

1.1. Background

1.1.1. Surface Water Acidification and the UK Acid Waters Monitoring Network

The quality of water draining the UK uplands has been profoundly affected by atmospheric pollution since the onset of the industrial revolution. Of primary concern, and the main subject of this report, has been the widespread acidification of lakes and streams by acid deposition, in the form of sulphur and nitrogen compounds derived primarily from fossil fuel combustion..

Controls on acidic emissions were initiated in the 1980s through the United Nations Economic Commission for Europe (UNECE) Convention on Long Range Transboundary Air Pollution (LRTAP) with the specific aim of reducing the impact of acid deposition on soils, vegetation and surface waters. As a result, over the last three decades there have been dramatic reductions in the emissions of S and N gases to the atmosphere in the UK and in Europe as a whole.

To assess the chemical and biological response of acidified lakes and streams in the UK to the planned reduction in emissions, the UK Acid Waters Monitoring Network (AWMN) was established by the UK Department of Environment (now Defra) in 1988 following the recommendations of the UK Acid Waters Review Group (AWRG, 1987).

The Network comprises 22 lake and stream sites across upland regions of the UK (Fig. 1.1). Water samples for chemical analysis are taken monthly and quarterly from streams and lake outflows, respectively. Biological monitoring involves annual surveys of diatoms, macroinvertebrates, salmonid fish populations and stream aquatic macrophytes, with lake aquatic macrophytes surveyed bi-annually. The design of the Network, sampling methodology and analytical protocols are provided by Patrick *et al.* (1995) and Monteith & Evans (2000) and further information is available via the AWMN website (awmn.defra.gov.uk).

The Network has evolved since its inception. In 1995, following recognition of nitrogen (N) deposition as a secondary driver for surface water acidification, measurement of total dissolved nitrogen (TN) was added to the suite of chemical determinands collected (as was total dissolved phosphorus, TP). At the same time one of the AWMN sites in north-east Scotland, Lochnagar, was set up to monitor mercury (Hg) in atmospheric deposition, water and aquatic plants, and in 1999, in response to concerns about the potential role of climate change, surface and deep-water thermistors were installed at all lake sites. A weather station was installed at Lochnagar in 2002 and an automatic hydro-meteorological monitoring buoy equipped with a thermistor chain and water quality sensors was deployed at the Round Loch of Glenhead in 2005. However, several stream sites still lack instrumentation to measure temperature and flow continuously, while the lake sites lack level recorders and thermistor chains necessary to monitor changes in thermal stratification. Instrumenting the Network to enable the potential future impact of climate change to be quantified is seen as a priority in developing the Network in future.

A unique feature of the AWMN is the use of sediment traps emptied annually in the lake sites and used to track changes in diatom assemblages and trace metals. In addition, sediment cores have been taken at all lakes on at least two occasions (cf. Battarbee *et al*. 1988, Juggins *et al*. 1996) providing a diatom, pH (diatom-inferred), geochemical and carbonaceous particle record of the lakes for the past 200 years. The combined sediment trap and core data enable the current conditions of the lakes to be placed in this longer term context, spanning pre-acidification reference conditions in the early 19th century, progressive acidification to the 1980s and improving conditions over approximately the last decade.

The data from the AWMN are also essential for calibrating and testing acidification models which are the primary tool for assessing likely future responses to mitigation measures. The combination of palaeoecological data, contemporary monitoring data and modelling enables the past, present and future status of UK acidified lakes to be assessed through the AWMN sites.

In addition to meeting UNECE requirements for monitoring the response of acidified surfaces waters to emissions reductions, AWMN data and the scientific insights gained from the Network are integral to a large range of national and international programmes. These are documented in Appendix 1, and include:

- the work of the International Cooperative Programme on Assessment of Rivers and Lakes (ICP Waters) and the Programme on Integrated Monitoring (ICP IM);
- Defra's Freshwater and Dynamic Modelling Umbrella Research Programmes;
- the development of acidification tools under the Water Framework Directive (WFD)
- the inclusion of several AWMN lake sites in the EA WFD Surveillance Network
- the current Review of Transboundary Air Pollution commissioned by Defra (RoTAP, in press),and previous reviews (e.g. NEGTAP 2001);
- the European Nitrogen Assessment (ENA) exercise under the European Science Foundation's "Nitrogen in Europe" programme, which contributes scientific input to both the International Nitrogen Initiative (INI) and the UNECE Task Force on Reactive Nitrogen (TFRN);
- NERC-funded and other projects focussed on upland water quality, ecological status and biodiversity.
- Provision of data to the UK Environmental Change Network (ECN)

The AWMN database now holds over 20 years of chemical and biological data. This interpretative report provides a state-of-the-art assessment of both chemical and biological trends based on analyses of the 20-year dataset. It is the fourth major interpretative report, following those produced after five (Patrick *et al*., 1995), ten (Monteith & Evans, 2000) and fifteen years (Monteith & Evans, 2005) each available from the AWMN website.

Until recently, the length of the AWMN time-series precluded the use of anything beyond simple linear statistical modelling to test whether the hydrochemistry and biological assemblages had changed significantly over time. While these approaches have been effective in discerning the prevalence and overall magnitude of trends, the AWMN time-series are now sufficiently long to allow more detailed analysis of temporal behaviour. In this report, therefore, we use a new combination of statistical techniques. Additive modelling has been used to assess univariate data, including deposition and hydrochemistry data, whilst a variety of ordination-based techniques have been applied to the multivariate biological data. Appendix 2 presents a detailed explanation of the statistical methods used.

1.2. AWMN Sites

The 22 AWMN sites are all located in relatively acid-sensitive regions, in upland areas with catchments underlain by base-poor soils and geology (Table 1.1). Although monitoring has been underway at most sites continuously since 1988, sampling at certain sites began later and there have also been a small number of interruptions in the record when sampling was not possible (Table 1.2). The Network originally comprised 10 stream and 10 lakes sites. In 1990 two sites in Northern Ireland were added (Blue Lough and Coneyglen Burn), supported by funding from the Department of Environment (Northern Ireland). At the start of 1991 the Nant y Gronwen (site 18) was removed from the Network following a request from the landowner and was replaced by a nearby moorland stream, Afon Gwy. More recently, as a result of water abstraction and damming by a local fish farm at Coire nan Arr (Site 1) a new 'control' site was added to the Network, Loch Coire Fionnaraich (Site 23).

At all sites, regular spot samples are taken for laboratory analysis of an extensive range of chemical determinands, including pH, conductivity, dissolved organic carbon and a standard suite of base cations, anions and metals. Epilithic diatoms, aquatic macrophytes and benthic invertebrates are sampled annually in the spring/summer and fish surveys for stream sites and the outflow streams of lakes are conducted each autumn.

Between 1988-2004 data collection and analyses at 20 of the AWMN sites were funded by Air Quality Division at Defra (previously Department of the Environment), with two sites in Northern Ireland being funded by the Department of Environment (Northern Ireland) (DoE(NI)). The Scottish Executive (SE) and subsequently Scottish Government (SG) contributed 50% of the funding for AWMN work by The Scottish Government's Marine Scotland Freshwater Laboratory (FRS). In 2001 DoE(NI) withdrew from the Programme and Defra took up funding of the Network in Northern Ireland.

Following a funding hiatus at Defra in mid-2007, chemical sampling and analyses at several sites were halted and, more widely, fish surveys and lake macrophyte surveys were cancelled for that year. The reduction in funding was formalised later in 2007 with the annual budget from Defra reduced in 2007-2010 by 78% over 2006-2007 levels.

The reduced Network of sites and analyses that remained after reductions in central funding has been sustained only as a result of significant contributions in kind from CEH and ENSIS-ECRC at UCL; financial assistance from the Welsh Assembly Government, Countryside Council for Wales (CCW), the Environment Agency (EA) and the Forestry Commission (FC); and assistance from Marine Scotland,, the School of Biological Sciences, Queen Mary University of London (QMUL) and several private individuals. The impact of the funding cuts has thereby been partly mitigated in the short term and consequently the monitoring programme that was in place between 1988-2007 has been maintained as far as possible at most sites in the period since 2007 (Table 1.2). Additional funding is essential to maintain and develop the Network in light of the potential impacts of

S and N deposition, land-use change, toxic substance deposition and climate change on the ecology and biodiversity of UK's upland waters.

The AWMN was set up explicitly to monitor responses to reduction of acidifying emissions of S and N, and compare responses along a gradient of deposition (essentially north to south) using acid-sensitive sites in the low-deposition region in the north-west as 'controls'. The Network was also designed to assess the differences between lakes and streams, especially with respect to differences in their respective hydrological regimes, and the differences between sites with afforested and moorland catchments. Site selection attempted to include sites in all the principal acidified regions across the UK. The North York Moors remains the only severely acidified upland region without a site.

The Network has proved to be robust, and today has evolved to include some but not all of the measurements and instrumentation needed to assess the additional and interacting effects of nutrient-N deposition and climate change. With multiple drivers operating together, patterns of chemical and biological response are complex. The chemical and biological changes that have taken place at the 22 sites, therefore, need to be analysed in the context of changes in a combination of different drivers. Acid deposition remains the dominant driver and this report is principally concerned with the response of upland waters to changes in acid deposition. But as acid deposition declines other drivers will become relatively more important. Upland water quality and biodiversity in future will be potentially also affected by the nutrient enriching effects of N deposition, by land-use change, by the behaviour of remobilised toxic substances and by climate change as described below and considered in more detail in Chapter 10.

1.3. Objectives

The primary objective of this report is to provide an assessment of the success of emission reduction policies for sulphur and nitrogen in facilitating recovery from acidification in surface waters since the introduction of emission reduction legislation. We also consider the extent to which the improvement in water quality that is now apparent will be sustained in future.

Chapter 2 uses the most recent bulk deposition data from ADMN sites situated closest to the AWMN sites to identify common trends in deposition patterns across the Network. In Chapter 3, we relate these trends to changes in water chemistry and summarise the variation and change in a number of key chemical determinands including xSO_4^{2-}, NO_3^-, chloride, pH, labile Al and DOC.

Chapters 4 to 7 summarise biological trends and include trends in the composition of epilithic diatom communities (Chapter 4), trends in the presence and absence of aquatic macrophyte species, including the appearance of species previously not recorded (Chapter 5), trends in the composition of benthic macroinvertebrate taxa (Chapter 6) and trends in salmonid fish populations (Chapter 7).

Chapter 8 presents a summary of trends in trace metal concentrations, in particular in bulk deposition, lake water and biota at Lochnagar and in sediment traps at all lake sites across the Network.

Chapters 9 and 10 are concerned with recovery. Chapter 9 focuses on evidence for recovery in the legislative context provided by the UNECE Protocols and EU Directives. It explains how the various recovery targets are defined, describes the approaches that have been used to define recovery targets, assesses progress that has been made towards the targets, and discusses reasons for the difference between the current status (2008) and the target status. Chapter 10 is concerned with the future and considers whether improvements to date will be sustained and the extent to which a full recovery may be confounded by other factors, such as climate change.

Chapter 11 summarises key outputs from the report and presents a series of recommendations for policy makers along with recommendations for extending the role and effectiveness of the AWMN in future.

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Table 1.1 Locations and physical characteristics of UK Acid Waters Monitoring Network sites

Site	Code	UK Grid Reference	Type	Altitude Range (m)	Geology	Soils	Catchment area (ha)	Forest area (%)	Lake area (ha)	Lake max. depth (m)
1. Loch Coire nan Arr	ARR	NG 808422	Lake	125 – 896	Sandstone	Podzol, gley, peat	897	-	12	12
2. Allt a' Mharcaidh	MHAR	NH 881045	Stream	325 – 1111	Granite	Podzol, peat	998	-	-	-
3. Allt na Coire nan Con	ANCC	NM 793688	Stream	10 – 756	Schist, gneiss	Peaty gley	790	48	-	-
4. Lochnagar	NAG	NO 252859	Lake	785 – 1155	Granite	Alpine podzol	92	-	10	27
5. Loch Chon	CHN	NN 421051	Lake	100 – 600	Schist, grits	Podzol, gley	1470	56	100	25
6. Loch Tinker	TINK	NN 445068	Lake	420 – 700	Schist, grits	Peat	112	-	11	10
7. Round Loch of Glenhead	RLGH	NX 450804	Lake	295 – 531	Granite	Peat, peaty podzol	95	-	13	14
8. Loch Grannoch	LGR	NX 542700	Lake	210 – 601	Granite	Gley, podzol, peat	1290	70	114	21
9. Dargall Lane	DARG	NX 449786	Stream	225 – 716	Shale, greywackes	Peaty podzol	210	-	-	-
10. Scoat Tarn	SCOATT	NY 159104	Lake	602 – 841	Volcanics	Peaty ranker	95	-	5	20
11. Burnmoor Tarn	BURNMT	NY 184044	Lake	252 – 602	Volcanics, granite	Ranker, podzol, peat	226	-	24	13
12. River Etherow	ETHR	SK 116996	Stream	280 – 633	Millstone grit	Peat	1300	-	-	-
13. Old Lodge	LODGE	TQ 456294	Stream	94 – 198	Sandstone	Brown podzol, gley	240	-	-	-
14. Narrator Brook	NART	SX 568692	Stream	225 – 456	Granite	Podzols	475	-	-	-
15. Llyn Llagi	LAG	SH 649483	Lake	380 – 678	Slate, shale, dolerite	Peaty podzol, peat	157	-	6	17
16. Llyn Cwm Mynach	MYN	SH 678238	Lake	285 – 680	Cambrian sedimentary	Rankers, peat	152	55	6	11
17. Afon Hafren	HAFR	SN 844876	Stream	355 – 690	Shale, gritstone	Peaty podzol, peat	358	50	-	-
18. Afon Gwy	GWY	SN 842854	Stream	440 – 730	Shale, gritstone	Peaty podzol, peat	210	-	-	-
19. Beagh's Burn	BEAH	D 173297	Stream	150 – 397	Schist	Peat	273	-	-	-
20. Bencrom River	BENC	J 304250	Stream	140 – 700	Granite	Peat	298	-	-	-
21. Blue Lough	BLU	J 327252	Lake	340 – 703	Granite	Peat	42	-	2	5
22. Coneyglen Burn	CONY	H 641884	Stream	230 – 562	Schist	Peat	1410	15	-	-
23. Loch Coire Fionnaraich	VNG9402	NG 945498	Lake	236 – 933	Sandstone, quartzite	Peat, peaty podsols	550	-	9	14

Table 1.2: **Monitoring record and funding status of AWMN sites (* no sampling in 2001 due to foot and mouth)**

Site Code	Chemistry	Inverts	Macrophytes	Diatoms	Fish	Sed traps	Current Funding
ARR	1988-2008	1988-2007	1988-1995, 1997, 1999	1988-2007	1989-2000	1991-1999, 2001, 2002	No longer monitored.
MHAR	1988-2008	1988-2008	1988-2007	1988-2008	1988-2006,2008	N/A	DEFRA, CEH, ENSIS, MS
ANCC	1988-2008	1988-2008	1988-2007	1988-2008	1988-2006,2008	N/A	Forestry Commission, CEH, ENSIS, MS, QMUL
NAG	1988-2008	1988-2008	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-2006, 2008	1991, 1993-2004, 2006-2008	DEFRA, CEH, ENSIS
CHN	1988-2008	1988-2008	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-2006, 2008	1991,1992, 1994-2008	Forestry Commission, CEH, ENSIS
TINK	1988-2008	1988-2008 *	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-1999, 2001-2006, 2008	1991-2008	CEH, ENSIS
RLGH	1988-2008	1988-2008 *	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-2006, 2008	1991-2008	DEFRA, CEH, ENSIS
LGR	1988-2008	1988-2008 *	1988-1995, 1997, 1999, 2001, 2005	1988-2008	1989-2004	1993-208	Forestry Commission, CEH, ENSIS, FRS
DARG	1988-2008	1988-2008 *	1998-2008	1988-2008	1988-2004, 2006, 2008	N/A	CEH, ENSIS, MS, QMUL
SCOATT	1988-2008	1988-2008 *	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-2005	1991-2008	DEFRA, CEH, ENSIS
BURNMT	1988-2008	1988-2008 *	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-2004,2008	1992-2008	EA, CEH, ENSIS
ETHR	1988-2008	1988-2008	1988-1997, 2000-2008	1988-2008	1989-1993	N/A	DEFRA, CEH, ENSIS
LODGE	1988-2008	1988-2008	1988-2006, 2008	1988-2008	1988-2008	N/A	DEFRA, CEH, ENSIS, QMUL
NART	1991-2008	1988-2007 *	1988-2006	1988-2006, 2008	1988-2006	N/A	CEH, ENSIS
LAG	1988-2008	1988-2008	1988-1995, 1997, 1999, 2001, 2003, 2005	1988-2008	1989-1999, 2001-2006, 2008	1993-2008	DEFRA, CEH, ENSIS
MYN	1988-2008	1988-2008	1988-1995, 1997, 1999, 2001, 2003, 2005, 2008	1988-2008	1989-2006, 2008	1991-2008	WAG/CCW/EA Wales, CEH, ENSIS
HAFR	1988-2008	1988-2008 *	1988-2008	1988-2008	1988-2006,2008	N/A	WAG/CCW/EA Wales, CEH, ENSIS
GWY	1991-2008	1991-2008 *	1991-1997, 1999-2008	1991-2008	1991-2006,2008	N/A	WAG/CCW/EA Wales, CEH, ENSIS
BEAH	1988-2008	1988-2007	1988-2000, 2002-2005	1988-2008	1988-2006	N/A	CEH, ENSIS
BENC	1988-2008	1988-2008	1988-2001, 2003-2006	1988-2008	1988-2006	N/A	CEH, ENSIS
BLU	1990-2008	1989-2008	1989-1995, 1997, 1999, 2001, 2003, 2005	1989-2008	1990-2006	1992-2008	DEFRA, CEH, ENSIS
CONY	1990-2008	1989-2007 *	1989-1999, 2001-2005	1989-2008	1990-2006	N/A	CEH, ENSIS
VNG9402	2001-2008	2002-2008	2003, 2005	2001-2008	2001-2006, 2008	2002-2008	DEFRA, CEH, ENSIS

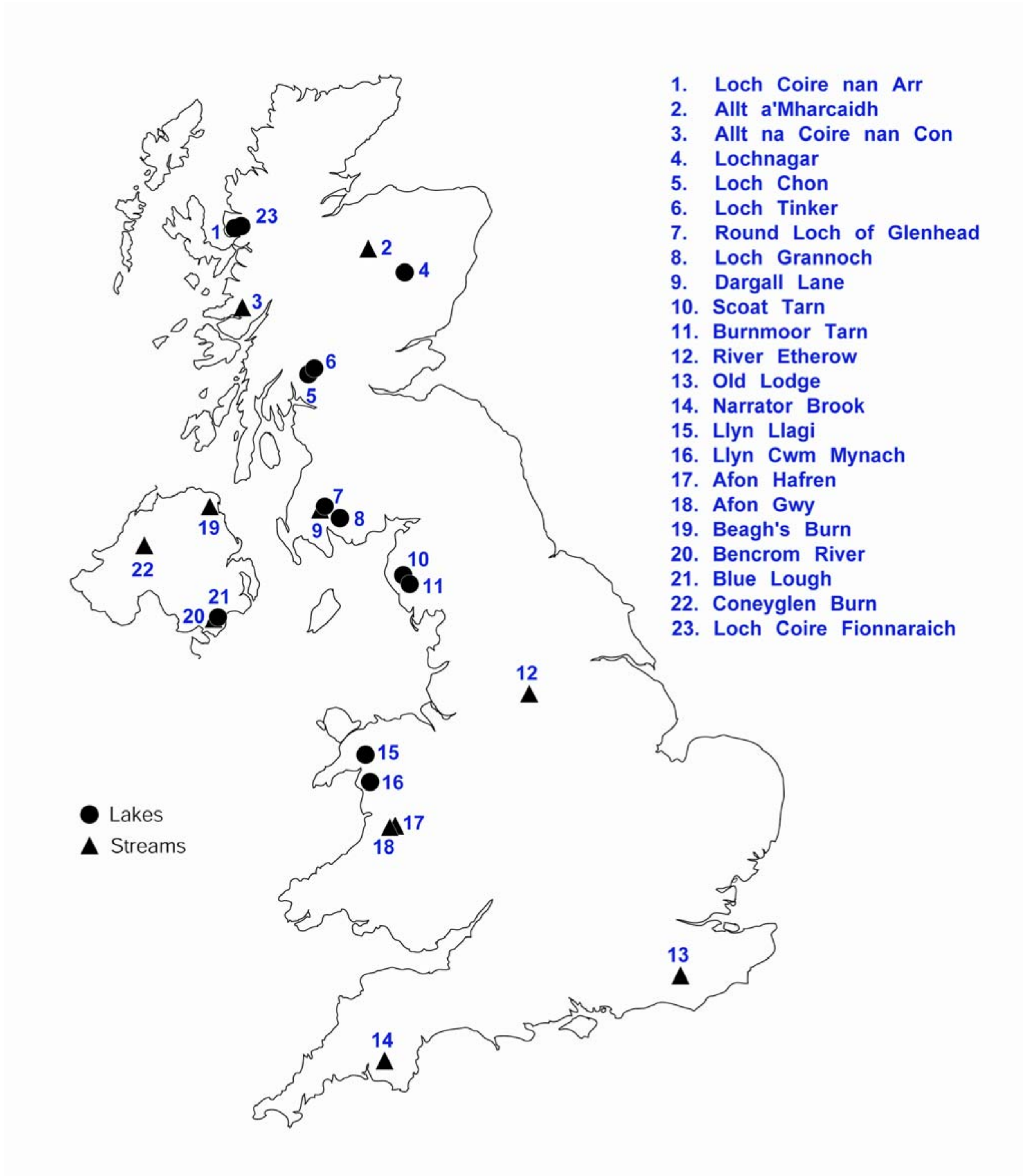

Figure 1.1 Map of Acid Waters Monitoring Network Sites

2. Acid Deposition Trends at AWMN Sites

Chris Curtis and Gavin Simpson.

2.1. Introduction and Previous Trend Analyses

The purpose of this chapter is to assess trends in deposition of pH, non-marine sulphate (xSO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) at Acid Deposition Monitoring Network (ADMN) sites located closest to Acid Waters Monitoring Network (AWMN) sites, using the most up to date deposition data available (i.e. up to 2007). The ADMN provides weekly or 2-weekly bulk deposition data for a network of sites around the UK.

The key question to be addressed in this chapter is:

- What are the trends in bulk deposition chemistry at ADMN sites most representative of the AWMN sites over the monitoring period?

Chapter 3 then compares the trends here with trends in the water chemistry at AWMN sites in an attempt to increase our understanding of the response of the hydrochemistry to changes in deposition and other drivers.

The draft report of the Defra Review of Transboundary Air Pollution (RoTAP, in press) summarised trends in acid deposition across the UK to 2006. Sulphur deposition in the UK declined by 80% from 1986 to 2006. Total N deposition did not change significantly through this period, remaining close to 400 kT per year throughout. Despite a decline in NO_x emissions, NH_3 emissions remained level and most of the reductions in NO_x deposition related to pollution that was exported overseas, with much lower reductions in deposition within the UK of only 15%. Concentrations of acidity, xSO_4^{2-} and non-marine chloride (Cl^-) decreased by 85%, 75% and 95% respectively, with xSO_4^{2-} accounting for 75% of the trend in deposited acidity.

Currently levels of reduced N deposition are similar to those for oxidised N. However, deposition of SO_x, NO_x and NH_y is predicted to decrease by 47%, 32% and 16% respectively by 2020 from 2005 levels so that reduced N deposition will form a progressively greater proportion of total N deposition.

For SO_x, NO_x and $NH_{y,}$ total deposition at the national scale is dominated by the wet deposition component, but there is great spatial variation with distance from sources. The relative importance of wet deposition inputs for xSO_4^{2-}, NO_x (as NO_3^-) and reduced N (as NH_4^+) deposition for the 5km grid square containing Acid Waters Monitoring Network (AWMN) site sampling locations in Great Britain is shown in Table 2.1. Figure 1.2 shows the location of AWMN and ADMN sites). Wet deposition of xSO_4^{2-} makes up between 70-95% of total non-marine inputs, with the lowest proportion at Old Lodge (south-east England) and the highest proportion in Scotland. A much greater range is found for the proportion of wet deposited NO_3^-, from 36% at Old Lodge and 53-66% in Wales to a maximum of 85% in the Trossachs of Scotland. For wet deposited NH_4^+ the proportion varies from 51% of total reduced N at Old Lodge up to a maximum of 91% at Coire nan Arr in north-west Scotland. For total N deposition these figures translate to 41% wet deposited at Old Lodge but >57% at all other sites, reaching a maximum proportion of 88% in the Trossachs.

The dominance of wet deposition at all sites except Old Lodge suggests that bulk deposition data should provide a robust estimate of deposition loads to the catchments of AWMN lakes and streams. Bulk deposition measurements capture wet deposition plus a component of dry deposition. For comparison of trends in AWMN surface water chemistry with the major driver of chemical change, acid deposition, the ADMN bulk deposition network provides input data which do not have to be aggregated to the annual time step. Hence trends in bulk deposition chemistry may be compared with AWMN time-series data without loss of temporal resolution.

Table 2.1: Breakdown of acid deposition (Concentration-Based Estimated Deposition 2004-06 averaged by landcover) for AWMN sites in Great Britain (S and N in kg ha^{-1} yr^{-1}).

Site Name	Non-marine S deposition				Oxidised N deposition				Reduced N deposition				Total N deposition	
	Wet	Dry	Total	% wet	Wet	Dry	Total	% wet	Wet	Dry	Total	% wet	TN	% wet
Loch Coire nan Arr	5.4	0.4	5.7	94.7	3.8	0.7	4.5	84.4	3.8	0.4	4.2	90.5	8.7	87.4
Allt a'Mharcaidh	3.6	0.6	4.2	85.7	3.3	2.4	5.7	57.9	2.9	1.1	4	72.5	9.7	63.9
Allt na Coire nan Con	4.9	0.6	5.5	89.1	3.9	1.1	5	78.0	3.8	0.8	4.6	82.6	9.6	80.2
Lochnagar	8.8	0.6	9.4	93.6	8.7	1.9	10.7	81.3	7.4	1	8.4	88.1	19.1	84.3
Loch Chon	11.8	0.8	12.6	93.7	10.3	1.8	12.1	85.1	10.4	1.2	11.5	90.4	23.6	87.7
Loch Tinker	11.8	0.8	12.6	93.7	10.3	1.8	12.1	85.1	10.4	1.2	11.5	90.4	23.6	87.7
Round Loch of Glenhead	10.1	0.7	10.8	93.5	7.7	3	10.7	72.0	11	3.1	14	78.6	24.7	75.7
Loch Grannoch	5.5	0.6	6.2	88.7	4.4	2.3	6.7	65.7	6.4	3.6	9.9	64.6	16.6	65.1
Dargall Lane	6.2	0.8	6.9	89.9	4.7	3.1	7.8	60.3	6.8	3.2	10	68.0	17.8	64.6
Scoat Tarn	7.9	1	9	87.8	7.2	3.3	10.5	68.6	9.9	3.5	13.4	73.9	23.9	71.5
Burnmoor Tarn	5.4	0.9	6.3	85.7	4.7	2.3	7	67.1	6.9	3.4	10.3	67.0	17.3	67.1
River Etherow	11	2.5	13.5	81.5	9.5	5.9	15.4	61.7	11.5	4.8	16.3	70.6	31.7	66.2
Old Lodge	4.2	1.8	6	70.0	3.2	5.9	9	35.6	2.8	2.7	5.5	50.9	14.5	41.4
Narrator Brook	6	1.1	7.1	84.5	6.1	3.7	9.8	62.2	6	5.1	11.1	54.1	20.9	57.9
Llyn Llagi	5.9	1.3	7.2	81.9	4.9	2.5	7.4	66.2	5.6	3.2	8.8	63.6	16.2	64.8
Llyn Cwm Mynach	5.2	1.2	6.4	81.3	4.2	3	7.2	58.3	5.2	3.2	8.4	61.9	15.6	60.3
Afon Hafren	7.1	1.3	8.4	84.5	5.7	5	10.7	53.3	7.1	4.3	11.4	62.3	22.1	57.9
Afon Gwy	7.1	1.3	8.4	84.5	5.7	5	10.7	53.3	7.1	4.3	11.4	62.3	22.1	57.9
Loch Coire Fionnaraich	6.2	0.4	6.6	93.9	4.3	0.9	5.2	82.7	4.1	0.5	4.6	89.1	9.8	85.7

Overall trends in ADMN bulk deposition have been reported up to 2007 in Lawrence *et al.* (2008). Using a linear least-squares approach, significant (in most cases strong or very strong) declining trends in xSO_4^{2-} are reported for all but one of 39 sites, with the rate of decline varying from c. -0.4 μeq l^{-1} yr^{-1} at Strathvaich Dam in northern Scotland to -4.1 μeq l^{-1} yr^{-1} at Jenny Hurn in the East Midlands. Only 14 of 39 sites show linear trends in NO_3^-, in all cases a declining trend, varying from -1.0 μeq l^{-1} yr^{-1} at Stoke Ferry in East Anglia to -2.4 μeq l^{-1} yr^{-1} at Loch Chon in the Trossachs (co-located with the AWMN site).

Here we select the ADMN sites with the longest continuous monitoring records located closest to AWMN lakes and streams (Table 2.2) that will allow comparisons between trends in bulk deposition and surface water chemistry (see Chapter 3), following the approach of Cooper (2005). While there are currently ADMN sites co-located with AWMN catchments which are not used here, they have much shorter records. In future they will be used to determine the extent to which extrapolated trends from the selected "matching" ADMN sites reflect actual trends in bulk deposition at these AWMN sites (Table 2.3). We have used the full length data series for ADMN sites even where this predates the start of AWMN records because this provides a longer, more robust assessment of deposition trends. Comparisons of trends in ADMN and AWMN sites are, however, based only on overlapping periods.

The results of trend analysis for the ADMN bulk deposition sites are shown in Table 2.2 using additive models for pH, xSO_4^{2-}, NO_3^-, NH_4^+ and total N (TN = NO_3^- + NH_4^+). Additive models take their form from the data and allow an assessment of whether trends fitted to the time-series data are significantly increasing or decreasing. The significance is estimated using the first derivatives of the fitted spline for the trend, computed using finite differences. A confidence interval, here 0.95 (95%), for the derivative is computed, which allows the identification of intervals of the spline where the derivative is significantly different from zero, i.e. significantly increasing or decreasing. The portions of the fitted trends that are significantly changing are identified in the plots using a thicker, coloured, line for the trend. In these plots, red indicates significantly decreasing and blue significantly increasing trends. Further details of model fitting can be found in Appendix 2.

2.2. Results

Trends for bulk deposition are described below for each ADMN site, for both primary concentration data and precipitation weighted data, expressed as deposition load in mg m^{-2} day^{-1} (concentration × precipitation / sampling period (days)). Samples with no data are omitted from the analysis. For rainfall trends, to allow data series containing genuine zero values to be log transformed, the transformation log (x + minimum recorded value) is used. Where bulk deposition sites are situated within, or on the fringe, of AWMN catchments they are referred to as "co-located". In the following summary the geographically closest AWMN sites are provided in parentheses.

2.2.1. Allt a' Mharcaidh (co-located with Allt a' Mharcaidh AWMN site)

The Allt a' Mharcaidh deposition site shows a significant linear increasing trend in bulk deposition pH throughout the period of monitoring (Fig. 2.1). This corresponds with a monotonic but non-linear decline in xSO_4^{2-} which is significant except during the early 1990s (Fig. 2.2a). There is no significant trend in any N species although concentrations of NO_3^- and NH_4^+ show apparent increases (Figs. 2.3a-2.5a). Deposition loads show a similar picture; xSO_4^{2-} shows a strong monotonic decline, while bulk deposition inputs of NO_3^-, NH_4^+ and TN show no significant trends, albeit with small apparent declines (Figs. 2.2b-2.5b).

2.2.2. Balquhidder / Balquhidder 2 (Lochs Chon and Tinker)

For this site the record for Balquhidder 2 was appended to that for the original Balquhidder location following relocation of the ADMN site by 2.4km up the same valley in 1994 (Table 2.2). The data are effectively a continuous series from 1986 to the present.

The pH of bulk deposition at this site showed a significant increase from the late 1980s to the present (Fig. 2.1). The monotonic trend follows the monotonic decline in xSO_4^{2-} though this is significant only after 1994 (Fig. 2.2a). Smoothed trends in concentrations of NO_3^-, NH_4^+ and TN are all downward but not statistically significant (Figs. 2.3a-2.5a). Deposition loads show rather different patterns, with significant declines in all acid anions. Non-marine SO_4^{2-} deposition declines significantly after 1991, while all N species decline significantly throughout the period of monitoring (Figs. 2.2b-2.5b).

Table 2.2: ADMN bulk deposition sites with linear trends to 2007 and matched AWMN sites

(Source: Lawrence *et al.*, 2008; trends ns = not sig., + significant, ++ moderate trend, +++ strong trend, ++++ very strong, +++++ exceptionally strong)

Code	Site Name	OS Grid Ref.	Alt. (m)	Matched AWMN sites	Monitoring Period (W=weekly; 2W = 2 weekly)	nss SO4 $\mu eq\ l^{-1}\ yr^{-1}$	NO3 $\mu eq\ l^{-1}\ yr^{-1}$
5103	Allt a' Mharcaidh	NH 876052	274	MHAR	16/12/85 – 5/11/01 (W); 2W to 24/12/07	-0.68^{++++}	-0.05 ns
5200 **5152**	Balquhidder Balquhidder 2	NN 521206 NN 545207	140 130	(Moved c. 2.4km in 1994) CHON, TINK	8/1/86 – 26/7/94 (2W) 2/8/94 – 28/10/01 (W); 2W to 24/12/07	- -0.89^{+++}	- -0.12 ns
5111	Bannisdale	NY 515043	265	SCOATT, BURNMT	8/1/86 – 26/12/07 (2W)	-1.33^{++++}	-0.14 ns
5007	Barcombe Mills	TQ 437149	10	LODG	8/1/86 – 12/12/07 (2W)	-0.96^{++}	-0.31 ns
5011	Glen Dye	NO 642864	185	NAGA	4/2/87 – 30/10/01 (W); 2W to 28/12/07	-1.66^{+++}	-0.25 ns
5119 **5153**	Beddgelert Llyn Llydaw	SH 556518 SH 638549	358 490	(Moved c. 9km in 1996) LAG, MYN	29/1/86 – 26/7/96 (W) 21/8/96 – 31/10/01 (W); 2W to 2/1/08	- -1.17^{+++}	- -0.20^{+}
5107	Loch Dee	NX 468779	230	BENC, BLU, DARG, LGR, RLGH	30/12/85 – 8/1/02 (W); 2W to 13/13/07	-0.95^{+++}	-0.16 ns
5006	Lough Navar	IH 065545	130	BEAG, CONY	4/2/87 – 29/10/01 (W); 2W to 24/12/07	-0.53^{++++}	-0.07 ns
5122 **5150**	Plynlimon Pumlumon	SN 822841 SN 823854	405 390	(Moved 1.3km in 1989) GWY, HAFR	25/2/86 – 17/1/89 (2W) 17/1/89 – 23/10/01 (W); 2W to 11/12/07	- -0.82^{++++}	- -0.18 ns
5010	Strathvaich Dam	NH 347750	270	ARR, ANCC, VNG9402	11/3/87 – 27/11/01 (W); 2W to 15/12/07	-0.44^{+++}	-0.09 ns
5120	Wardlow Hay Cop	SK 177739	350	ETHR	5/1/86 – 31/12/01 (W); 2W to 23/12/07	-2.79^{+++++}	-0.28 ns
5008	Yarner Wood	SX 786789	119	NART	6/2/86 – 31/10/10 (W); 2W to 26/12/07	-0.67^{++}	0.14 ns

Table 2.3: ADMN bulk deposition sites co-located with AWMN sites, with monitoring period and linear trends (see Table 2.2 for explanation)

Code	Site Name	OS Grid Ref.	Alt.	Monitoring Period	nss SO4 $\mu eq\ l^{-1}\ yr^{-1}$	NO3 $\mu eq\ l^{-1}\ yr^{-1}$
5103	Allt a' Mharcaidh	NH 876052	274	16/12/85 – 5/11/01 (W); 2W to 24/12/07	-0.68^{++++}	-0.05 ns
5104 **5157**	Lochnagar Lochnagar	NO 274858 NO 252859	680 785	1/7/86 - 12/12/88 (2W) (moved 2km) 25/3/99 - 31/12/07 (2W)	- -1.68^{++}	- -0.74 ns
5122 **5150**	Plynlimon (GWY) Pumlumon (GWY)	SN 822841 SN 823854	405 390	25/2/86 – 17/1/89 (2W) (moved 1.3km) 17/1/89 – 23/10/01 (W); 2W to 11/12/07	- -0.82^{++++}	- -0.18 ns
5133	Silent Valley (BENC)	J 306243	150	8/1/86-16/1/90 (2W)	-	-
5155	Beagh's Burn	ID 165283	250	28/1/99 - 31/12/07 (2W)	-2.14^{+}	-0.14 ns
5156	Loch Chon	NN 429084	150	24/2/99 - 24/12/07 (2W)	-0.87^{+}	-0.58^{+}
5158	River Etherow	SK 125986	485	4/3/99 - 27/12/07 (2W)	-1.96^{++}	-0.77 ns
5159	Scoat Tarn	NY 158103	595	3/3/99 – 23/12/07 (2W)	-0.84^{+}	0.02 ns
5160	Llyn Llagi	SH 647483	380	1/3/99 – 21/12/07 (2W)	-0.67^{+}	0.06 ns

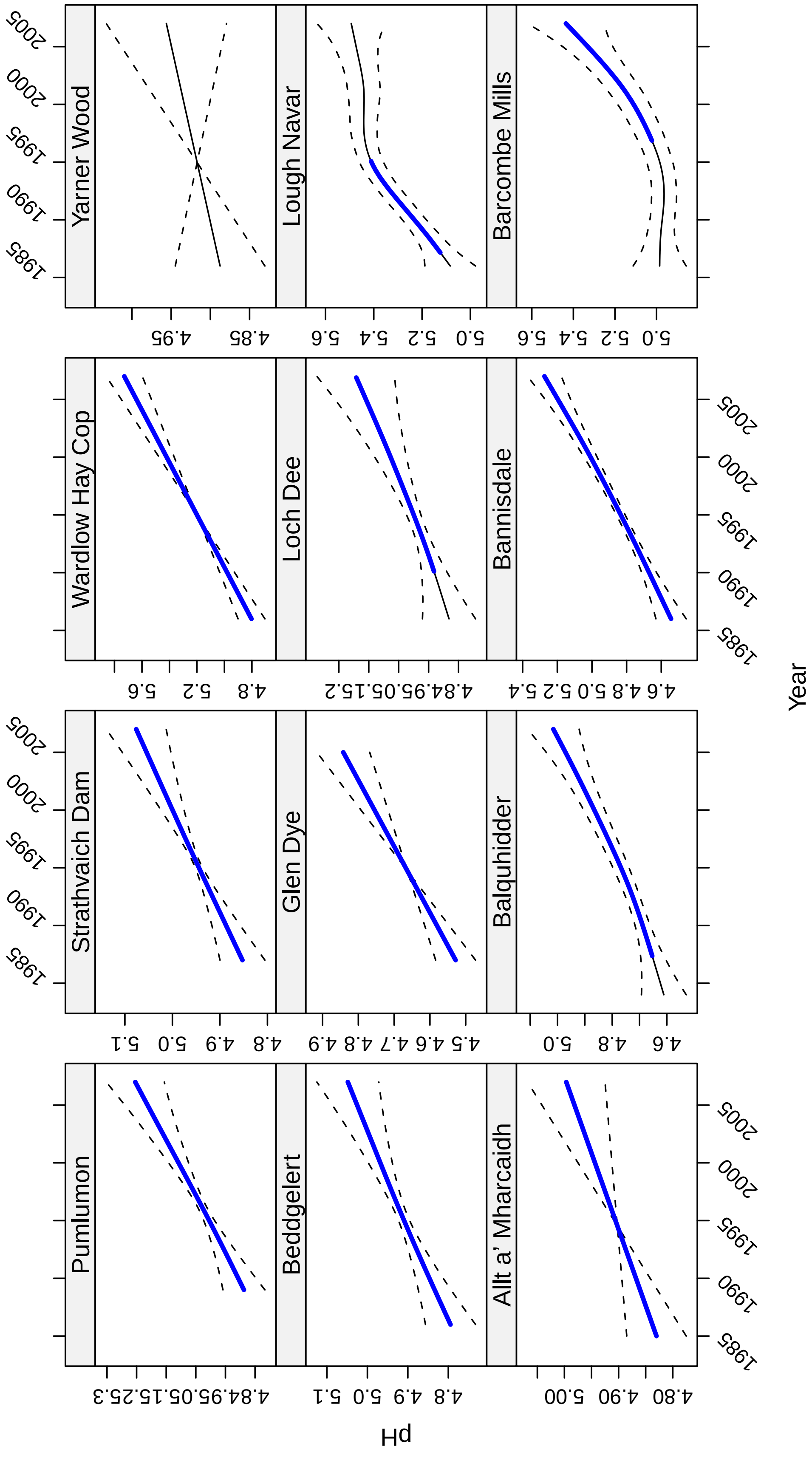

Figure 2.1: Trends in pH of bulk deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively

2.2.3. Bannisdale (Scoat Tarn and Burnmoor Tarn)

Bulk deposition pH increases significantly throughout the period of monitoring (Fig. 2.1) corresponding with significant monotonic declining trends in xSO_4^{2-} and NO_3 concentrations from the early 1990s and NH_4^+ and TN concentrations throughout the record (Figs. 2.2a-2.5a). Trends in deposition loads provide a very similar picture.

2.2.4. Barcombe Mills (Old Lodge)

Unlike most other ADMN sites, there is no significant increase in bulk deposition pH at Barcombe Mills until the late 1990s, after which levels increase steadily to the present (Fig. 2.1). The absence of trend over the first 15 years of monitoring is difficult to explain because the other key acid species (xSO_4^{2-} and NO_3^-) show significant monotonic declines throughout the monitoring period, as does NH_4^+ and hence TN (Figs. 2.2a-2.5a). Furthermore, this site is close to major deposition sources and has the highest proportion of dry deposition of all selected ADMN sites. It is therefore possible that other components of deposition play a role at this site. When concentrations are precipitation-weighted, both xSO_4^{2-} and NH_4^+ deposition show significant declining trends throughout, but it is evident that NO_3^- deposition only began to decline after around 2000.

2.2.5. Beddgelert / Llyn Llydaw (Llyn Llagi and Llyn Cwm Mynach)

This record comprises appended data from Beddgelert and Llyn Llydaw, with the ADMN site being moved 9km in 1996 (Table 2.2). Despite the relatively large distance and altitude increase of 130m associated with the relocation, there are no obvious step changes in the data and the equivalent composite dataset was used in the previous analyses of Fowler *et al.* (1995) and Lawrence *et al.* (2008).

Bulk deposition pH shows a significant linear increasing trend throughout the period of monitoring (Fig. 2.1). This corresponds largely with a significant, near linear decline in xSO_4^{2-} concentration after 1991 to the present. Trends in NO_3^- follow a similar pattern to Pumlumon (see below) but with only a very short period of significant increasing trend around 1991 (Fig. 2.2a). An apparent increasing trend is reversed around 1995 with a smaller apparent decline and levelling off to the present. For NH_4^+ and TN, apparent decreasing trends are not significant (Figs. 2.3b-2.4b).

Similarities in trends with the Pumlumon site disappear when precipitation-weighting is applied. Both xSO_4^{2-} and NO_3^- deposition show a significant monotonic decline throughout the period of monitoring, while an early significant decline in NH_4^+ levels off after 1995 (Figs. 2.2b-2.4b). The trend in total N deposition is intermediate between NO_3^- and NH_4^+ (Fig. 2.5b).

2.2.6. Glen Dye (Lochnagar)

The pH trend in bulk deposition at Glen Dye shows a significant increase throughout the period of monitoring (Fig. 2.1). Non-marine SO_4^{2-} concentration only declined significantly from the mid-1990s (Fig. 2.2a), while there is no significant trend in any of the N species (Figs. 2.3a-2.5a) though all show an apparent decline over this period. Deposition loads show a similar pattern to concentrations, with the only significant trend being a decline in xSO_4^{2-} from about 1995 but there is no evidence of changes in N species (Figs. 2.2b-2.5b).

2.2.7. Loch Dee (Bencrom River, Blue Lough, Dargall Lane, Loch Grannoch, Round Loch of Glenhead)

The acidity of bulk deposition at Loch Dee follows the same general pattern modelled at most other Scottish ADMN sites, although the significant increase in pH only starts in around 1990 (Fig. 2.1). The pH increase broadly corresponds with significant decreases in xSO_4^{2-} concentration (Fig. 2.2a) but there are no significant trends in concentrations of N species, despite an apparent decline in NO_3^- after the early 1990s. When expressed as deposition loads using precipitation-weighting, trends in xSO_4^{2-} are very similar but the apparent declines in N species become significant throughout the whole period for NH_4^+, but only for a period in the late 1990s for NO_3^- and TN (Figs. 2.2b-2.5b).

2.2.8. Lough Navar (Beagh's Burn and Coneyglen Burn)

Trends in bulk deposition pH at this site are unique, with levels increasing significantly from the late 1980s to around 1995, but then levelling off (Fig. 2.1). This pattern cannot be explained by concentrations of xSO_4^{2-}, which only decline significantly after 1995, or by NO_3^- which shows a short but significant decline from the mid-1990s after a period of significant increase at the start of the 1990s (Fig. 2.2a). Trends in NH_4^+ concentration are not significant but appear to broadly follow NO_3^- (Figs. 2.3a-2.5a).

Precipitation-weighted trends show a brief but significant increase in xSO_4^{2-} from 1989 to 1991, which is followed by a significant decrease from 1995 to the present (Fig. 2.2b). The deposition load of NO_3^- shows the longest sustained period of significant increase of any site in the late 1980s and early 1990s, but then a reversal to a period of significant decline from 1995 to 2000 (Fig. 2.3b). Similar but much smaller and shorter trends are observed for NH_4^+ deposition, while the trends in TN are very similar to those for NO_3^-.

2.2.9. Pumlumon (co-located with Afon Gwy and Afon Hafren)

The trend in pH at Pumlumon shows a significant linear increase throughout the period of monitoring (Fig. 2.1). This increase corresponds largely with a significant decline in xSO_4^{2-} from 1995 to 2002 (Fig. 2.2a). Trends in NO_3^- concentrations are complex, with a short significant increase in the early part of the record followed by a significant decrease in the late 1990s (Fig. 2.3a). Concentrations of NH_4^+ follow a similar pattern to NO_3^- in the first ten years of monitoring with a significant decline from 1996 to 1999, but show an apparent, if non significant, increase thereafter (Fig. 2.4a). Trends in TN deposition largely follow those for NO_3^- but are moderated in the last few years by opposing trends in NH_4^+ (Fig. 2.5a). When converted to deposition loads using precipitation, all trends are very similar to their corresponding concentrations (Figs. 2.2-2.5b).

2.2.10. Strathvaich Dam (Loch Coire nan Arr, Allt na Coire nan Con and Loch Coire Fionnaraich)

Trends in bulk deposition pH at Strathvaich Dam show a significant linear increase throughout the period of monitoring (Fig. 2.1). Like many other sites, concentrations of non-marine SO_4^{2-} were approximately constant until a significant decline which began in 1995 and continued to the end of the record (Fig. 2.2a). There is an apparent cyclicity in NO_3^- concentrations as observed at Pumlumon, with significant increases in the early 1990s followed by significant decreases in the late 1990s (Fig. 2.3a). Ammonium concentrations show a non-significant rising tendency in the first five years (Fig. 2.4a) followed by a general decline after 1994 which becomes significant from 1995 to 2003. The pattern in TN is intermediate between those for NO_3^- and NH_4^+ concentrations (Fig. 2.5a). Trends in precipitation-weighted deposition levels are very similar to concentrations for all species, though there is no period of significant increase in NO_3^- (Figs. 2.2b-2.5b).

2.2.11. Wardlow Hay Cop (River Etherow)

There is a very strong, linear, significant increase in bulk deposition pH at this site for the whole monitoring period (Fig. 2.1). This is matched by a significant and almost linear decline in both xSO_4^{2-} and NO_3^- concentrations (Fig. 2.2a and 3.3a, respectively). Ammonium concentrations show apparent cyclicity, peaking in 1993 before reaching a minimum in 2002 (Fig. 2.4a). Higher concentrations of NH_4^+ relative to NO_3^- at this site mean that the TN trend closely follows that for NH_4^+ (Fig. 2.5a). Trends in deposition of the major acid anions are not linear. Deposition of xSO_4^{2-} shows a monotonic, mostly significant decline except for a level period in the early 1990s (Fig. 2.2b). An apparent decline in NO_3^- deposition is not significant, while for NH_4^+ and TN deposition a period of apparent increase to 1995 is followed by a decrease which is not significant (Figs. 2.3b-2.5b).

2.2.12. Yarner Wood (Narrator Brook)

Yarner Wood is the only site which shows no period of significant trend in the pH of bulk deposition, despite an apparent small increase (Fig. 2.1). While xSO_4^{2-} concentration declines significantly from around 1992 to the present there is no significant trend in N species, although NO_3^- shows a small apparent increase (Figs. 2.2a-2.5a). Precipitation-weighted trends show significant declines of differing length for each species during the late 1990s (Figs. 2.2b-2.5b).

2.3. Discussion

2.3.1. Trends in concentrations

Trends in bulk deposition pH show significant increases at all sites except Yarner Wood in south-west England, although the timing and pattern vary regionally (Fig. 2.1). Most sites with trends show a near linear increase throughout, except for Lough Navar which shows a significant increase in the first half of monitoring which then levels off, while Barcombe Mills shows increasing pH only after 1996.

Trends in pH appear to be largely driven by trends in xSO_4^{2-} concentration which show a significant decline at all sites (Fig. 2.2a), although, unlike pH, the xSO_4^{2-} trend at most sites is only significant after 1995. A possible explanation for the decline in acidity of rainfall prior to 1995 could be a reduction in the deposition of hydrochloric acid (HCl), although this pollutant is generally not expected to have travelled further than 100 km from the larger coal-burning power plants of central England. Further work would be required to test this hypothesis.

Trends in NO_3^- concentration are very mixed, with only six out of 12 ADMN sites showing significant trends. Bannisdale, Barcombe Mills and Wardlow Hay Cop show near linear declining trends in NO_3^- for a large part or all of the monitoring period. Lough Navar, Pumlumon and Strathvaich Dam all show short periods of significant increase in the early 1990s followed by significant declines after 1995. Only five sites show significant trends in NH_4^+ concentration, with declines of varying length from one year in the late 1990s at Wardlow Hay Cop to the whole record for Bannisdale and Barcombe Mills. Trends in total N concentrations closely track NH_4^+ except at Wardlow Hay Cop where the decline is significant throughout.

2.3.2. Deposition loads (precipitation-weighted) and rainfall trends

The use of precipitation data to convert concentrations into deposition loads has a major impact on trends at some sites for N species, while xSO_4^{2-} trends show almost identical patterns to concentrations.

For NO_3^- deposition the major changes are seen at Wardlow Hay Cop (significant decline in NO_3^- concentration but not deposition throughout), Beddgelert and Balquhidder (no trend in concentration, declining deposition throughout), and Loch Dee and Yarner Wood, both showing no trend in concentrations but with periods of significantly declining deposition at the end of the 1990s.

Trends in NH_4^+ deposition are generally similar to those for NO_3^- albeit less significant in most cases (Fig. 2.4b). The major differences from concentration trends are seen at Balquhidder, Beddgelert and Loch Dee, where there is no trend in concentration but long periods of declining deposition.

In an attempt to understand these differences we re-examined the rainfall data recorded in the ADMN collectors using the same statistical methods as previous trend analyses.

Additive modelling of the bulk collector rainfall data (log-transformed, daily means calculated by averaging over sample period) in general show declining trend components of the model fitted, which are significant for much or all of the monitoring period for all sites except Strathvaich Dam (Fig. 2.6). There are major caveats associated with these trend components, however. The additive models fitted explain only a small proportion of the variance in the observed data, of the order of 10%, and the trend component (rather than the seasonal smoother) accounts for only a part of the variance explained. Hence the interpretation of the trend components in Figure 2.6 suggests that there has been a small decline in observed rainfall amount. This small decline largely disappears when the data are analysed at the annual time step. Figure 2.7 shows annual sum rainfall amounts for each ADMN site addressed. Additive models with a single covariate (year) were fitted to these data for each site to identify trends in annual sum rainfall. In this analysis, only two sites (Loch Dee and Lough Navar) show significant declining trends in annual rainfall amount, with a third (Yarner Wood) a borderline significant declining trend ($p = 0.063$). In only one case (Loch Dee) does there appear to be a consistent decline in annual rainfall amount recorded in the ADMN collector.

Interpretation of the modelled trends is further complicated by methodological changes in the ADMN whereby sampling frequency over the monitoring period at most sites was switched from weekly in the first half of the period to 2-weekly sampling at the end of 2001. This may lead to at least three potential sources of variation in the data:

- doubling the sampling interval effectively halves the "detection limit" for rainfall measurement, i.e. if the minimum detectable sample is 1mm of rainfall in the collector, then after 2 weeks this corresponds to half the daily rainfall as the same amount collected over a 1 week period;
- evaporative losses of sample are likely to increase with increasing sample interval potentially leading to an apparent decline in rainfall captured and;
- increased loss or under-representation of peak rainfall events may occur, owing to over-topping of sampling bottles at the reduced sampling frequency.

While it is likely that these factors have affected the rainfall trend determinations, they are less likely to have affected the deposition flux trends (precipitation-weighted concentrations) because any loss of sample volume by evaporation should be matched by a proportional increase in concentrations in the remaining sample. However, if evaporation were shown to have increased, caveats would then need to be attached to the concentration trends. Further work on the potential impacts of changing sample regime on trend detection is merited, though the overall effect appears to be small.

This chapter highlights trends in deposition data at selected ADMN sites across the UK. There are widespread increasing trends in bulk deposition pH which are largely driven by declining xSO_4^{2-} concentrations from the late 1990s and to a lesser degree by declining NO_3^- at some sites. Earlier declines in bulk deposition pH cannot be explained by xSO_4^{2-} or NO_3^- at most sites and it is possible that other components of deposition, not assessed here, may account for these earlier trends in acidity.

2.4. Key Points

Additive modelling techniques have been used to determine trends in both concentrations and deposition loads (precipitation-weighted) at 12 Acid Deposition Monitoring Network sites most closely co-located with AWMN sites. Periods of significant increase or decrease over the period of monitoring were identified.

All bulk deposition sites with significant trends in pH show increases (11 out of 12 ADMN sites).

Concentrations of non-marine sulphate (xSO_4^{2-}) show significant decreasing trends at all sites and appear to be the main driver of changes in bulk deposition pH after the late 1990s, while earlier trends in deposition pH remain unexplained.

Trends in concentrations of N species are mixed, but where significant show an overall decline for NO_3^- and/or NH_4^+.

Precipitation-corrected deposition loads show very similar trends to concentrations for xSO_4^{2-}, but for N species there are changes to the significance of trends at some sites.

Small declining trends in precipitation measured in the bulk deposition collectors may reflect changes in sampling methodology as sampling frequency changed from weekly to 2-weekly during the ADMN monitoring period.

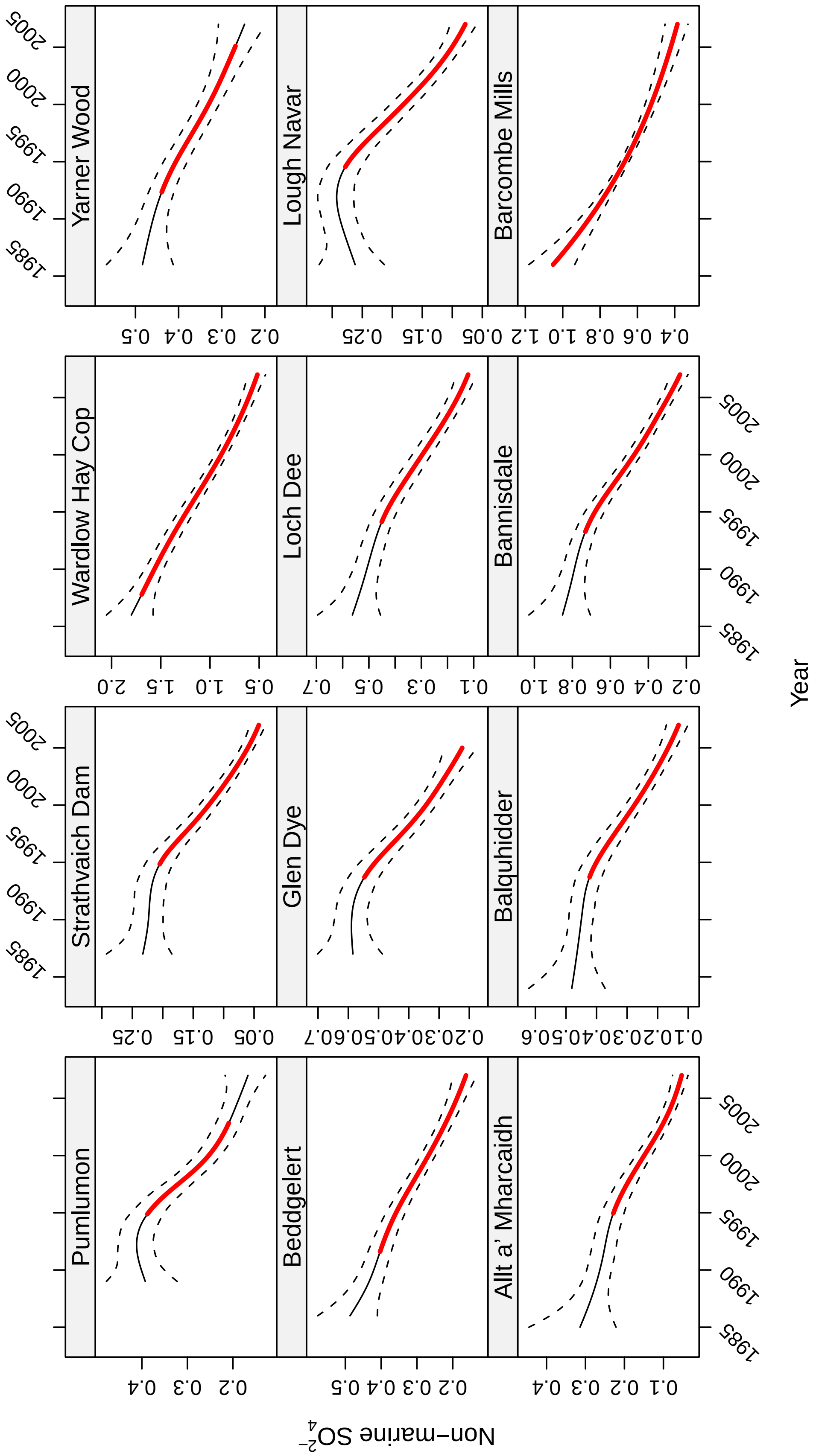

Figure 2.2a: Trends in xSO_4^{2-} concentration (mg S l^{-1}) in bulk deposition at 12 ADMN bulk deposition sites. Red lines indicate significant decreasing trends.

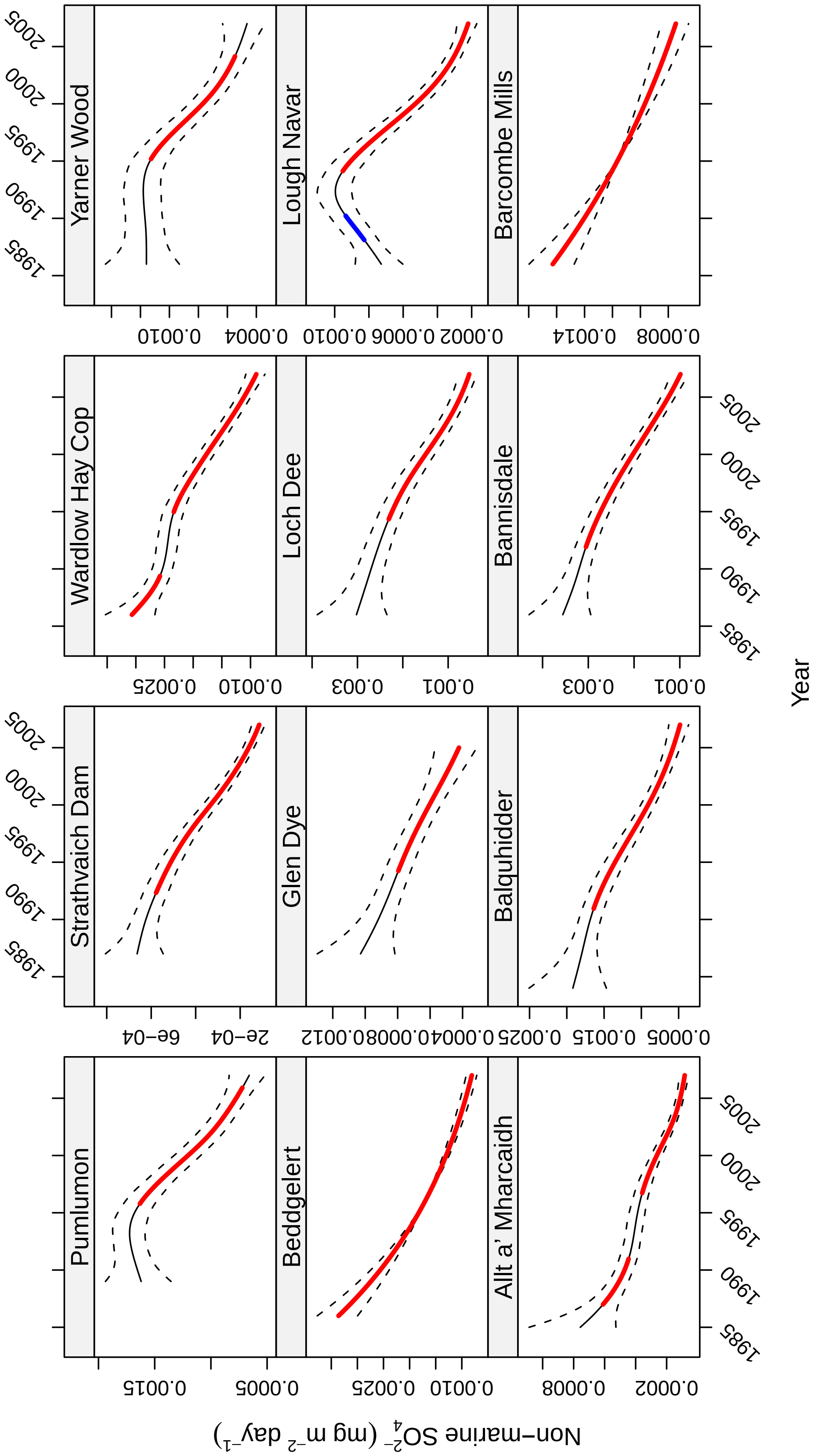

Figure 2.2b: Trends in precipitation weighted xSO_4^{2-} in bulk deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively

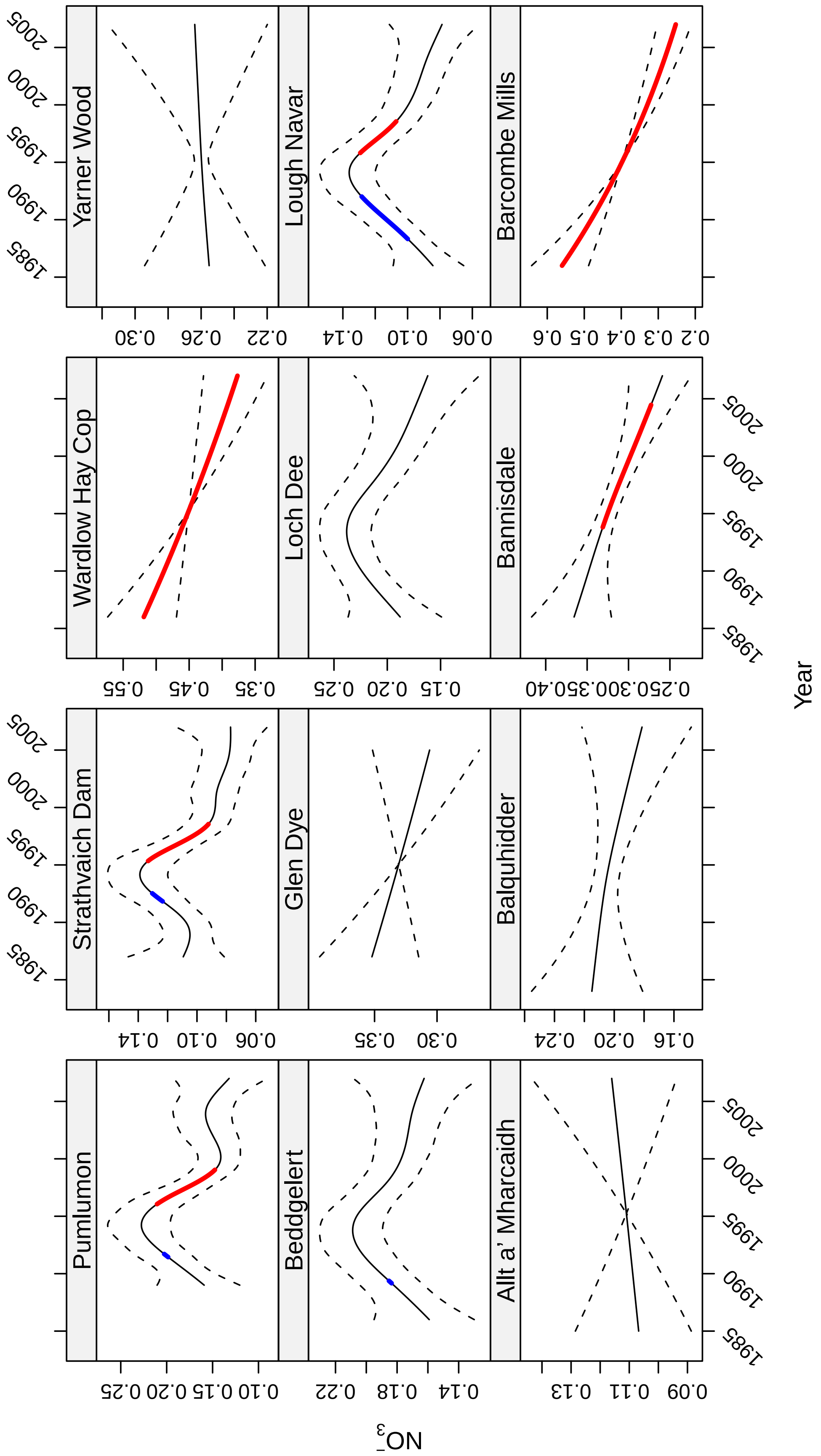

Figure 2.3a: Trends in NO_3^- concentration (mg N l^{-1}) in deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively.

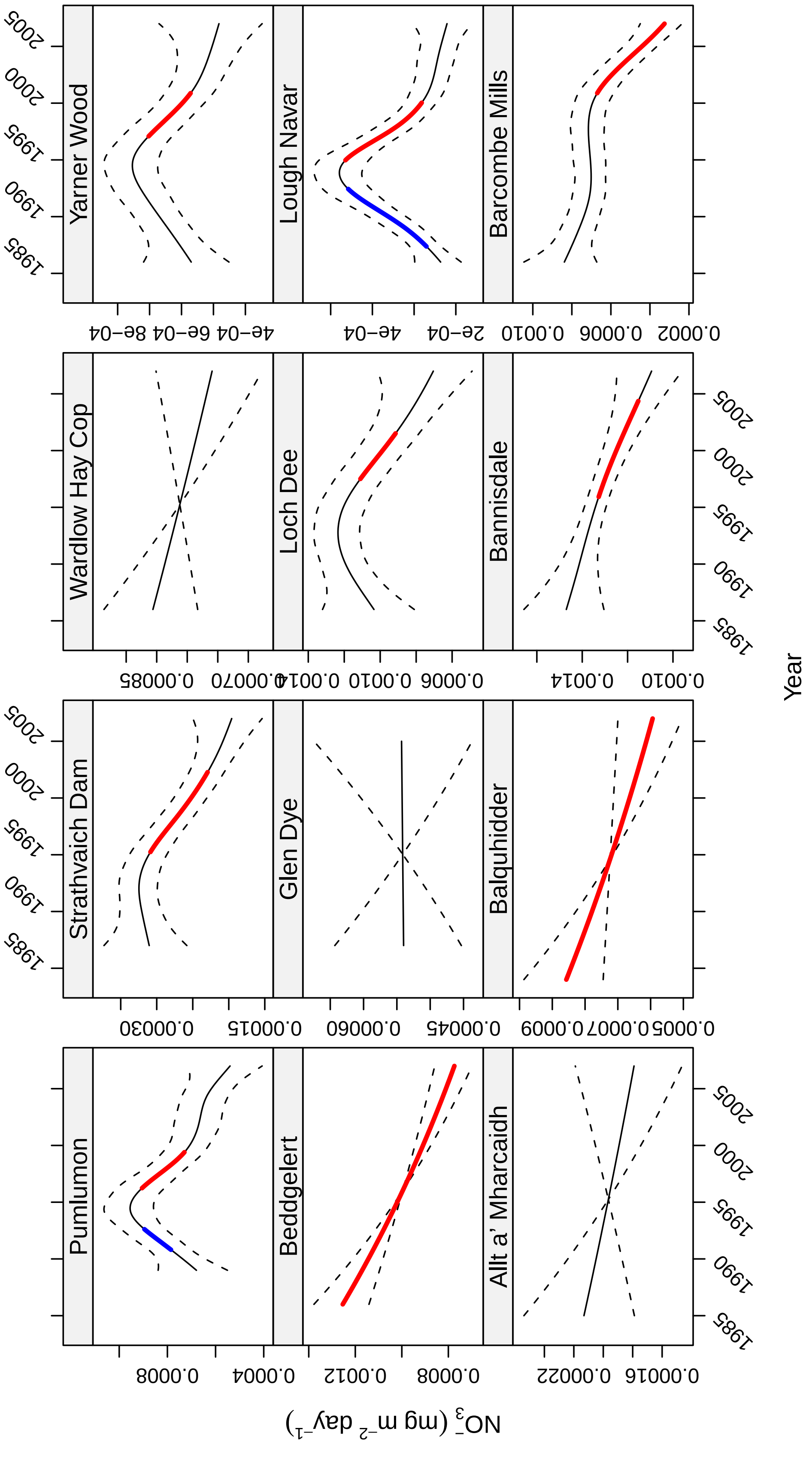

Figure 2.3b: Trends in precipitation weighted NO_3^--N in bulk deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively.

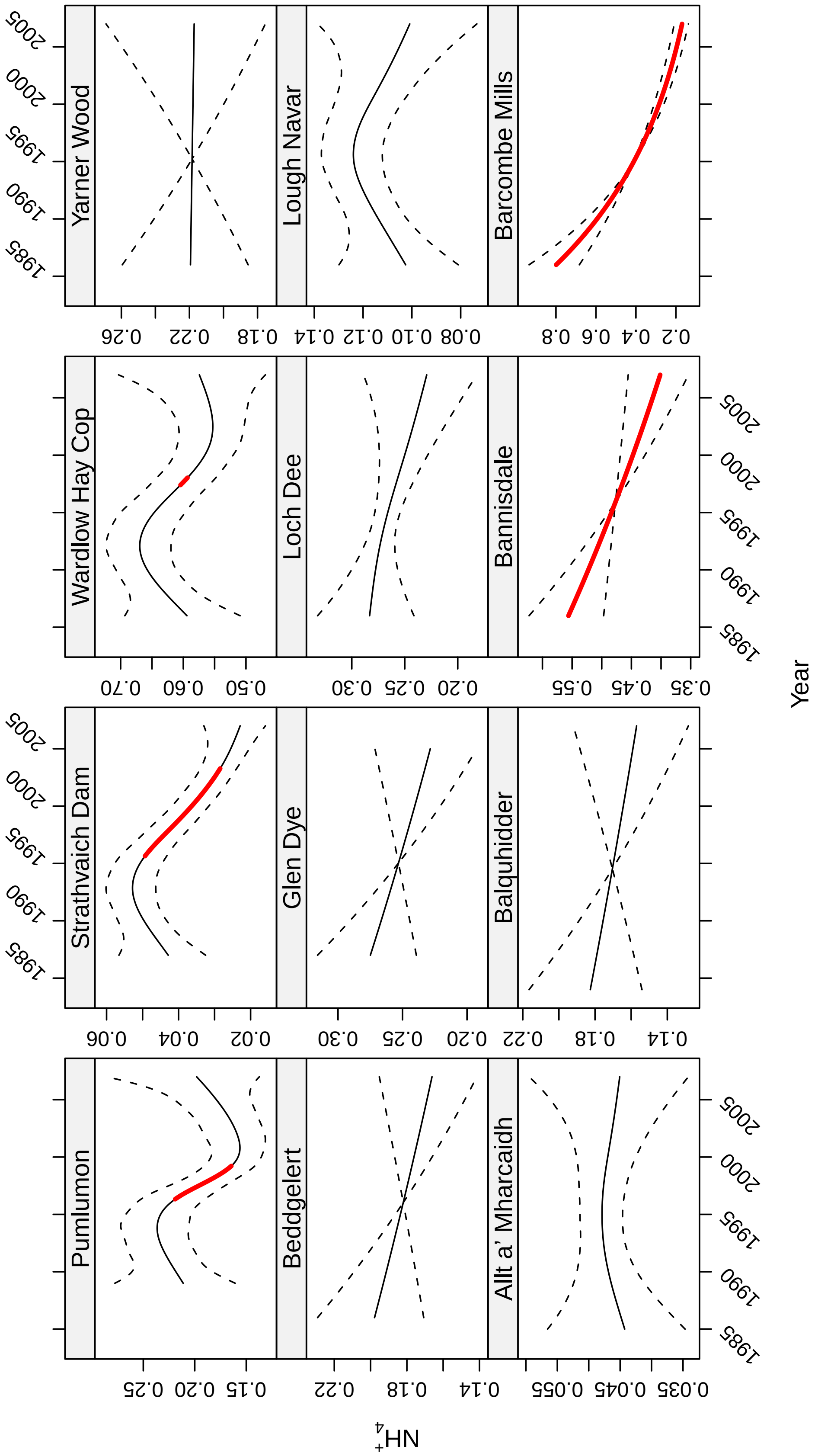

Figure 2.4a: Trends in NH_4^+ concentration (mg N l^{-1}) in bulk deposition at 12 ADMN bulk deposition sites. Red lines indicate significant decreasing trends.

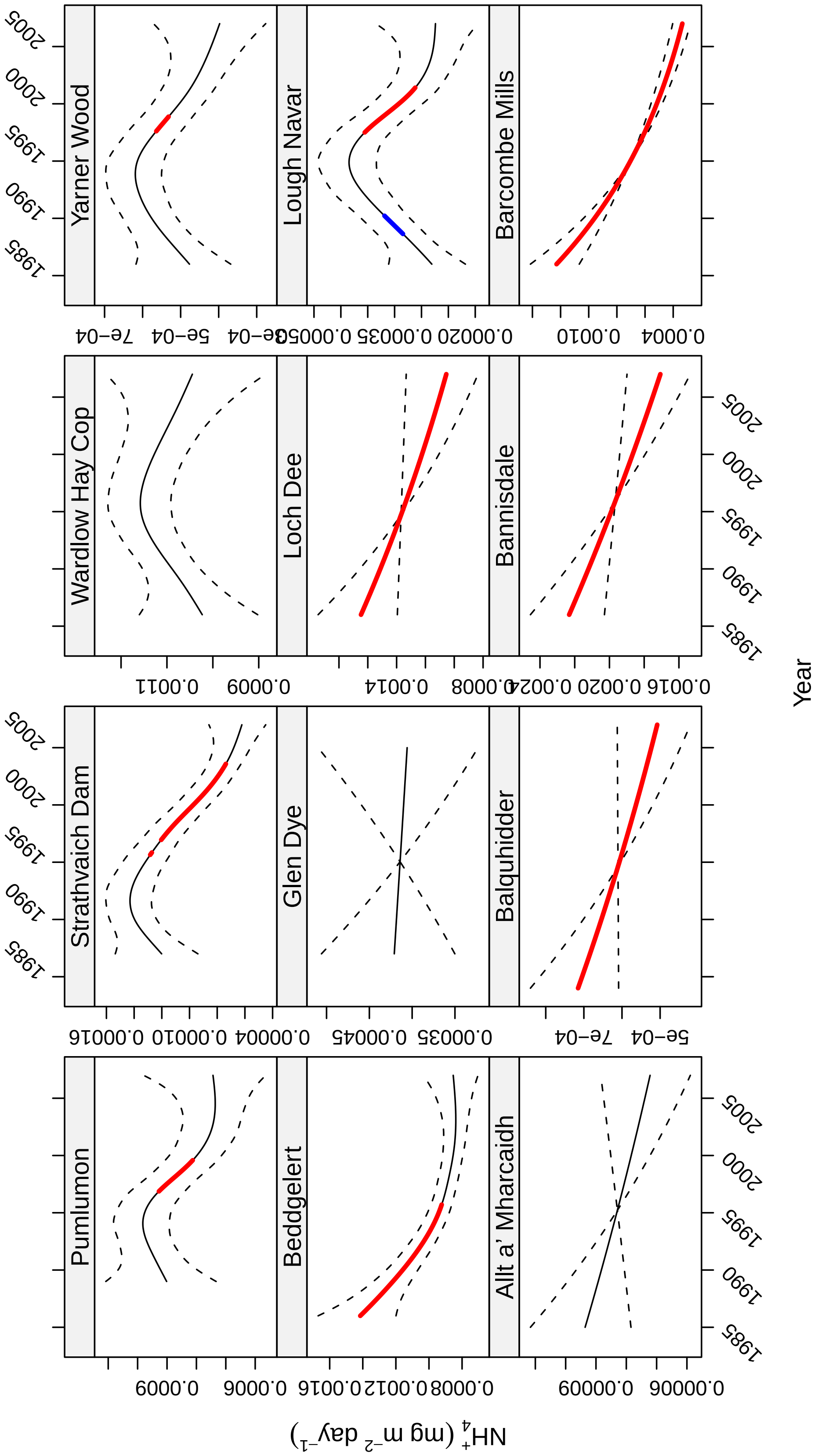

Figure 2.4b: Trends in precipitation weighted NH_4^+-N in bulk deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively.

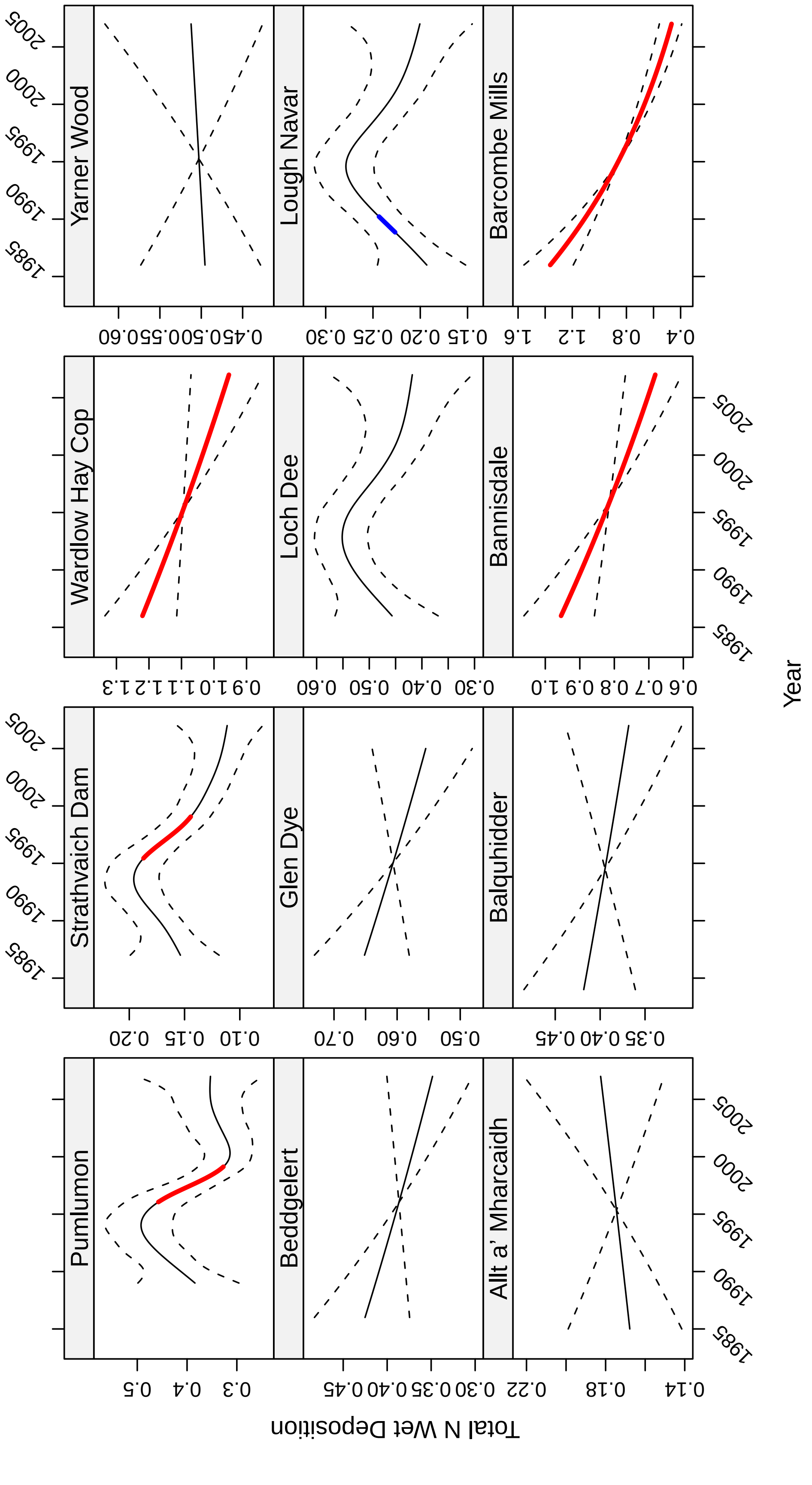

Figure 2.5a: Trends in total nitrogen (mg N l^{-1}) concentration in bulk deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively.

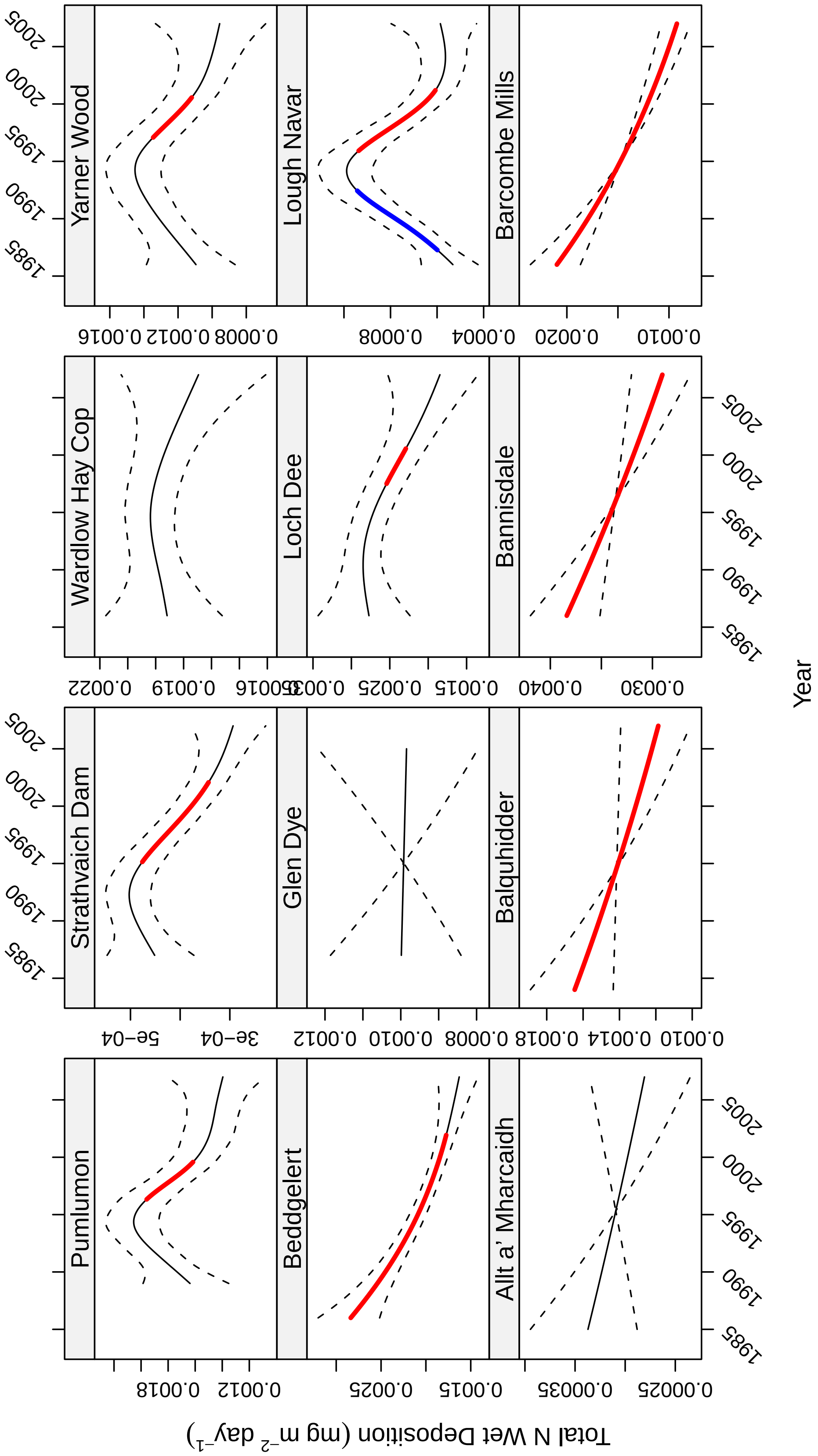

Figure 2.5b: Trends in precipitation weighted total nitrogen in bulk deposition at 12 ADMN bulk deposition sites. Blue and red lines indicate significant increasing and decreasing trends, respectively.

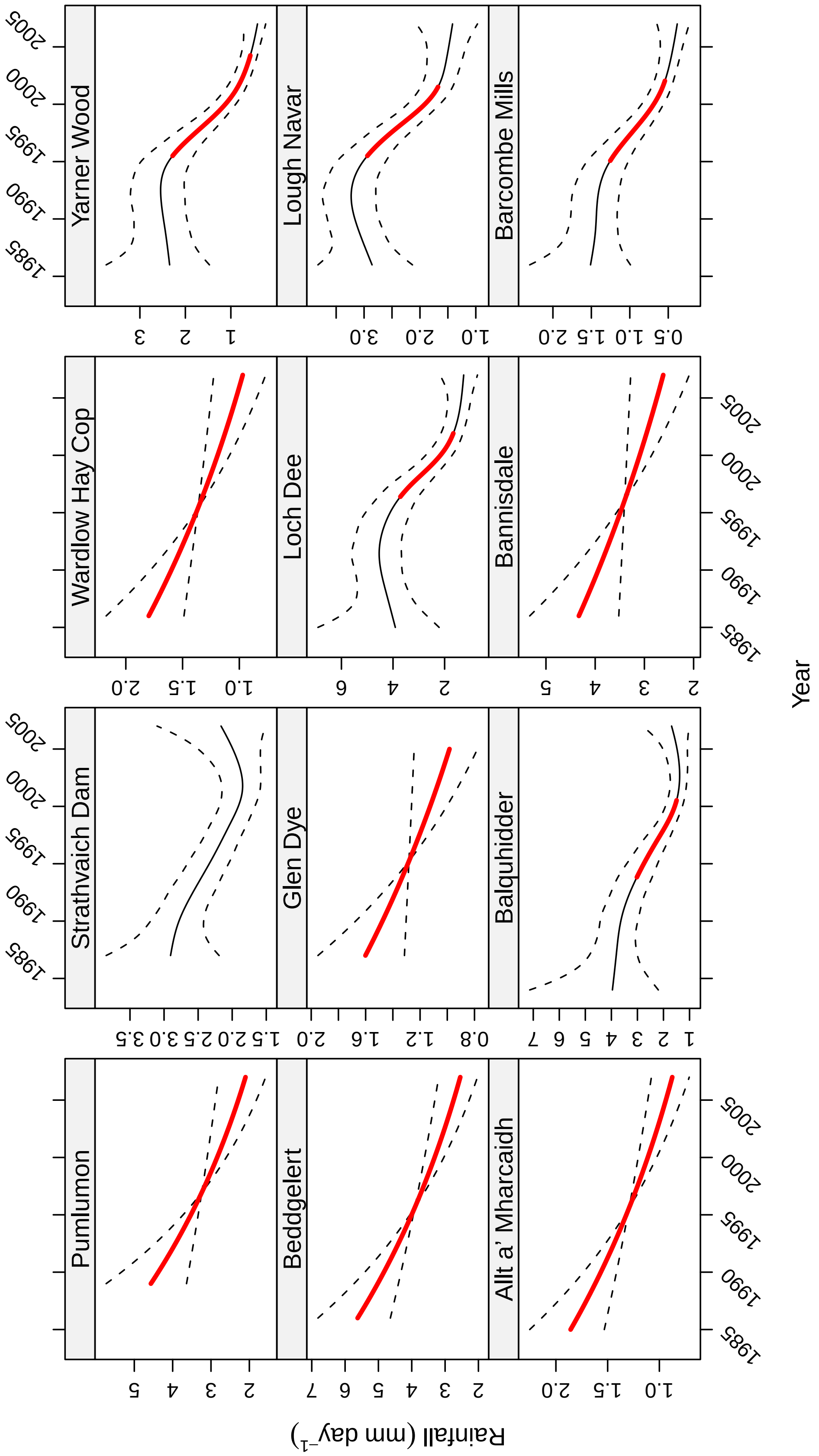

Figure 2.6: Fitted trends in daily mean rainfall (from bulk collectors) at ADMN sites matched to AWMN sites – see text for explanation.

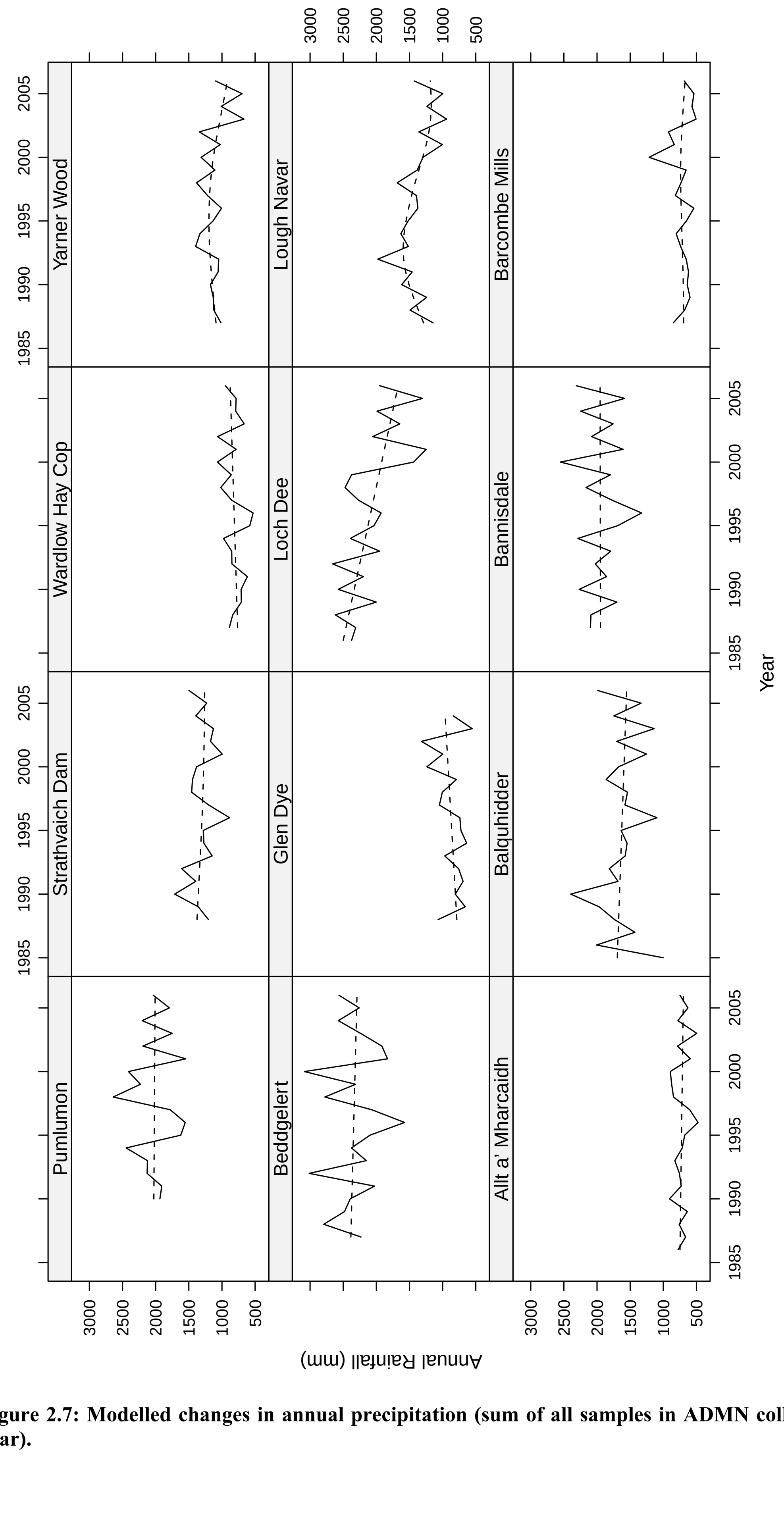

Figure 2.7: Modelled changes in annual precipitation (sum of all samples in ADMN collector within a year).

2.5. References

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3. Hydrochemistry

Don Monteith, Chris Evans, Gavin Simpson and Chris Curtis.

3.1. Introduction

In the three previous Acid Water Monitoring Network (AWMN) five yearly interpretative reports (i.e, Patrick *et al*., 1995; Monteith & Evans, 2000; Monteith & Evans, 2005) hydrochemical data were assessed by non-parametric Mann-Kendall analysis to determine the likelihood of monotonic change over time, while the strength of trends were described using the Sen statistic, to provide an estimate of the average change in units of concentration per year. The latter is a linear statistic (i.e. a slope) and has been valuable, for example, in describing geographical variation in the rate of change in non-marine sulphate concentration ($xSO4^{2-}$), or assessing the relationship between rates of change in drivers and responses, e.g. xSO_4^{2-} versus acid neutralising capacity (ANC) across the Network.

While these methods have been effective in quantifying the extent and relative magnitude of hydrochemical changes, AWMN time-series are now sufficiently long to merit the use of statistical techniques that enable a more detailed investigation of temporal behaviour. This has several benefits:

While long-term reductions in the chief agent of acidification, xSO_4^{2-}, are clear across the Network, change has been far from linear.

Some variables, e.g. nitrate (NO_3^-), show substantial inter-annual variability that is very poorly characterised by a linear trend.

For these long time-series, linear statistics alone have limited application for investigating the links between drivers and responses at the individual site scale.

Here we use a combination of additive modelling, derivative estimates and estimates of the long-term change to summarise variation and change in a range of key hydrochemical determinands. Additive models extend the linear regression model to include arbitrary smooth functions of one or more model covariates. This allows flexible relationships between response and covariates to be modelled whilst allowing the form of the relationship to be determined from the data themselves. In the case of the time-series models fitted here, it is necessary to know whether features in the fitted trends are significantly increasing or decreasing. This significance is estimated using the first derivatives of the fitted spline for the trend, computed using finite differences. A confidence interval, here 0.95 (95%), for the derivative is computed, which allows the identification of intervals of the spline where the derivative is significantly different from zero, i.e. significantly increasing or decreasing. The portions of the fitted trends that are significantly changing are identified in the plots using a thicker, coloured, line for the trend. In these plots, red indicates significantly decreasing and blue significantly increasing trends.

Box-plots are used within this chapter to summarise the data in a way that emphasises inter-annual variability and long-term trends. Data are often not available for the full first year, while records from all sites terminate at the end of the first quarter of 2008. In some cases this results in extreme values at the beginning and end of these records. These are unlikely to be representative of the full year and should be ignored when assessing these plots by eye. The absence of complete years of data at either end of these records at most sites has no influence on the shape of the fitted smoothed trend. The primary time-series data for a range of key hydrochemical parameters are provided in Appendix 3, Figure 1.

This chapter comprises two sections. In the first we explore the nature of variability in individual hydrochemical variables, representing monthly or quarterly water samples for streams and lakes respectively, using statistical analyses to answer the following questions:

- Has chemistry changed significantly over time in any manner, i.e. what is the likelihood that the data show change beyond seasonality and random variability?
- Where chemical change is statistically significant, is it monotonic or characterised by oscillations with no obvious long-term change?
- Where data indicate long-term change:
    - By how much have measurements changed between the beginning and end of the record?
    - Is the change linear or restricted to specific periods?
    - To what extent are trends coherent between sites?

We also consider the extent to which surface water hydrochemical trends may be linked to those in bulk deposition, by relating results to those in the previous chapter.

In the second section we provide a more detailed Network-level assessment of trends and relationships between variables

Time-series plots of the observed data for each of the chemical determinands discussed here can be found in Appendix 3 together with the fitted trends (shown in this chapter) and the residuals for each of the models (see Appendix 3 Figs. 1-33). Appendix 3 also includes tables showing the Sen slope estimates, expressed per year, for key determinands observed at AWMN sites (Appendix 3, Table 1), change estimates for key determinands observed at AWMN sites based on Sen slopes (Table 2) and summary of trends for each of the key determinands discussed here (Tables 3-13).

3.2. Trends in Hydrochemistry

3.2.1. Acid anions

3.2.1.1. Non-marine sulphate

In keeping with convention, non-marine sulphate (xSO_4^{2-}) concentration in this assessment is estimated by assuming that SO_4^{2-} ions accompany chloride (Cl^-) ions in sea-salt aerosol in fixed proportion. It is assumed that all Cl^- in water samples is derived from sea-salt.

The concentration of xSO_4^{2-} in AWMN lakes and streams, representing the chief acidifying anion in most sensitive UK freshwaters, has fallen substantially across the Network over the 20-year period (Fig. 3.1), largely in line with reductions observed in bulk deposition concentrations at corresponding Acid Deposition Monitoring Network (ADMN) sites.

Comparisons with deposition data support earlier observations that xSO_4^{2-} concentrations are generally highly responsive to reductions in xSO_4^{2-} deposition at most sites (Cooper *et al.*, 2005). Surface water concentrations are markedly higher, but have also declined most rapidly, at sites in central and southeast England, close to major sulphur (S) emission sources. Concentrations and rates of change decline in a north-westerly direction. Deposition loads based on bulk precipitation are mostly consistent with these observations.

At several sites, reductions in xSO_4^{2-} concentration are relatively monotonic, but are far from linear. Derivative analysis of trends indicates that concentrations at most sites showed significant declines in a five-year period in the latter half of the 1990s only (Fig. 3.2). This pattern is also seen in deposition loads at most sites, although in many cases the deposition trend continues to the present (Chapter 2).

Many sites show irregular declines in xSO_4^{2-}, in some cases with a slight increase early in the record which is not seen in the bulk deposition trends. An exception is the ADMN site Lough Navar, which shows an early increase in xSO_4^{2-} that broadly matches the trend at the corresponding AWMN site Coneyglen Burn.

The early increases in estimates of xSO_4^{2-} concentration in AWMN sites are confined to sites close to the Irish Sea. Given these increases are not observed in bulk deposition it is possible that concentrations were underestimated in the early phase of monitoring as a result of complications caused by high sea-salt inputs at the time. One explanation provided in earlier reports is that SO_4^{2-} ions behaved less conservatively (i.e. they adsorbed more to the soil) during periods of high sea-salt deposition. Sulphate is derived both from industrial pollutants and from sea-salt. Adsorption of SO_4^{2-} to sesquioxide surfaces in the mineral soil is pH dependent and could be enhanced during sea-salt deposition events. Chloride ions are not significantly affected by this process and therefore pass more quickly into surface waters, but as the component of SO_4^{2-} deemed to be of marine origin is determined from the Cl^- concentration, the xSO_4^{2-} fraction could be underestimated at this time. Conversely the xSO_4^{2-} fraction might later be overestimated as soil acidity declines and some SO_4^{2-} is desorbed.

Uniquely for the AWMN, surface-water concentrations at Narrator Brook in south-west England show an overall slight increase in xSO_4^{2-} although this is not monotonic and includes a period of decline between 1995 and 2000. Bulk deposition trends at nearby Yarner Wood show stable loads to 1995 with a subsequent significant downturn. The soils at Narrator Brook, a site that was not glaciated, appear to have a greater capacity for S adsorption than elsewhere in the Network (older soils tend to have greater S adsorption capacity). This may account for the low degree of temporal variation, and lack of clear response to changes in deposition at this site.

Since 2000 most sites show little further significant trend in xSO_4^{2-} concentration despite continuing declines in bulk deposition, and for the majority, concentrations remain between three to six times higher than those recorded in the least deposition-impacted sites in the AWMN, Loch Coire nan Arr and Loch Coire Fionnaraich in the far north-west of Scotland.

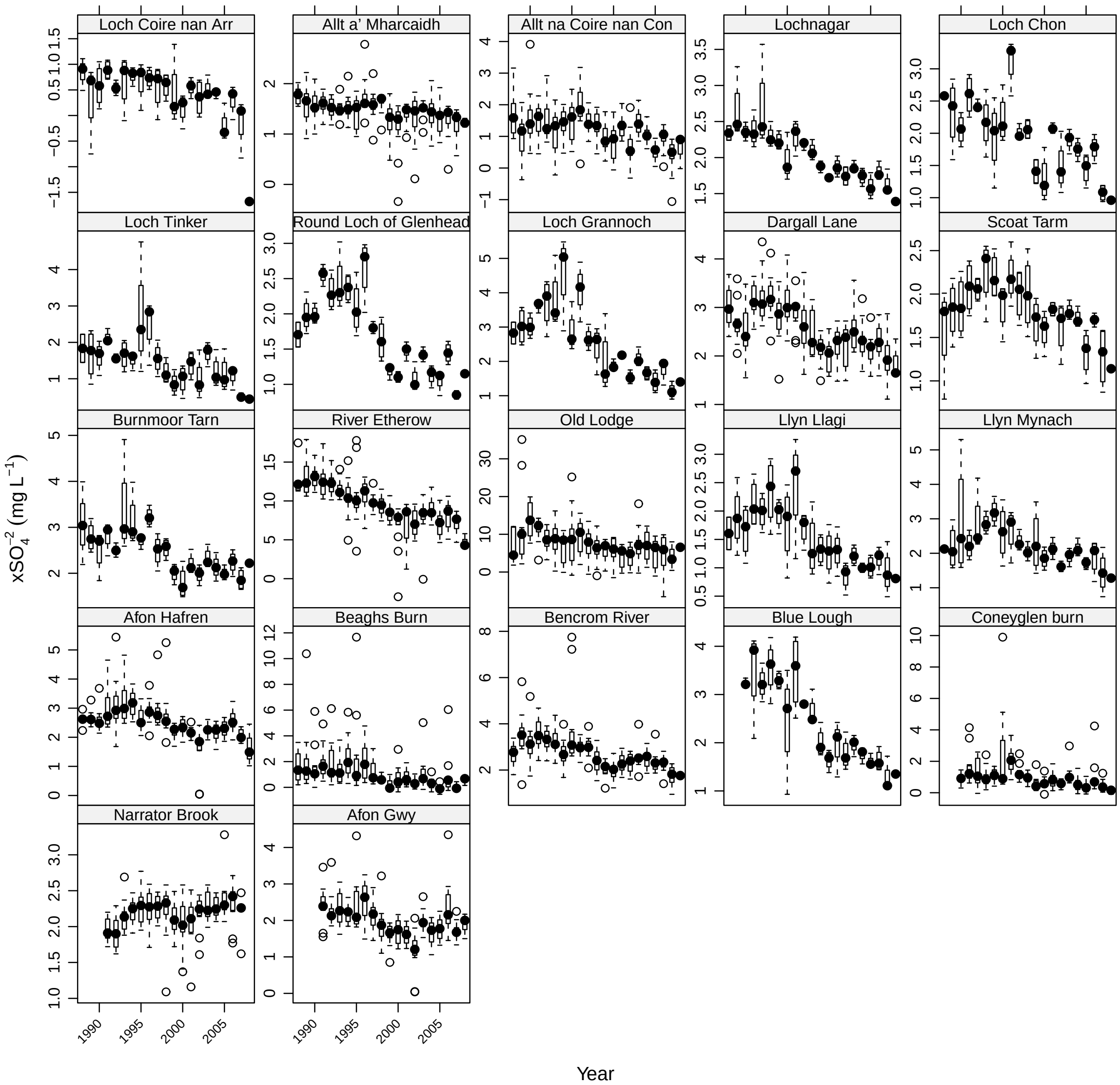


Figure 3.1: **Box plots of mean annual xSO_4^{2-} concentration (mg l^{-1}) by year. The mean for the last year of monitoring is based on Jan/Feb/March data only.**

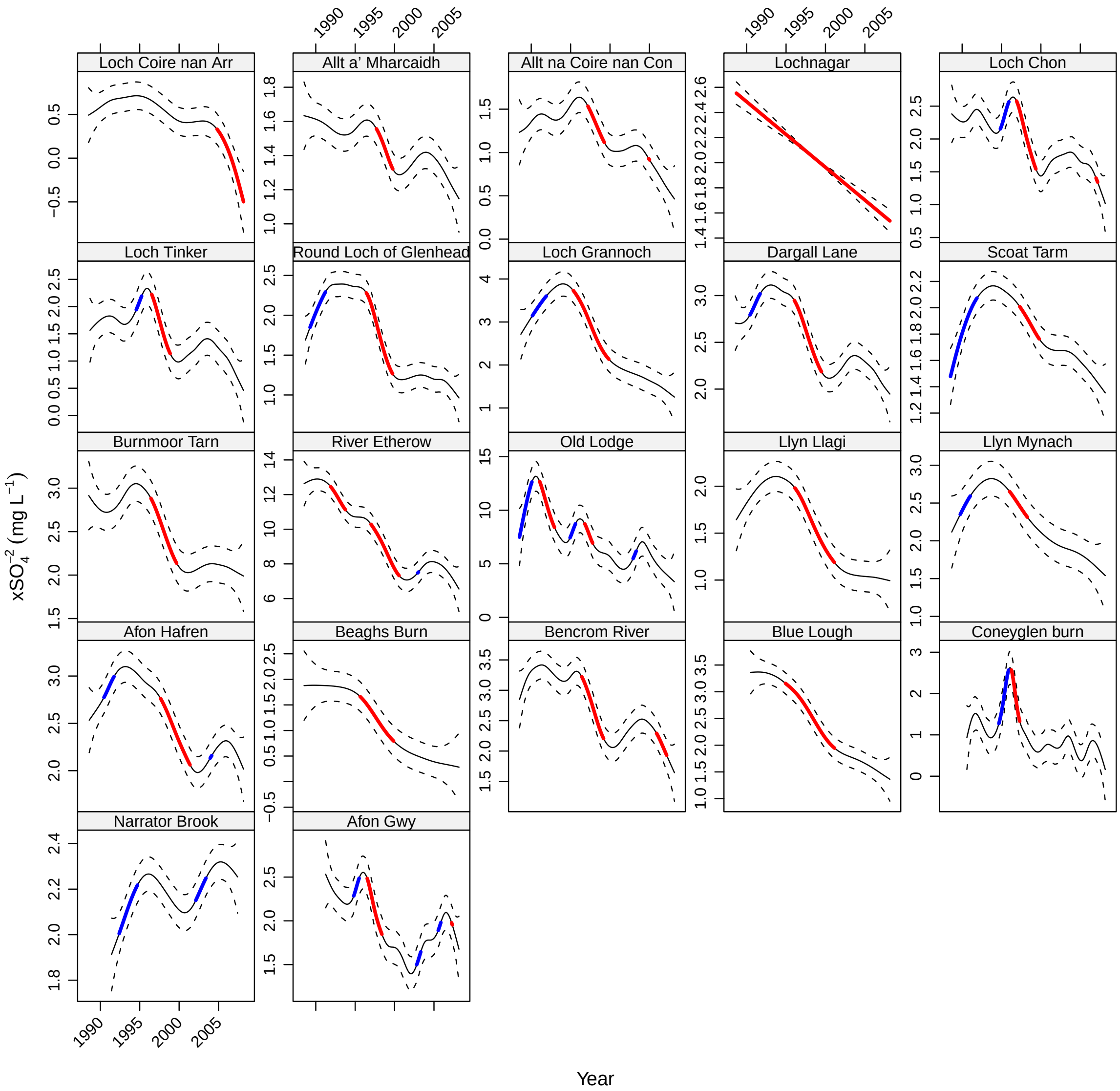


Figure 3.2: **Fitted trends in xSO_4^{2-} (mg l^{-1}). Periods of significant change in the fitted trend, determined by derivative analysis, are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).**

3.2.1.2. Nitrate

The concentration of NO_3^-, the secondary acidifying anion at most AWMN sites, shows substantial inter-annual variability at all sites where concentrations rise above the limit of detection for at least part of the year (Fig. 3.3).

Concentrations show marked seasonality at all sites, at least in part due to seasonal variation in N mineralization and biological uptake, with peak concentrations normally occurring in early spring. However, bulk deposition shows a corresponding seasonal pattern when modelled across all sites, suggesting that patterns in surface waters may not be dictated solely by terrestrial processes (Fig. 3.4). This is a potentially significant observation not previously reported.

Fifteen sites show statistically significant long-term trends, i.e. significant temporal variation that is neither seasonal nor random, and seven of these (the River Etherow, Scoat Tarn, Llyn Llagi, Afon Hafren, Afon Gwy, Beagh's Burn, and Blue Lough) show evidence for a long-term slight decline in concentrations (Fig. 3.5). Concentrations and/or loads of NO_3^- in bulk deposition decline significantly for at least short periods in most sites, with Beddgelert (for Llyn Llagi and Llyn Cwm Mynach) and Balquhidder (for Lochs Chon and Tinker) showing near linear declining trends in deposition load throughout the period of monitoring. In all cases Sen slopes are small relative to those for xSO_4^{2-}. The NO_3^- trend at Llyn Llagi matches that in bulk deposition load at Beddgelert, though Llyn Cwm Mynach does not.

Temporal variation in NO_3^- concentration is relatively coherent among AWMN lakes, and most lakes and streams show a common peak in concentrations in the spring of 1996 following the coldest and driest winter during the 20-year monitoring period. Previously it has been postulated that the high NO_3^- levels in AWMN sites in 1996 resulted from effects of soil freezing (causing the rupture of plant cells and release of nutrients), and restricted terrestrial demand during the relatively cold spring (Monteith *et al.*, 2000). However, trends have diverged since 1996. Several sites have shown subsequent decreases, but concentrations at two, Round Loch of Glenhead and Loch Chon, remain elevated resulting in an overall significant long-term increase. Consequently, as xSO_4^{2-} concentrations have fallen sharply at both sites, the contribution of NO_3^- to the "total acidity" of these surface waters (i.e., $xSO_4^{2-} + NO_3^-$) has risen substantially over the 20 years.

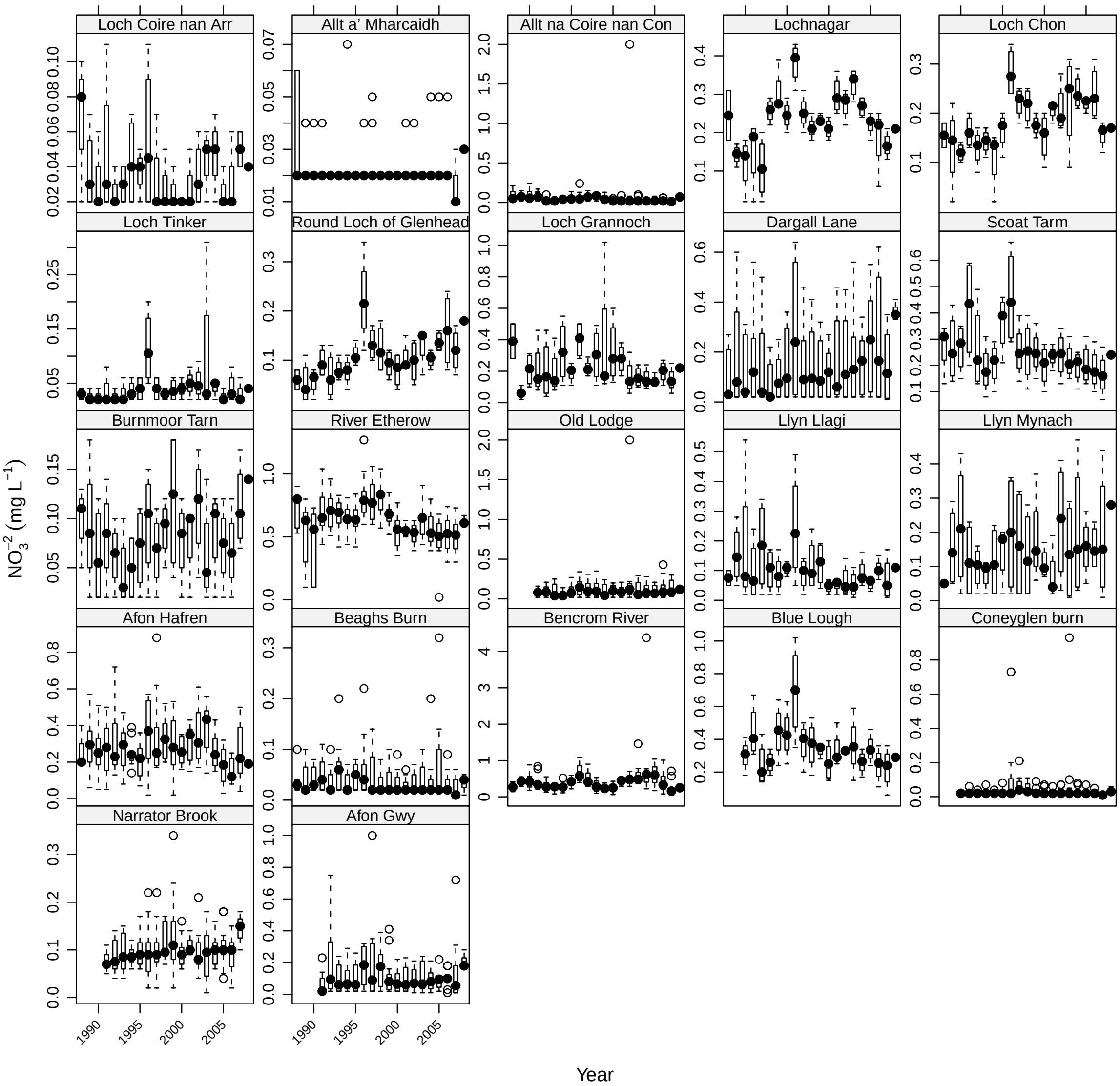


Figure 3.3: Box plots of mean annual NO_3^- concentration (mg l^{-1}) by year. The mean for the last year of monitoring is based on Jan/Feb/March data only.

There is evidence for links between long-term patterns in bulk deposition NO_3^- and surface water concentrations at several co-located sites, but in most cases there appears to be a time lag of 1-2 years, which is too long to be explained solely by hydrological residence times. At other sites there is no obvious relationship between surface water and bulk deposition trends, although some of these ADMN sites are relatively distant from their AWMN 'pairs' and may not be sufficiently representative of the local deposition regime. There is a clear need to investigate these relationships with more rigorous statistical assessments of shorter records from several co-located AWMN sites (e.g. Llyn Llagi, Scoat Tarn, River Etherow, Lochnagar, Beagh's Burn, Loch Chon).

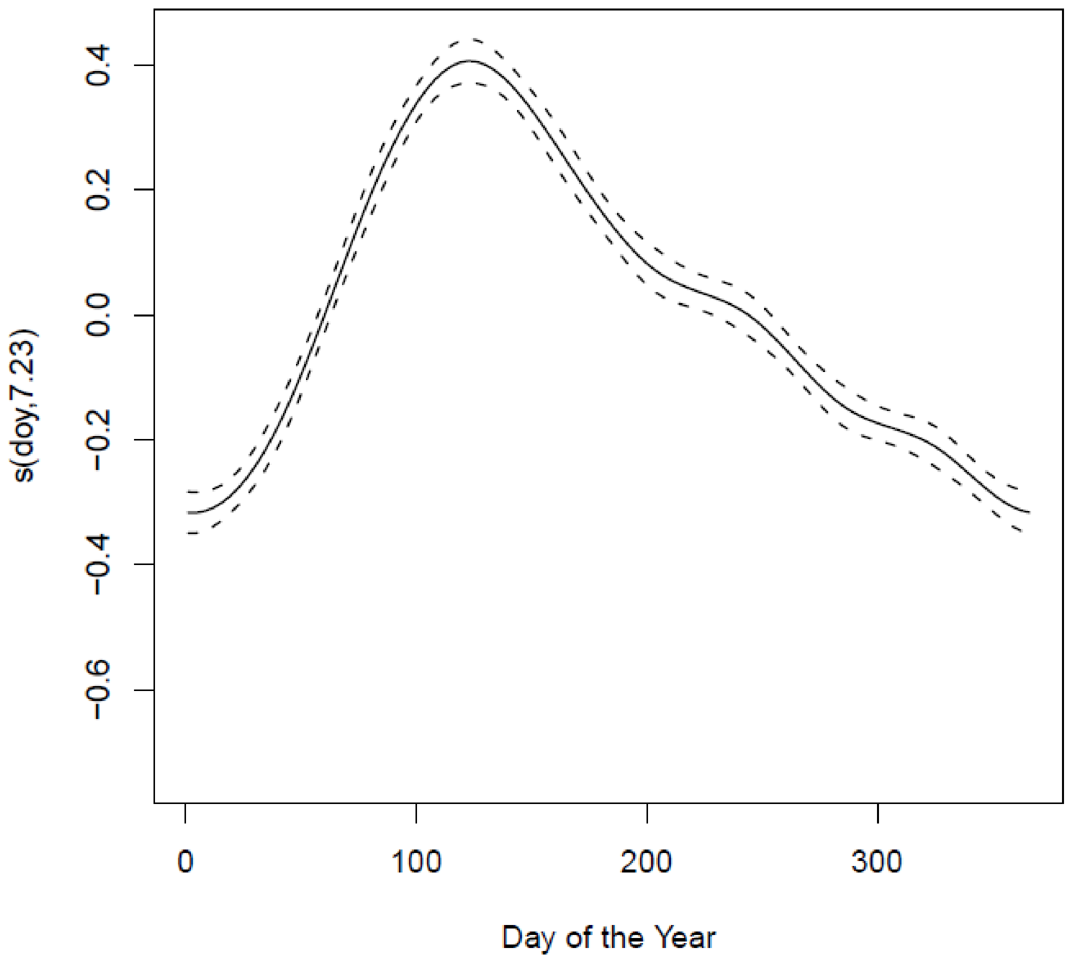


Figure 3.4 Seasonal pattern in N deposition for all co-located ADMN sites. The y axis is the centred smooth function for day of the year (7.32 degrees of freedom).

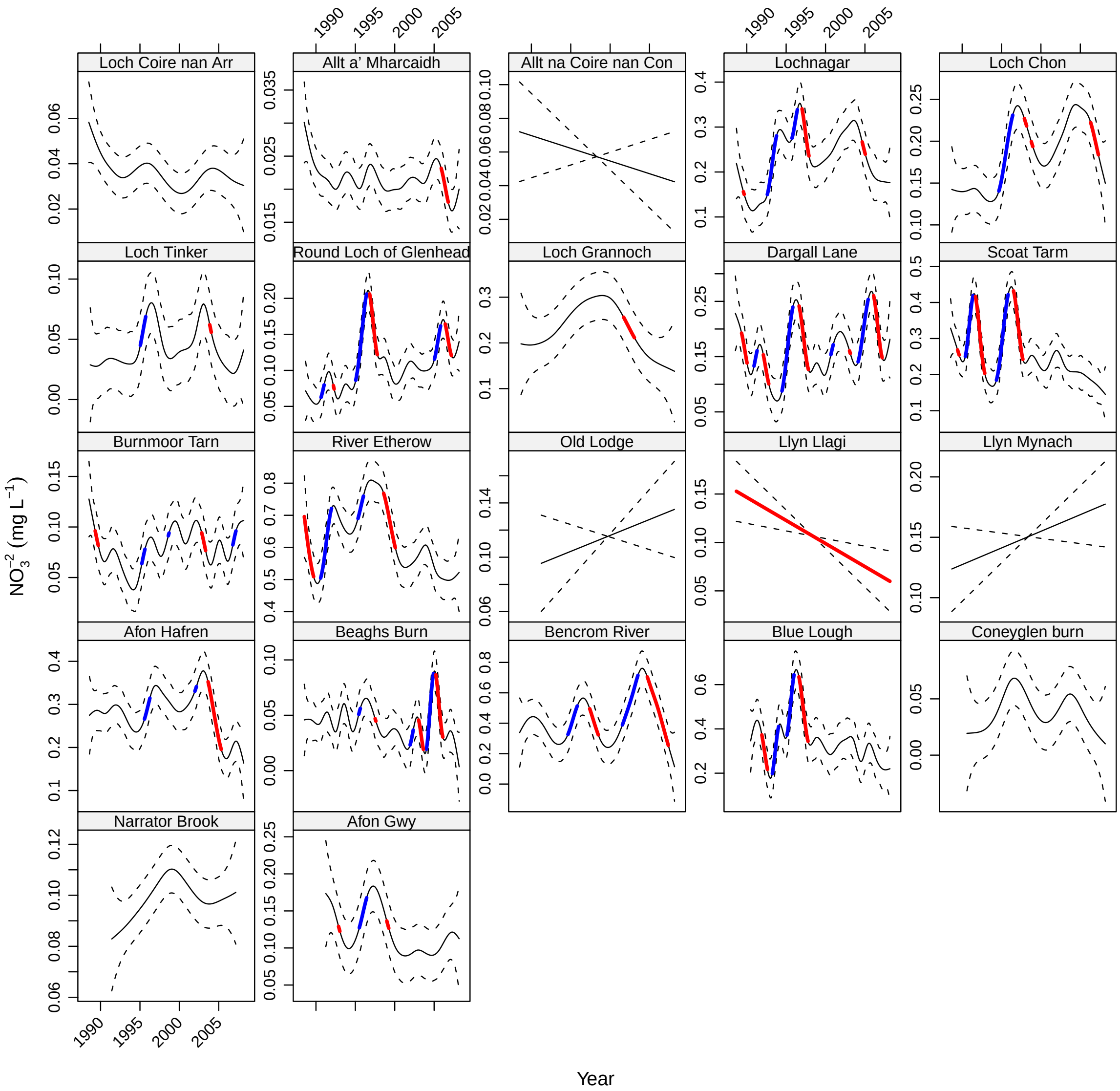


Figure 3.5: Fitted trends in NO_3^- (mg l^{-1}). Periods of significant change in the fitted trend, determined by derivative analysis, are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).

3.2.1.3. Chloride

Chloride in AWMN lakes and streams, as noted above, is derived primarily from sea-salt which is deposited episodically, mainly during winter storms and predominantly in areas close to the coast. In general, Cl^- ions are thought to behave relatively conservatively in catchments, being less affected by anion adsorption, biological retention and redox processes than SO_4^{2-} and NO_3^-, and thus more mobile within soils. Chloride concentration in AWMN waters therefore provides an indication of the frequency and intensity of sea-salt episodes, during which cations from sea-salt displace hydrogen and aluminium ions from soil exchange sites resulting in short term acidifying events.

The state of UK winter climate around the onset of AWMN monitoring was unusually extreme. Evans *et al*. (2001) have previously identified a link between sea-salt events and a winter high North Atlantic Oscillation (NAO) Index, and argued that as a result, sea-salt episode activity is likely to follow a similar decadal periodicity to that shown by the NAO. An even stronger relationship is now apparent between Cl^- concentrations at several AWMN sites and the Arctic Oscillation (AO) Index (see Chapter 10). The AO Index has shown a gradual ramping toward more positive values since the 1950s and this has been attributed to anthropogenic forcing from either atmospheric CO_2 increases and/or stratospheric ozone decline (Yukimoto and Kodera, 2005). The relationship identified between Cl^- concentrations and the AO suggests that conditions for generating frequent and intense sea-salt events in the early part of the AWMN record were perhaps unprecedented in the past 60 years at least, and are therefore likely to have added, with unprecedented effect, to the acid stress imposed by anthropogenic pollution (from S and N) over this period.

Fifteen AWMN lakes and streams show significant trends in Cl^- concentration. Most show reductions of between -0.8 and -3.0 μeq l^{-1} yr^{-1}.

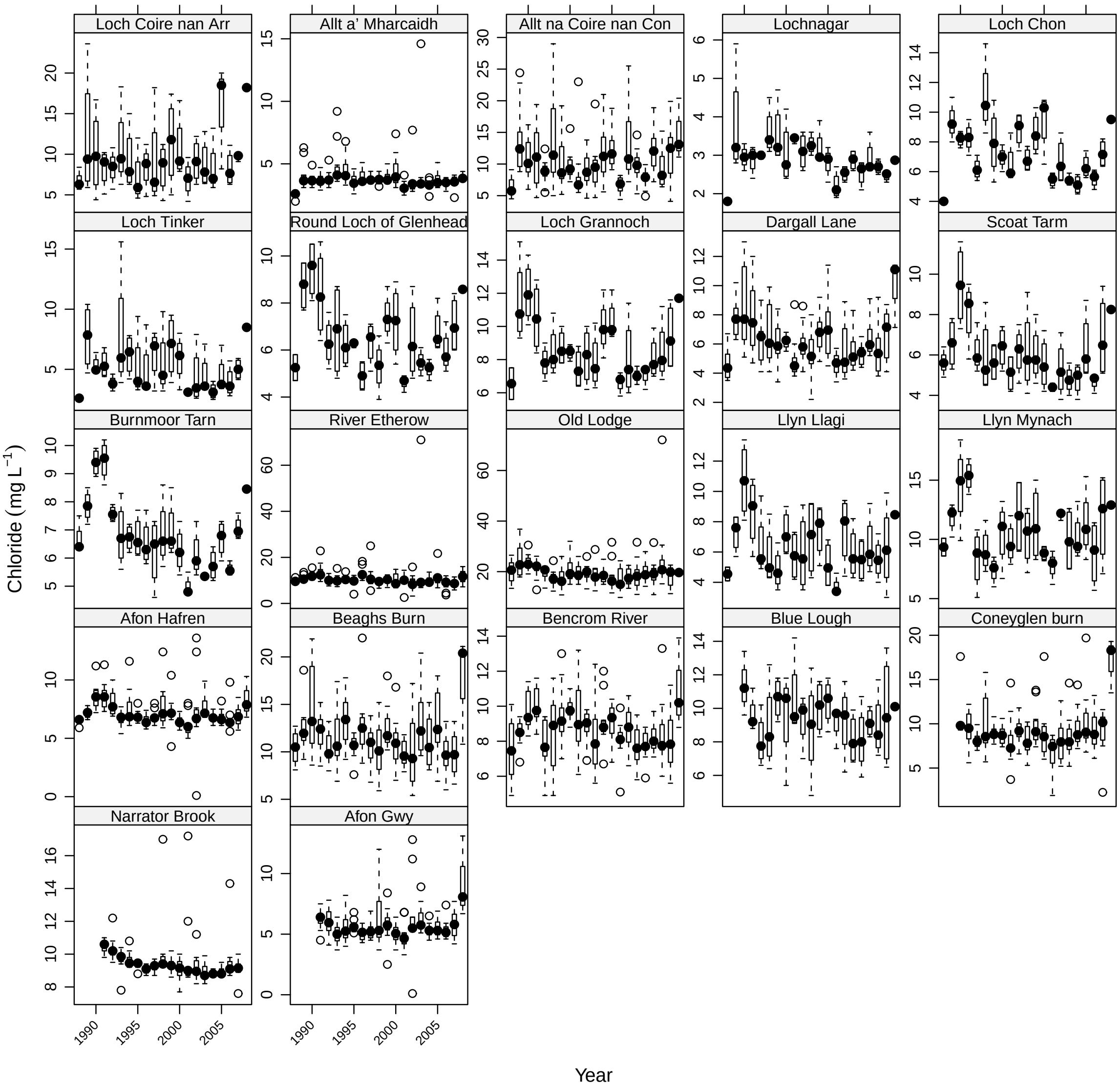


Figure 3.6: Box plots of mean annual Cl^- concentration (mg l^{-1}) by year. The mean for the last year of monitoring is based only on Jan/Feb/March data only.

Several sites close to the east coast of the Irish Sea, (including Round Loch of Glenhead, Loch Grannoch, Dargall Lane, Scoat Tarn, Burnmoor Tarn, Llyn Llagi, Afon Hafren), Bencrom River in the Mourne Mountains and Old Lodge in the Ashdown Forest show similar long-term trends with a particularly large peak in concentration centred around 1990, slightly smaller peaks around the turn of the century and, most recently, during the winter and spring of 2007 and 2008 (Figs. 3.6 & 3.7). This apparent decadal periodicity corresponds closely to that anticipated by Evans *et al.* (2001) with respect to the NAO influence.

Two of the strongest Sen slopes were recorded for the central and southern England sites, River Etherow and Old Lodge, where xSO_4^{2-} concentrations fell most rapidly. This raises the question as to whether a proportion of Cl^- decline in some regions may have been derived from reductions in anthropogenically derived Cl^-, i.e. in the form of hydrochloric acid (HCl) from the burning of coal with high Cl^- content.

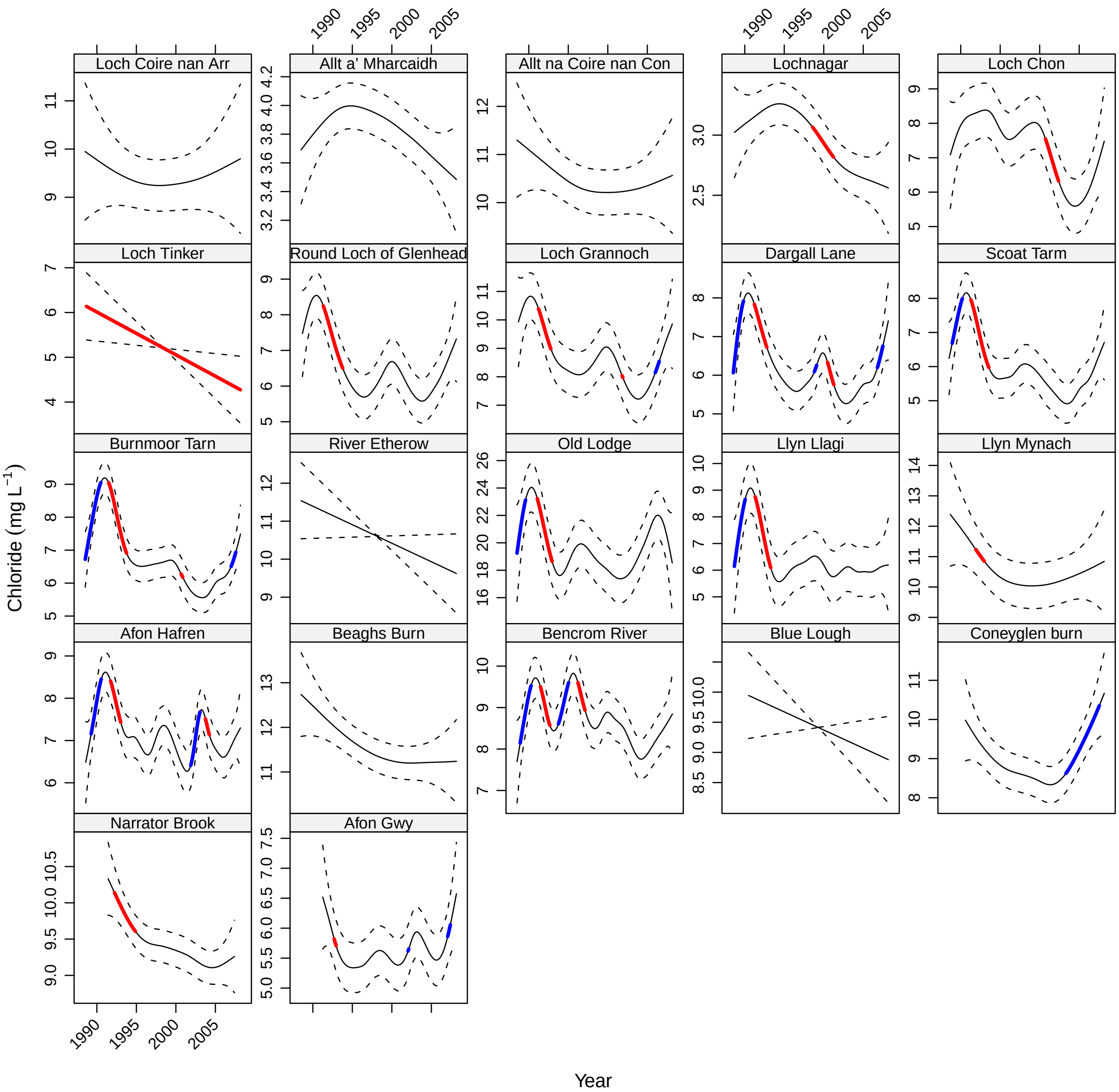


Figure 3.7: Fitted trends in Cl^- (mg l^{-1}). Periods of significant change in the fitted trend, determined by derivative analysis, are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).

Ongoing analyses suggest a significant role of this decreasing non-marine chloride in contributing to recovery from acidification. HCl emissions decreased by over 90% during the 1990s, but changes in non-marine Cl^- are hard to disentangle from fluctuating marine inputs in the AWMN dataset. However, analysis of other datasets (i.e. the Acid Deposition Monitoring Network and the Environmental Change Network) suggest that reductions in non-marine Cl^- deposition in some areas may have been of comparable magnitude to those in non-marine SO_4^{2-}, thus representing an important additional driver of recovery.

Trends in Cl^- are not discernible for sites in northern Scotland (Loch Coire nan Arr, Allt na Coire nan Con or Allt a' Mharcaidh), at the River Etherow in the southern Pennines, Llyn Cym Mynach in north Wales or Blue Lough in the Mourne Mountains. The Afon Gwy also shows no indication of a trend but these measurements only began in 1991 after the highest concentrations were recorded at several other westerly sites.

Importantly, sea-salt inputs were uncharacteristically low at many AWMN sites for the three years leading up to March 2006, the cut-off for the last AWMN research report (Monteith & Shilland, 2007). The combination of low xSO_4^{2-} and absence of major sea-salt episodes led to exceptionally benign water chemistry over this period.

3.2.2. Trends in acidity

3.2.2.1. pH

Seventeen AWMN sites show statistically significant trends in pH and most of these are effectively monotonic, demonstrating a progressive improvement in water quality (Figs. 3.8 & 3.9) and matching the general trend of increasing bulk deposition pH.

Only five sites do not show significant changes in pH. These are situated in northern Scotland (Loch Coire nan Arr, Allt a' Mharcaidh and Allt nan Coire nan Con), and north Northern Ireland (Beagh's Burn and Coneyglen Burn), the least deposition-impacted regions of the UK. However, bulk deposition pH values at Strathvaich Dam (for Coire nan Arr and Allt na Coire nan Con), Lough Navar (for Beagh's Burn and Coneyglen Burn) and the co-located Allt a' Mharcaidh do show a general increase in pH.

Eight sites (Loch Tinker, Dargall Lane, Scoat Tarn, Burnmoor Tarn, River Etherow, Afon Hafren, Afon Gwy and Blue Lough) show either linear or curvilinear increases in pH. These sites show Sen slopes ranging from 0.017 (Blue Lough) to 0.04 (Llyn Llagi) pH units per year.

For a minority of these sites, (Loch Chon, Scoat Tarn, Afon Gwy and Blue Lough) the change in pH appears significant throughout the monitoring period, but AWMN monitoring at Afon Gwy and Blue Lough began later than most other sites. The progressive rise in pH from 1988 in Loch Chon and Scoat Tarn can mostly be explained by the combined effects of reductions in sea-salt inputs over the first few years, followed by xSO_4^{2-} decline.

Derivative analysis suggests that for the majority of sites showing significant trends (Lochnagar, Round Loch of Glenhead, Loch Grannoch, Dargall Lane, Old Lodge, Afon

Hafren), the most significant improvement in pH occurred in the latter half of the 1990s, over the period that xSO_4^{2-} declined most strongly (Fig. 3.9).

Several sites provide indications of recent reversals in pH from around 2005, but with the exception of Allt na Coire nan Con none of these shifts is significant. There are no corresponding declines in bulk deposition pH at any site, and this behaviour most likely reflects an increase in sea-salt deposition in 2007 and 2008.

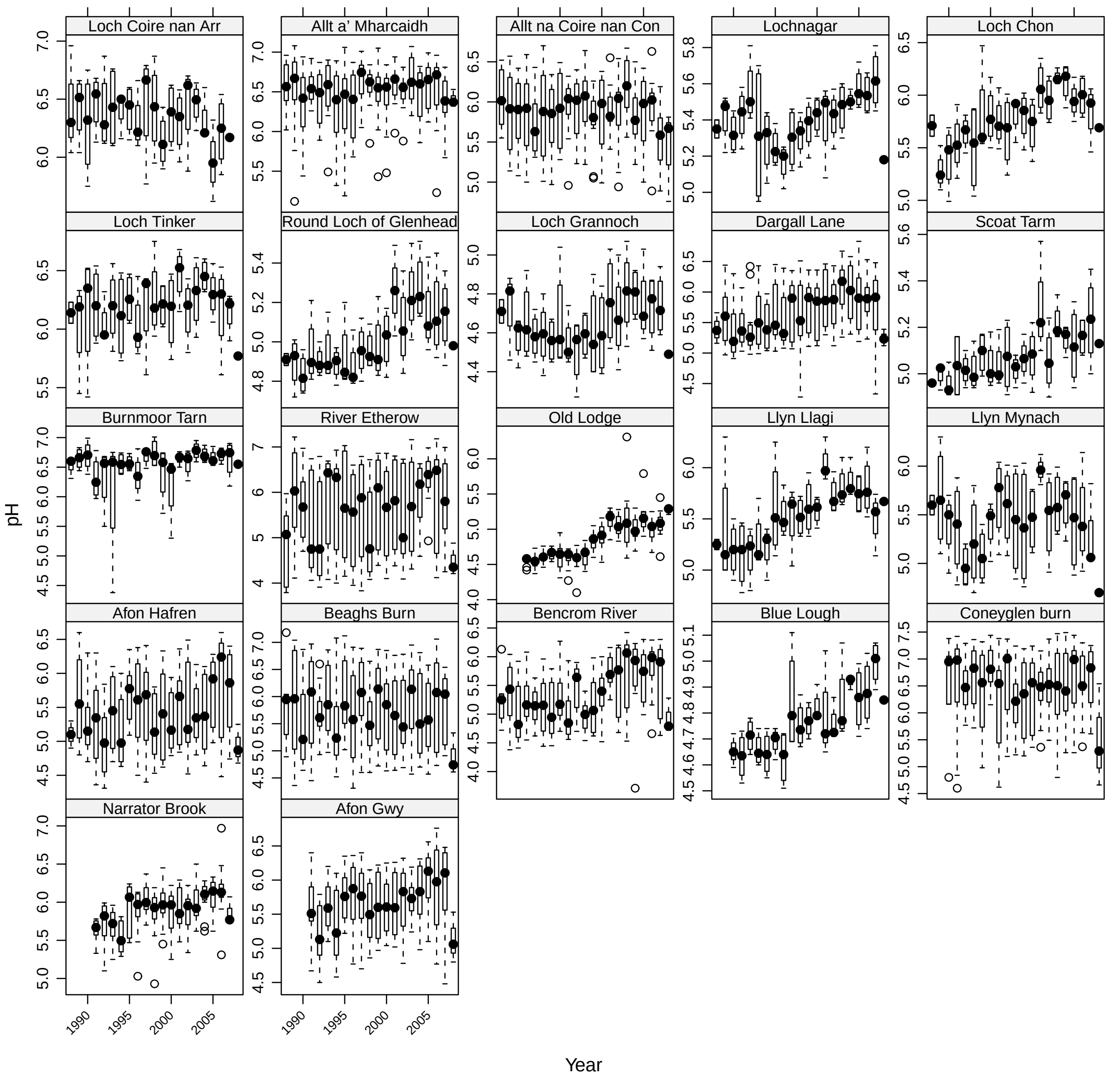


Figure 3.8: Box plots of mean annual pH by year. The mean for the last year of monitoring is based on Jan/Feb/March data only.

Two afforested sites (Loch Grannoch and Llyn Cwm Mynach), and the high montane site Lochnagar show initial declines in pH over the first decade followed by more recent improvement. These sites show no relationship to trends in bulk deposition pH at the corresponding ADMN sites at Loch Dee, Beddgelert and Glen Dye respectively.

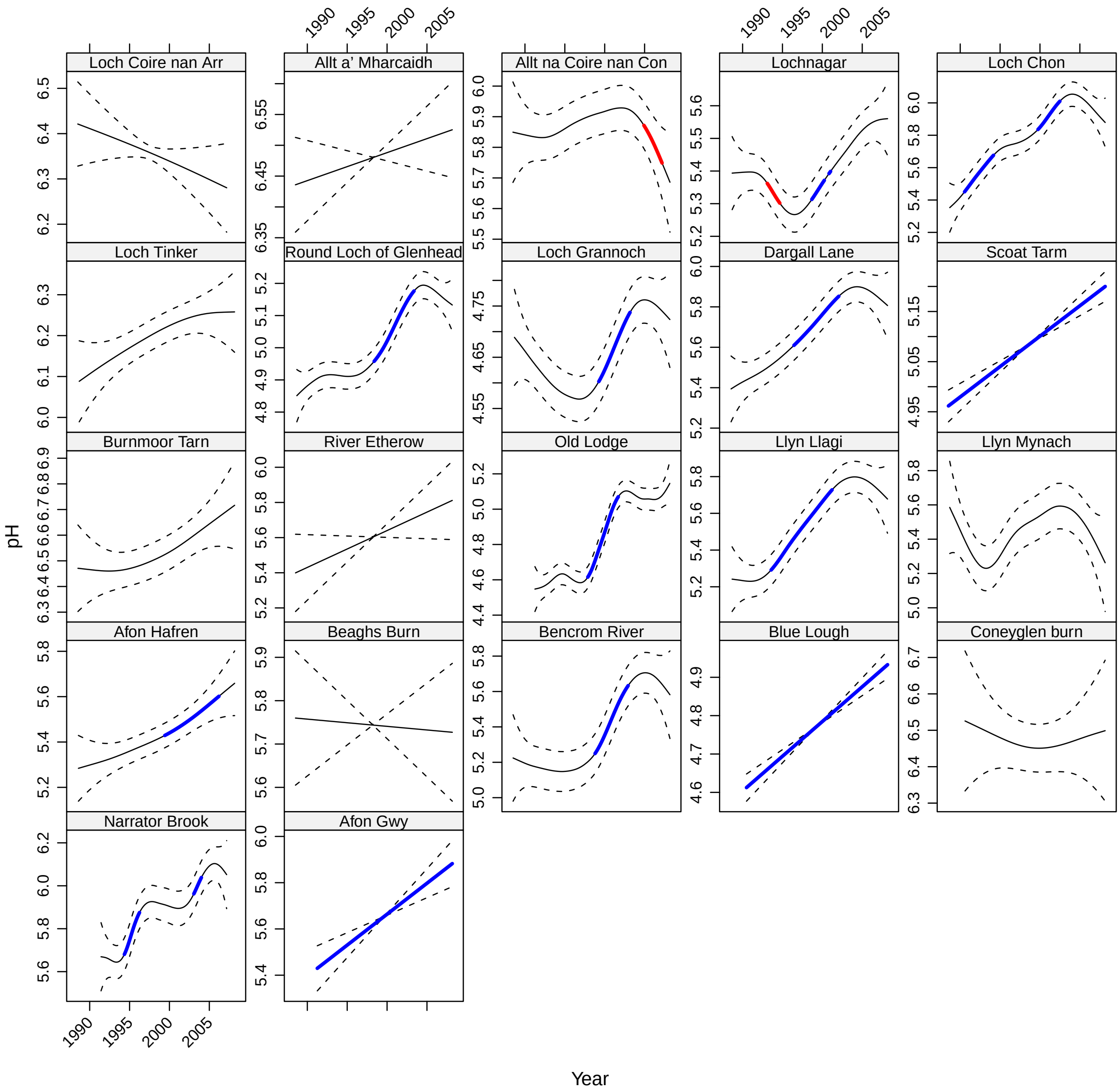


Figure 3.9: Fitted trends in pH. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).

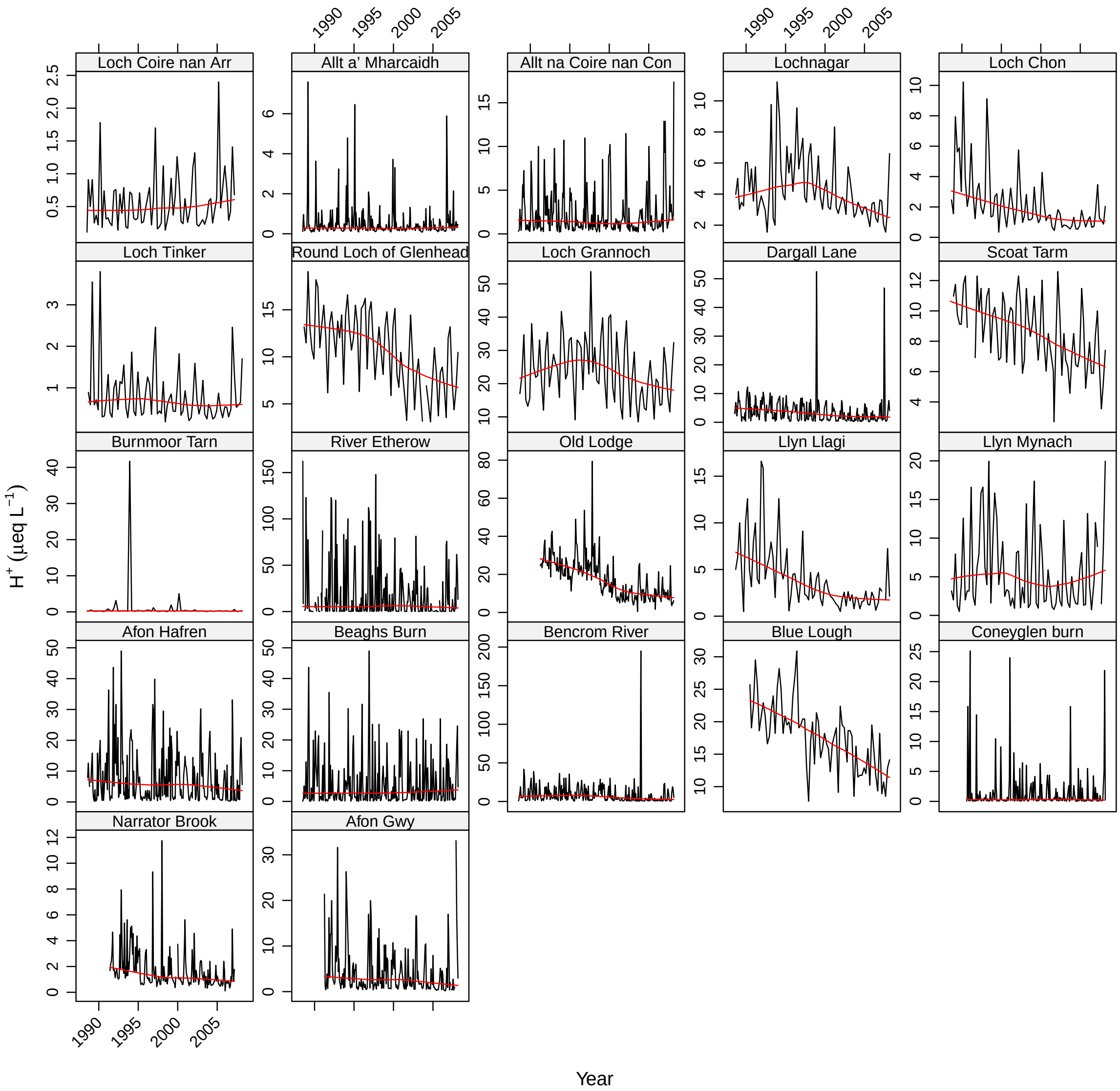


Figure 3.10: Time-series of hydrogen-ion concentration (µeq l^{-1}) in AWMN lakes and streams, with a LOESS smoother fitted as a red line, illustrating the sharp decline in peak concentrations in some sites.

The reduction in acidity at several stream and lake sites is apparent not only in the smoothed trend but also in the magnitude of short term peaks (i.e. the strength of acid episodes that occur during high flow and sea-salt deposition events). This is more clearly seen in the reduction in peak hydrogen-ion concentrations (Fig. 3.10), and is of considerable ecological importance as it is likely that the intensity of acid episodes imposes the limit for biological recovery and the re-establishment of acid-sensitive organisms at stream sites.

3.2.2.2. Labile Aluminium (Labile Al)

Aluminium in ionic form (labile aluminium) is normally only present in freshwater if mineral acids associated with SO_4^{2-}, NO_3^- or Cl^- are passing unneutralised through catchment soils. It is therefore always associated with waters of low pH and is highly toxic to many aquatic organisms in concentrations above *c.* 10 µeq l^{-1}.

Labile Al concentrations have changed significantly at sixteen sites. As with pH, the majority of sites show either linear or curvilinear declines in concentration indicating long-term improvement in water quality (Figs. 3.11-3.13).

The reduction in labile Al is greatest in the more acid sites that initially had the highest concentrations, and declines have been particularly dramatic in Blue Lough, River Etherow, Scoat Tarn and Dargall Lane. The derivative analysis (Fig. 3.11) indicates that at several of these sites, significant reductions in labile Al have occurred throughout most of the monitoring period, in response to early declines in sea-salt deposition and later declines in xSO_4^{2-}.

At some sites, (Allt na Coire nan Con, Round Loch of Glenhead, Afon Hafren and Old Lodge) long-term decline is prefaced by an initial increase in concentrations, while several sites show small increases since 2005. Both are best explained by heightened sea-salt deposition during these periods. However, it is clear that the effect that sea-salt events now have in causing short term peaks in labile Al concentrations is considerably smaller than it was prior to the reduction in xSO_4^{2-} in the late 1990s.

As reported for hydrogen ion concentration, falling labile Al concentrations are accompanied by large reductions in the concentrations of short term peaks (Fig. 3.12) driven by sea-salt and hydrological episodes, and this again is likely to be highly conducive to biological recovery (also see Section 3.3.4).

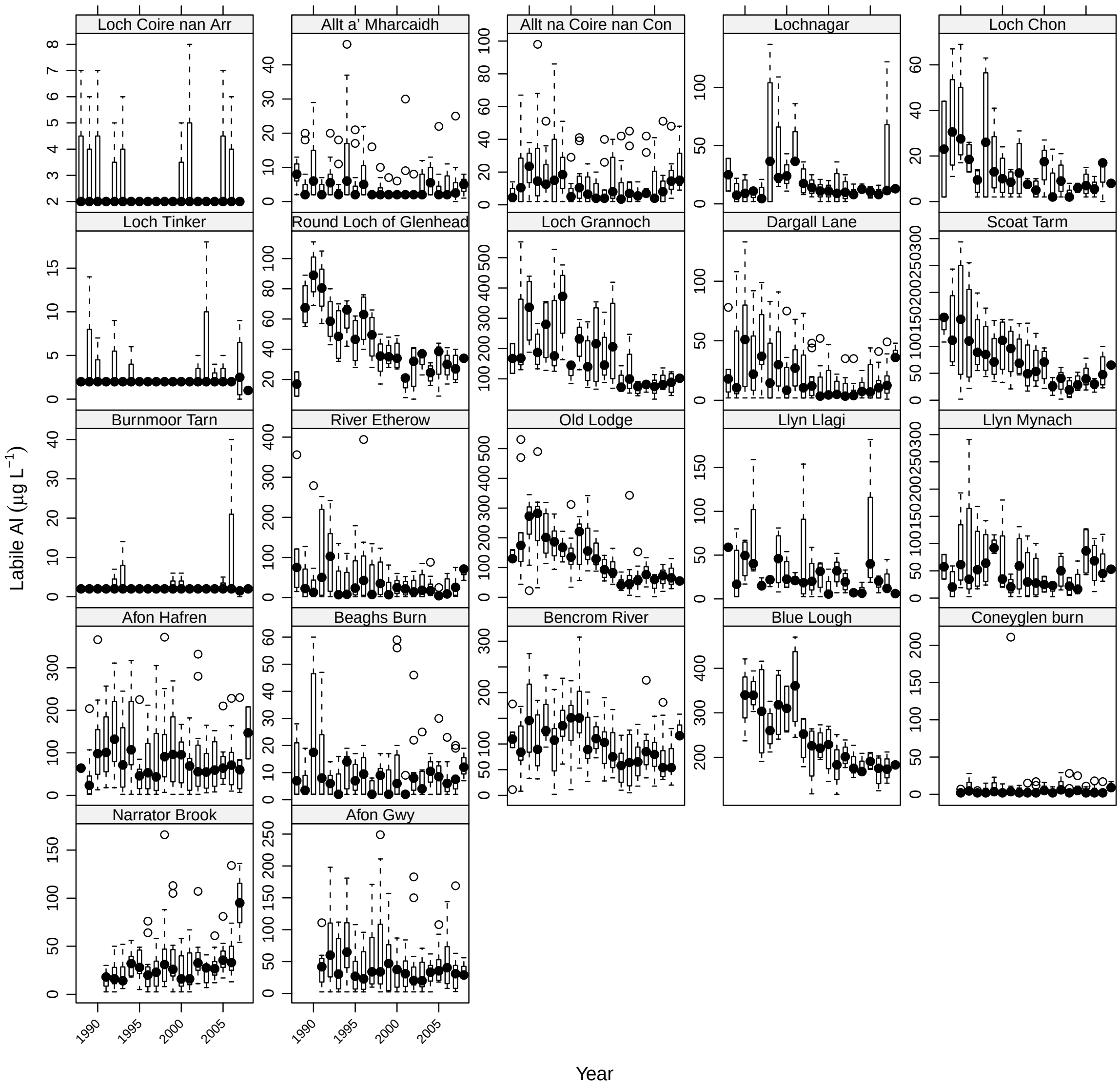


Figure 3.11: Box plots of mean Labile Aluminium concentration ($\mu g\ l^{-1}$) by year. The mean for the last year of monitoring is based on Jan/Feb/March data only.

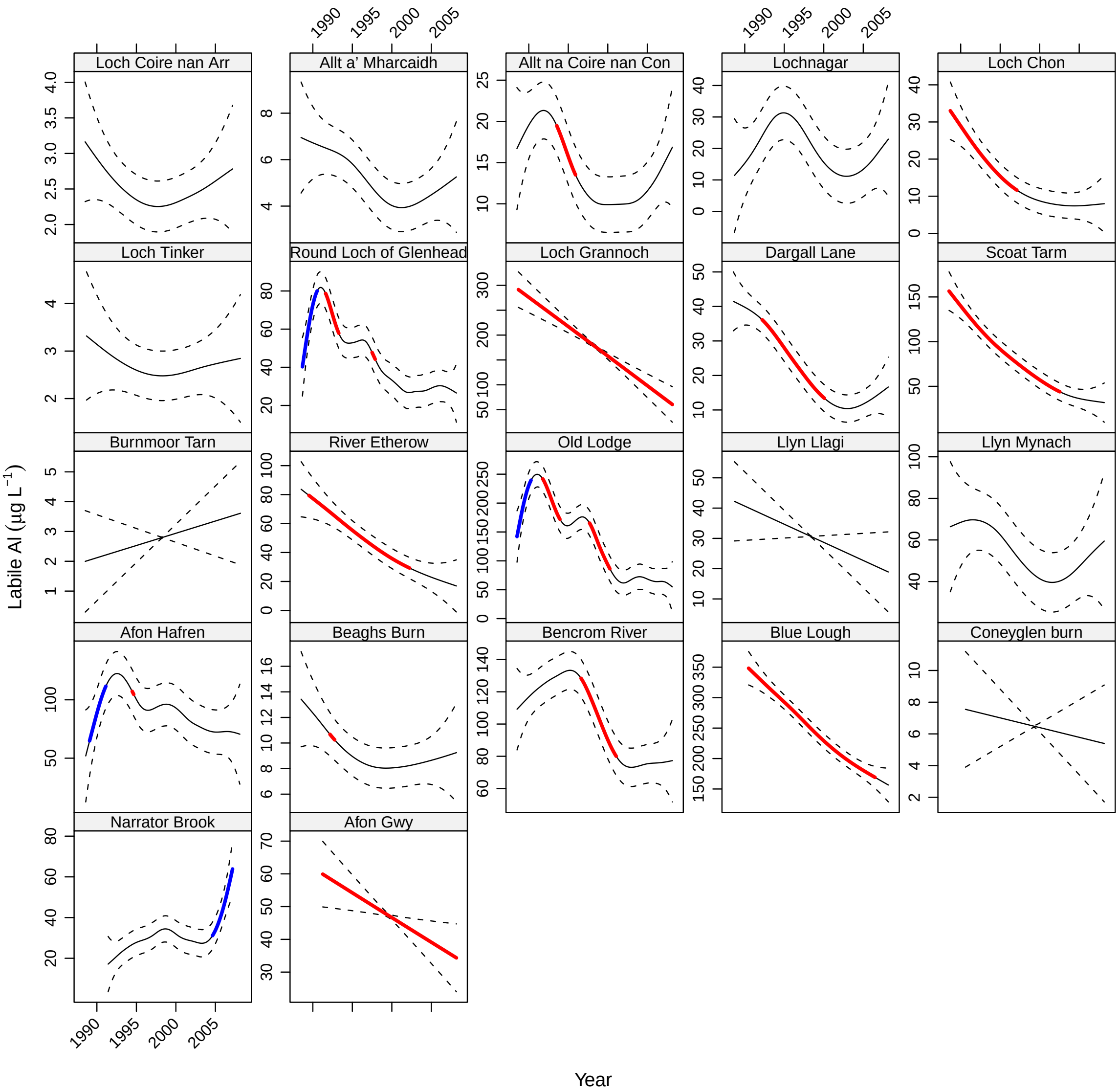


Figure 3.12: Fitted trends in labile Aluminium (Labile Al) concentration (µg l^{-1}). Periods of significant change in the fitted trend, determined by derivative analysis, are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).

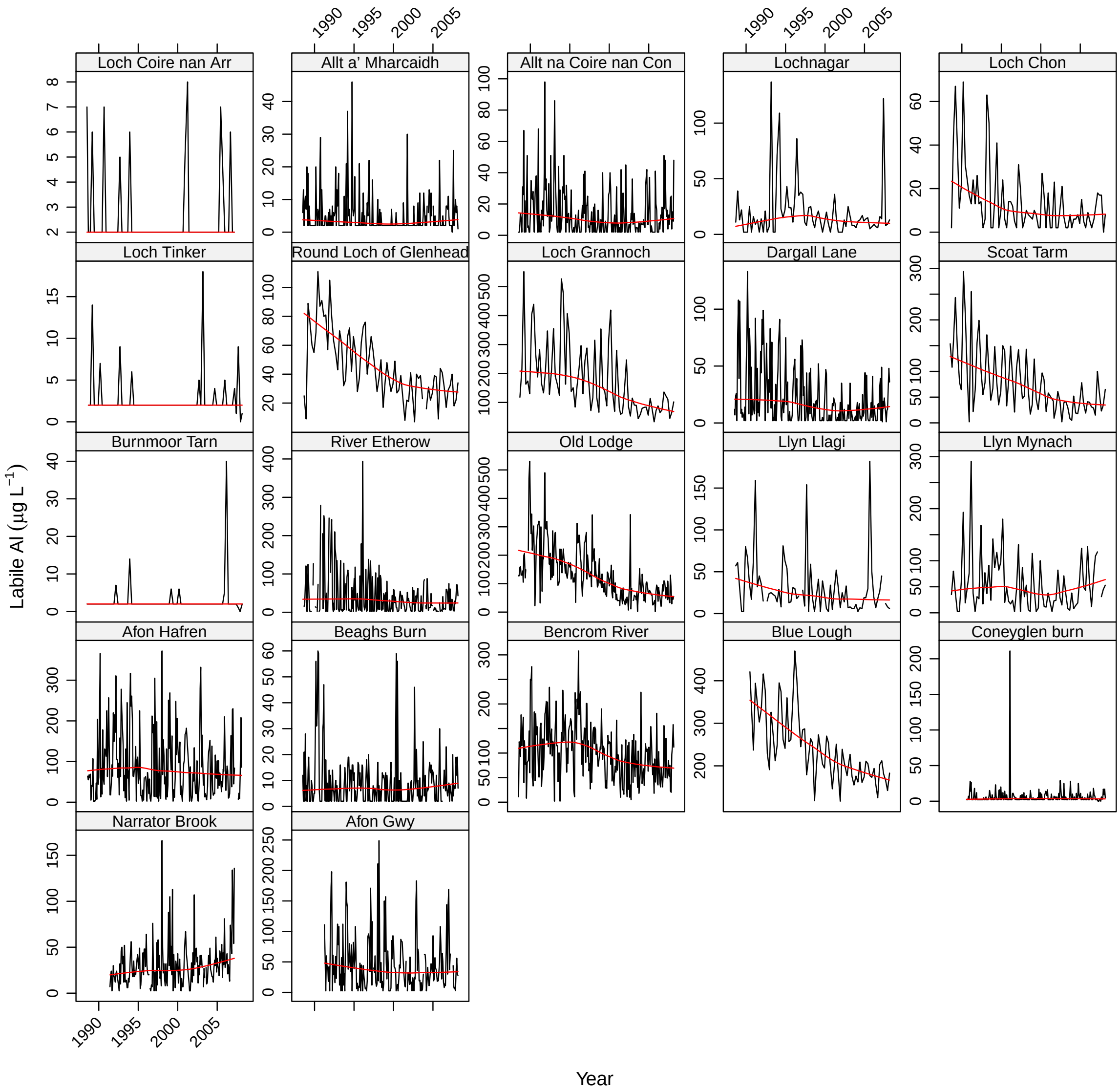


Figure 3.13: Time-series of labile Aluminium concentration (µg l^{-1}) in AWMN lakes and streams, with a LOESS smoother fitted as a red line, illustrating the sharp decline in peak concentrations in some sites.

3.2.2.3. Acid Neutralising Capacity

Acid Neutralising Capacity (ANC) describes the ability of water to resist acidification by a strong acid. As such it is a powerful indicator of acidification status. Waters with negative ANC for example are almost certainly in an acidified condition. ANC is the variable most readily predicted by process-based acidification models such as MAGIC (Model for Acidification of Groundwater in Catchments). ANC is often determined from the difference between the concentration of base cations (i.e. Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and strong acid anions (SO_4^{2-}, NO_3^{-} and Cl^{-}) in units of equivalence. In this report ANC is calculated according to an alternative expression of this relationship applied to AWMN data by Davies *et al.* (2005) where ANC = Alkalinity + (F x DOC) – (3 x labile Al), where ANC and Alkalinity are expressed in µeq l^{-1}, labile Al is in µmol l^{-1} and DOC (dissolved organic carbon) is in mg l^{-1}. F is a charge density function for DOC that is assumed to be 4.5 for water between pH 4.5 – 5.5, and 5.0 for water above pH 5.5.

Eighteen lakes and streams show significant trends in ANC. Only the low deposition sites Loch Coire nan Arr and Coneyglen Burn, and two Welsh sites, Afon Gwy and Llyn Cwm Mynach, show no change. On the basis that Llyn Cwm Mynach is one of the most transparent lakes on the AWMN (summer Secchi disc depths range from 6-9 metres) while DOC concentrations are not particularly low (mean circa 3 mg l^{-1}) it is likely that, uniquely for the Network, the ANC calculation for this site is confounded by the presence of significant amounts of DOC of low molecular weight. The absence of a clear trend at the Afon Gwy is surprising, although the *p* value of 0.07 for the trend is close to the significance threshold of 0.05 and the shape of the fitted trend is similar to most other sites.

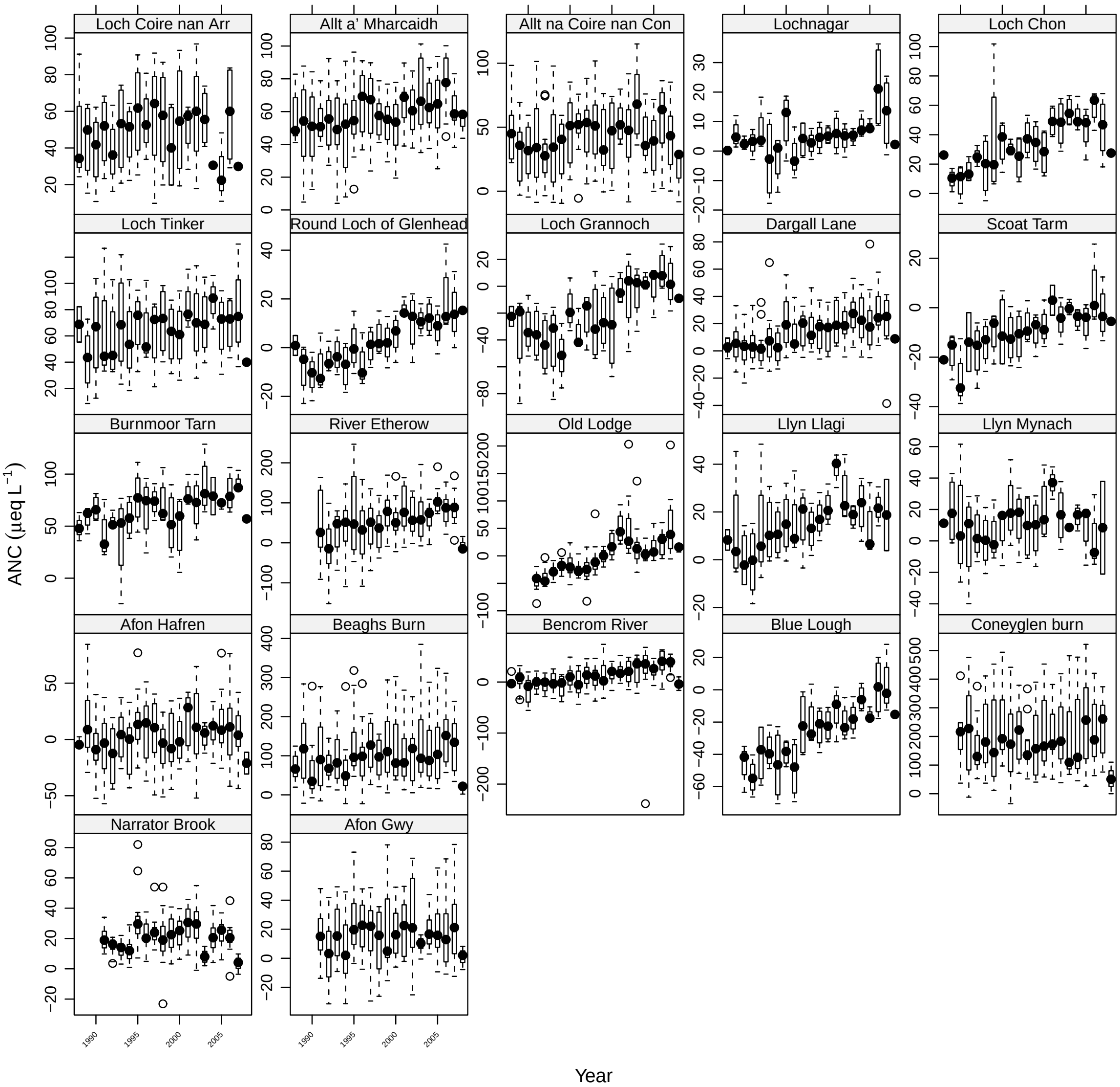


Figure 3.14: Box plots of mean Acid Neutralising Capacity (µeq l^{-1}) by year. The mean for the last year of monitoring is based on Jan/Feb/March data only.

Most sites show either linear or curvilinear increases (Figs. 3.14 & 3.15) in ANC indicating that chemical improvement results both from the reduction in sea-salt deposition in the early years of monitoring and following the post-1995 reduction in xSO_4^{2-}. This is supported by the derivative analysis that suggests that significant change has occurred at many of these sites throughout most of the monitoring record.

The shape of recovery in ANC at Lochnagar, one of the few sites with very little sea-salt influence, differs from that for the majority of sites. Here, xSO_4^{2-} has declined almost linearly, but in the first few years the reduction was nullified by an increase in the concentration of NO_3^- that levelled out in the mid-1990s. The net effect of these changes in drivers is that ANC has only recently begun to increase significantly.

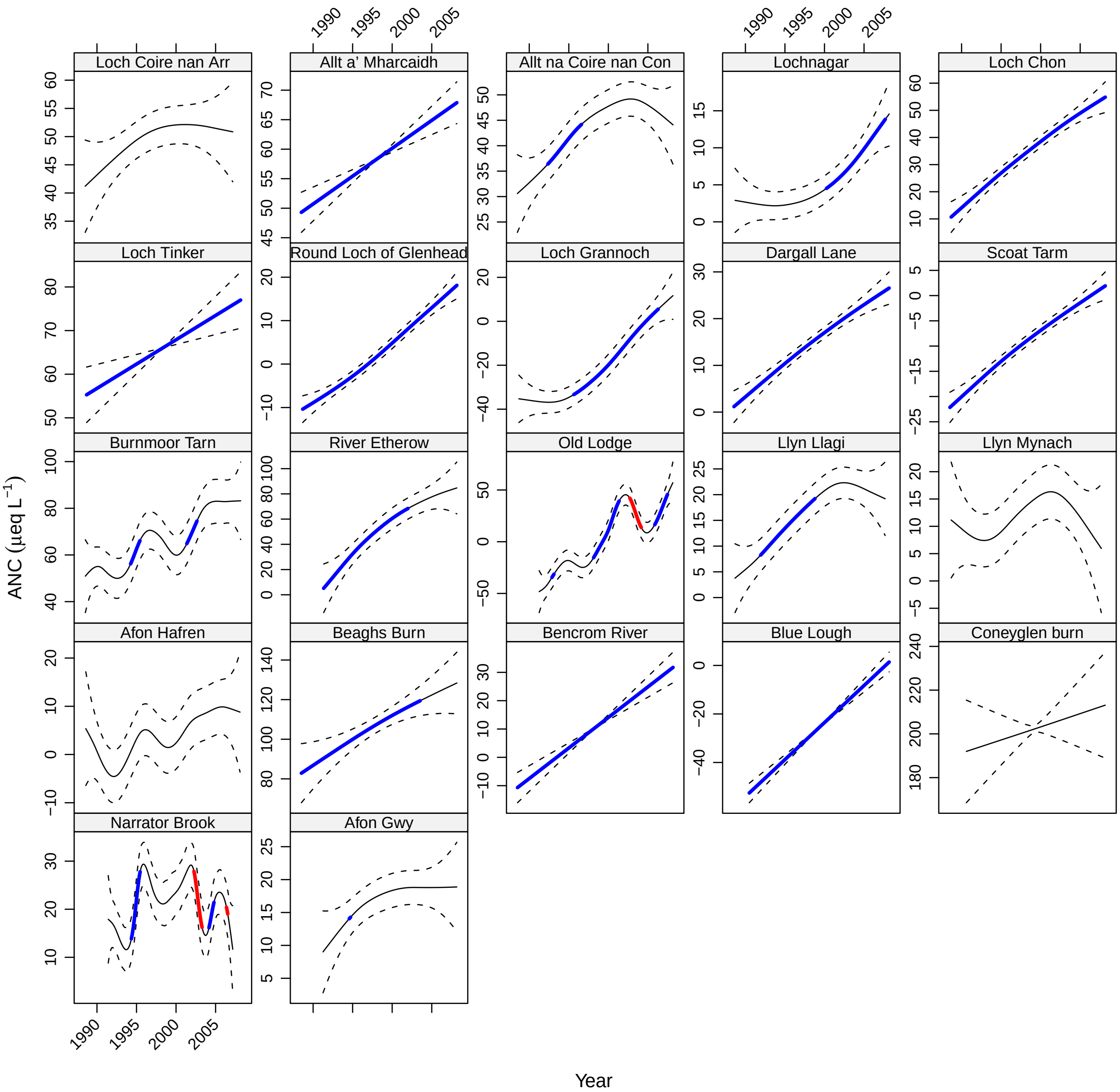


Figure 3.15: Fitted trends in Acid Neutralising Capacity (μeq l^{-1}). Periods of significant change, determined by derivative analysis, in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).

3.2.3. Trends in chemical buffering: Base Cations

The base cation concentrations of AWMN sites result mainly from inputs from catchment soils (a product of geochemical weathering) and from sea-salt, while trace amounts are also deposited as non-marine particulate matter (i.e. in the form of dust from both natural and anthropogenic sources). The majority of sites show significant downward trends in base cation concentrations. This is an expected response to declining acid inputs, although ANC will increase only if the decline in base cation concentration is less than the decline in acid anions (i.e. the sum of trends in SO_4^{2-}, NO_3^- and Cl^-). Trends for calcium (Ca^{2+}) are presented in Appendix 3, Figure 13.

Approximately two-thirds of sites show periods of significant decline in Ca^{2+}, although the clearest reductions are seen in the earlier part of the record (e.g. at Dargall Lane, Scoat Tarn, Burnmoor Tarn, Llyn Llagi, Llyn Cwm Mynach, Afon Hafren) and are therefore probably dominated by reductions in sea-salt inputs as opposed to reductions in mobilisation due to reductions in acid inputs. However, Lochnagar, one of few sites with minimal sea-salt influence, is the only site to show a significant linear reduction in Ca^{2+} concentration throughout the monitoring period, and this can only be explained by the linear decline in SO_4^{2-} at the site (Fig. 3.2) and/or any accompanying reduction in deposited Ca^{2+} from anthropogenic sources.

Reductions in Ca^{2+} in Loch Chon and Loch Tinker are not significant, despite a considerable long-term reduction in the acid load (Appendix 3, Fig. 13).

3.2.4. Dissolved Organic Carbon

Dissolved organic carbon (DOC) in AWMN sites is derived largely from the degradation of plant and soil organic material and is dominated by high molecular weight humic matter in the form of humic and fulvic acids. These compounds are efficient at absorbing light and exert a control on water transparency.

DOC concentrations show significant monotonic, and largely linear, increasing trends at almost all sites other than Narrator Brook (Fig. 3.16). Derivative analysis indicates that the rate of change for the majority of sites is significant throughout most of the monitoring period (Fig. 3.17).

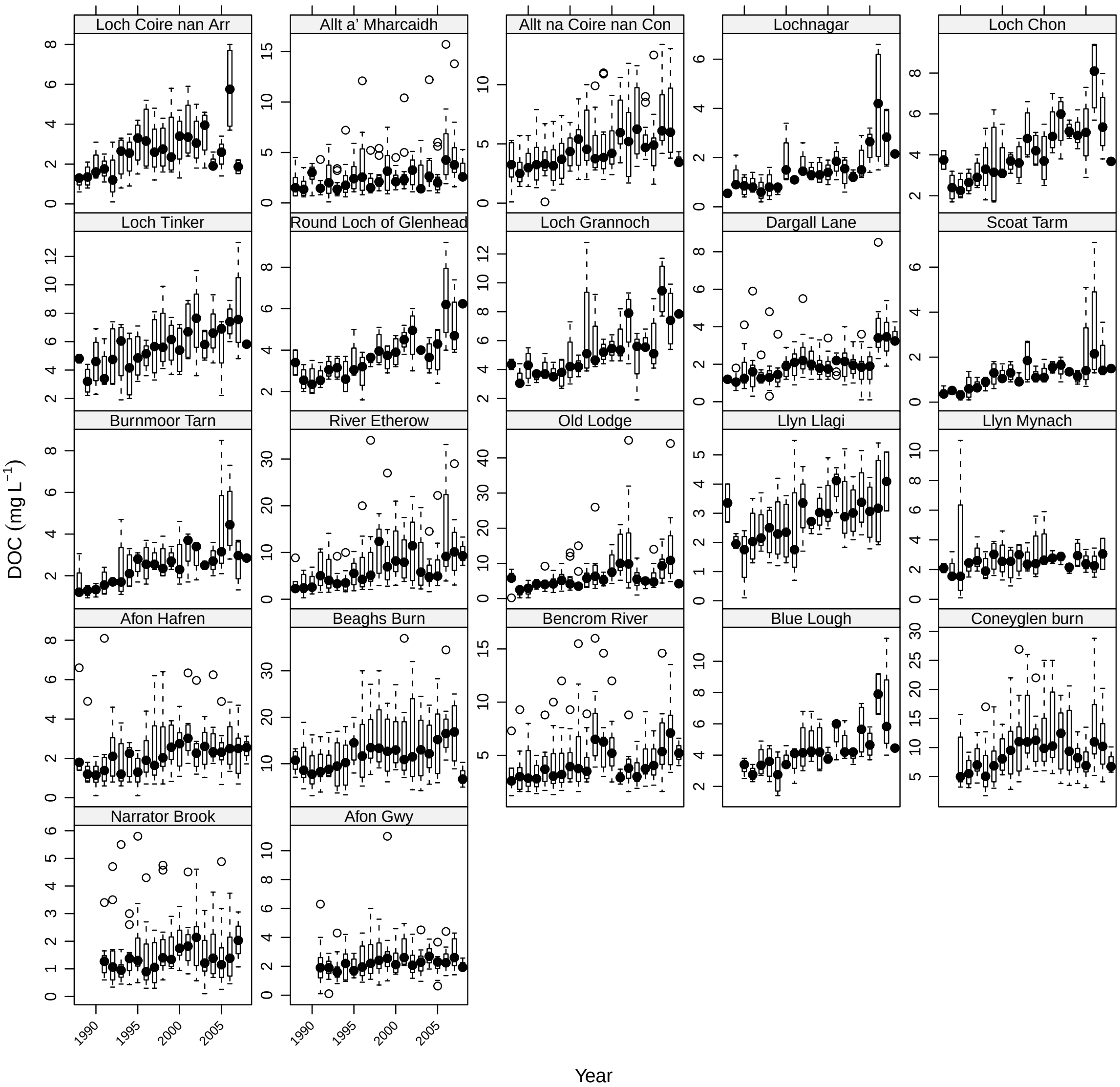


Figure 3.16: Box plots of mean Dissolved Organic Carbon (mg l^{-1}) by year. The mean for the last year of monitoring is based on Jan/Feb/March data only.

These long-term upward trends are very clearly linked to the reduction in sea-salt and xSO_4^{2-} deposition over the monitoring period (Evans *et al*., 2005; Monteith *et al*., 2007). It has been postulated that the solubility of soil organic matter has increased as a result of an increase in soil pH and/or a reduction in soil-water ionic strength. Laboratory work conducted at the University of Leeds under a NERC Standard Grant on soil cores taken from AWMN site catchments is currently underway to test these hypotheses (P. Chapman, pers. comm.). However, recent, unusually pronounced, peaks in DOC in the autumn of 2006 and 2007 cannot be linked solely to declining deposition, but could reflect very unusual climatic conditions particularly during the summer of 2006, when exceptionally high summer temperatures and a prolonged period of dry weather was followed by heavy rains in the days before the September sampling.

The increase in DOC is an indication of recovery from acidification as DOC is expected to increase as xSO_4^{2-} decreases (Monteith *et al*., 2007). This linkage explains in part why the increases in pH have been somewhat smaller than expected, compared to the increases in ANC.

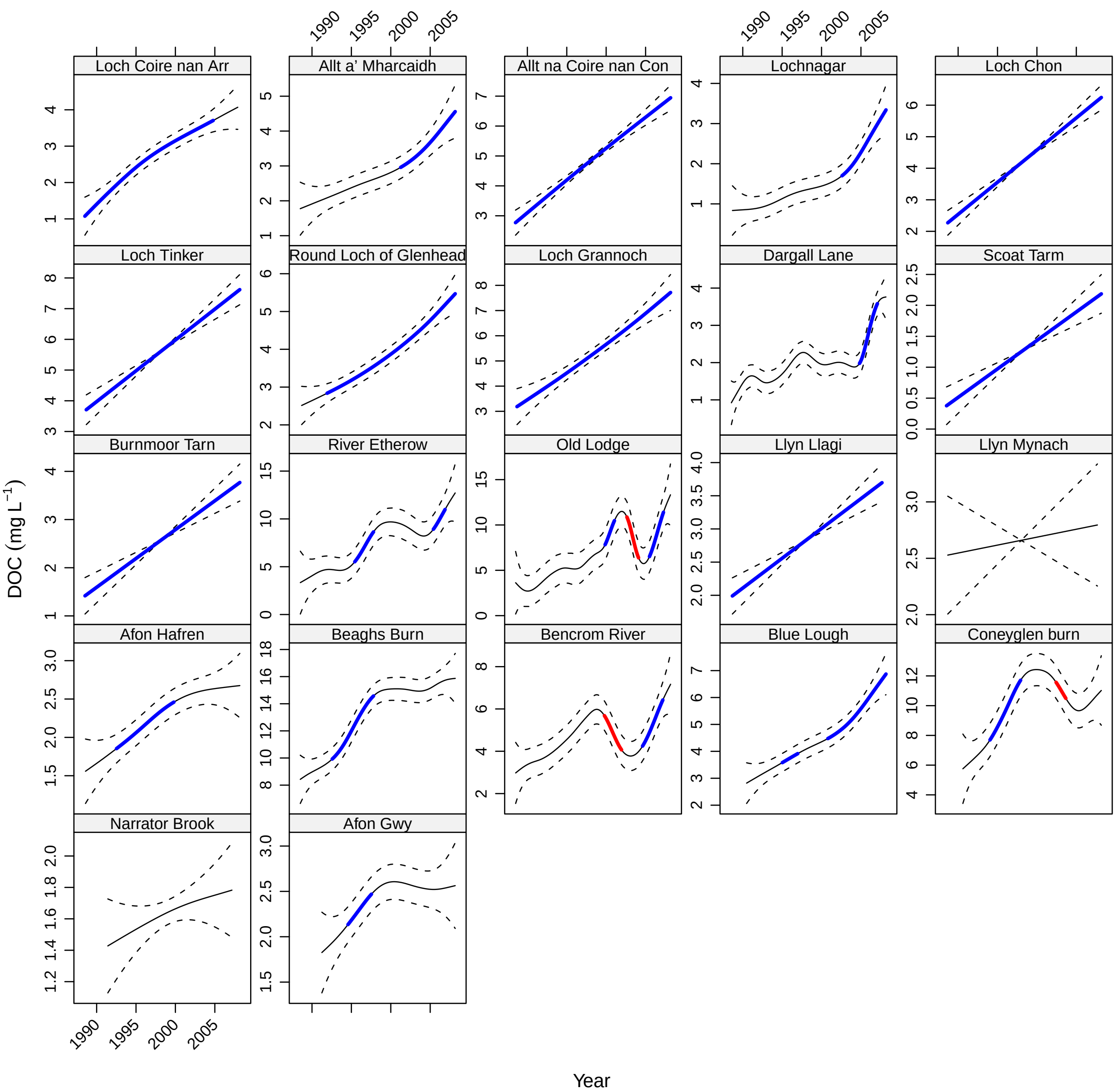


Figure 3.17: Fitted trends in Dissolved Organic Carbon (mg l^{-1}). Periods of significant change in the fitted trend, determined by derivative analysis are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease).

3.3. Synthesis of Chemical Trends

3.3.1. Key temporal patterns

This assessment provides the strongest evidence to date of widespread chemical improvement of the acidified lakes and streams comprising the AWMN, as indicated by increases in pH and ANC and reductions in labile Al concentrations.

Chemical recovery, with respect to direct anthropogenic pollutant effects, has clearly been a non-linear process at the majority of sites. Reductions in the deposition of the main acidifying pollutant, xSO_4^{2-}, have been restricted mostly to a relatively short period between 1995 and 2000, and this is reflected in the pattern of lake and stream water concentrations, as illustrated by the pattern in the standardised smooth functions in Figure 3.18. Declines in xSO_4^{2-} are more linear at sites further from the coast, including the River Etherow in the southern Pennines and Lochnagar in the Grampian Mountains.

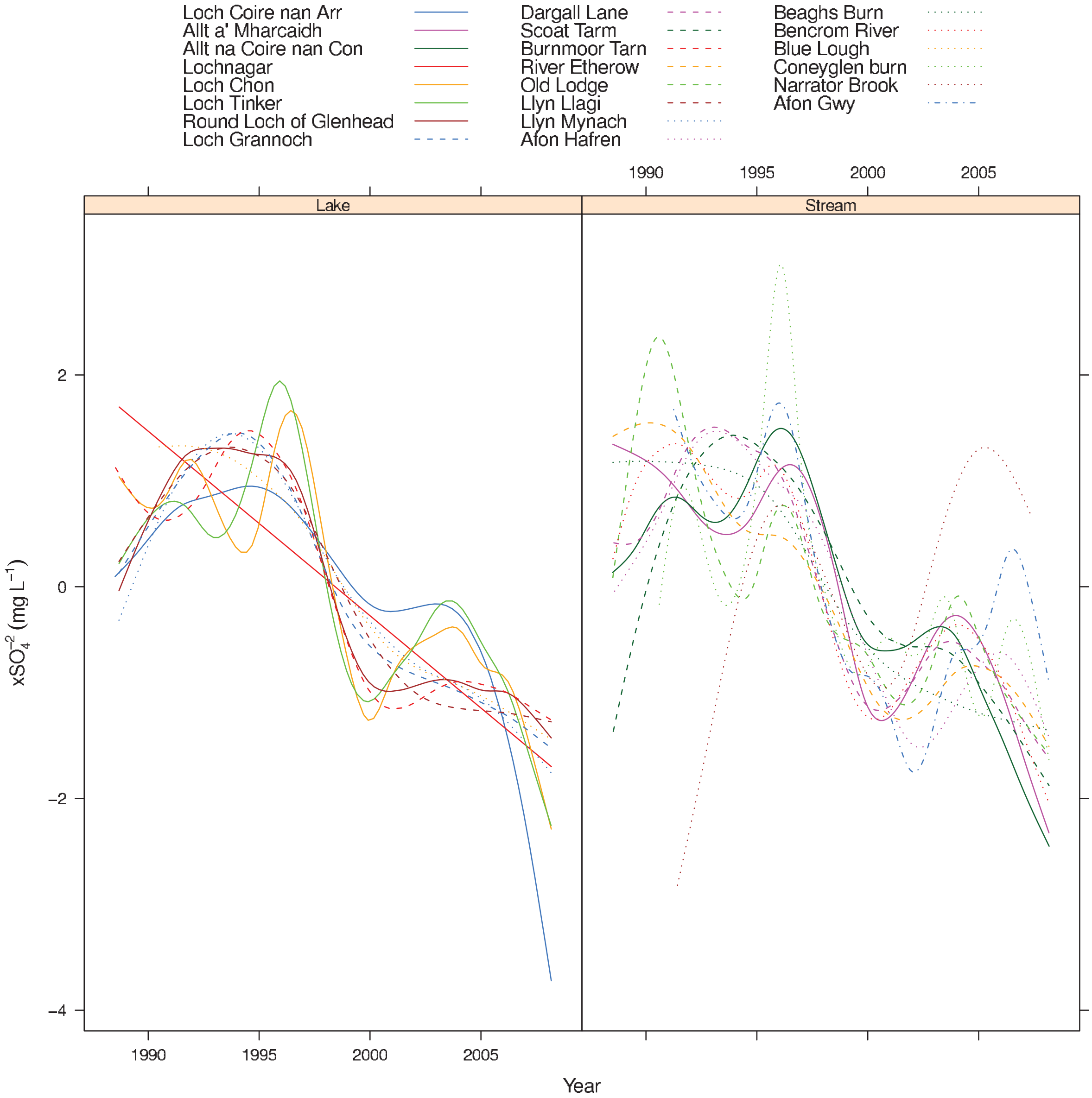


Figure 3.18. Centred and standardised smoothed functions for non-marine sulphate for AWMN lakes and streams.

Despite the large reductions in xSO_4^{2-}, concentrations at most sites remain markedly higher than those in "reference" UK surface waters most distant from major pollutant sources. Average concentrations for the majority of sites over the last five years range between three to six times higher than that for Loch Coire Fionnaraich in north west Scotland (the record for this site only extends back to 2000), and are two to four times higher than the concentration observed in the neighbouring site, Loch Coire nan Arr, over the first five years of monitoring (i.e. 1988-1993).

Prior to this assessment there was no indication of any reduction in NO_3^-, usually the second most important acidifying anion. In previous reports we have reported strong coherent inter-annual variation in NO_3^- concentration and that concentrations peaked at several sites in the spring of 1996 following an exceptionally dry and cold winter. Here, for the first time, we have observed an overall long-term decline in NO_3^- concentration at several sites from central Wales to the English Lake District and the eastern coast of Northern Ireland, although this is not seen in the average tendency for all AWMN sites (Fig. 3.19). At some sites there are similarities between the smoothed trends in NO_3^- concentration and the regional modelled volume-weighted concentration of NO_3^- in wet deposition, albeit with lags of 1-2 years. Significant increases in NO_3^- at Loch Chon and Round Loch of Glenhead demonstrate that deposited N remains a threat to further recovery.

The lack of overall consistency in NO_3^- trends may reflect the competing (and spatially variable) impacts of (modest) overall reductions in N deposition, set against the continuing enrichment of catchment soils with deposited N, which may ultimately lead to greater NO_3^- leaching as a consequence of N 'saturation'. This would imply that NO_3^- concentrations may increase more widely in future, where N deposition remains above the long-term N retention capacity of the ecosystem. Currently NO_3^- levels at most sites remain relatively low, and while there is much uncertainty in this prediction, both monitoring and modelling evidence suggests that the development of N saturation is a slow process (see Chapter 10).

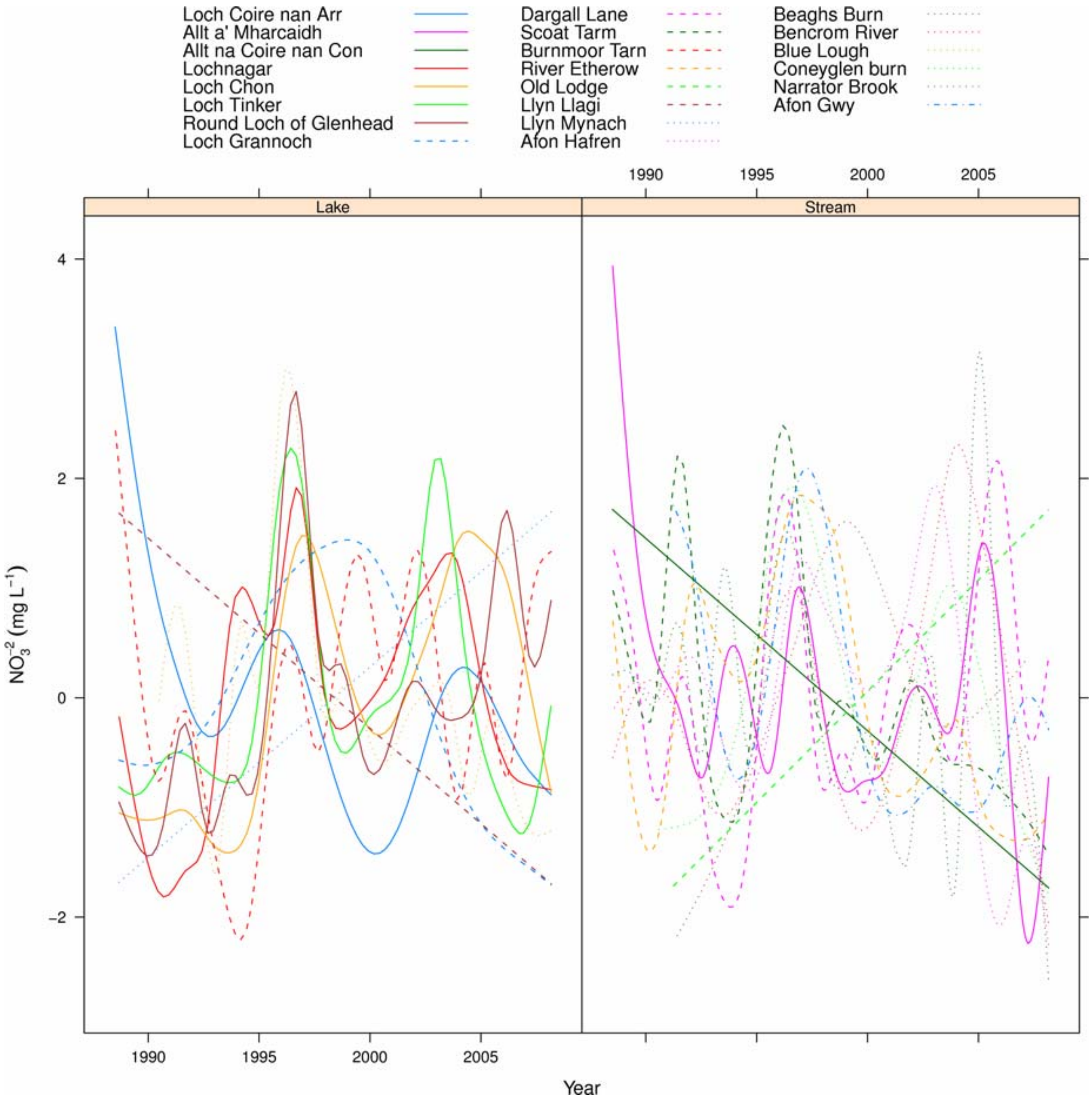


Figure 3.19. Centred and standardised smoothed functions for NO_3^- for AWMN lakes and streams.

Exceptionally stormy weather in the first few years of monitoring resulted in substantial inputs of sea-salt and high levels of runoff at west coast sites. This led to the temporary displacement of hydrogen and aluminium ions by marine base cations, and a switch to more surface dominated hydrological pathways. Both effects are likely to have raised acidity levels over this period – possibly to unprecedented levels at some sites (see Chapter 9). The elevated input of sea-salt at the majority of sites is clear from the pattern in standardised smooth functions (Fig. 3.20). The more linear reductions over time in acidity (i.e. pH and ANC increases and labile Al decreases) seen at some of these lakes and streams are therefore likely to represent a combination of declining sea-salt inputs (and associated declines in rainfall) in the early years of monitoring followed by the direct anthropogenic effects of reduced sulphur loading. Ongoing research suggests that in the more deposition-impacted regions, early reductions in Cl^- concentrations may also reflect reductions in HCl deposition which would also have contributed to the decline in acidity over this period (C. Evans, pers. comm.).

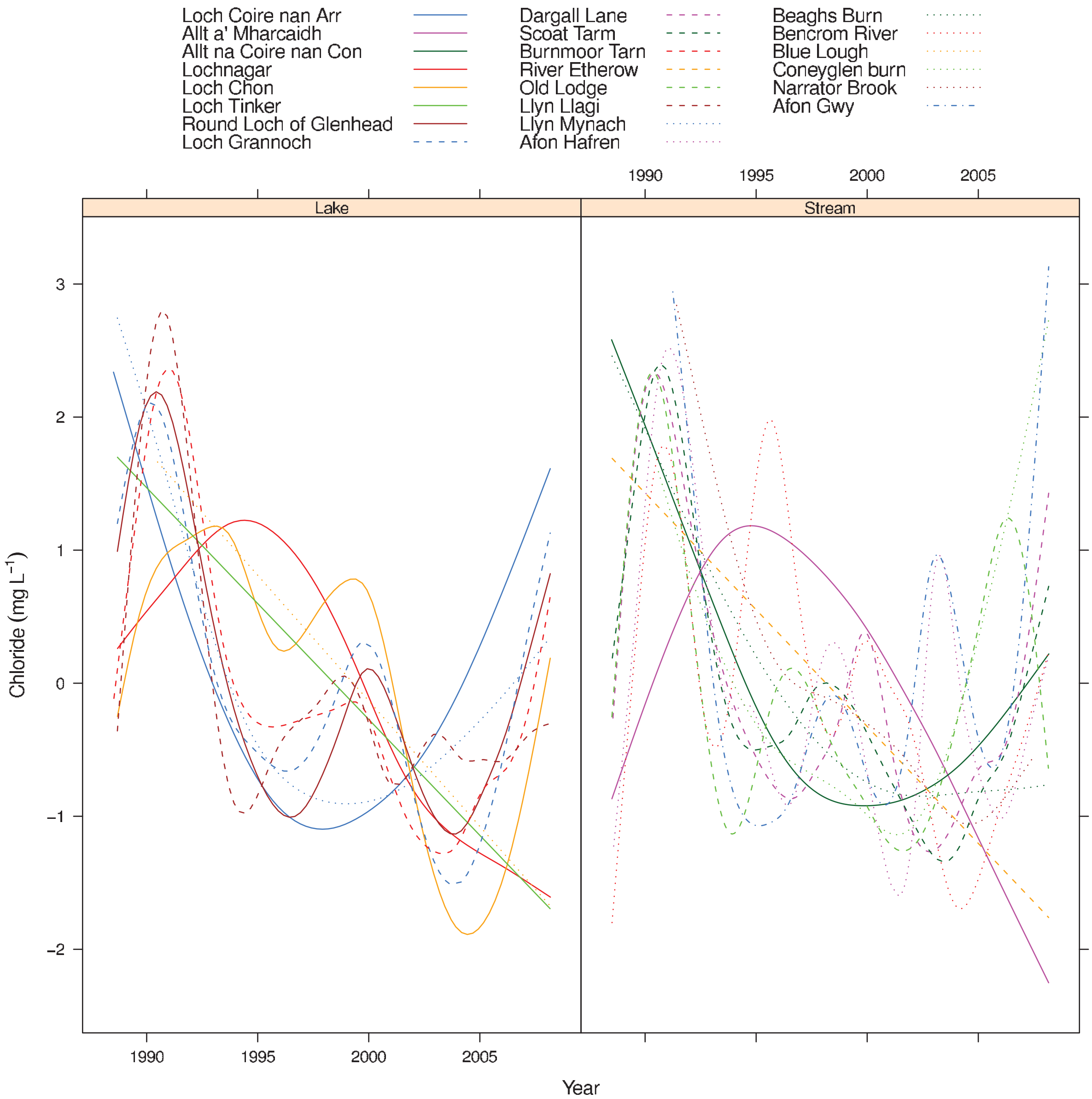


Figure 3.20 Centred and standardised smoothed functions for chloride for AWMN lakes and streams.

The rate of change in ANC is a generic indicator of the combined effects of changes in inorganic aluminium, pH and bicarbonate alkalinity. The Sen slope estimates for ANC for the 22 AWMN sites is strongly correlated with the Sen slope for xSO_4^{2-} (Fig. 3.21a), demonstrating the chemical sensitivity of these sites to the strength of change in xSO_4^{2-}. Much of the residual variation in this relationship can be explained by the change in Cl^-. The combined slopes for xSO_4^{2-} and Cl^- provide an even stronger predictor of the change in ANC (Fig. 3.20b), emphasising the contributions of reductions in both anthropogenic pollution and climatic effects to the overall chemical improvement seen across most of the Network.

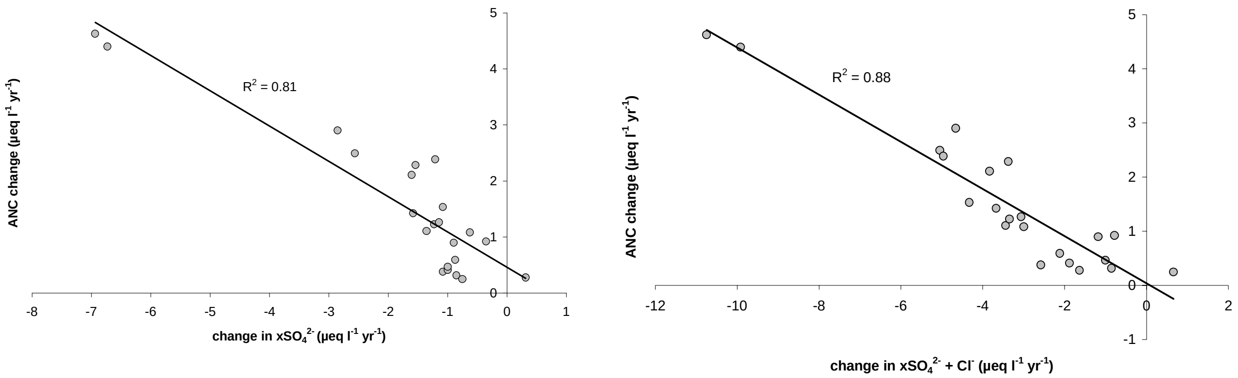


Figure 3.21. Relationship between the rate of change in ANC and (a) the rate of change in $xSO4^{2-}$ and (b) the net rate of changes in xSO_4^{2-} and Cl^-, at the 22 AWMN sites.

The merging of the two slopes in this way is artificial as the effect of a unit change in xSO_4^{2-} is unlikely to equate to a unit change in Cl^- . However, by applying the two as explanatory variables in a multiple regression the resulting equation is:

change in ANC = 0.11 - 0.51*change in xSO_4^{2-} - 0.31*change in Cl^-
(R^2 =0.89; p for both variables <0.01)

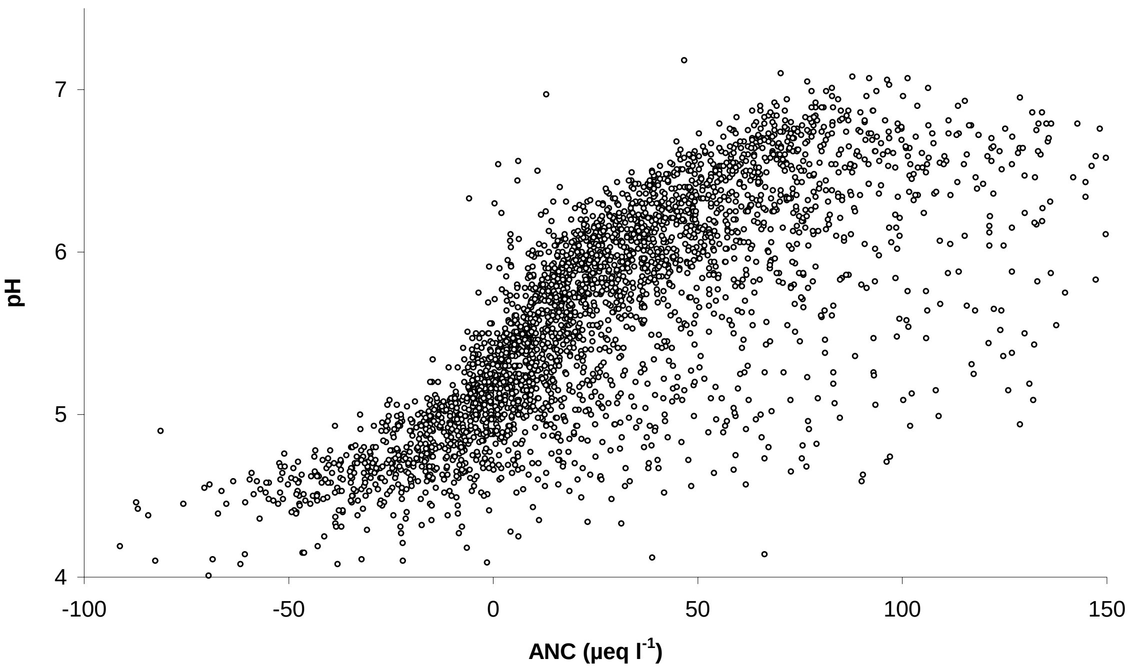
On the basis of this regression, therefore, each 2 μeq l^{-1} reduction in xSO_4^{2-} has, on average for the Network, resulted in a 1 μeq l^{-1} increase in ANC. But around a third of the ANC change can be linked to the decline in Cl^- associated with declining levels of sea-salt deposition. The consequences for any future return to higher levels of sea-salt deposition, as experienced in the first few years of monitoring, are considered in Chapter 10.

3.3.2. pH increases and implications for recovery to date

At some of the most acidic sites on the Network the rise in ANC has been expressed mainly through large reductions in labile Al (i.e. inorganic aluminium) and increases in DOC, which have buffered pH. However, in more recent years pH has begun to respond more clearly to the chemical improvement as labile Al levels have begun to flatten out. This is illustrated in Figure 3.22, in which pH is plotted in relation to ANC for: (a) all sites; and (b) selected sites, to illustrate the current status of some of the more acidic lakes. Most of the more acid streams are omitted from this Figure because large variations in DOC result in much greater scatter of data points which clouds the relationship. Figure 3.22a demonstrates the sigmoidal relationship between pH and ANC that is typical for low alkalinity surface waters. The spread of points at a given ANC level is caused by differences in DOC between sites, with the lowest DOC levels showing the highest pH. pH remains relatively stable at low ANC, but begins to climb once ANC exceeds *c.* 0 μeq l^{-1} and continues to increase until ANC exceeds *c.* 40 μeq l^{-1}.

As ANC has shown broadly linear improvement with time the relationships for individual sites in Figure 3.22b can be roughly interpreted as time-series running from left to right. At Scoat Tarn and Blue Lough the early improvement in ANC had little influence on pH but now that ANC has become positive pH has begun to rise rapidly. This is important as it demonstrates that only small additional reductions in acid inputs (from xSO_4^{2-} or NO_3^-), and the consequent small increase in ANC, should be necessary to induce further significant improvements in pH. As pH is often shown to be the key variable determining the viability of acid sensitive species and communities, these more acidic AWMN sites could be argued to be at a critical stage in their chemical and biological recovery. This chemical characteristic of recovering waters might also provide a partial explanation for the wide gap seen between contemporary diatom communities in some of the more acidified lakes and the diatom assemblages found in the pre-acidification levels of sediment cores (Chapter 9). In other words the biological recovery is expected to follow changes in pH rather than changes in ANC.

a)



b)

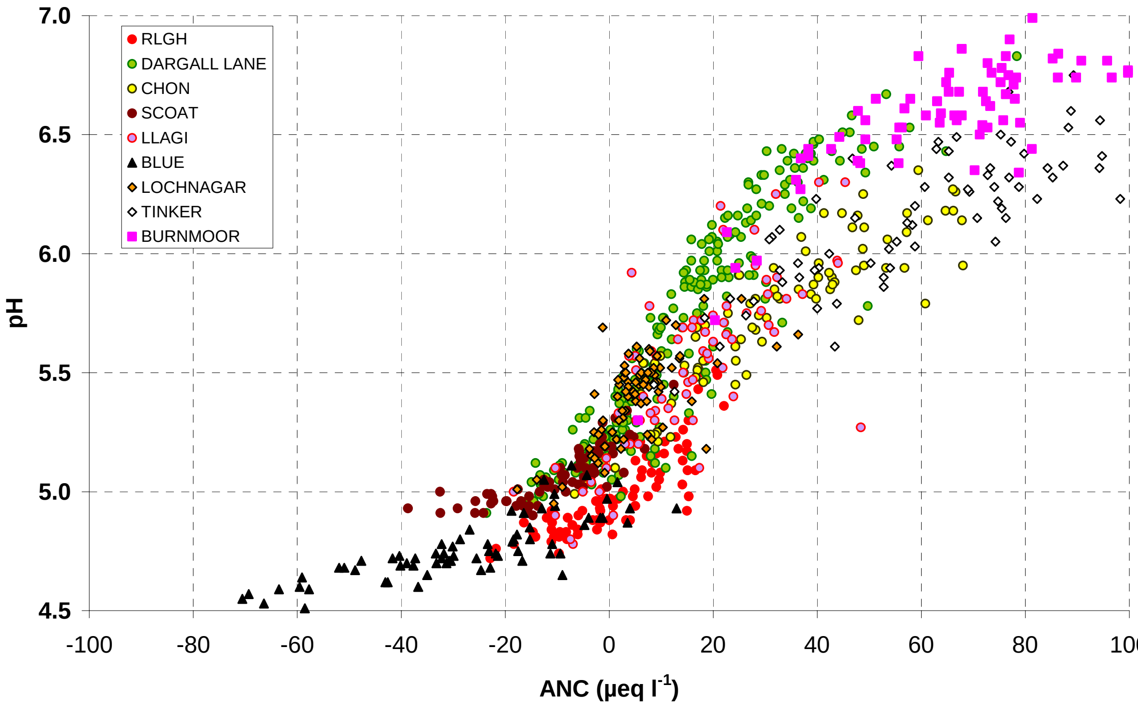


Figure 3.22. Relationship between pH and ANC (a) for all samples in the AWMN database and (b) for selected sites.

3.3.3. Comparisons between the water chemistry of afforested and non-afforested (moorland) sites

The co-location of pairs of afforested and non-afforested sites was central to the initial design of the AWMN. They were included in order to test hypotheses regarding interactions between forest management and acidification recovery. Three geographically close pairs are: the moorland site Loch Tinker and afforested site Loch Chon in the Scottish Trossachs; the moorland site Round Loch of Glenhead and afforested site Loch Grannoch in Galloway, southwest Scotland; and the moorland stream Afon Gwy and the afforested Afon Hafren in the Plynlimon region of mid-Wales. A fourth pair, with weaker co-location (the moorland site Llyn Llagi in Snowdonia, and the afforested Llyn Cwm Mynach in the Welsh Rhinog Mountains – some 30 km to the south) is also included in the following analysis. There are two additional afforested sites in the Network which are not paired with an adjacent moorland site; Allt na Coire nan Con and Coneyglen Burn. Further details regarding future management plans for the afforested sites are presented in Chapter 10.

While there are inevitably other physical differences between sites (for example, underlying geology, altitude and size) that prevent categoric assumptions being drawn about the influence of forestry in individual cases, comparisons across the Network are instructive with respect to differences in both long-term acidity status and differences in responses to declining acid deposition. Comparisons of the first three pairs were made in the AWMN 10 Year Interpretative report (Monteith & Evans, 2000). This revealed several common characteristic differences within pairs, with the afforested site in each showing higher concentrations of SO_4^{2-}, NO_3^- and Cl^- and higher levels of acidity.

In Figures 3.23a – 3.26a we present time-series of annual mean levels of a range of key chemical determinands as time-series for the four pairs of sites. Figures 3.23b – 3.26b represent time-series of the difference between the non-afforested and afforested site in each case.

The site pairs share several long-term characteristics as previously described (Monteith & Evans, 2000). SO_4^{2-}, NO_3^- and Cl^- concentrations are all higher in the afforested sites, consistent with the increased interception of pollutants and sea-salts by the forest canopy. The water draining the afforested sites tends to be of lower pH in all cases with the exception of the first three years of monitoring of Llyn Llagi, and at the outset, at least, run-off from the afforested catchments contained far higher concentrations of labile Al. With the exception of the Trossachs pair, run-off from the other afforested sites had higher concentrations of base cations (calcium and magnesium), and although this characteristic will be dependent on catchment geology, elevated levels are consistent with higher inputs of acid anions and suggest that base cation depletion by tree growth has not been a major factor at the Network scale.

With respect to changes with time, SO_4^{2-} concentrations in three out of the four pairs are converging strongly as a result of more rapid declines in the afforested (historically more acidified) sites relative to the non-afforested sites. This behaviour is entirely consistent with the wider national pattern of convergence in SO_4^{2-} concentrations as a result of the positive correlation between mean concentrations and rate of decline. The exception in this case is the Welsh lake pair for which SO_4^{2-} concentrations are falling at a similar rate.

Trends in the relationship between paired sites differs more with respect to NO_3^- and there is no consistency between the direction of trend and land use. The difference in two pairs has increased over time but decreased in the other two. For the Trossachs pair, NO_3^- concentration is increasing in afforested Loch Chon while concentrations in Loch Tinker remain low and unchanged. For the Welsh lake pair, concentrations in Llyn Llagi are declining while afforested Llyn Cwm Mynach shows no trend. In Galloway the difference in concentrations between Loch Grannoch and the Round Loch of Glenhead has declined as a result of falling concentrations at the afforested site and rising concentrations at the moorland site. There is no obvious trend in the relationship between the Plynlimon streams although concentrations have become more similar in the last three years of the record as a result of a sudden decline in concentrations at the afforested sites. The most plausible explanation for the heterogeneity of these relationships is that forest management is having an influence on NO_3^- concentrations and that sites are at different stages in management cycles. Recent reductions in concentrations in Loch Grannoch and Afon Hafren, for example, may reflect increased terrestrial demand as a result of recent replanting in these catchments.

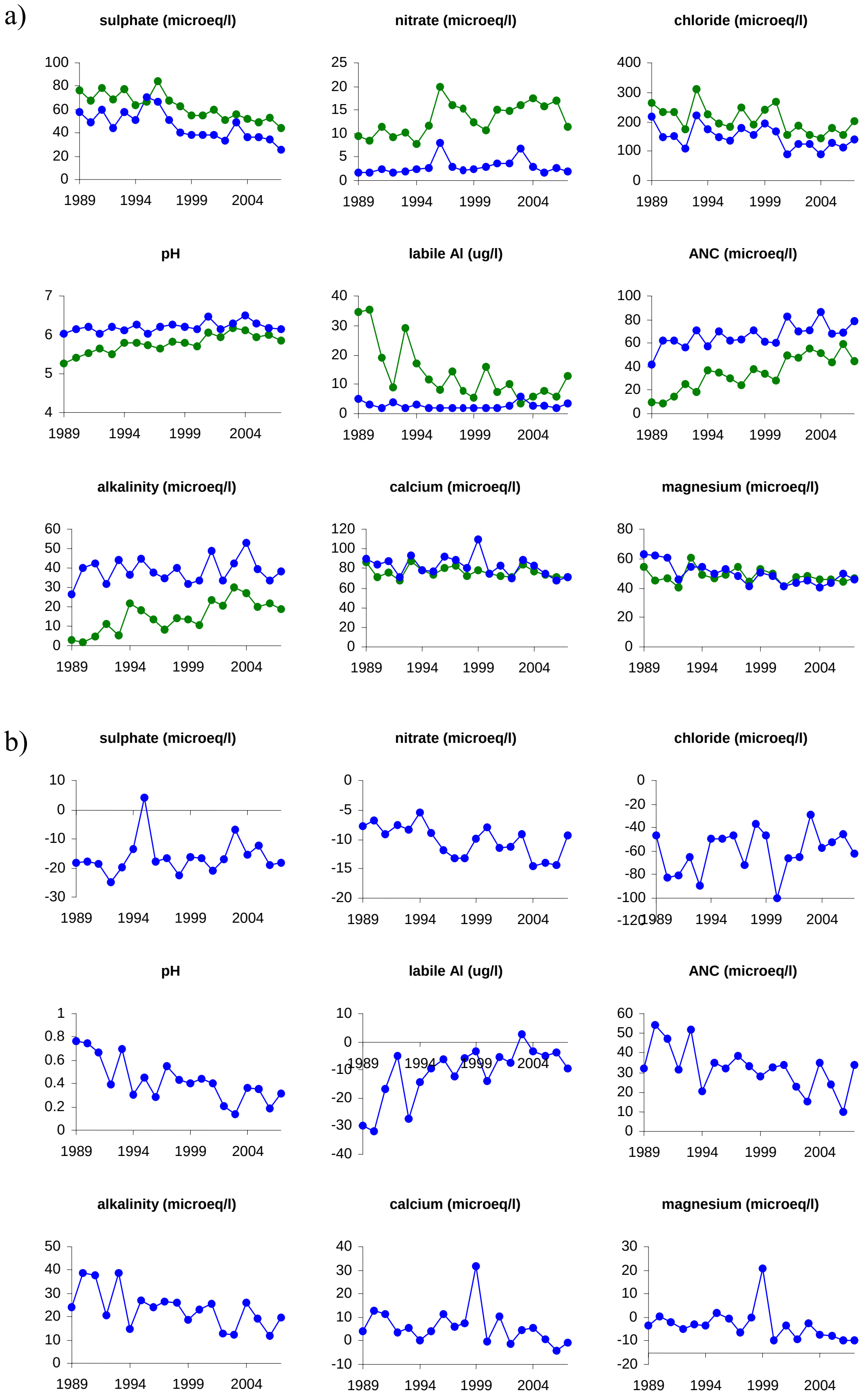
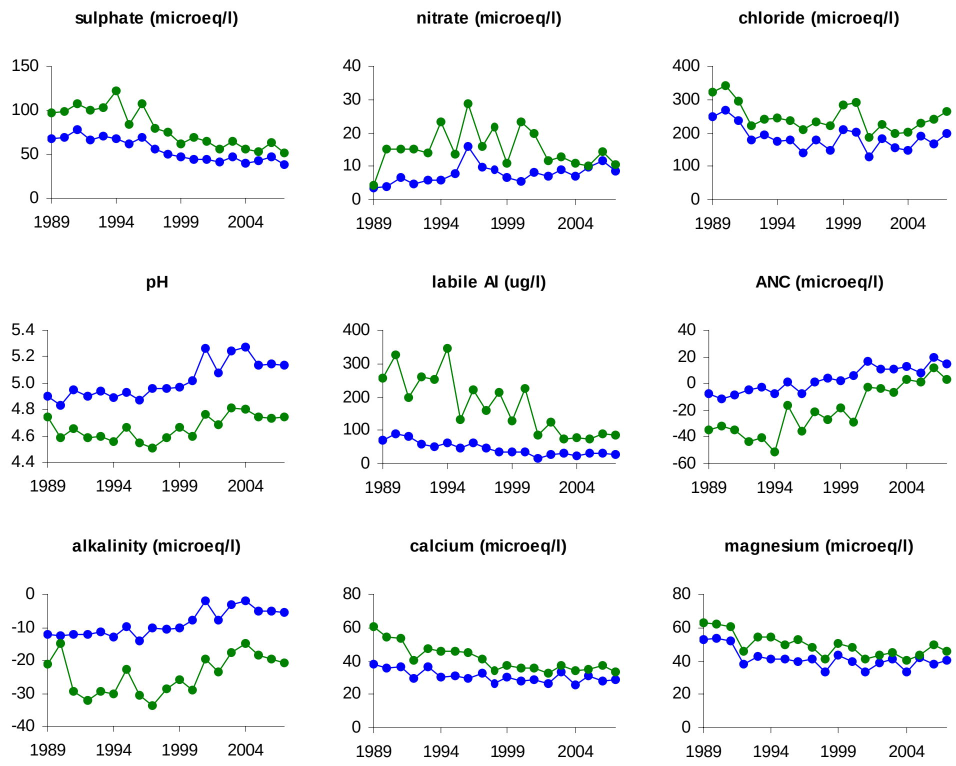


Figure 3.23 a) Comparison of mean annual chemistry time-series for a range of key determinands at the moorland site Loch Tinker (blue) and the neighbouring afforested site Loch Chon (green) in the Scottish Trossachs; b) time-series of the difference between annual mean levels for Loch Tinker and Loch Chon

a)



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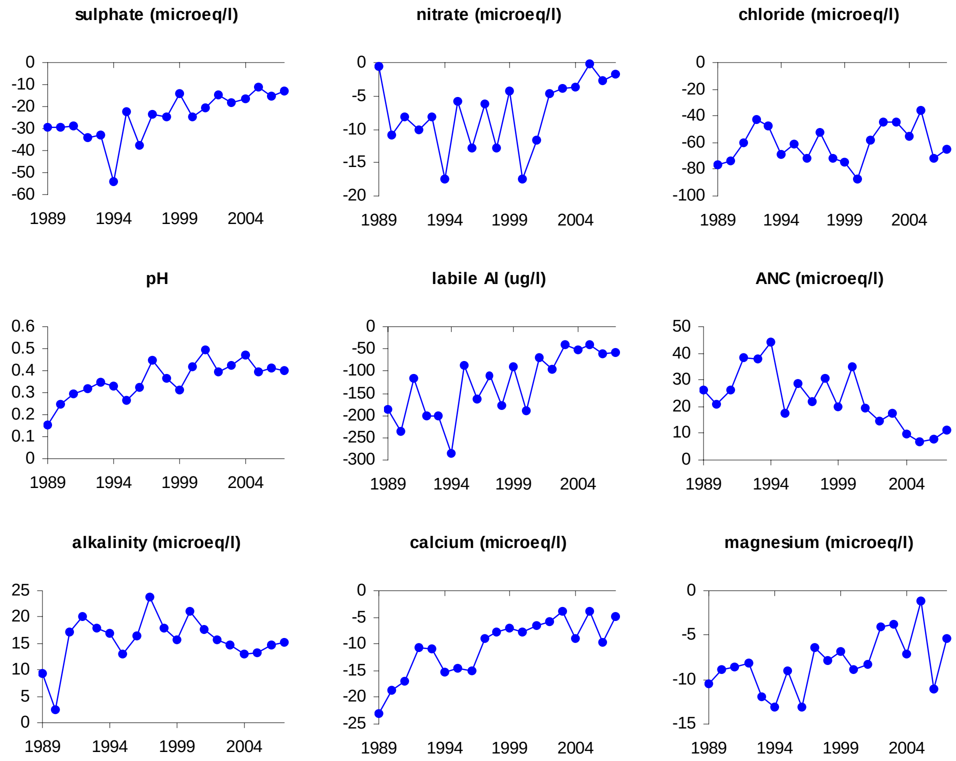
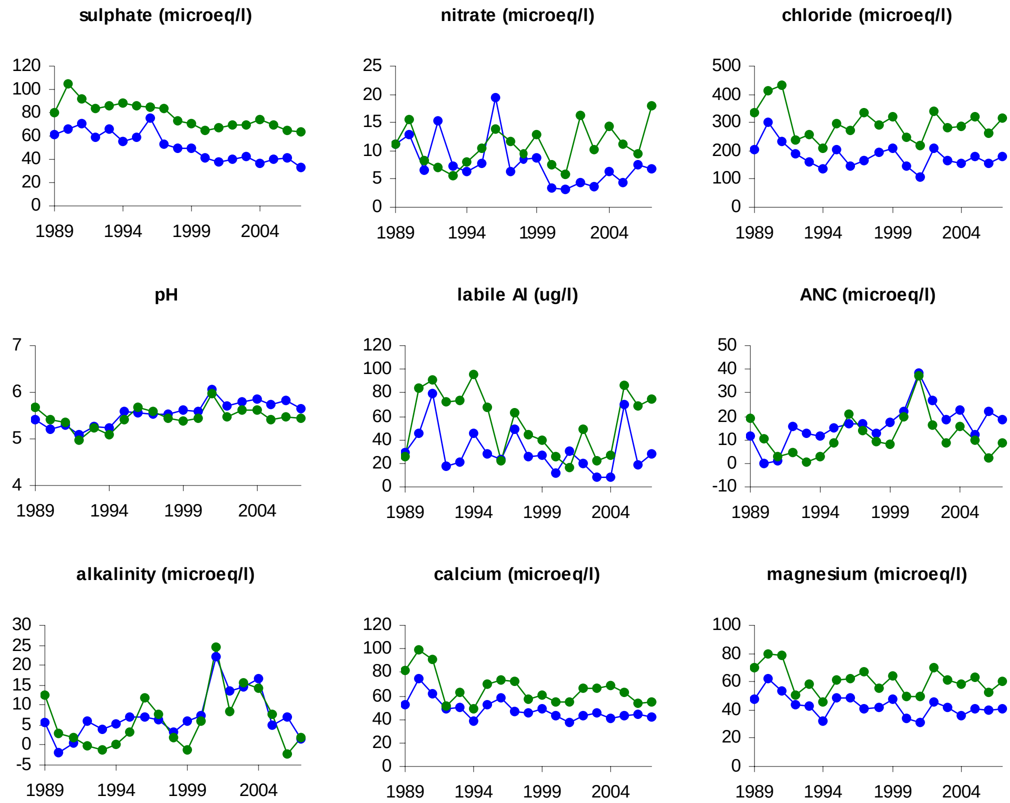


Figure 3.24 a) Comparison of mean annual chemistry time-series for a range of key determinands at the moorland site Round Loch of Glenhead (blue) and the neighbouring afforested site Loch Grannoch (green) in Galloway, southwest Scotland; b) time-series of the difference between annual mean levels for Round Loch of Glenhead and Loch Grannoch

a)



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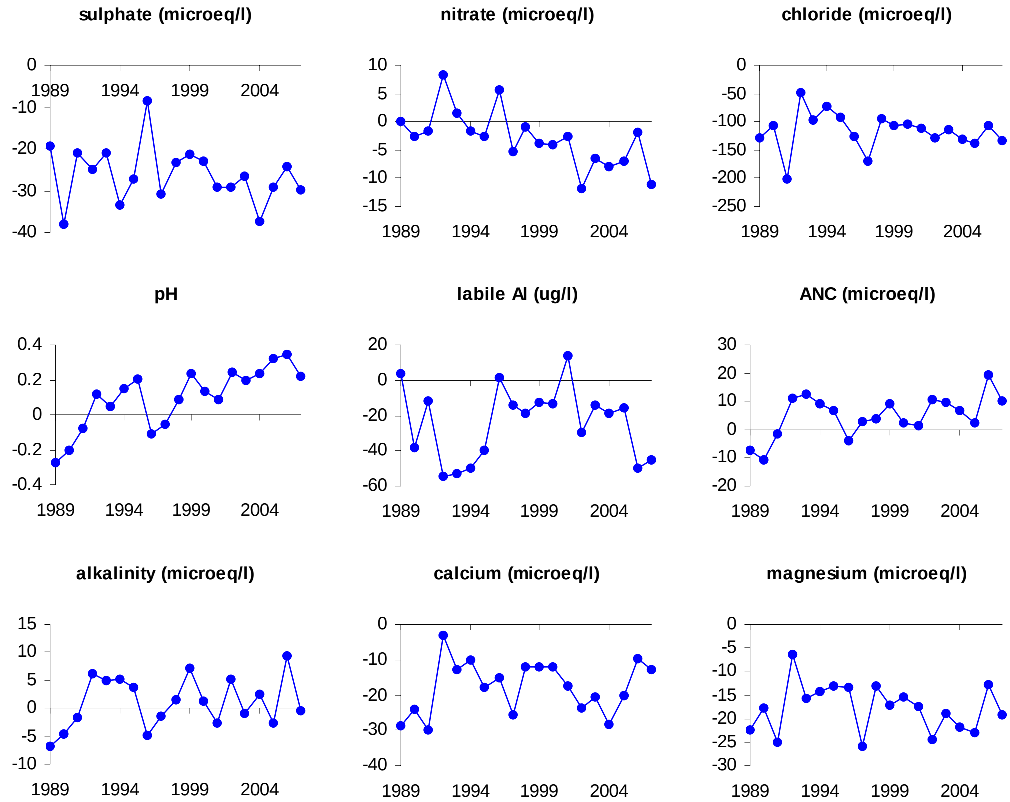
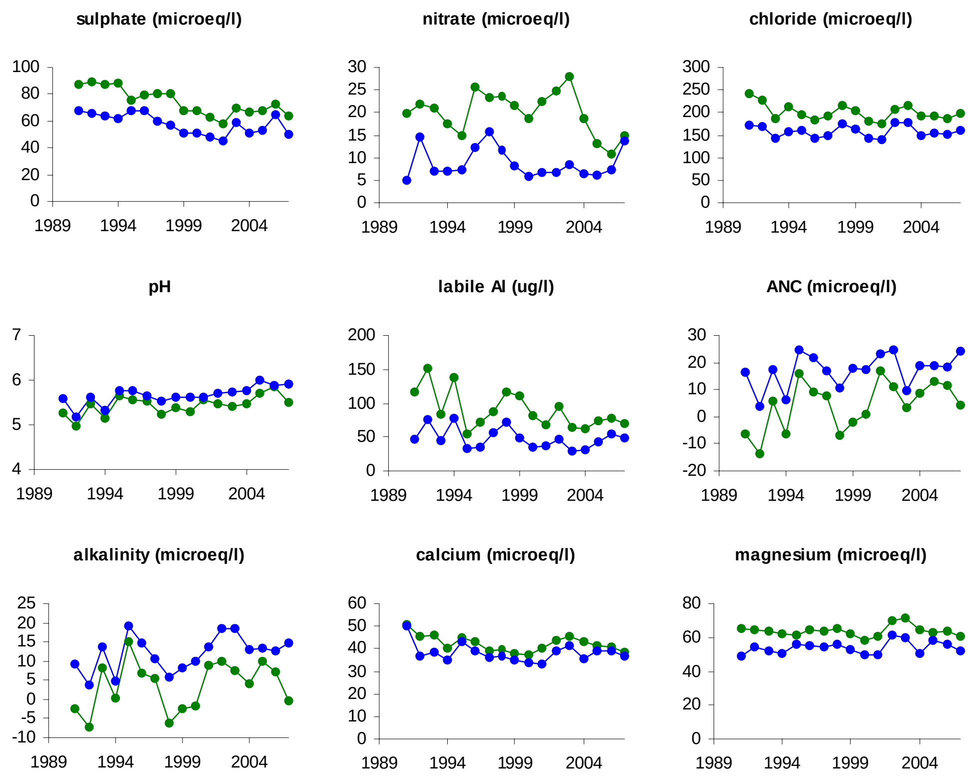


Figure 3.25 a) Comparison of mean annual chemistry time-series for a range of key determinands at the moorland site Llyn Llagi (blue) in Snowdonia and the afforested site Llyn Cym Mynach (green) in the Welsh Rhinogs; b) time-series of the difference between annual mean levels for Llyn Llagi and Llyn Cwm Mynach.

a)



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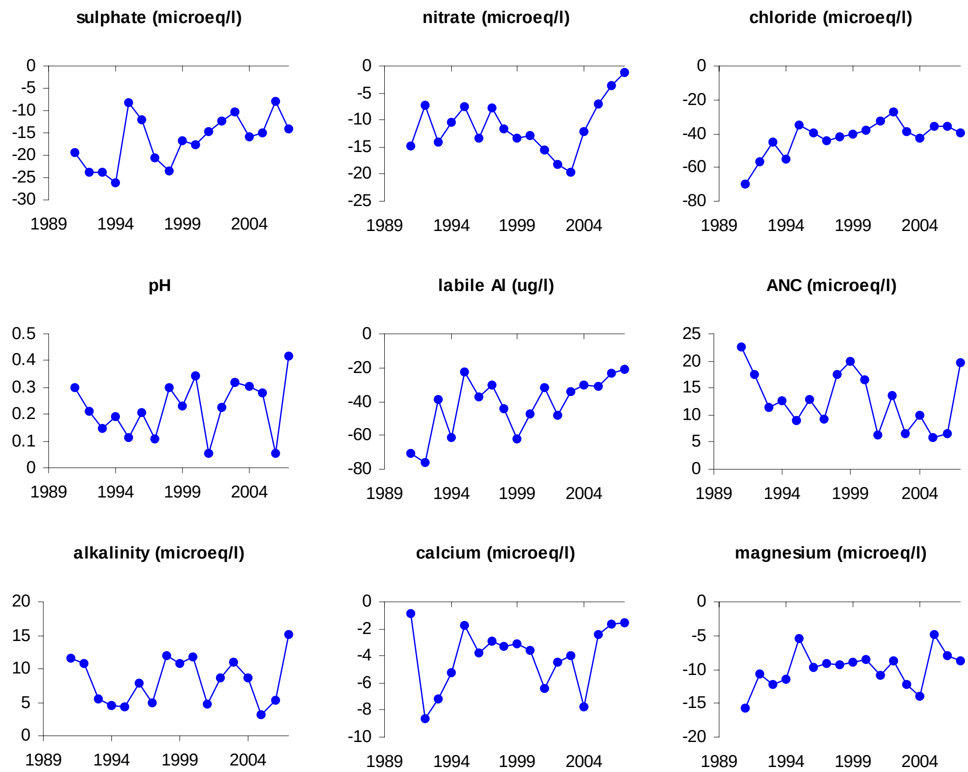

Figure 3.26 a) Comparison of mean annual chemistry time-series for a range of key determinands at the moorland site the Afon Gwy (blue) and the neighbouring afforested site the Afon Hafren (green) in Plynlimon mid-Wales; b) time-series of the difference between annual mean levels for Afon Gwy and Afon Hafren.

The most striking change for within-pair relationships for chemical response variables is seen for labile Al. In three of the four pairs there has been rapid convergence in concentrations as the more acidic (i.e. afforested) of each pair has fallen more strongly than the moorland partner. This is the expected consequence of two factors: the initially higher starting concentrations and the larger reduction in sulphur inputs in the afforested sites. The exception is Llyn Cwm Mynach where there has been a rise in labile Al concentrations in recent years that is not well understood.

All sites show long-term increases in pH. The Galloway and Welsh lake pairs show an increasing within-pair difference in pH over time reflecting more rapid increases in pH in the moorland sites. The more muted recovery in pH in the afforested sites most likely reflects the more acidic starting conditions and the fact that the predominant response in these more acid sites has been a reduction in labile Al concentration (Fig. 3.22). In the Trossachs, the moorland Loch Tinker is too alkaline to show much response in pH and here, the relatively mildly acidic afforested site, Loch Chon, shows a more rapid increase (note the much lower starting concentrations for labile Al in Loch Chon relative to other afforested sites). There is no clear difference in rate of response in pH between the Plynlimon streams.

While ANC has increased at all eight sites, three out of four pairs show more rapid increases in the afforested sites. This is consistent with the larger reductions in acid anions in the afforested sites, and there is little difference in rates of change in ANC relative to change in acid anion concentrations between afforested and non-afforested sites (Fig. 3.27). The only pair not to exhibit this behaviour is the Welsh lake pair, but here trends in ANC are difficult to interpret as a result of the problem calculating ANC for the Llyn Cwm Mynach site (see above).

The only pair to show a strong trend in the relationship between base cation concentrations is the Galloway lakes. Here, calcium concentrations particularly have fallen much more rapidly in afforested Loch Grannoch than in the Round Loch of Glenhead (Appendix 3, Fig. 13).

To summarise, this pairwise comparison indicates that chemical recovery is underway in both afforested and moorland catchments and, if anything, ANC is rising more quickly in the afforested sites, most probably because of the larger reduction in acid inputs resulting from the amplifying effect of pollutant interception. However, because the afforested sites are generally considerably more acidified as a result of much larger acid inputs historically, the dominant response at all but Loch Chon has been a reduction in labile Al, and pH increases to date are relatively muted. The likely implications for biological recovery in afforested catchments depend, at least in part, on the degree of biological response at different stages in the ANC gradient illustrated in Figure 3.22. Labile Al concentrations remain high in Loch Grannoch and Afon Hafren particularly, and are perhaps still too extreme for many acid sensitive organisms to survive. At these sites there has been a relatively small change in pH to date, although the change in hydrogen ion concentration is still considerable. In Loch Chon however, labile Al concentrations have declined to background levels in recent years, and the combined effect of this and the consequent strong pH response would seem to be conducive to substantial ecological improvement (see Chapters 4 – 7).

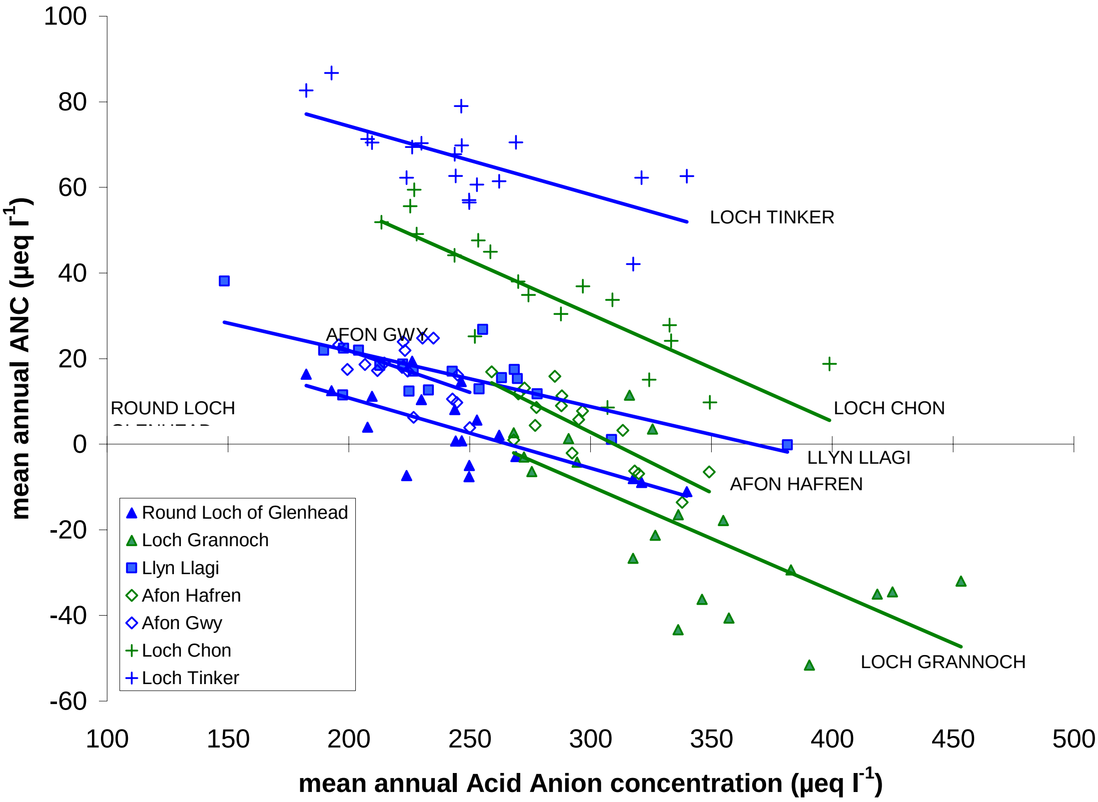

Figure 3.27. Comparison of relationships between annual mean ANC and the sum of annual mean acid anion concentration (i.e. $[SO_4^{2-}] + [NO_3^-] + [Cl^-]$ for the afforested and non-afforested pairs. Llyn Cwm Mynach is excluded from the plot due to uncertainties associated with ANC estimates for the site. Lines fitted by linear regression.

3.3.4. Evidence for the reduction in severity of acid episodes in AWMN streams

Acidified streams represent a particularly hostile environment for acid-sensitive biota, as a result of the more acidic flow-paths and base cation dilution, and/or increased supply of H^+ and Al ions from the catchment soils, that follow periods of high rainfall and/or sea-salt deposition respectively. It is likely that conditions experienced during these events represents the physico-chemical "ceiling" for the rate of recovery of acid-sensitive biota (Lepori *et al.*, 2003) and it has been suggested that repeated acid episodes may explain why biological recovery has progressed so slowly in some systems (Kowalik *et al.*, 2007).

Freshwater macroinvertebrates and salmonids are known to be highly sensitive to elevated levels of labile Al and H^+ ions that affect gill function and ionic regulation (see Section 7.1 with respect to salmonids), even over the relatively short episodes triggered by high flow or seasalt. For salmonids at least it is thought that Al normally exerts the greater toxic effect unless the water is exceptionally acidic (Gensemer and Playle, 1999; Rosseland and Staurnes, 1994).

Sensitivity to elevated acidity is often dependent on life-cycle stage. For example, acidic episodes during smoltification of Atlantic salmon in spring are more detrimental than events of similar severity and duration occurring (Staurnes *et al.*, 1995) at other times of year. Kroglund *et al.* (2008) found that while salmon smolt were capable of surviving in elevated gill Al concentrations (300µg Al g^{-1} dw) for several days, a 3-day exposure of 25 to 60 µg Al g^{-1} dw reduced smolt to adult survival by 20 to 50%.

The impact of individual acid episodes on recovering biological communities is relatively poorly documented. However, Lepori and Ormerod (2005) showed that the abundance of the acid sensitive mayfly species, *Baetis alpinus,* was reduced significantly in Southern Alpine streams following episodic increases in acidity relative to populations of the same species in well buffered streams in the same region. Mortality levels in the episodic streams were dependent on exposure, with depressions of 2-4 days not resulting in significant damage while exposure for 15 days reduced the population to between 1-20% of pre-impact levels.

Univoltine macroinvertebrate species must endure the full winter period in the immersed nymph stage and are hence their populations are particularly exposed to chemical conditions during what is often the most episodic time of year (Kowalik and Ormerod, 2006). In contrast species that have more generations are more able to establish during the spring and summer. Biological effects of an individual episode also depend on the recent chemical history, with greater damage occurring when fish health has already been compromised by previous events (Henriksen *et al*., 1984).

In summary, therefore, while episodic increases in acidity have been widely shown to be detrimental to a range of acid-sensitive biota, precise effects of individual events are difficult to quantify and clearly dependent on the organism, stage in the life cycle, and the duration, intensity and history of events.

Here we examine the extent to which the severity of acidic episodes has declined in response to deposition reductions, in the context of the wider reduction in average levels of acidity reported previously. Our analysis is restricted by the temporal resolution of the data (monthly samples) that is insufficient to record either the maximum levels of acidity reached during these episodes or their duration.

The chemistry data for AWMN stream sites were grouped into five four-year periods. “Extreme” acidity for each period was based on the 10th percentile for pH and ANC and the 90th percentile for labile Al.

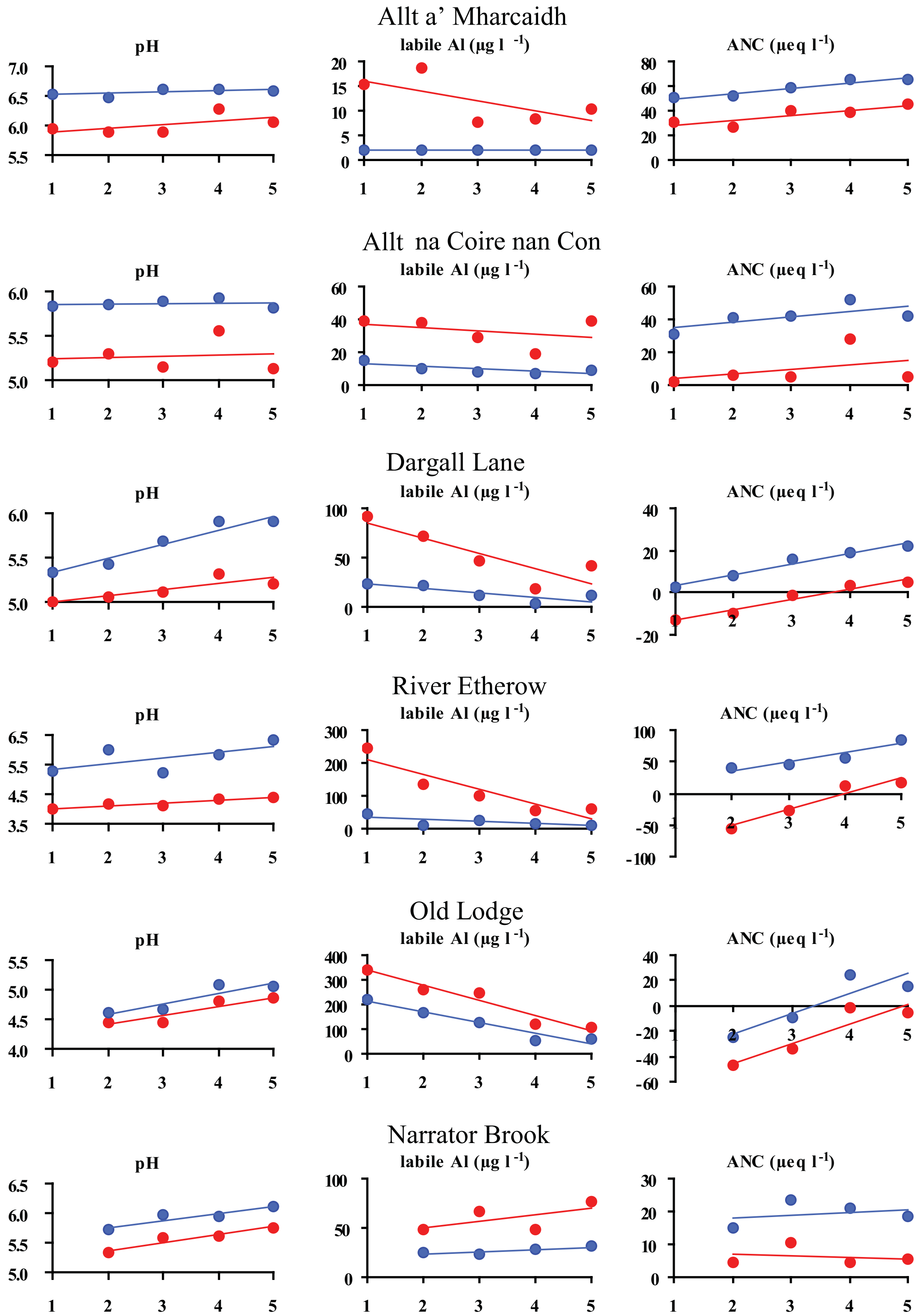

Figure 3.28. Trends in median (blue) and extreme (red) acidity in AWMN streams over five four-year periods: 1. pre-March 1992; 2. April 1992-March 1996; 3. April 1996-March 2000; 4. April 2000-March 2004; 5. April 2004-March 2008. Extreme acidity represented by 5th percentile of pH and ANC, and 90th percentile for labile Aluminium.

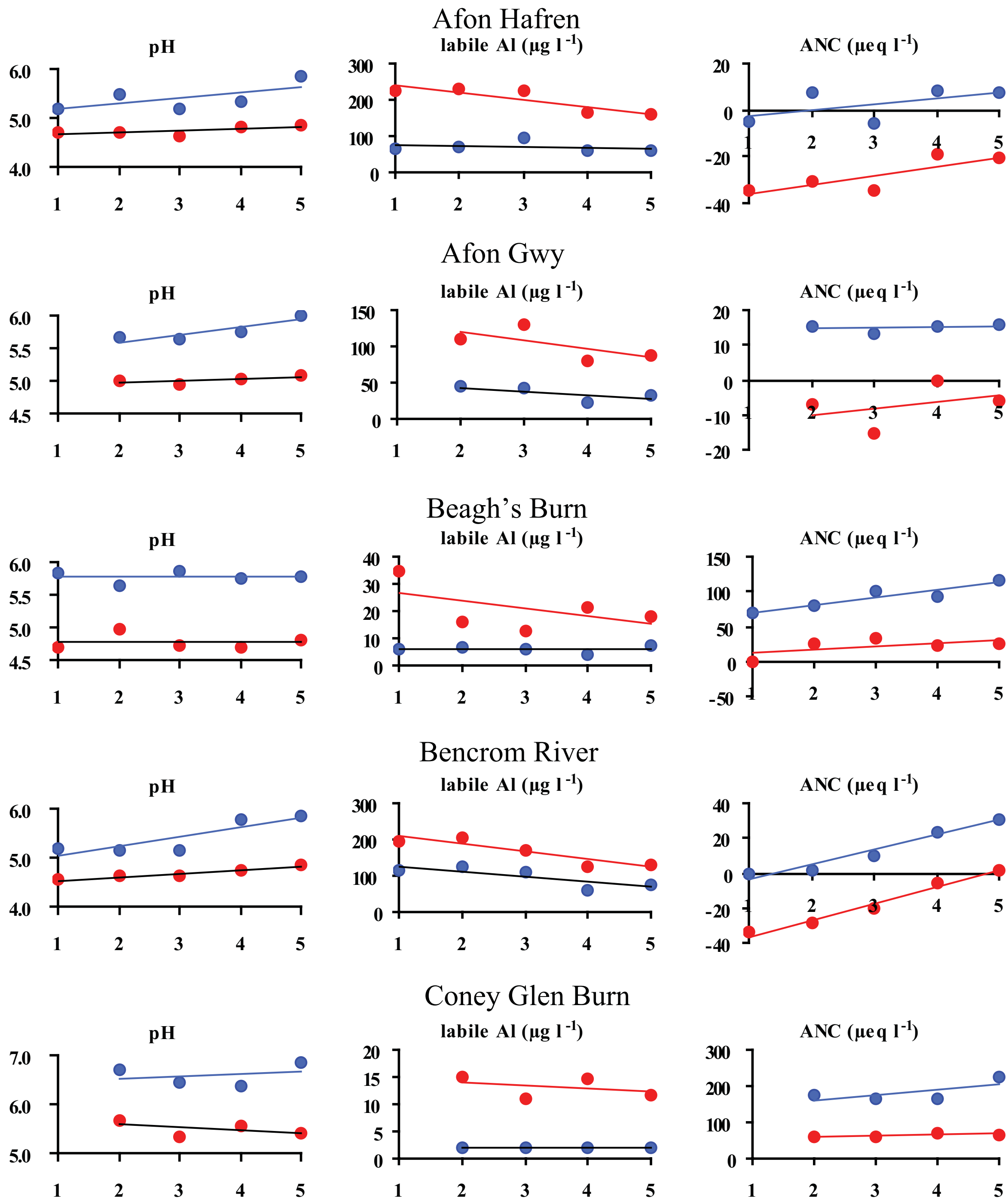

Figure 3.28 Cotd.

Linear regression was used to provide a rough approximation for change both in these extreme levels and in median levels over the 20 years of monitoring. The time-series are shown in Figure 3.28 and regression slopes are provided in Table 3.1.

Extremes and median ANC tend to parallel each other suggesting that the ANC depressions during acid episodes are mostly recovering as quickly as average annual levels. However, Figure 3.28 shows that 10th percentile ANC values in the most recent period still remain below zero in Old Lodge, Afon Hafren and Afon Gwy, while in addition those for Dargall Lane, the River Etherow and Bencrom River remain below the widely applied "critical limit" of 20 μeq l^{-1}.

Extreme (90th percentile) labile Al concentrations at several of the more acidic sites have been declining more rapidly than the median. Particularly sharp reductions in episodic labile Al are seen in Dargall Lane Burn, the River Etherow and Old Lodge, while slower rates of decline occur in the Afon Hafren, Afon Gwy and Bencrom River. Extreme levels in the River Etherow, Old Lodge, Afon Hafren, Afon Gwy and Bencrom River in the last period remain substantially above 50 μg l^{-1}, and could still represent toxic conditions for a range of acid-sensitive species.

Recovery in extreme pH (10th percentile) in the more acidic streams appears generally muted in relation to recovery in the median, but this mostly reflects the logarithmic relationship between pH and H^+. Recovery in H^+ is occurring at a similar rate in both cases.

Table 3.1. Linear regression slopes in median and extreme acidity in AWMN streams over five four-year periods. Extreme acidity represented by 5th percentile of pH and ANC, and 90th percentile for labile Aluminium.

	pH		**labile Al (μg l^{-1} yr^{-1})**		**ANC (μeq l^{-1} yr^{-1})**	
	10th percentile	median	90th percentile	median	10th percentile	median
Allt a' Mharcaidh	0.016	0.005	-0.5	0.0	1.0	1.0
Allt na Coire nan Con	0.003	0.000	-0.5	-0.4	0.7	0.8
Dargall Lane Burn	0.017	0.040	-3.9	-1.1	1.2	1.3
River Etherow	0.025	0.050	-11.2	-1.6	6.4	3.7
Old Lodge	0.038	0.044	-15.4	-10.6	3.9	3.9
Narrator Brook	0.033	0.030	1.7	0.6	-0.1	0.2
Afon Hafren	0.011	0.029	-4.8	-0.4	1.0	0.6
Afon Gwy	0.008	0.029	-2.9	-1.3	0.5	0.1
Beagh's Burn	-0.001	0.000	-0.7	0.0	1.2	2.7
Bencrom River	0.018	0.049	-5.4	-3.7	2.4	2.2
Coneyglen Burn	-0.014	0.010	-0.1	0.0	0.7	3.6

In summary, while several stream sites continue to show extremely acidic conditions during hydrological and sea-salt episodes that are likely to limit the rate of biological recovery, the reduction in severity of these is of similar magnitude to, and in the case of labile Al often faster, than, the reduction in "average" acidity. The continued occurrence of acid episodes should not therefore be considered as a significant additional factor preventing biological improvement. However it is clear that "extreme" levels of acidity are still very high in some AWMN stream sites. A clearer understanding of the tolerance of sensitive organisms to the effects of both H+ and aluminium, separately and synergistically, are still required before true "critical limits" can be established for acid-sensitive organisms in episodic systems.

Both duration of exposure and seasonal variations in sensitivity need to be taken into account when determining this sensitivity.

3.4. Key Points

The conclusions to be drawn from this analysis are consistent with those in the last major interpretative report (Monteith & Evans, 2005) in that chemical recovery is clearly underway and sites are continuing to respond to reductions in acid deposition. However this analysis has benefited from the application of a more sophisticated approach to trend analysis that has revealed new relationships and raised new hypotheses that need to be explored further.

Non-marine sulphate concentrations have fallen markedly in line with changes in S deposition, but changes with time are clearly non-linear with the bulk of the decline in concentrations occurring in the latter half of the 1990s. This is broadly consistent with patterns in xSO_4^{2-} deposition described in the previous chapter.

Since 2000, xSO_4^{2-} concentrations have mostly stabilised but concentrations at most sites remain several times higher than those in the least impacted region of northwest Scotland. As the contribution of long-term soil-stored SO_4^{2-} to most sites is thought to be small, the implication is that most regions continue to receive a significant acidifying load of xSO_4^{2-}.

Nitrate concentrations show great inter-annual variability, which in previous reports has been attributed solely to effects of variability in climate. There is now some evidence for direct responses to variability in N deposition and these require further investigation.

Few sites show indications of long-term upward or downward trends in NO_3^-. However there is a geographically discrete group of sites in the western Great Britain and eastern Northern Ireland that show small overall reductions. Concentrations in the moorland site Round Loch of Glenhead and the partly afforested site Loch Chon show evidence of gradual long-term increases, and given the declines in xSO_4^{2-} at both, the contribution of NO_3^- to “total acidity” has increased substantially at these sites.

Chloride concentrations also show long-term downward trends which are again non-linear. These changes are largely attributed to a long-term decline in sea-salt inputs associated with decreasing storminess, but there are indications that the decline at some sites is at least in part due to reductions in HCl deposition from anthropogenic sources. Research into this phenomenon is continuing.

AWMN sites show several strongly coherent temporal patterns in water chemistry, particularly with respect to xSO_4^2 and Cl^- concentrations, and as these tend to be the main drivers of surface water acidity this also results in clear similarities in trends in measures of acidity, and particularly ANC, for many sites. This degree of coherence will benefit prediction of chemical recovery for acidified UK waters more widely. In contrast NO_3^- concentrations, that were relatively coherent over the first 10 years of monitoring now show more heterogeneous behaviour. Further investigation into this divergence should improve our understanding of nitrogen cycling in upland systems.

There are clear improvements in pH and reductions in labile Al in most sites. Reductions in acidity are seen both in smoothed trends and in the severity of acid episodes, and the latter is likely to be of particular importance for biological recovery. However, labile Al concentrations at several sites, although much lower than 20 years ago, may still be too toxic for some acid-sensitive organisms, and to date there has only been a relatively small improvement in pH in these systems.

Responses in acidity and ANC are often more linear than drivers and demonstrate combined responses to falling levels of sea-salt deposition in the early period and a later response to falling xSO_4^{2-}.

In the last 2 years there has been a gradual rise in sea-salt deposition that has depressed pH and increased Al at more acid sites.

Several of the more acidic sites are at a critical stage in their chemical recovery, where small reductions in the acid load are expected to result in relatively large improvements in pH.

Chemical recovery is occurring in afforested and non-afforested sites alike. However, our rather restricted comparison of site pairs indicates that the legacy of much higher acid inputs in afforested sites (resulting from enhanced interception of atmospheric pollutants) may account for some afforested sites remaining in a more acidified condition.

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4. Epilithic Diatoms

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4.1. Introduction

The 'acid rain' issue served to highlight the importance of diatoms in assessing the acidification status of surface waters and stimulated the development of methods: (i) to reconstruct past lake-water pH from sediment cores using transfer functions (e.g. Birks *et al.*, 1990); and (ii) to monitor changes in acidity in streams and lakes. In both stream and lake systems experimental studies have shown that diatoms respond sensitively to pH and pH-related environmental factors, and that forms, concentrations and interactions of aluminium and DOC, as well as pH, can have a large influence on diatom species composition and biomass (Planas *et al.*, 1996; Junger & Planas, 1993; Gensemer & Payle, 1999). These findings are corroborated by field studies (e.g. Round, 1991, Kovács *et al.*, 2006; Passy & Legendre, 2006) and by the statistical analysis of diatom-chemistry training sets (cf. Birks *et al.*, 1990; Kingston & Birks, 1990). In addition there have been studies that show how rapidly species composition can change in response to a change in water chemistry (e.g. Cameron, 1995; Hirst *et al.*, 2004).

Diatoms are found in a range of different habitats in streams and lakes, each supporting highly diverse floras, and as community composition can vary seasonally, difficult choices need to be made to design a cost-effective monitoring strategy. This is especially so with respect to the timing and location for routine sampling and the selection of diatom habitats to be sampled. In oligotrophic soft water streams and lakes, the diatom epilithon (diatoms growing on rocks and stones) is usually the most diverse, and, as rock and stone substrates can be found in both lakes and streams, the epilithon was selected as the best community to use for monitoring in the AWMN.

Key questions to address after 20 years of sampling are:

- Have there been any significant changes in diatom assemblages across the Network?
- Are there differences between lakes and streams in terms of the extent of change?
- How can the different responses at individual sites be explained with reference especially to changes in acidity?

Data for each year of diatom epilithon sampling are detailed in the AWMN annual reports (e.g. Shilland *et al.*, 2009). This chapter summarises the results of epilithic diatom analyses carried out at the 22 AWMN lake and stream sites during the 1988 - 2008 monitoring period.

4.2. Results

The diatom data were analysed using Redundancy Analysis (RDA) and Principal Response Curves (PRC). The results of these analyses are shown on a site by site basis in Appendix 4 (Figs. 1-23 and Figs. 24-46, respectively). Here we describe the statistical methods used, summarise the results and describe the key findings at each site.

4.2.1. Redundancy Analysis

Diatom percentage frequency data were aggregated across the three replicate samples within a single site for each year. Prior to analysis the diatom count data were converted to percentages and $\log_{10}$ transformed with a constant of 1 added to zero values. The data were centred by samples and species. Principal Components Analysis (PCA) was applied to the log-transformed, double-centred data for each site individually to investigate the main patterns in the data. Based on these initial analyses, RDA, with sampling year as an explanatory variable, was carried out using log-transformed data as before. The resulting plots (Appendix 4, Figs. 1-23) show the results of the series of multivariate statistical analyses of the epilithic data for each site where the annual sample points are identified according to year of sampling and the points are linked together to establish a time-track of floristic change. RDA axis 1 generally reflects a shift in diatom assemblages characteristic of more acidic water to those found in less acidic conditions. The gradient of sample scores from lower to higher values along axis 1 through time since 1988 can therefore be regarded as corresponding to a pH gradient.

To test for the presence of a trend in the species percentage abundances a restricted permutation test was used in which the ordering of samples was maintained with starting samples selected via random cyclic shifts of the time-series. The maximum number of permutations is equal to the number of samples within each time-series, which, for the data here, is between 20 and 21, with the exception of Loch Coire Fionnaraich (VNG9402) for which only eight samples were available. The minimum *p*-value obtainable under such tests is 1/N where N is the number of permutations (number of samples), and is generally ~0.05 for most of the AWMN sites. The single constrained eigenvalue from each RDA ($RDA_{\lambda time}$) was compared to the eigenvalue of the first PCA axis ($PCA_{\lambda 1}$), i.e. the maximum amount of between-year variance that might be explained by a single variable or a fixed combination of variables. As $RDA_{\lambda time}$ approaches $PCA_{\lambda 1}$ the variance in the species data explained by a linear change in time is increasingly likely to be the single most important pattern of variance in the full species data.

The results of significance tests on the trend changes in diatom species abundances at each of the twenty-two sites over the duration of sampling are summarised in Table 4.1. A large amount of variation in the species data is accounted for by the temporal trend. In the majority of sites, the trend is strongly associated with the main axis of variation in the species data, illustrated by the large value of $RDA_{\lambda time}$ in comparison to $PCA_{\lambda 1}$. The table indicates that 14 sites (highlighted in dark grey) show significant trends in species composition at $\alpha = 0.05$ level, and a further four sites at the $\alpha = 0.10$ level (highlighted in light grey) during the twenty year monitoring period. Compared to the 1988-2003 series assessed in the 15 Year Interpretative Report (Monteith & Evans, 2005) two more sites are included within the group of sites showing a significant trend change. Significant floristic change trends ($\alpha = 0.05$) in the diatom epilithon were found in ten of the eleven lakes that have been monitored for most of the last 20 years while the time-trend at Loch Tinker is only significant at the $\alpha = 0.1$ level (Table 4.1). The maximum achievable significance of the trend test at Loch Coire Fionnaraich was restricted by the small number of observations. Four of the eleven streams showed significant linear trends in diatom epilithon (Allt a' Mharcaidh, Dargall Lane, River Etherow, and Afon Hafren) at the $\alpha = 0.05$ level with three (Afon Gwy, Beagh's Burn and Old Lodge) at the $\alpha = 0.1$ level. The four stream sites showing no significant trend are Allt na Coire nan Con, Bencrom River, Coneyglen Burn and Narrator Brook.

Table 4.1: Results of the Redundancy Analysis (RDA) trend analysis for the AWMN samples. $PCA_{\lambda 1}$ is the Eigenvalue of the first Principal Component Analysis (PCA) axis; $RDA_{\lambda time}$ is the Eigenvalue of the RDA axis; % PCA_1 and % RDA_1 are the variances in the species data explained by PCA axis 1 and time (RDA); *F* is the pseudo-*F* statistic; *n* is the number of samples in the series; min *p* is the minimum achievable *p*-value, and *p* is the exact permutation p value rounded to two decimal places.

Site Name	$PCA_{\lambda 1}$	$RDA_{\lambda time}$	% PCA1	% RDA1	F	n	min p	p
Allt na Coire nan Con	0.64	0.24	32.3	12.2	2.65	21	0.0476	0.19
Loch Coire nan Arr	0.32	0.25	24	18.6	4.12	20	0.05	<0.05
Beagh's Burn	0.74	0.33	25.6	11.4	2.46	21	0.0476	0.1
Bencrom River	0.14	0.04	27.5	7.4	1.52	21	0.0476	0.48
Blue lough	0.36	0.25	32.5	22.2	5.13	20	0.05	0.05
Burnmoor Tarn	0.3	0.22	22.6	16.9	3.86	21	0.0476	<0.05
Loch Chon	0.77	0.66	43.4	36.8	11.04	21	0.0476	0.05
Coneyglen Burn	0.75	0.22	27.6	8.1	1.59	20	0.05	0.3
Dargall Lane	0.33	0.25	45.9	35.3	10.36	21	0.0476	<0.05
River Etherow	0.95	0.71	34.1	25.5	6.52	21	0.0476	<0.05
Afon Gwy	0.23	0.12	32.4	17.1	3.29	18	0.0556	0.06
Afon Hafren	0.53	0.47	48.8	43	14.31	21	0.0476	0.05
Llyn Llagi	0.87	0.78	46.1	41.4	13.43	21	0.0476	0.05
Loch Grannoch	0.78	0.49	39.6	25	6.33	21	0.0476	0.05
Old Lodge	0.31	0.17	25.5	13.8	3.04	21	0.0476	0.1
Allt a' Mharcaidh	0.29	0.2	23.1	15.7	3.54	21	0.0476	0.05
Llyn Cwm Mynach	0.46	0.41	26.2	23.7	5.91	21	0.0476	0.05
Lochnagar	0.41	0.24	19.5	11.5	2.48	21	0.0476	0.05
Narrator Brook	0.34	0.11	23.3	7.8	1.51	20	0.05	0.35
Round Loch of Glenhead	0.42	0.38	35	31.1	8.58	21	0.0476	<0.05
Scoat Tarn	0.35	0.26	20.3	14.9	3.32	21	0.0476	0.05
Loch Tinker	0.28	0.18	21.2	13.9	3.06	21	0.0476	0.1
Loch Coire Fionnaraich	0.43	0.27	36.5	22.8	1.77	8	0.125	0.13

Figure 4.1 shows RDA axis 1 sample scores for the diatom data constrained by sampling year in order to construct fitted RDA trend models for each site. A LOESS smoother was fitted through each series to illustrate the trend in sample scores. Most sites show a strong trend in the diatom epilithon data through the period of sampling (1988-2008).

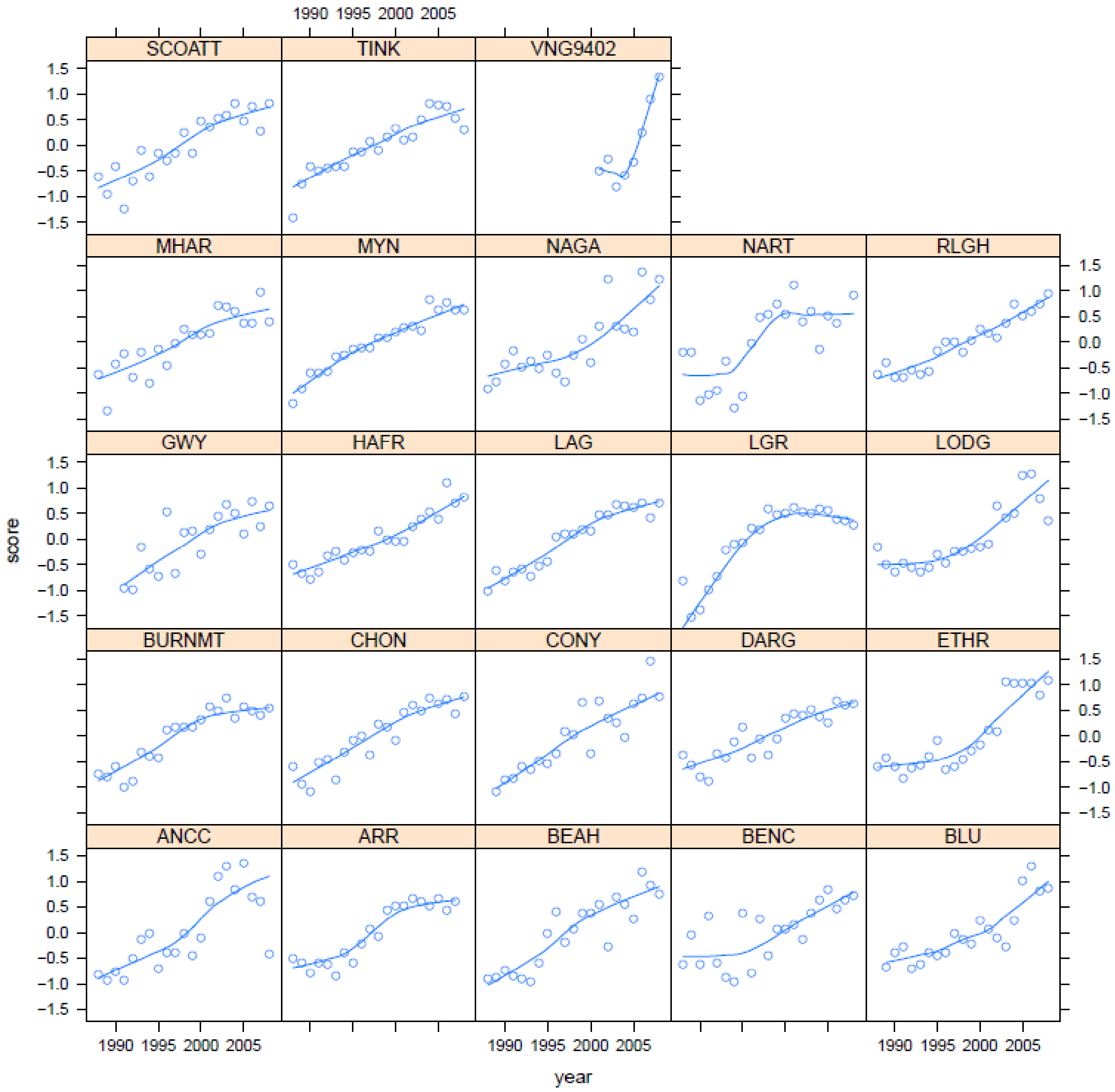

Figure 4.1. Axis 1 scores from Redundancy Analyses (RDA) fitted to the diatom epilithon data constrained by sampling year. The solid line in each plot is a LOESS smoother

4.2.2. Principal Response Curves

Principal response curves (PRC) were derived for all sites to illustrate the temporal variation in community structure at each site relative to an initial reference point, or control, based on the average species composition for the first three years within each series (i.e. 1988, 1989 and 1990). Diatom species counts were reset to 1 for those taxa not present in all samples, i.e. those that have a count in the "control" sample of < 1. As for the PCA (above), all manipulations were performed on the primary data which were subsequently converted to percentages, log-transformed and double-centred prior to analysis. In the sequence of PRC plots (Appendix 4, Figs. 24-46) time is oriented along the horizontal (x) axis, whilst the vertical axis represents the sample scores. The "control" is represented by the horizontal grey line positioned at 0 on the y-axis. The plotted points are therefore the sample scores on the first PRC axis. The distance between these plotted points and the "control" line represents the magnitude of compositional change relative to the "control" in the diatom assemblage at each time point. The plots are supplemented by a labelled rug plot on the right-hand axis (representing the species scores on the y-axis). If the sample scores are positive then those taxa with positive species scores become more abundant and those with negative species scores become less abundant. The opposite is true when sample scores are negative. Only the most significant taxa, i.e. those that show the strongest linear relationships with time at each site, are shown.

The PRCs for all 22 sites show changing RDA sample scores that are either negative or positive depending on species changes. The species showing the greatest positive or negative abundance changes are indicated by those taxa at the upper and lower extremes of the 'rug' (species code) lists shown on each PRC plot in Appendix 4, Figures 24-46. Most of the sites show changes compared to the 1988-1991 'control' period. At some sites the changes are not necessarily indicative of decreasing acidity, but in most cases the PRC changes are associated with increases in the abundance of more acid-sensitive taxa such as *Tabellaria flocculosa* and *Brachysira* species and relative declines in the abundance of acidobiontic species such as *Tabellaria binalis* and *Tabellaria quadriseptata*. Species scores from Loch Tinker, Afon Gwy, Beagh's Burn, Allt a' Mharcaidh, Scoat Tarn, Round Loch of Glenhead, Llyn Cwm Mynach, Dargall Lane, Loch Chon, Burnmoor Tarn, Llyn Llagi, River Etherow and Loch Coire nan Arr all show statistically significant floristic change consistent with decreasing acidity. Species compositional changes at several other sites are less clearly associated with reduced acidity according to our current understanding of the acidity preferences of species. These sites fall into two groups: (i) very acidic sites where the main chemical response to falling acid deposition to date has been falling labile aluminium concentrations rather than rising pH (i.e. Lochnagar, Loch Grannoch, Afon Hafren, Old Lodge, Bencrom River and Blue Lough; and (ii) some of the least acidified sites on the Network which have shown little change in acidity (i.e. Narrator Brook, Allt na Coire nan Con and the relatively short record for Loch Coire Fionnaraich).

4.3. Site Specific Summaries

Here we summarise the epilithic diatom changes that have taken place at each site over the monitoring period. The pH optima data for individual species presented are derived from the Surface Waters Acidification (SWAP) database (Stevenson *et al*., 1991). Diagrams showing the changes in species composition for epilithon are presented by Shilland *et al*. (2009).

4.3.1. Lakes

4.3.1.1. Loch Coire nan Arr (ARR)

Since the late 1990s the level of the loch has been regulated in order to ensure water supply at times of low rainfall. By 2005 the loch was being subjected to water-level changes of several metres. This has had a major impact on all aspects of the biology and for the past four years monitoring has been undertaken at a nearby site, Loch Coire Fionnaraich. This latter loch is now the control site for the Network replacing Loch Coire nan Arr.

From the start of monitoring until 2006 the diatom epilithon of this loch has shown relative stability with the relative abundances of *Brachysira vitrea* remaining similar throughout the sampling period (Shilland *et al.*, 2009). Some changes in relative abundances occurred with *Achnanthes minutissima* being common in the years between 1997 and 2005. At least eight less common diatom species have disappeared from the count data since 2004 but several new species were recorded after the mid-1990s. Because of the previously described disturbances, interpretation of these latter species changes is problematic.

4.3.1.2. Lochnagar (NAG)

The diatom assemblages sampled in this loch have been dominated throughout by *Achnanthes marginulata*, *Tabellaria flocculosa* and *Eunotia incisa* (Shilland *et al.*, 2009), none of which shows any obvious sustained long-term changes in relative abundances, although there is considerable inter-annual variability. The abundance of *Aulacoseira distans* var. *nivalis* (SWAP pH optimum = 5.0) increased progressively until about 2002, while *Peronia fibula* (SWAP pH optimum = 5.3) and *Eunotia naegelii* (SWAP pH optimum = 5.0) have both declined since around 2000. Several diatom taxa have become more abundant since 2002 including *Fragilaria virescens, F. vaucheriae* and *Diatoma hiemale*, all species indicative of less acid conditions. Palaeoecological work has shown previously that *Achnanthes marginulata* and *A. distans* var. *nivalis* increased in relative abundance in the sediments as the loch acidified during the 20th century. Over the latter period of monitoring (since 2004) both these taxa have declined, providing further evidence of recent recovery.

4.3.1.3. Loch Chon (CHN)

The epilithic diatom community of this loch showed clear changes in the abundances of common species during the monitoring period (Shilland *et al.*, 2009). The diatom assemblages have changed from those dominated by *Navicula leptostriata* (SWAP pH optimum = 5.1) and *Achnanthes marginulata* to those dominated by *Tabellaria flocculosa* and *Brachysira vitrea* (SWAP pH optima = 5.4 and 5.9 respectively). This indicates a switch to less acid conditions. 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. However, after 2006 its abundance has declined as *Tabellaria flocculosa* and *Cymbella lunata* expanded. Also, with respect to recovery trends, the loch experienced an increase in the acid-sensitive species *Achnanthes minutissima* after 2003. The abundance of this species has not been sustained and very low abundances were recorded for 2007 and 2008. Overall, recovery is indicated from the mid-1990s to mid-2000s but this is not supported by the most recent data for 2007-2008.

4.3.1.4. Loch Tinker (TINK)

The epilithic diatom community of this loch showed modest changes in the abundances of common species during the monitoring period (Shilland *et al.*, 2009). The most important changes have been the gradual increase in the acid-sensitive species *Achnanthes minutissima* (SWAP pH optimum = 6.3) and *Cymbella microcephala* (SWAP pH optimum = 6.3) since the mid-1990s. During the monitoring period declines in the relative abundances of *Fragilaria vaucheriae* (SWAP pH optimum = 6.3) and the acid-indicating diatom *Navicula subtilissima* from low to undetectable levels have been observed. *Brachysira vitrea* was the common diatom at this site but abundances show a fluctuating trend. Overall, the above diatom changes indicate only a small improvement in water quality. However, post-2006 changes do suggest further recovery is underway and data for the next five years should help confirm this.

4.3.1.5. Round Loch of Glenhead (RLGH)

The epilithic diatom community of this loch has undergone substantial change during the monitoring period (Shilland *et al.*, 2009) with species shifting from an assemblage dominated by the acidobiontic species *Tabellaria quadriseptata* (SWAP pH optimum = 4.9), and to a lesser extent *Eunotia incisa* (SWAP pH optimum = 5.1), to one increasingly dominated by *Navicula leptostriata* (SWAP pH optimum = 5.1) since 1994. *N. leptostriata* was not recorded in 1988 and 1990 but by 2008 this species comprised circa 50% of the entire epilithic assemblage.

4.3.1.6. Loch Grannoch (LGR)

The epilithic diatom assemblages in this loch exhibit considerable fluctuations in species abundances during the monitoring period (Shilland *et al.*, 2009). At the onset of monitoring the assemblage was dominated by *Asterionella ralfsii* (SWAP pH optimum = 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 while *Frustulia rhomboides* var. *saxonica* (SWAP pH optimum = 5.2) and *Eunotia incisa* (SWAP pH optimum = 5.1) increased temporarily. In 1993 the acidobiontic species *Tabellaria quadriseptata* (SWAP pH optimum = 4.9) was abundant in one sample, and subsequently this species became dominant in most samples until 2006. In the last two years of monitoring *Tabellaria quadriseptata* has declined strongly whilst *T. flocculosa, E. incisa* and *Peronia fibula* have increased. Perhaps significantly, the key declining taxa, *A. ralfsii* and *T. quadriseptata,* share the same SWAP pH optimum of 4.9, indicating that the floristic changes in the first five years of monitoring may not be directly related to recovery from acidification.

4.3.1.7. Scoat Tarn (SCOATT)

The epilithic diatom assemblages in this Lake District tarn show some consistent but modest changes in species abundance during the monitoring period (Shilland *et al.*, 2009). There are small increases in proportional abundances of some species e.g. *Peronia fibula* (SWAP pH optimum = 5.3) and clear declines in others with lower pH optima, including *Eunotia exigua* (SWAP pH optimum = 5.1) and *Tabellaria binalis* (SWAP pH optimum = 4.7).

4.3.1.8. Burnmoor Tarn (BURNMT)

The epilithic diatom assemblages in this tarn show some consistent but modest changes in species abundance during the monitoring period (Shilland *et al.*, 2009). Several species have increased in proportional abundance, particularly *Denticula tenuis* (SWAP pH optimum = 6.8), *Cymbella microcephala* (SWAP pH optimum = 6.3), *Cymbella cesatii* (SWAP pH optimum = 6.4) and, since 1996, the planktonic diatom *Cyclotella kuetzingiana* var. *minor*. Expansion of the latter species in the epilithon probably reflects the deposition of dead or dormant cells around the lake littoral. The clearest reduction in abundance is for *Nitzschia perminuta* (SWAP pH optimum = 5.7); *Tabellaria flocculosa* also becomes less common. However, the most common diatom *Achnanthes minutissima* shows relatively little change in abundance during the monitoring period.

4.3.1.9. Lyn Llagi (LAG)

The epilithic diatom assemblage of this lake was dominated by the acidobiontic species, *Tabellaria quadriseptata* (SWAP pH optimum = 4.9), *Eunotia incisa* and *T. flocculosa* during the first five years of monitoring (Shilland *et al.*, 2009). The former showed a sharp increase in abundance in a sediment core from the lake in levels dated to the latter half of the 20th century and it remained abundant in the epilithon until around 1995. After the mid-1990s other species including *Nitzschia perminuta* (SWAP pH optimum = 5.7), *Brachysira vitrea* (SWAP pH optimum = 5.9) and *Cymbella minuta* (SWAP pH optimum = 6.1) became more abundant, with *B. vitrea* dominating the assemblages after 2005. Overall, the diatom epilithon at this site shows strong evidence for a sustained improvement in water quality but it is to be noted that the increase in the relative abundance of *B. vitrea* is not continued after 2006.

4.3.1.10. Llyn Cwm Mynach (MYN)

The epilithic diatom flora of this lake has shown considerable and sustained change over the monitoring period (Shilland *et al.*, 2009). Most noticeably there has been a gradual replacement of *Eunotia rhomboidea* (SWAP pH optimum = 5.1) and *Eunotia vanheurkii* var. 1 (SWAP pH optimum = 5.1) by a range of generally slightly less acid indicating species. Initially these included *Brachysira brebissonii* (SWAP pH optimum = 5.3), *Eunotia denticulata* (SWAP pH optimum = 5.2) and *Navicula tenuicephala* (SWAP pH optimum = 5.3). After 1993 a further increase in less acid-tolerant taxa was observed, including *Brachysira vitrea* (SWAP pH optimum = 5.9) and *N. leptostriata*. These two taxa dominated the assemblage in 2008.

4.3.1.11. Blue Lough (BLU)

The epilithic diatom data for this lake show that the acidibiontic diatom *Tabellaria quadriseptata* (SWAP pH optimum = 4.9) dominated the assemblages between 1988 and 2003 (Shilland *et al.*, 2009). The distribution of the other acidobiontic species *Tabellaria binalis* (SWAP pH optimum = 4.7) is also generally similar but this species is present only at very low frequency after 2004. *Brachysira brebissonii* (SWAP pH optimum = 5.3) generally increases in frequency after 1993 and several less common species (e.g. *Semiorbis hemicyclus, Navicula subtilissima*) also increase in later years. Overall, the epilithic diatoms in this lake indicate a slight decline in acidity as the classic acidification indicators *T. quadriseptata* and *T. binalis* have both decreased in abundance. However, they have been replaced by other species also indicative of high acidity suggesting that there has been little overall improvement.

4.3.1.12. Loch Coire Fionnaraich (VNG9402)

This loch was added to the research Network in 2001 to replace the increasingly disturbed Loch Corrie nan Arr and hence there are no pre-2001 data for this site. The site was selected to be similar to its redundant counterpart and unsurprisingly the diatoms, *Brachysira vitrea* and *Tabellaria flocculosa* are common in both lochs. Abundances of *Achnanthes minutissima* and *Peronia fibula* were however different with the former being of low abundance in Loch Fionnaraich. Despite this loch being selected as a ‘reference site’, being in an area of low atmospheric deposition in north western Scotland, the diatom assemblages indicate a significant shift in species abundances since 2005 when the relative abundance of *Tabellaria flocculosa* expanded while other species (*P. fibula, B. vitrea* and *B. brebissonii*) declined. A few valves of *Tabellaria flocculosa* f. IIIp, a planktonic variety of the species, were noticed in the 2008 samples but counts were combined with those of the nominate form for present purposes. In summary, the diatoms at this site show clear changes but the eight-year monitoring period is insufficient to demonstrate a significant trend.

4.3.2. Streams

4.3.2.1. Allt a' Mharcaidh (MHAR)

During the twenty-year monitoring period there has been a small but significant change in the composition of the epilithic diatom flora (Shilland *et al.*, 2009). The common species *Synedra minuscula, Achnanthes minutissima* and, to a lesser degree, *Fragilaria vaucheriae* and *Tabellaria flocculosa,* are present throughout the sampling period. However, *S. minuscula* tended to be most common during the middle years of the sampling period. Other species showed fluctuations with *A. minutissima* increasing moderately since 2005. There has also been a small increase in the acid tolerant species *Eunotia incisa* (SWAP pH optimum = 5.1) possibly indicating lower pH values.

4.3.2.2. Allt na Coire nan Con (ANCC)

The epilithic diatom community of the Allt na Coire nan Con has varied substantially since the onset of monitoring (Shilland *et al.*, 2009). The data show a switch from a dominance by *Achnanthes saxonica* in the first half of the record to *Tabellaria flocculosa* and *Synedra minuscula* in the middle period of monitoring. *Eunotia incisa* tended to increase in the first five years of the 21st century but has declined after 2007. Overall, only small chemical changes have occurred at this site and despite the substantial variability in the diatom flora the overall trend indicated by the diatoms is also modest, possibly indicating slightly higher acidity in the early 2000s. The latter is consistent with the increase in stream-water DOC but further years of data are needed to clarify the underlying causes of diatom changes at this site.

4.3.2.3. Dargall Lane Burn (DARG)

The epilithic diatom assemblage in this stream shows a clear long-term trend in species abundance changes with considerable fluctuations in species abundances during the monitoring period (Shilland *et al.*, 2009). The most common diatoms throughout the monitoring period are *Tabellaria flocculosa* (SWAP pH optimum = 5.4) and *Peronia fibula* (SWAP pH optimum = 5.3) and both fluctuate in abundance with a tendency for reciprocal dominance, with the former showing abundance peaks around 2000 and in 2008 and the latter in the mid-1990s and in 2006. A marked reduction in the relative abundances of *Eunotia naegelii* (SWAP pH optimum = 5.0) and *Eunotia incisa* (SWAP pH optimum = 5.1) occurred between the late 1980s and around 1996. *Brachysira vitrea* (SWAP pH optimum = 5.9) an acidification recovery indicator for many acidified sites, shows a small but clear increase in abundance in years 2007 and 2008. Overall, this site shows considerable changes that are consistent with recovery from acidification.

4.3.2.4. River Etherow (ETHR)

The epilithic diatom community of this stream showed more inter-annual variability than any other site on the Network (Shilland *et al.*, 2009). The most notable floristic changes have been a reduction in the acidophilous/acidobiontic species *Eunotia exigua* (SWAP pH optimum = 5.1) during monitoring, and progressive increases in the more acid-sensitive species *Gomphonema angustatum* (SWAP pH optimum = 5.8) and *Achnanthes saxonica* (SWAP pH optimum = 5.7). *A. minutissima* has usually dominated but species fluctuations have resulted in *Eunotia rhomboidea* and *E. exigua* also being dominant at times. The large fluctuations in species abundances encountered during the monitoring period possibly reflect hydrologically driven variability in acidity at this site. The diatom flora nevertheless provides clear evidence of a biological response to falling acidity levels.

4.3.2.5. Old Lodge (LODG)

In common with the other more acidic streams on the Network, the epilithic diatom assemblage of this stream shows clear, fairly consistent changes in species abundances throughout the monitoring period (Shilland *et al.*, 2009). The assemblages were usually dominated by the acidophilous/acidobiontic species *Eunotia exigua* (SWAP pH optimum = 5.1). However, since around 2000 frequencies of this species have declined. The assemblages have become more diverse since the mid-1990s with increases in *Frustulia rhomboides* var. *viridula* (SWAP pH optimum = 5.3), *Nitzschia gracilis* and *Surirella linearis* (SWAP pH optimum = 5.3). Although there is some evidence that the assemblage has responded since 2000 to the recent rise in water pH that began in the late 1990s, the last 2008 sample marks a return to high abundance of *Eunotia exigua*.

4.3.2.6. Narrator Brook (NART)

The epilithic diatom flora of this stream shows strong inter-annual variation with the acid-sensitive *Achnanthes minutissima* dominant in most samples and in most years (Shilland *et al.*, 2009). Between 1998-2003 *A. minutissma* relative abundances were depressed relative to *Fragilaria vaucheriae, Surirella linearis* and *Eunotia vanheurkii* var. *intermedia* (the last species has a considerably lower pH optimum). These changes coincide with a period of higher xSO_4 and labile aluminium concentrations but no obvious change in pH. In 2008, the acidophilous species *E. vanheurkii* var. *intermedia* again dominated the assemblage. Overall, the diatoms exhibit considerable variability in species changes but these do not correspond with a significant trend change during the monitoring period. The marked increase in *E. vanheurkii* var. *intermedia* in the 2008 samples could indicate a return to more acid conditions and a decline in water quality but data for the next five years are needed to verify this.

4.3.2.7. Afon Hafren (HAFR)

The epilithic diatom community in this stream has been dominated by one acidophilous/acidobiontic species (Shilland *et al.*, 2009), *Eunotia exigua* (SWAP pH optimum = 5.1). Only in years 1990 and 2005 did frequencies of this diatom fall below 40% and in most samples, in most years, *E. exigua* formed >70% of the assemblage. In 1990 its abundance was suppressed by *Achnanthes austriaca* var. *minor* (SWAP pH optimum = 5.1) and in 2005 by *Tabellaria flocculosa* (SWAP pH optimum = 5.4). Since 1997, abundances of this latter species have progressively increased from trace amounts to becoming the dominant species in 2006. In 2008 another marked change occurred with the arrival of *Fragilaria virescens* at the site and by 2008 its abundance was second only to *E.*

exigua. In general, these epilithic diatom changes are consistent with a gradual recent improvement in pH. However, the strikingly high abundances of *T. flocculosa* in 2006 may also reflect the influence of other factors affecting pH, especially the low sea-salt inputs during the winter and spring of that year. The unusual abundance of *Fragilaria virescens* in 2008 could indicate the onset of other significant water quality changes but further monitoring would be needed to verify this.

4.3.2.8. Afon Gwy (GWY)

Similar to the Afon Hafren, in the early years of monitoring the acidophilous / acidobiontic species *Eunotia exigua* (SWAP pH optimum = 5.1) dominated the epilithon diatom community of this stream. However, abundances have declined from peak levels in the late-1990s, as *Tabellaria flocculosa* (SWAP pH optimum = 5.4), again in common with the Afon Hafren, has increased from very low abundances in the early 1990s. The epilithon changes at this site are consistent with a gradual improvement to elevated water pH after about 1995. There has been a general decline in representation of less common taxa at this site, so that diversity has declined.

4.3.2.9. Beagh's Burn (BEAH)

The epilithic diatom flora of this stream shows major changes in floristic composition with increasing frequencies of *Eunotia exigua* and *Gomphonema angustatum* in the first five years of monitoring followed by very high abundances of *Achnanthes minutissima* (>70%) in 1994 and immediately by high abundance of *Synedra minuscula* (>70%) in 1995 (Shilland *et al.*, 2009). These major floristic fluctuations are followed by a more progressive increase since 1996 in the relative abundance of *Achnanthes saxonica* (SWAP pH optimum = 5.7). This species was scarce in the early years of monitoring and never exceeded 10% relative abundance, but by 2006 it comprised over 60% of the assemblage. Few species show clear reductions in abundance but by 2008 *A. minutissima* had virtually disappeared from the assemblage. In the last three years of monitoring *A. saxonica* has declined as the acid indicating *E. exigua* has increased. Overall, this stream shows no significant progressive pattern of change during the monitoring period and major species fluctuations are likely to be at least partly explained by extreme hydrological episodes. Species less tolerant to acid conditions are however associated with the mid-1990s to the mid-2000s period but acid tolerant *E. exigua* has increased in years 2007 and 2008 perhaps indicating a recent decline in water quality.

4.3.2.10. Bencrom River (BENC)

The epilithic diatom flora of this stream has been dominated by *Eunotia naegelii* (SWAP pH optimum = 5.0) and *Brachysira brebissonii* (SWAP pH optimum = 5.3) throughout the monitoring period (Shilland *et al.*, 2009). However, the frequencies of the former increased during the 1988-2003 period while those of the latter species have declined. After 2003, *E. naegelii* declined as abundances of *Frustulia rhomboides* var. *saxonica* (SWAP pH optimum = 5.2) and *B. brebissonii* tended to increase. In the last year of monitoring both *E. rhomboidea* and the less acid tolerant *Brachysira vitrea* (SWAP pH optimum = 5.9) both show increased abundances. Overall, the diatom changes in this stream show a significant trend change but only a slight decrease in acidity over the last four years. The highest frequency of the less-acid indicator *B. vitrea* occurred in the last year of sampling but data for the next five years are needed to verify this change.

4.3.2.11. Coneyglen Burn (CONY)

The epilithic diatom data for this stream shows that although *Achnanthes minutissima*, *Synedra minuscula* and *Gomphonema angustatum* were the most common, their frequencies varied quite considerably (Shilland *et al.*, 2009). *A. minutissima* declined after the first year of monitoring as *S. minuscula* increased in frequency. In years around 1990, *G. angustatum* tended to increase in frequency while those of *S. minuscula* declined. This latter species recovered in abundance, becoming the most common species in 2004. In the last three years of monitoring *S. minuscula* was replaced by *G. angustatum, Eunotia tridentata* and several *Achnanthes* species. The epilithic diatom data show strong inter-annual variability, reflecting similar variability in water chemistry data. The diatom changes, though quite marked, do not constitute a significant trend change and there is no clear indication of any change in acidity. This is an expected result at a relatively high alkalinity site in a low acid deposition region.

4.4. Discussion

At most sites progressive change in assemblage composition is apparent throughout most of the twenty year period of observation and this is broadly consistent with linear changes in pH seen at the same sites (see Chapter 3, Fig. 3.9). At some sites diatom communities show relative stability in the early years of monitoring (Bencrom River, River Etherow, Old Lodge, Narrator Brook) but change later (again consistent with pH change, with the possible exception of the River Etherow), while others exhibit initial trends in epilithon followed by periods of little floristic change (Loch Coire nan Arr, Burnmoor Tarn, Loch Grannoch). The changes in Loch Coire nan Arr may reflect the major disturbance to the littoral habitat in the lake following the installation of a permanent dam around the turn of the century. Uniquely for the Network, the change in Loch Grannoch is indicative of several years of deteriorating acidity followed by more recent improvement, and this again is reflected in the pH trend for this site.

The nature of diatom change is broadly similar to that reported in the 1988-2003 diatom epilithon data report (Monteith *et al.*, 2005). Biological improvement, as inferred by increasing abundances of diatom species indicative of less acid conditions relative to those indicative of more acid conditions, has occurred at most of the sites showing significant floristic change. But for the first time we are able to show that the timing of floristic change differs between sites, and at most sites this is consistent with the timing of change in pH.

The overall pattern of recovery is summarised in Table 4.2, where the floristic changes are compared to catchment afforestation, measured pH change and diatom-inferred pH change as defined by Shilland *et al.* (2009). The sites that show no statistically significant floristic change are all stream sites in low deposition areas where little or no change is expected.

Other factors which may be influencing compositional change in the diatom epilithon potentially include the catchment land-use, especially at the afforested sites, climate change (precipitation, temperature and sea-salt incursions), nutrient enrichment from atmospherically deposited nitrogen and changes in dissolved organic carbon concentrations (see Chapter 9). However, none of these factors is as yet sufficiently important to disguise the influence of pH increase as the dominant driver.

Table 4.2. Summary of site data for the 1988-2008 period showing degree of catchment afforestation (>2%) and indicating recovery in measured pH, the significant diatom changes and recovery in diatom inferred pH. pH recovery significance refers to all or part of the monitoring period (see Chapter 3). *indicates significance at the < 95% level or, for diatom inferred pH, indicates only a slight recovery in the last five years of monitoring (see Shilland et al. 2009).

	Catchment afforested	Significant pH recovery	Significant diatom floristic change	Diatom inferred pH recovery
Allt na Coire nan Con	Yes			
Loch Coire nan Arr			Yes	
Beagh's Burn			Yes*	
Bencrom River		Yes		Yes
Blue lough		Yes	Yes	Yes*
Burnmoor Tarn			Yes	Yes
Loch Chon	Yes	Yes	Yes	Yes
Coneyglen Burn	Yes			
Dargall Lane		Yes	Yes	Yes
River Etherow		Yes*	Yes	Yes
Afon Gwy		Yes	Yes*	
Afon Hafren	Yes	Yes	Yes	Yes*
Llyn Llagi		Yes	Yes	Yes
Loch Grannoch	Yes	Yes	Yes	
Old Lodge		Yes	Yes*	
Allt a' Mharcaidh		Yes*	Yes	Yes
Llyn Cwm Mynach	Yes		Yes	Yes*
Lochnagar		Yes	Yes	Yes
Narrator Brook		Yes		
Round Loch of Glenhead		Yes	Yes	Yes
Scoat Tarn		Yes	Yes	
Loch Tinker		Yes*	Yes*	Yes*
Loch Coire Fionnaraich		na	na	na

4.5. Key Points

At most sites there have been marked changes in the diatom epilithon data throughout the period of observation (1988-2008). At some sites, however, the trend change has occurred following a period of relative stability at the beginning of monitoring while others have changed most in the first few years of monitoring.

A large amount of variation in the species data is accounted for by the temporal trend. A statistically significant trend in diatom epilithon species change was observed in 18 of the 23 sites. In the majority of sites, the trend is strongly associated with the main axis of variation in the species data, illustrated by the large value of $RDA_{\lambda time}$ in comparison to $PCA_{\lambda 1}$.

Principal response curves (PRCs) (See Appendix 4) show that the magnitude of the compositional change in diatom assemblages varies considerably between sites. The timing of floristic change also varies according to site location within the twenty-year monitoring period. There is also evidence that the stream assemblages are more variable than lake assemblages and that, as a result, underlying trends at some stream sites are more difficult to detect.

Compositional changes are displayed in the PRCs using the first three years of data as a 'control'. These changes are often associated with increases in the abundance of more sensitive taxa such as *Tabellaria flocculosa* and *Brachysira* species, relative to acidobiontic species such as *Tabellaria binalis* and *T. quadriseptata*.

Following compositional changes that provide evidence for decreasing acidity, the diatom flora at some sites stabilise (Llyn Llagi) or undergo different trajectories of change, particularly in the most recent samples (Loch Chon, Afon Hafren, Old Lodge) suggesting that the effect of increasing pH is being offset by other factors.

Other factors which may be influencing compositional change in the diatom epilithon are hydrological variation (especially in streams), catchment land-use (especially forest management practices), climate change, nutrient enrichment (from N deposition) and changes in dissolved organic carbon concentrations.

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5. Aquatic Macrophytes

Ewan Shilland and Don Monteith.

5.1. Introduction

Macrophytes are the larger plants of fresh water, readily distinguished by the naked eye and include angiosperms (flowering plants), pteridophytes (ferns, horsetails and quillworts), bryophytes (mosses and liverworts), charophytes (stoneworts) and filamentous algae. The growth within a particular site of individual species, and species groups, is controlled by a complex interplay of environmental conditions such as water chemistry, depth, temperature and flow, nutrient and light availability as well as competition and disturbance. The UK Acid Waters Monitoring Network (AWMN) sites are largely upland, acid and oligotrophic and thus host macrophyte species specialised to grow in cooler water with low pH and low nutrient levels. Changes in these key parameters affect species composition and abundances. Monitoring at AWMN sites is undertaken to determine whether macrophyte species have responded to changes in chemical conditions at these sites.

Attempts have been made to classify rivers and lakes within the UK on the basis of their plant species and associated physical and environmental characteristics (e.g. Rodwell, 1995; Palmer, 1992; Holmes, 1999; Duigan *et al*., 2007). The AWMN streams fall into Group D "acid and nutrient-poor rivers" in the framework provided by Holmes (1999), and more specifically the DXa, DXd and DXe classifications. Lakes are mainly classed as Types 2 and 3 from Palmer (1992), Types C1 and C2 after Duigan *et al* (2007), National Vegetation Classification types A7, A14, A9c, A22, A23 and A24 (Rodwell 1995), and EU Habitats Directive Annex 1 Habitat 3130 "Oligotrophic to mesotrophic standing waters with vegetation of the Littorelletea uniflorae and/or of the Isoëto-Nanojunceteae".

Key questions to address after 20 years of sampling are:

- Have there been any significant changes in macrophyte assemblages across the Network?
- Are there differences between lakes and streams in terms of the extent of change?
- Can the different responses at individual sites be explained with reference especially to changes in water chemistry?

5.2. Methods

The macrophyte flora of each site is sampled in an easily replicated fashion so that broad qualitative changes in both floristic composition and relative abundance can be assessed. Within the period mid-June to September each stream is sampled annually while lakes are sampled biannually, and, since 2007, triannually. Sampling is undertaken centrally by ENSIS-ECRC at UCL and quality control is ensured by the collection and preservation of voucher specimens and the exchange of specimens with botanical experts based at the Natural History Museum London, The Royal Botanical Gardens Edinburgh and the University of Bergen.

5.2.1. Lakes

Each lake is sampled by three methods:

Inshore survey
As much of the inshore zone as possible is viewed either by walking the shoreline, wading or from a slow-moving boat. Emergent, floating and submerged macrophytes in the shallow inshore zone are recorded and major stands annotated on a large-scale map. Major vegetation types fringing the lake are also recorded.

Trawl survey
Two transverse trawls (four in larger lakes) are made across the lake by trawling a grapnel (double-headed rake) attached to a long rope behind a boat travelling at a steady speed. Each traverse is sub-divided into five approximately equal trawl sections for which the amount of plant material recovered and relative abundance of individual macrophyte taxa are estimated. Trawls are carefully situated away from coring sites and sediment traps.

Transect survey
Three sites in each lake (four in larger lakes) are chosen for more detailed survey transects of 50-60 m in length aligned perpendicular to the shore. At least one transect is located on a steeply shelving and/or exposed shore. A fixed line is deployed along the transect and Ekman grab samples are taken from the sediment surface at 10 m intervals with an additional site 5 m from the shore. Water depth, substrate type, amount of plant material and relative abundance of species are recorded for each Ekman grab sample and the exercise is duplicated at each sample point along the transect.

The location of end stations of both lake trawls and transects are recorded by GPS to ensure that subsequent sampling occurs in the same areas. Since the trawls and transect survey are destructive sampling methods, sampling exactly along previous survey lines is avoided as far as possible. In practice however the process of setting the transect can result in overlaps between visits.

The combination of the three survey methods provides information to assess the relative abundance of individual macrophytes occurring in each lake. Moreover, the profiles generated by the transects indicate the approximate maximum depth to which living macrophytes extend. This information is transferred to the central biological database and summarised in the annual reports of the Monitoring Network as a list of taxa together with DAFOR abundance estimates (e.g. Shilland *et al*., 2009).

5.2.2. Streams

Dry-weather flow is a pre-requisite for sampling in-stream macrophytes. A 50 m section of stream containing a representative range of aquatic macrophytes is selected. Every 5 m from 0-50 m inclusive, a transect is laid across the water-filled section of the channel and water depth, substrate and macrophyte taxa (if any) are recorded at three equidistant points along that transect. In the 5 m stream sections between each transect the stream bed is surveyed and the total amount of plant cover (expressed as a percentage of submerged stream bed) and floristic composition of the plant assemblages are estimated visually; the substrate composition of the stream-bed is also recorded in these sections, which are easily replicated in subsequent surveys.

Major morphological features and the location of notable growths of plants in the channel are annotated on large-scale sketch maps. Plants growing in the channel and on the banks not submerged during dry-weather flow are also recorded. All submerged plants are recorded; data are transferred to the central biological database and appear in the annual report of the Monitoring Network as a summary list which indicates the estimated percentage of submerged stream bed throughout the 50 m length covered by each taxon (e.g. Shilland *et al*., 2009).

5.3. Results

5.3.1. Lakes

5.3.1.1. Loch Coire nan Arr

At the onset of monitoring Loch Coire nan Arr contained a diverse plant assemblage. By 1997 disruption of water levels resulted in a loss of almost all emergent macrophytes, as well as declines in some submerged species, and surveying ceased in 1999 with efforts redirected at the nearby replacement site, Loch Coire Fionnaraich.

5.3.1.2. Lochnagar

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 dissolved organic carbon (DOC) and a slight concomitant reduction in transparency, *I. lacustris* has expanded its depth range from little more than 1 m initially to around 3 m in some parts of the loch more recently. Unlike other lakes in the Network, e.g. Loch Tinker, the depth range of this species is clearly not limited by light availability which remains high (e.g. Secchi disc depths regularly reach 8-10 m), and its success at greater depths is more likely to reflect higher water temperatures or nutrient availability.

J. bulbosus var. *fluitans* only occurred in very limited stands at the outset of monitoring but now occupies substantial areas, particularly along the eastern shore of the loch. This area also now hosts a population of *Subularia aquatica*, first observed in the loch in 2009. *Fontinalis antipyretica*, extremely localised in two small patches next to lake-side seeps when monitoring began, has now spread out from both locations.

5.3.1.3. Loch Chon

The aquatic macrophyte flora at Loch Chon has remained largely constant since monitoring started, and exhibits a relatively diverse submerged and emergent assemblage of typically oligotrophic species. The acid-sensitive angiosperm *Subularia aquatica*, not detected prior to

1995, has since been recorded in several locations in all sampling years. Likewise, the charophyte *Chara virgata* was found for the first time in 1999 and recorded at the same location in all subsequent surveys.

5.3.1.4. Loch Tinker

There has been little change in the aquatic macrophyte composition at Loch Tinker during the monitoring period. Of note, however, is the appearance of the acid-sensitive species *Subularia aquatica*, not detected until 1995 after which 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 subsequently but has become constant since 1999. *Chara virgata* was found for the first time in 2005 but was not observed in 2009.

5.3.1.5. Round Loch of Glenhead

Whilst some emergent species have declined slightly, the submerged aquatic macrophyte composition at Round Loch of Glenhead has remained relatively constant, with the exception of the detection in 2003 of the acid-sensitive elodeid species *Myriophyllum alterniflorum* (Fig. 5.1). This species was detected at a single open water location that year 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.

5.3.1.6. Loch Grannoch

The typically acidified oligotrophic macrophyte flora of Loch Grannoch is dominated by the acid-tolerant species *Littorella uniflora*, *Lobelia dortmanna*, *Isoetes lacustris* and *Juncus bulbosus* var *fluitans*. The liverwort *Nardia compressa* and the moss *Sphagnum auriculatum* are also common, the latter particularly in deeper water at the northern end of the loch where it forms a dense carpet over the lake bottom. Emergent species such as *Carex rostrata* and *Phragmites australis* and the floating-leaved water lily *Nymphaea alba* are restricted to sheltered bays, mostly on the eastern side of the loch. There were no major changes in the assemblage up until the last survey performed in 2005.

5.3.1.7. Scoat Tarn

The aquatic macroflora of Scoat Tarn is typical for an upland oligotrophic and acidified lake, being dominated mostly by isoetid taxa (predominantly *Isoetes lacustris*), mosses including *Sphagnum* sp. and *Hyocomium armoricum*, and liverworts such as *Nardia compressa*. The isoetid *Lobelia dortmanna*, that is common in lower altitude AWMN sites is sparse and is considered to be close to its altitudinal limit. There has been no indication of change over the monitoring period.

5.3.1.8. Burnmoor Tarn

The aquatic macrophyte assemblage of Burnmoor Tarn has been dominated throughout by isoetid taxa but has also included acid-sensitive species such as *Myriophyllum alterniflorum* and the charophyte *Nitella flexilis* var. *flexilis* agg., both absent from the more acid AWMN lakes. Two more acid-sensitive charophytes have established during recent years; *Chara virgata* has been recorded since 2003 and has increased in abundance during subsequent surveys and, in 2008, *Nitella translucens* was found in deeper water, the first occurrence of the species at any site across the Network. The expansion of charophytes may be linked to the marked increase in bicarbonate alkalinity in this lake which is too well buffered to have undergone much change in pH.

5.3.1.9. Llyn Llagi

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 has been found again in surveys from 2003 onwards. A further increase in the numbers of more sensitive species was observed in 2009, with the discovery of *Nitella flexilis* var. *flexilis* agg. and *Elatine hexandra*. The spatial distribution of the acid-tolerant *Juncus bulbosus* var. *fluitans* appears to have expanded slightly over the full monitoring period.

5.3.1.10. Llyn Cwm Mynach

The aquatic macrophyte flora in Llyn Cwm Mynach is relatively diverse for an AWMN lake, partly as a result of the range of habitats at this site. There are two distinct basins with a shallow limb separated from the deeper main basin by a stone causeway. 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 genus has a preference for elevated levels of heavy metals (John *et al*., 2002) and may indicate the influence of some small abandoned manganese mine workings within the catchment on the water chemistry. *Plectonema* has formed a thick blanket over other submerged vegetation to the extent that *Juncus bulbosus* var. *fluitans* plants in parts of the lake were unable to survive and now form substantial rafts of decaying debris around the shore of the lake. Despite 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. Small amounts of *Isoetes lacustris* were first recorded in 1999 and it has been found again in all but the most recent survey.

5.3.1.11. Blue Lough

The aquatic macroflora of Blue Lough remains dominated by an acid tolerant assemblage of the isoetid species *Isoetes lacustris* and *Lobelia dortmanna*, the aquatic rush *Juncus bulbosus* var. *fluitans,* the moss *Sphagnum* sp. and liverwort *Cephalozia bicuspidata*. Species composition and abundances have been stable since 1989.

5.3.1.12. Loch Coire Fionnaraich

As the replacement 'control site' for Coire nan Arr in the AWMN this loch has only been surveyed three times, in 2003, 2005 and 2009. Within this period the aquatic flora has remained very stable. The aquatic macrophytes are typical for a relatively unimpacted acid oligotrophic loch, with *Lobelia dortmanna* and *Littorella uniflora* abundant in the shallows, *Myriophyllum alterniflorum* and *Juncus bulbosus* var. *fluitans* growing in the slightly deeper water and *Isoetes lacustris* furthest down, reaching a maximum depth of about 3 m. The more acid sensitive species *Subularia aquatica*, *Callitriche hamulata* and *Nitella flexilis* agg. are also found but at lesser abundances. Of note is the absence of any major beds of emergent plants, even in more sheltered locations. As a reference site in the AWMN, the flora of this loch provides an example of the range of species that could have occurred previously at many acidified sites in the Network and that might be expected to return during the recovery process.

5.3.2. Streams

5.3.2.1. Allt a' Mharcaidh

The aquatic macrophyte flora of Allt a' Mharcaidh has been dominated largely by the acid-sensitive aquatic moss, *Hygrohypnum ochraceum* since the onset of monitoring in 1988. While there has been virtually no species losses or gains, overall bryophyte cover of the stream bed has increased, mainly as a result of greater abundances of 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 of increased coverage.

5.3.2.2. Allt na Coire nan Con

The aquatic macrophyte characteristics of the survey stretch at Allt na Coire na Con have changed substantially over the monitoring period. In the first four years of monitoring the acid-sensitive moss *Hygrohypnum ochraceum* was common, with substantial coverage in some permanently submerged parts of the survey stretch. After 1992, however, the submerged flora was reduced to a few sparse patches of this moss and the acid-tolerant liverwort, *Scapania undulata*. Although the main change has been a reduction in the coverage of a sensitive species, it is possible this resulted primarily from changing hydrological characteristics of the system. Forestry felling that commenced around the time of the observed changes may have influenced flow rates and the frequency and magnitude of episodic events as a result of the reduced precipitation retention capacity of the forest. An increase in flow energy and release of brush during spates may have resulted in increased scouring of the stream bed and attached bryophytes. Although the rest of the assemblage has remained relatively constant since 1992, the moss *Fontinalis antipyretica* colonized the survey stretch in small amounts in 2007, persisting at similar levels into 2009.

5.3.2.3. Dargall Lane

Until 2003 the aquatic macrophyte flora of this stream was almost exclusively represented by acid-tolerant liverworts. Since that date small amounts of the upland moss *Blindia acuta* have also been identified in the survey section. The cover of *Nardia compressa* (which is only dominant within the AWMN in the seasonally highly acidic Bencrom River) has declined substantially post 2003 and has been replaced by the more ubiquitous *Scapania undulata*. There has been a slight increase in the coverage of *Marsupella emarginata* over the same period.

5.3.2.4. River Etherow

Like several of the more acidic streams in the Network, the aquatic macrophyte flora in the Etherow survey stretch has been restricted largely to one acid tolerant and ubiquitous liverwort species, *Scapania undulata*. This is sensitive to occasional very high flow events that scour the stream-bed, and there is an overall downward trend over the full monitoring period that could be due to an increased frequency of these episodes, although there are no data available to confirm this. Recently, however, two more 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). The acid-sensitive moss *Hygrohypnum ochraceum*, generally confined to the circumneutral AWMN streams, was first recorded at low levels in 2005 and regularly since 2007.

5.3.2.5. Old Lodge

As with the River Etherow the macrophyte flora of the Old Lodge survey stretch has been dominated by the 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 almost all years, indicative of the gradual reduction in acidity and, possibly, the return of ANC to positive values (Fig. 5.2). The coverage of filamentous algae has also declined from high levels in some years in the early 1990s.

5.3.2.6. Narrator Brook

The aquatic macrophyte community of Narrator Brook includes a diverse range of bryophytes including acid-sensitive moss species such as *Rhyncostegium riparioides*. Up until monitoring ceased in 2006 there was no indication of any significant change in the community over the study period of monitoring.

5.3.2.7. Afon Hafren

The aquatic macrophytes in the survey stretch at Afon Hafren have been restricted largely to one acid tolerant and ubiquitous liverwort species, *Scapania undulata*, which after many years of limited coverage has expanded slightly since 2003. 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.

5.3.2.8. Afon Gwy

In common with the Afon Hafren, the River Etherow and Old Lodge, the aquatic macrophyte flora in the survey stretch of the Afon Gwy is restricted largely to one acid tolerant liverwort species, *Scapania undulata,* which has shown no indication of long-term changes in coverage. No acid-sensitive mosses have been recorded in the survey stretch. However the acid-sensitive red alga, *Lemanea* sp., which is common in the circumneutral AWMN streams, the Allt a' Mharcaidh and Narrator Brook, was recorded for the first time in several locations in 2006 and found again in 2009.

5.3.2.9. Beagh's Burn

Beagh's Burn is another AWMN site dominated throughout the monitoring period 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.

5.3.2.10. Bencrom River

The aquatic macrophyte flora of Bencrom River has been dominated throughout the study period by the liverwort *Nardia compressa*. This calcifuge thrives in acidic streams (Porley & Hodgetts, 2005). There has been no evidence for any change in the assemblage up until monitoring was last undertaken in 2006.

5.3.2.11. Coneyglen Burn

The macrophyte composition and abundance at Coneyglen Burn reflect the fact that the water chemistry of this site is relatively well buffered. Bryophytes predominate, with the acid-sensitive mosses *Hygrohypnum ochraceum* and *Fontinalis squamosa* being most abundant. The liverwort *Scapania undulata* is also common in patches. On occasion substantial levels of filamentous algae have been recorded but otherwise the flora has been stable over time.

5.4. Key Points

Several acid-sensitive taxa have been recorded in AWMN sites only recently after several years of not having been detected. Most "new" records occurred in the second half of the monitoring period.

New taxa have been found in seven out of eleven lake sites; Lochnagar, Loch Chon, Loch Tinker, Round Loch of Glenhead, Burnmoor Tarn, Llyn Llagi and Llyn Cwm Mynach and four out of eleven stream sites; Allt na Coire nan Con, Dargall Lane, Old Lodge and Afon Hafren (Table 5.1; Fig. 5.3). Of the sites with new taxa seven are non-afforested and four afforested.

Species composition at eleven sites has not changed significantly since the study onset. Whilst this includes a few low deposition "control" sites it also includes sites with significant improving trends in deposition chemistry (Chapter 2) and surface water chemistry (Chapter 3).

No sites are exhibiting significant species losses. Where change is occurring macrophyte diversity is generally increasing.

In general most AWMN lakes were dominated at the outset by isoetid species such as *Isoetes lacustris* and *Lobelia dortmanna*. Isoetids are adapted to waters with very low levels of carbon, nitrogen and phosphorus, by being able to exploit nutrients within the lake sediment. Despite very low growth rates, the paucity of nutrients in the open water prevents competition from various branching, leafy, elodeid species that derive their nutrients via the water column. Several of the new records are for elodeid species and other species that are less able to access sedimentary sources of nutrients. It is conceivable that recovery from acidification has raised inorganic carbon concentrations in the water column. However, elodeid changes may also reflect changes in the availability of phosphorus and nitrogen resulting from wider changes in water chemistry.

Llyn Llagi shows the greatest signs of macrophyte recovery and has gained several new submerged plant species. Accordingly the site has moved from the C1 to the C2 category in Duigan *et al*'s. (2007) lake classification scheme.

The elodeid species *Myriophyllum alterniflorum,* increasingly established in the Round Loch of Glenhead after 2003 (Fig. 5.1), should contribute to an enhancement of the available habitat structure for other biological groups within the site.

The 2009 appearance of *Subularia aquatica* in Lochnagar is noteworthy. The discovery equals the JNCC macrophyte database altitude record for the species in the UK, from a 1988 survey at the nearby Sandy Loch. This may be linked both to the gradual reduction in acidity in Lochnagar since 2006 and to reductions in the duration of ice-cover in recent years, and the effect this might have on the seasonal light climate. The species is an annual, seeds prolifically, is considered ruderal in its habit (Farmer & Spence, 1986) and can readily colonise environmentally suitable lakes (Birks, 2000). These attributes combined with the nearby source site of Sandy Loch may have allowed *S. aquatica* to become established in Lochnagar very soon after conditions became favourable for its growth.

The primary changes observed in AWMN streams have been the recent detection of aquatic mosses, albeit in very small amounts, at sites previously dominated almost solely by acid tolerant liverworts. In both Old Lodge and the Afon Hafren *Hyocomium armoricum* has been recorded when average ANC in the streams has risen above around 10 $\mu eq\ l^{-1}$ (Fig. 5.2). Aquatic mosses tend to dominate the least acidic streams on the Network. Species change in the AWMN streams has tended to be more subtle than in the lake sites.

The exploration of reference conditions at lake sites through the study of sediment macrofossils and the floras of analogue reference sites would be instructive in establishing whether sites are on trajectory to return to their original pre-acidification status or are gaining new species due to temperature or enrichment changes. Sediment macrofossil work would also test the viability of seed banks as a means of site re-colonisation rather than traditional dispersal, which may facilitate recolonisation once suitable chemical conditions have been reached.

Table 5.1. Records of aquatic macrophyte taxa not detected in AWMN sites until 1995 or later

site	species	sample years														
		95	96	97	98	99	00	01	02	03	04	05	06	07	08	09
LAKES																
Lochnagar	*Subularia aquatica*	X	•	X	•	X	•	X	•	X	•	X	•	•	•	✓
Loch Chon	*Elatine hexandra*	✓	•	✓	•	✓	•	X	•	X	•	X	•	•	•	•
	Subularia aquatica	✓	•	✓	•	✓	•	✓	•	✓	•	✓	•	•	•	•
	Chara virgata	X	•	X	•	✓	•	✓	•	✓	•	✓	•	•	•	•
Loch Tinker	*Subularia aquatica*	✓	•	✓	•	X	•	X	•	✓	•	✓	•	•	•	✓
Round Loch of Glenhead	*Myriophyllum alterniflorum*	X	•	X	•	X	•	X	•	✓	•	✓	•	•	•	✓
Burnmoor Tarn	*Chara virgata*	X	•	X	•	X	•	X	•	✓	•	✓	•	•	✓	•
	Nitella translucens	X	•	X	•	X	•	X	•	X	•	X	•	•	✓	•
Llyn Llagi	*Callitriche hamulata*	X	•	X	•	✓	•	✓	•	✓	•	✓	•	•	•	✓
	Nitella flexilis agg.	X	•	X	•	X	•	X	•	X	•	X	•	•	•	✓
	Elatine hexandra	X	•	X	•	X	•	X	•	X	•	X	•	•	•	✓
Llyn Cwm Mynach	*Eleogiton fluitans*	X	•	X	•	✓	•	✓	•	✓	•	✓	•	•	✓	•
	Isoetes lacustris	X	•	X	•	✓	•	✓	•	✓	•	✓	•	•	X	•
STREAMS																
Allt na Coire nan Con	*Fontinalis antipyretica*	X	X	X	X	X	•	X	X	X	X	X	X	✓	•	✓
Dargall Lane	*Blindia acuta*	X	X	X	X	X	X	X	X	✓	✓	✓	✓	✓	✓	✓
Old Lodge	*Hyocomium armoricum*	X	X	X	X	X	✓	X	✓	✓	✓	✓	✓	✓	✓	✓
Afon Hafren	*Hyocomium armoricum*	X	X	X	X	X	X	X	✓	✓	X	✓	✓	✓	✓	✓

Key. ✓ species recorded during survey, X species not recorded during survey, • no survey

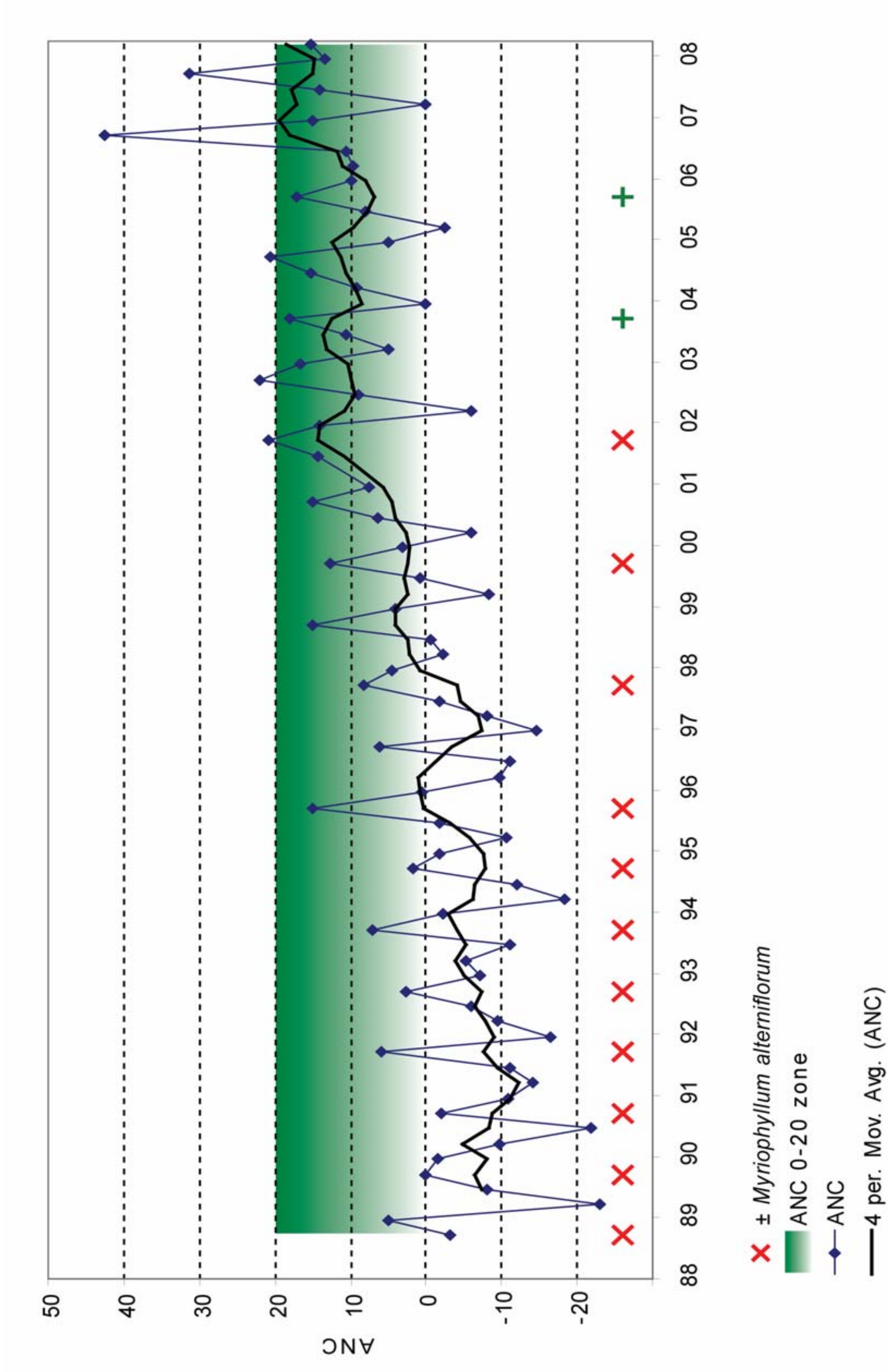

Figure 5.1 Occurrence of *Myriophyllum alterniflorum* in relation to quarterly ANC at Round Loch Of Glenhead

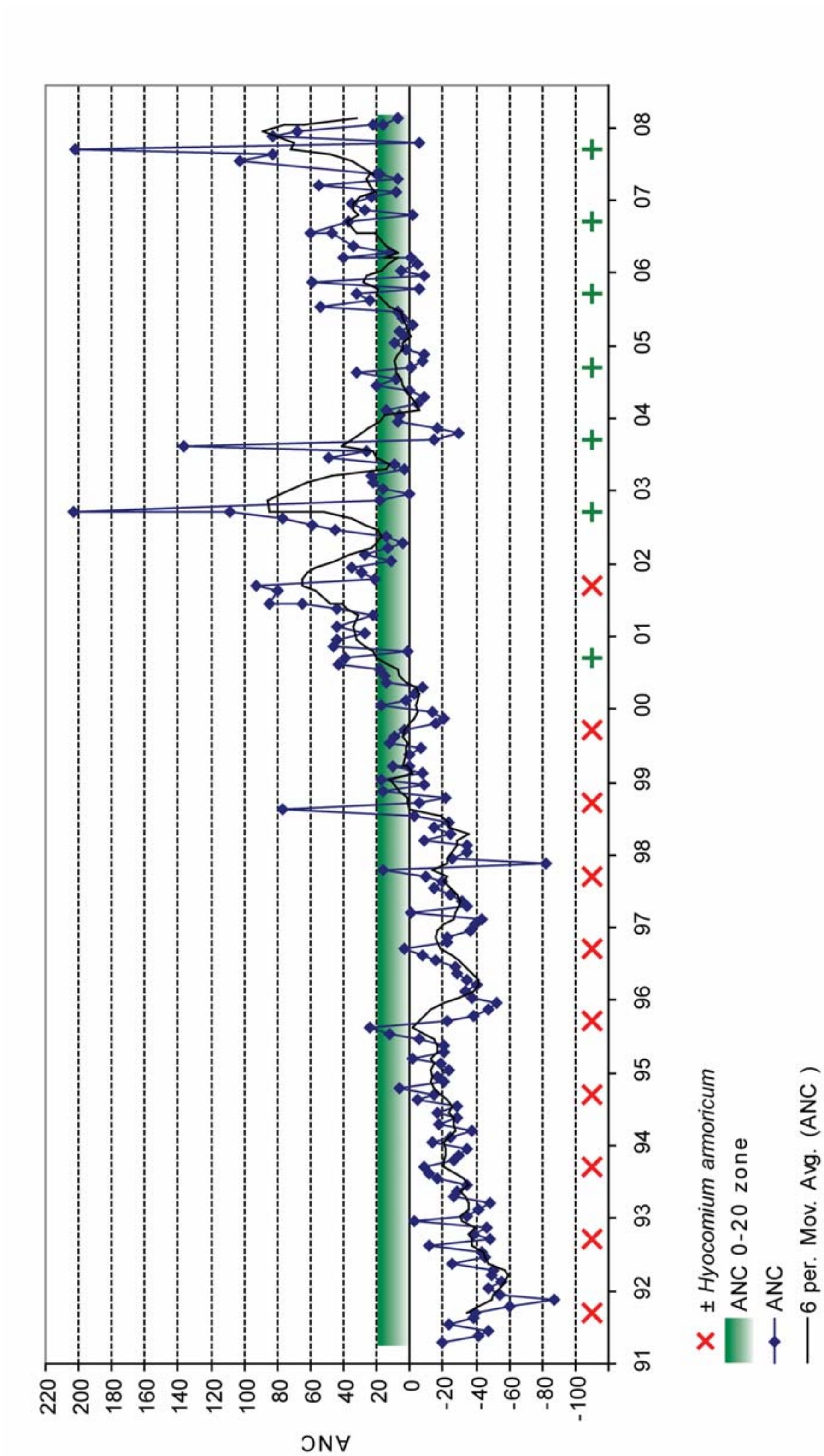

Figure 5.2 Occurrence of *Hyocomium armoricum* in relation to monthly ANC at Old Lodge

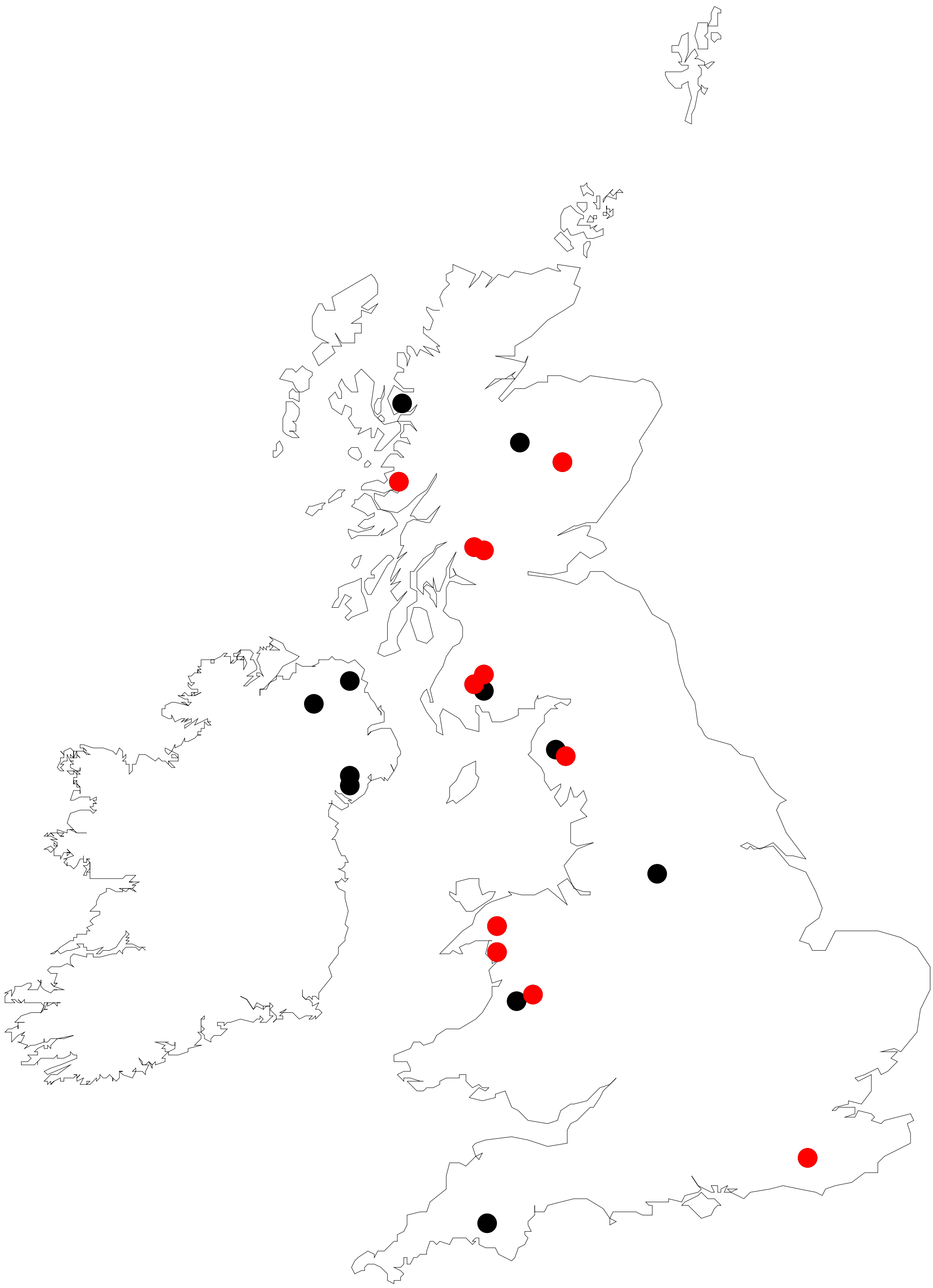

Figure 5.3. UK Acid Waters Monitoring Network Sites with new macrophyte taxa since 1995 (Red Dots)

5.5. References

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6. Macroinvertebrates

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6.1. Introduction

Macroinvertebrates constitute one of the main groups of freshwater organisms used for the biological monitoring of streams and rivers worldwide. They are useful in detecting a variety of forms of pollution, including organic matter and eutrophication, but also acidity and acidification. Macroinvertebrates have been collected regularly, systematically and semi-quantitatively at AWMN Network sites since 1988 (sampling every spring at all streams and lakes, with consistent methods and processing). An analysis of the first 15 years of data showed encouraging, though patchy and modest, signs of recovery at several sites (Monteith *et al*., 2005). The present analysis adds five more years of data and allows an assessment of whether these changes are continuing. The general objective is to provide the latest available view of the course of recovery from acidification for this important group of organisms as major drivers of patterns in biodiversity and ecological status across the AWMN.

Specifically we asked:

Have there been any directional changes in benthic invertebrates across the Network, consistent with recovery from acidification?
Are there any systematic differences between lake and streams?
Can we relate changes at particular sites to recovering water chemistry?

6.2. Methods

6.2.1. Samples

At each site, five one-minute kick (streams) or sweep (lakes) samples were taken with a 330μm mesh net, with the objective of obtaining consistent replicate samples from the same habitat year after year. We did not attempt to maximise the species list, but aimed at sampling consistency. Thus, the same stony riffles were sampled for streams and the same dominant habitat for lakes. In the latter, this was normally the stony or sandy littoral at c 0.3 - 0.5m depth, including sweeping through rooted macrophytes where present. The samples were placed in bags and preserved in the field in 70% Industrial Methylated Spirit, until sorting and identification according to standard AWMN protocols (Patrick *et al.,* 1991).

6.2.2. Analysis

Samples of macroinvertebrates across the whole time-series were subject to Principal Components Analysis, following conversion of the data to relative abundances (percent composition) and log-transformation. Redundancy analysis (RDA), with sampling year as explanatory variable, was used to test for trends in the macroinvertebrate community at each site. The presence of a trend was determined using a restricted permutation test, in which the ordering of samples (years) was maintained but the 'starting sample' selected via random cyclic shifts of the time-series. The maximum number of permutations is equal to the number of samples within each times-series (normally 20 or 21, except for Loch Coire Fionnaraich). Appendix 2 provides a more detailed description of the statistical techniques and Appendix 5 presents RDA and Principal Response Curve (PRC) plots of the macroinvertebrate data.

A new tool, Acid Water Indicator Community, (AWIC) for detecting recovery from acidification in streams based on macroinvertebrates has been developed by Davey-Bowker *et al*. (2005). AWIC was initially applied at the family level but here we use a version that assigns species and other taxa (AWIC*sp*) a 'score' in terms of acid tolerance (higher for progressively less acid-tolerant species) (Table 6.1). A similar model for lake littoral invertebrates has been developed by ENSIS-ECRC at University College London (Acid Waters Invertebrate Status Tool, AWIST) and measures deviation from an expected 'reference state' as Ecological Quality Ratios (EQRs).

Table 6.1. The species-level Acid Water Indicator Community index (AWIC*sp*).

Taxon	Score		Taxon	Score
Dinocras cephalotes (Curtis, 1827)	9		*Pisidium* sp.	9
Dixa sp.	9		Ceratopogonidae	9
Perla bipunctata Pictet, 1833	9		*Leuctra fusca* (Linnaeus, 1758)	9
Caenis rivulorum Eaton, 1884	9		*Protonemura praecox* (Morton, 1894)	9
Hydropsyche instabilis (Curtis, 1834)	9		Hydracarina	9
Alainites muticus (Linnaeus, 1758)[1]	9		*Chloroperla tripunctata* (Scopoli, 1763)	9
Odontocerum albicorne (Scopoli, 1763)	9		*Baetis scambus* group[6]	9
Wormaldia sp.	9		Gyrinidae	9
Gammarus pulex (Linnaeus, 1758)	9		*Isoperla grammatica* (Poda, 1761)	9
Ephemera danica Müller, 1764	9		*Asellus meridianus* Racovitza, 1919	9
Limnebius truncatellus (Thunberg, 1794)	9		*Atherix* sp.	9
Philopotamus montanus (Donovan, 1813)	9		*Crangonyx pseudogracilis* Bousfield, 1958	8
Perlodes microcephalus (Pictet, 1833)	9		*Brachyptera risi* (Morton, 1896)	8
Esolus parallelepipedus (Müller, 1806)	9		Empididae	8
Paraleptophlebia submarginata (Stephens, 1835)	9		*Calopteryx virgo* (Linnaeus, 1758)	8
Glossosoma sp.	9		Dytiscidae (including Noteridae)	8
Rhithrogena sp.	9		*Cordulegaster boltonii* (Donovan, 1807)	7
Electrogena lateralis (Curtis, 1834)[2]	9		*Polycelis felina* (Dalyell, 1814)	7
Ecdyonurus sp.	9		*Rhyacophila dorsalis* (Curtis, 1834)	7
Baetis rhodani (Pictet, 1844)	9		Limoniidae/Pediciidae[7]	7
Serratella ignita (Poda, 1761)[3]	9		*Tabanus* group[8]	7
Sialis fuliginosa Pictet, 1836	9		*Nigrobaetis niger* (Linnaeus, 1761)[9]	7
Caenis robusta Eaton, 1884	9		*Baetis vernus* Curtis, 1834	7
Hydraena gracilis Germar, 1824	9		Oligochaeta	7
Habrophlebia fusca (Curtis, 1834)	9		Simuliidae	6
Agapetus sp.	9		*Oulimnius* sp.	6
Ancylus fluviatilis O.F. Müller, 1774	9		*Leuctra inermis* Kempny, 1899	6
Athripsodes bilineatus (Linnaeus, 1758)	9		*Sialis lutaria* (Linnaeus, 1758)	6
Heptagenia sulphurea (Müller, 1776)	9		*Amphinemura sulcicollis* (Stephens, 1835)	6
Lype sp.	9		*Oecetis testacea* (Curtis, 1834)	6
Hydropsyche pellucidula (Curtis, 1834)	9		*Crenobia alpina* (Dana, 1766)	6
Silo pallipes (Fabricius, 1781)	9		Limnephilidae	6
Scirtidae	9		*Rhyacophila munda* McLachlan, 1862	6
Potamopyrgus antipodarum (J.E.Gray, 1843)[4]	9		Chironomidae	6
Sericostoma personatum (Spence in K. & S., 1826)	9		*Protonemura meyeri* (Pictet, 1841)	5
Helobdella stagnalis (Linnaeus, 1758)	9		*Siphonoperla torrentium* (Pictet, 1841)[10]	5
Leuctra geniculata (Stephens, 1836)	9		*Phagocata vitta* (Duges, 1830)	5
Amphinemura standfussi Ris, 1902	9		*Leptophlebia marginata* (Linnaeus, 1767)	5
Elmis aenea (Müller, 1806)	9		Hydroptilidae	4
Radix balthica (Linnaeus, 1758)[5]	9		Polycentropodidae	4
Glossiphonia complanata (Linnaeus, 1758)	9		*Leuctra nigra* (Olivier, 1811)	4
Erpobdella octoculata (Linnaeus, 1758)	9		*Nemoura* sp.	3
Diplectrona felix McLachlan, 1878	9		*Capnia bifrons* (Newman, 1838)	3
Mystacides sp.	9		*Leuctra hippopus* (Kempny, 1899)	3
Hydropsyche siltalai Döhler, 1963	9		*Diura bicaudata* (Linnaeus, 1758)	2
Limnius volckmari (Panzer, 1793)	9		*Nemurella picteti* Klapálek, 1909	1
Lepidostoma hirtum (Fabricius, 1775)	9			

[1]formerly Baetis muticus (Linnaeus, 1758); [2]formerly *Heptagenia lateralis* (Curtis, 1834); [3]formerly *Ephemerella ignita* (Poda, 1761); [4]formerly *Potamopyrgus jenkinsi* (Smith, 1889); [5]formerly *Lymnaea peregra* (Müller, 1774); [6]comprising *Baetis scambus* Eaton, 1870 and *Baetis fuscatus* (Linnaeus, 1761); [7]formerly Limoniidae but now two separate families; [8]comprising *Tabanus* sp. and *Haematopota* sp.; [9]formerly *Baetis niger* (Linnaeus, 1761); [10]formerly *Chloroperla torrentium* (Pictet, 1841).

6.3. Results

The amount of variation in the community data explained by the temporal trend varied from site to site (Table 6.2). In several sites, the temporal trend was strongly associated with the main axis of variation in the species data. Significant linear trends were apparent at 16 sites (where *P* was *c.* 0.05 and the minimum attainable at the site: sites highlighted in dark grey in Table 6.2). These comprised eight streams and eight lakes. Three further sites (Blue

Lough, Lochnagar and Scoat Tarn, highlighted in light grey) were also significant at $P \leq 0.1$. Triplots of the results of applying RDA to each of the macroinvertebrate time-series from the AWMN sites were produced to highlight major shifts in species composition over time (see Figs. 2-24 in Appendix 6).

Table 6.2: Results of the RDA trend analysis for the AWMN samples. $PCA_{\lambda 1}$ is the eigenvalue of the first PCA axis; RDA $_{\lambda time}$_time is the Eigenvalue of the RDA axis; % PCA_1 and % RDA_1 are the variances in the species data explained by PCA axis 1 and time (RDA); *F* is the pseudo-*F* statistic; *n* is the number of samples in the series; min *p* is the minimum achievable *p*-value, and *p* is the exact permutation *p* value. Sites with significant linear trends at p = 0.05 are highlighted in dark grey and at p = 0.10 in light grey.

Site code	Site name	$PCA_{\lambda 1}$	RDA $_{\lambda time}$	%PCA_1	% RDA_1	F	n	min p	p
ANCC	Allt na Coire nan Con	0.58	0.4	24	16.8	3.82	21	0.0476	0.04762
ARR	Loch Coire nan Arr	0.64	0.33	32.1	16.7	3.62	20	0.05	0.2
BEAH	Beagh's Burn	0.33	0.09	32.8	8.5	1.68	20	0.05	0.55
BENC	Bencrom River	0.29	0.16	26.2	14.4	3.03	20	0.05	0.05
BLU	Blue Lough	0.59	0.37	45.5	28.6	6.82	19	0.0526	< 0.053
BURNMT	Burnmoor Tarn	0.74	0.58	36.9	28.8	7.29	20	0.05	0.05
CHN	Loch Chon	0.44	0.29	24.7	16.5	3.75	21	0.0476	0.04762
CONY	Coneyglen Burn	0.56	0.37	37.7	24.9	5.3	18	0.0556	0.05556
DARG	Dargall Lane	0.37	0.26	35.8	25.7	6.23	20	0.05	0.05
ETHR	River Etherow	0.46	0.3	33.3	21.8	5.29	21	0.0476	0.04762
GWY	Afon Gwy	0.52	0.3	40.5	23.5	4.6	17	0.0588	0.1176
HAFR	Afon Hafren	0.42	0.31	38.4	27.6	6.87	20	0.05	0.05
LAG	Llyn Llagi	0.58	0.47	36.5	29.6	7.98	21	0.0476	0.04762
LGR	Loch Grannoch	0.52	0.3	36.6	21.6	4.97	20	0.05	0.05
LODG	Old Lodge	0.31	0.12	37	14.1	3.13	21	0.0476	0.1429
MHAR	Allt a' Mharcaidh	0.17	0.1	29.3	16.3	3.7	21	0.0476	0.04762
MYN	Llyn Cwm Mynach	0.41	0.32	33	25.8	6.61	21	0.0476	0.04762
NAGA	Lochnagar	0.52	0.2	29.1	11.3	2.42	21	0.0476	0.09524
NART	Narrator Brook	0.29	0.23	26.9	20.8	4.47	19	0.0526	0.05263
RLGH	Round Loch of Glenhead	0.3	0.19	40.1	25.5	6.16	20	0.05	0.05
SCOATT	Scoat Tarn	0.14	0.07	44.6	23.9	5.65	20	0.05	0.1
TINK	Loch Tinker	0.35	0.21	30.1	18.3	3.8	19	0.0526	< 0.053
VNG9402	Loch Coire Fionnaraich	0.49	0.31	42.4	27.1	1.86	7	0.1429	0.1429

Of the 16 sites with significant time-trends (at p = 0.05), nine were also significant in the 15-year dataset (Monteith *et al*., 2005), while in seven the time-trend appeared for the first time. For a few sites (Afon Gwy, Old Lodge, Scoat Tarn) time-trends apparent after 15 years were narrowly insignificant after 20 years at the p = 0.05 level.

AWIC scores were calculated for all stream sites in the Network. There was a statistically significant increasing temporal trend in AWIC*sp* index values at five of the 11 sites (Allt na Coire nan Con; Dargall Lane Burn; River Etherow; Narrator Brook; Afon Gwy; Table 6.3, Fig. 6.1), while site 2 was close to significance. At none of the 11 stream sites was there any significant or marked decreasing trend in AWIC*sp* scores, while site Allt a' Mharcaidh is close to significance.

Table 6.3. Mann-Kendall trend test on AWIC*sp* time-series at AWMN stream sites. Also included are the upper and lower 95% confidence limits for the distribution of n=999 bootstrapped estimates of tau.

Stream	Mann-Kendall *tau*	2-sided *P*<	Lower 95% CL	Upper 95% CL
MHAR	0.287	0.08	-0.622	0.056
ANCC	0.383	0.02	-0.754	-0.015
DARG	0.649	0.001	-1.098	-0.206
ETHR	0.727	0.001	-1.180	-0.248
LODG	0.258	0.11	-0.540	0.002
NART	0.582	0.001	-1.027	-0.115
HAFR	0.265	0.11	-0.591	0.081
GWY	0.478	0.01	-0.837	-0.095
BEAH	0.255	0.13	-0.574	0.066
BENC	0.027	0.90	-0.373	0.306
CONY	-0.046	0.82	-0.282	0.412

One site (Afon Gwy) shows significant evidence of recovery but did not have a linear time-trend, though it did in the 15-year dataset (Monteith *et al*., 2005), while the other recovering sites all had significant time-trends. Thus, around half the Network stream sites show clear evidence of both trends in time and recovery from acidification.

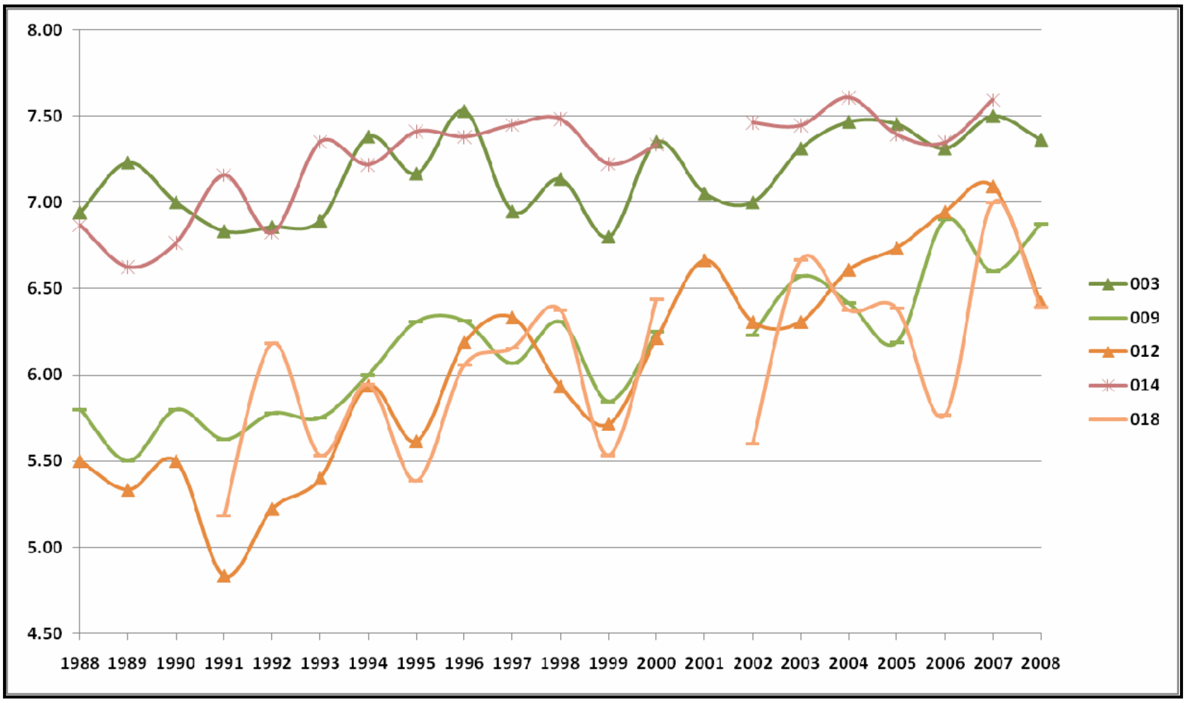

Figure 6.1. The significant increasing trend in AWIC*sp* scores for five AWMN stream sites (3 = Allt na Coire nan Con; 9 = Dargall Lane; 12 = River Etherow; 14 = Narrator Brook; 18 = Afon Gwy)

Time plots of 'AWIST' scores for the Network's lake sites suggest that sites with significant time-trends are indicative of recovery from acidification (Round Loch of Glenhead, Loch Tinker, Llyn Llagi, Burnmoor Tarn, Loch Chon; Fig. 6.2). The 'family' version of AWIC also suggests recovery at Llyn Llagi. A few sites have significant time-trends but no evident recovery from acidification (Loch Grannoch, Llyn Cwm Mynach, Blue Lough; Fig. 6.2). Trends at such sites are evidently either stochastic, associated with other environmental or biological drivers, or recovery is occurring but is not yet detectable with the tools available. These observations concur with those from the analysis of diatom trends (Chapter 4).

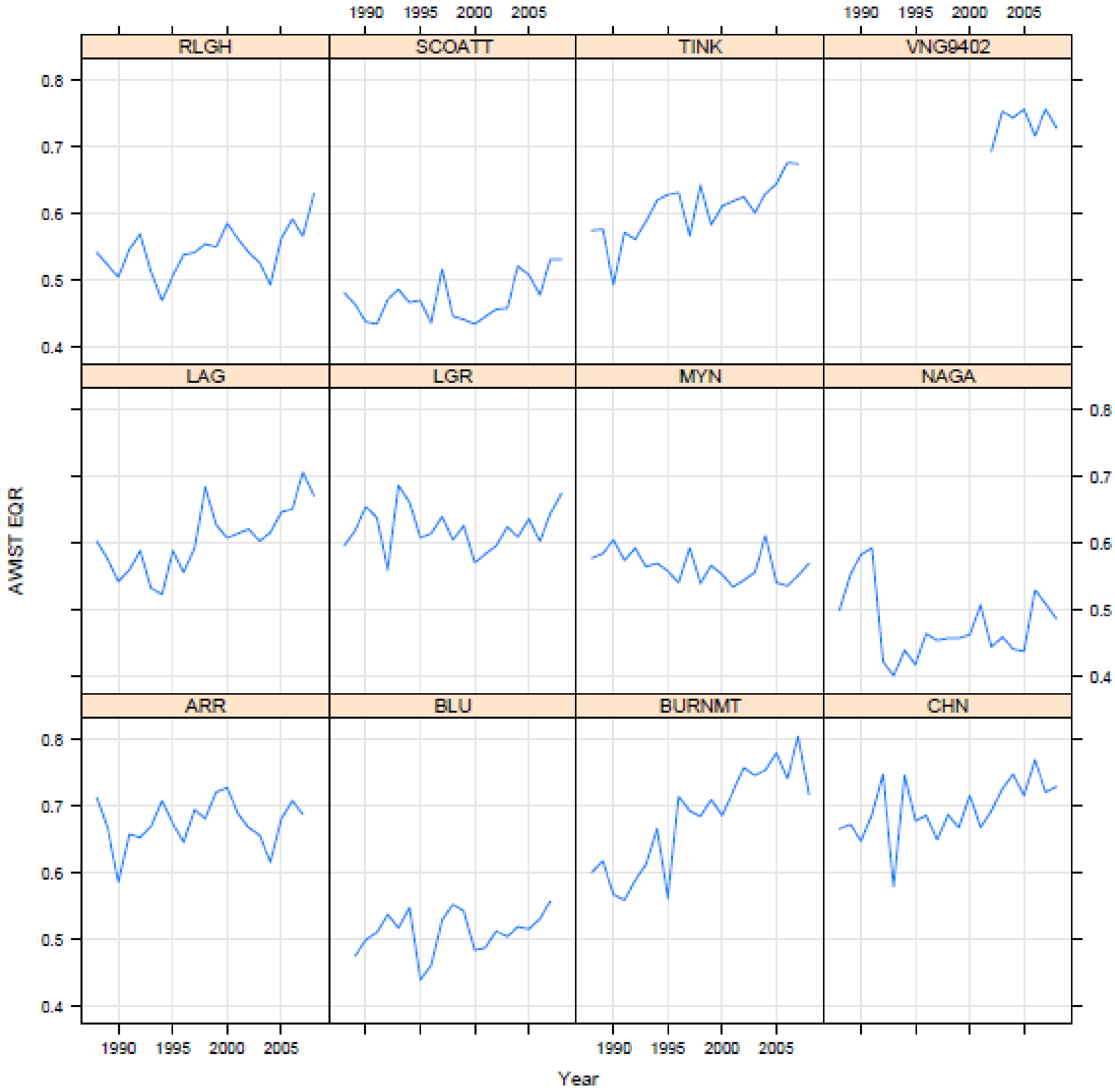

Figure 6.2. Time-series of AWIST EQRs for AWMN lake sites. Higher EQRs represent invertebrate assemblages that are closer to the reference or unimpacted state on a scale of 0, . . . , 1. See Table 6.2 for site codes.

In general, inspection of the primary data and ‘Principal Response Curves’ (Appendix 5, Figs. 25-47) confirms that acid acid-tolerant taxa have declined, and/or acid-sensitive taxa have increased, at sites showing recovery. However, faunal change at most sites remains fairly modest and recovery, while now clearly apparent at about half the Network sites, would still appear to be in the early stages.

6.4. Site Specific Assessments

6.4.1. Lakes

6.4.1.1. Loch Coire nan Arr (ARR)

This 'control' site is no longer monitored due to changes in water level (see Chapter 1). It showed no significant time-trend and, not surprisingly, no recovery. It had among the most diverse littoral faunas, notably with several genera of (acid-sensitive) mayflies (*Ameletus, Centroptilum, Baetis, Siphlonurus, Procloeon*), as befits its status as a non-acidified control.

6.4.1.2. Lochnagar (NAG)

There was neither a significant time-trend not evidence of recovery from acidification at Lochnagar, in contrast to the diatoms, which did indicate some recovery from about 2002/3. The only substantial change to aquatic macrophyte populations over the period is a large expansion of the acid-tolerant rush, *Juncus bulbosus* var. *fluitans*. The Lochnagar littoral fauna consists of a sparse assemblage of trophic generalists, and changes over the monitoring period mainly reflect shifts in their relative abundance rather than in composition. The chemistry of Lochnagar has shown signs of recovery, though pH first declined before increasing from the mid-1990s, and there has been no significant trend in labile Al. The shifts in abundance of the cores species do probably indicate early signs of recovery, but these are not yet detectable with the AWIST tool.

6.4.1.3. Loch Chon (CHN)

This site provides evidence of both time-trends and recovery from acidification. The fauna is very species rich, and there has been a good deal of turnover, though with a diverse core of consistently present taxa. While much of this dynamism is not obviously associated with acidity, markedly acid-sensitive species that have increased include the stonefly, *Leuctra geniculata*, the snail, *Radix balthica* and the mayfly, *Caenis*, while the acid-tolerant stonefly, *Leuctra nigra,* has recently declined. These biological changes are consistent with the chemistry, which has shown clear recovery, with mean annual pH rising from below 5.5 to around 6.0 (although with some indication of reversal post 2005) and with respect to changes in diatom and aquatic macrophyte populations.

6.4.1.4. Loch Tinker (TINK)

Loch Tinker shows a significant time-trend with AWIST scores indicating recovery from acidification. A number of acid-sensitive species have increased, including the caddis *Mystacides* and *Tinodes waeneri*, although several moderately acid-tolerant species persist (including nemourid stoneflies). The biology and chemistry exhibit consistent trends as the Loch Tinker chemistry has shown a modest increase in pH over the period.

6.4.1.5. Round Loch of Glenhead (RLGH)

There was a significant time-trend at this site and AWIST scores also suggested recovery from acidification, change being particularly marked late in the record. Of particular note is that the snail, *Radix balthica,* was found for the first time in 1996. It was at first sporadic but has been present every year from 2002. Such taxa are associated with water plants, and we note that the aquatic macrophyte *Myriophyllum alterniflorum* established strongly from 2003. It seems highly likely that colonization by the plant encouraged population growth by this acid-sensitive snail. Recovery at this site is consistent with chemical trends, where pH and acid-neutralising capacity has risen, while labile Al concentration has fallen during the period.

6.4.1.6. Loch Grannoch (LGR)

The littoral benthos of Loch Grannoch showed a significant time-trend, but this was the second such site at which we did not detect recovery from acidification. In this case this is consistent with the diatom record, which also shows changes in composition but no clear recovery, and is possibly attributable to forestry activities in the catchment. The chemical record shows some overall recovery but a clear decline in pH over the first decade, which was only then followed by an increase. There was a definite decline in taxon richness at this site up to last two years of the record (2007 & 2008), when it recovered, so there are signs of an ecological lag in response. In general, the fauna is one of moderately or extremely acid-tolerant species (where their tolerance is known).

6.4.1.7. Scoat Tarn (SCOATT)

The linear time-trend at Scoat Tarn was significant after 15 years but was marginally insignificant in the 20-year record. The AWIST score did not indicate recovery from acidification. Not surprisingly, therefore, while there has been some species turnover in the littoral fauna, this is not clear over time nor consistent with recovery or decline. The assemblage is dominated by Chironomidae and is otherwise a mixture of moderately acid-tolerant species (e.g the predatory *Sialis lutaria*, the omnivorous stonefly *Siphonoperla torrentium*, and the herbivorous stonefly *Leuctra hippopus*). There is no evidence for change in the aquatic macrophyte population here. This site has shown chemical recovery, but largely in the form of reductions in labile Al that remain relatively high, and pH is still relatively low (annual means of *c.* 5.2 or less), so it may be that biological recovery awaits further chemical improvement.

6.4.1.8. Burnmoor Tarn (BURNMT)

This is another site at which the littoral fauna show a significant time-trend and is, perhaps, the lake with clearest evidence of recovery based on littoral macroinvertebrates. Never strongly acidified, Burmoor Tarn has shown modest but significant increases in pH and alkalinity. Several acid-sensitive taxa show clear increases near the end of the record, including mayflies in the genus *Caenis*, the caddis *Lepidostoma* and a few snails (*Radix balthica*), while the acid-tolerant beetle *Platambus maculatus* declined. The apparent sensitivity of the fauna to declining acidity, in addition to evidence for recovery in diatoms and aquatic macrophytes, raises interesting issues regarding the suitability of 20 $\mu eq\ l^{-1}$ ANC as the universal critical level for acidity. ANC at Burnmoor Tarn has remained consistently above this throughout the monitoring period but continues to rise as acid deposition declines.

6.4.1.9. Llyn Llagi (LAG)

The fauna here showed both a significant (and particularly clear) time-trend and also recovery from acidification, consistent with the diatom record and also with chemical trends, with mean pH now clearly exceeding 5.5. While taxonomic changes have not been entirely consistent with recovery, some markedly acid-sensitive genera have appeared in the last few years (*Mystacides*, *Athripsodes*, both Trichoptera), and two species of the net-spinning polycentropodid caddis *Cyrnus*.

6.4.1.10. Llyn Cwm Mynach (MYN)

This site showed a significant time-trend but this was not associated with recovery from acidification although there has been considerable species turnover. Some rather acid-tolerant species have declined (the stonefly, *Nemurella pictetii* and *Plectrocnemia* sp, but were never very abundant) and, right at the very end of the record, some acid-sensitive mayflies appeared in very small numbers (*Siphlonurus* and baetids), while Leptophlebiidae (probably the moderately tolerant *Leptophlebia marginata*) have also declined. It may be that the first signs of recovery in the littoral fauna are appearing, although the chemical record at this afforested site is also rather equivocal, with an early decline in pH followed by a subsequent recovery.

6.4.1.11. Blue Lough (BLU)

There was a clear linear time-trend at Blue Lough, but no significant recovery from acidification as measured by AWIST. This site was characterised by an increase in the relative abundance of leptophlebiid mayflies (probably *Leptophlebia marginata*, which is moderately acid-tolerant). The record is also marked by species turnover of water bugs and beetles (Corixidae and Agabidae) and a modest increase in diversity. We have little information on acid tolerance of these groups, and this might explain why we did not detect recovery in this lake where there were clear signs of chemical recovery. As at Scoat Tarn, most chemical recovery to date has been with respect to falling labile Al concentrations rather than rising pH.

6.4.1.12. Loch Coire Fionnaraich (VNG9402)

Loch Coire Fionnaraich was added to the Network in 2001 to replace Loch Coire nan Arr. A number of prominent species are found in both sites, including the mayflies *Centroptilum luteolum* and *Siphlonurus lacustris*. While this site is a suitable replacement as a 'control', it is too early to look for trends in the macroinvertebrate data.

6.4.2. Streams

6.4.2.1. Allt a' Mharcaidh (MHAR)

This site shows a significant time-trend, that was not detectable after 15 years, but no recovery from acidification. Further, there has been no trend in pH. Not surprisingly therefore, while there has been some turnover at this species-rich site, this has involved species that make up a small fraction of the benthos, with no clear pattern in acid sensitivity, and the core community of abundant taxa has remained the same (a mixture of mayflies, stoneflies, chironomids and simuliids). This is broadly consistent with the lack of evidence for change in the aquatic macrophyte flora and very slight shifts in the diatom assemblage that are not obviously linked to recovery.

6.4.2.2. Allt na Coire na Con (CON)

This site showed both a significant time-trend and some recovery from acidification. There has been substantial species turnover, and some of this appears consistent with changes in acidity, such as the appearance, from the mid-90s, of the acid-sensitive mayfly *Electrogena lateralis*. Other changes are much less obviously related to acidification, however, and several moderately tolerant species have increased through the record, including the stonefly *Siphonoperla torrentium*, while the mayfly *Rhithrogena semicolorata* has declined. There is little evidence for recovery responses in diatoms or aquatic macrophytes at this mildly acidic site, where a slight reduction in acidity up to around 2000 has since partly reversed apparently in response to increased sea-salt inputs.

6.4.2.3. Dargall Lane (DARG)

The benthos at Dargall Lane showed a significant time-trend and the AWIC score indicates very clear recovery from acidification. Species that increased included the acid-sensitive *Hydropsyche siltalai* (a filter-feeding caddis), the stoneflies *Brachyptera risi* and *Perlodes microcephala* (sensitive/highly sensitive), while those that declined included the acid-tolerant stonefly *Leuctra hippopus*. Changes at this site suggest that the macroinvertebrate fauna is showing recovery from acidification, which supports the significant increase in pH observed at the site, particularly during the middle period of the record. The changes in macroinvertebrates at this site also match those in the diatoms, and are also consistent with a gradual change in bryophyte species composition.

6.4.2.4. River Etherow (ETHR)

The benthos of the River Etherow shows both time-trends and very significant recovery from acidification, consistent with both the diatom and chemical trends (particularly in aluminium). Several acid-tolerant taxa have declined (the stoneflies *Leuctra hippopus* and *Nemoura*), while the acid-sensitive stonefly *Brachyptera risi* and the highly sensitive mayfly *Electrogena lateralis*, have increased. This site provides one of the clearest indications of recovery (from a strongly acidified baseline) of any site in the Network, although again the core assemblage, consisting here prominently of *Leuctra inermis* and *Amphinemura sulcicollis* (both stoneflies), consists mainly of moderately tolerant species, and has remained unchanged. This observation is particularly pertinent given that the site is one of the most chemically episodic on the Network, and suggests that the continued occurrence of acid episodes is not necessarily restrictive providing the magnitude of these events is declining. Diatoms and aquatic macrophytes also show recovery responses in the River Etherow, although the effects of extreme high-flow events and wet summers depressing acidity are evident in these time-series.

6.4.2.5. Old Lodge (LODG)

The macroinvertebrates at Old Lodge show no time-trend or recovery from acidification (though a time-trend was evident after 15 years). This is at odds with the clear chemical recovery (pH, ANC and labile Al) at this site, while evidence from the aquatic macrophytes and, to a lesser extent, the diatoms does indicate a fragile recovery. The clearest indicator of biological recovery at Old Lodge is the colonisation and evidence of recruitment by brown trout in this previously fishless stream. The invertebrate community remains one typical of acidified streams, the commonest species being the highly tolerant stoneflies *Nemoura* spp, *Leuctra nigra* and *Nemurella pictetii*. We note that the alderfly *Sialis fuliginosa* is common in the acid streams of this area (including Old Lodge), although classed as highly sensitive in AWIC. It is feasible that labile Al levels are still too high to allow the return of more acid-sensitive species.

6.4.2.6. Narrator Brook (NART)

At Narrator Brook there are significant time-trends and change consistent with recovery from acidification. There has been chemical recovery at this site, though the evidence from the diatoms in this case is equivocal and no trend is seen in the aquatic macrophytes. Narrator Brook has a species-rich benthos and is one of the least acidic streams in the Network. The core community has again persisted and includes some markedly acid-sensitive species, including *Hydropsyche siltalai* (net-spinning caddis) and the predatory stonefly *Isoperla grammatica,* plus a mixture of more tolerant taxa. There has been an overall increase in the number of species at this site (pH has risen above the biologically significant threshold of *c*. 5.5; Sutcliffe & Hildrew, 1989), some (though not all) of which are acid-sensitive (e.g. *Chloroperla tripunctata, Ecdyonurus* sp).

6.4.2.7. Afon Hafren (HAFR)

Here the macroinvertebrates exhibit a time-trend but no recovery from acidification, despite there being a modest increase in pH over the period. The diatom and macrophyte records are also rather equivocal for this site. The dominant species (the moderately acid-tolerant stonefly *Leuctra inermis*) has recently declined in the record, whereas the acid-sensitive predatory stonefly *Isoperla grammatica* has appeared and increased in numbers, as has the beetle *Oreodytes sanmarkii* (whose acid-sensitivity is not fully known). There has also been an overall increase in diversity in the benthos. There are indications, therefore, though hitherto not detectable with the statistical tools available, of the early onset of biological recovery at this site.

6.4.2.8. Afon Gwy (GWY)

This site showed a significant time-trend in the 15-year dataset, although this is not quite evident after 20 years, while it does show significant recovery from acidification. This is the only site in the Network with this contradictory combination of trends. The fauna is typical of an oligotrophic upland stream, with a mixture of moderately acid-tolerant species persisting throughout the record. Nevertheless, the significant recovery from acidification detected by AWIC may be partially accounted for by the appearance of the acid-sensitive predatory stonefly *Isoperla grammatica* and by the decline in the tolerant *Leuctra hippopus*. It is consistent with the changes in the diatom community and the clear increase in pH at this site.

6.4.2.9. Beagh's Burn (BEAH)

The benthos at this site showed a marginally significant time-trend, but no significant recovery from acidification. There has been no increase in pH. Neither does the diatom record indicate any clear trends, although fluctuations in the flora may be attributed to hydrological events (as may changes in the fauna). Indeed, a large fraction of the community is accounted for by Simuliidae and Chironomidae, which often indicates the role of physical (e.g. flow) disturbances.

6.4.2.10. Bencrom River (BENC)

The macroinvertebrates of the Bencrom River exhibit a significant linear time-trend but no recovery from acidification, despite the chemistry showing a modest increase in pH (but with a marked reversal at the end of the record). In this respect, the invertebrates are similar to the diatoms, which showed trends but only marginal evidence of recovery. No trends were apparent in the liverwort dominated macrophyte flora. There has been some increase in the number of taxa, and the fauna remains dominated by moderately acid-tolerant taxa (mainly stoneflies).

6.4.2.11. Coneyglen Burn (CONY)

Macroinvertebrates at Coneyglen Burn showed a significant time-trend but no sign of recovery from acidification, again reflecting the lack of change in pH at this site, where there is no trend for diatoms or aquatic macrophytes. There was no overall trend in diversity at this site, although there was considerable species turnover. The core community was dominated throughout by the acid-tolerant stonefly *Siphonoperla torrentium*, plus chironomids and simuliids.

6.5. Discussion

There has been a substantial further accrual of evidence from the macroinvertebrate data over the last five years that biological recovery of surface waters is occurring. Overall, there is good agreement between chemical and biological trends; sites showing biological recovery also show chemical recovery, though with a lag in the former. This is despite the still relatively short sequence of samples, in terms of time-series analysis, with which to detect trends. While such evidence is encouraging, and inspection of the data shows that at sites with significant trends species known to be acid-tolerant are often in decline while more acid-sensitive species are gradually appearing, recovery is still fragile and at an early stage. Certainly, no wholesale shift in the core community is evident at any AWMN site, though species replacements seem to be occurring at many.

There is a debate about why macroinvertebrate recovery is modest (e.g. Monteith *et al*., 2005; Hildrew, 2009; Chapter 9). Hypotheses include: (i) the extent and persistence of chemical recovery, (ii) the difficulty of acid-sensitive species dispersing to acid-sensitive sites, and (iii) whether there are ecological interactions that resist a straightforward recovery of the community following the same trajectory along which it declined.

The biological and chemical threshold of pH 5.5 seems to be important, and sites that have moved across this threshold show the clearest recovery (Sutcliffe & Hildrew, 1989). The episodic chemistry of streams also clearly plays a role in their slow recovery from acidification, and a good deal of evidence for this has been gathered (Kowalik & Ormerod, 2006; Kowalik *et al*., 2007). However, biological recovery in lakes is similar to that in streams, and lakes are far less chemically episodic.

The ‘dispersal hypothesis’ can largely now be rejected, at least for mobile species including most aquatic insects. There is now much direct and indirect evidence of long distance dispersal sufficient to recolonise recovering freshwaters (e.g. Masters *et al*., 2007; Hildrew, 2009), with the possible exception of very large areas containing uniformly acidified freshwater systems. The evidence that ecological interactions limit the recovery of communities and ecosystem processes is circumstantial, and needs more research. Intriguingly, predatory species, both invertebrates and fish, are prominent in the recovery process (Monteith *et al*., 2005). Generalist herbivore/detritivores may inhibit the return of acid-sensitive specialist algal grazers (Ledger & Hildrew, 2005). Further, recent modelling by Layer *et al.* (in press) suggests greater dynamic stability in the simplified food-webs of acid waters, which implies indeed that they can resist invasion. This strengthens the findings of Townsend *et al*., (1987) that, of stream communities along a gradient of acidity, those of acid streams were most persistent. Such biological mechanisms would only delay recovery, however, and would not prevent it if the chemical conditions continue to ameliorate. The evidence from the macroinvertebrates, therefore, is encouraging even if recovery is far from complete.

6.6. Key Points

In a report based on the first 15 years of AWMN data on macroinvertebrates, 'significant time-trends' were observed at 12 of the 22 sites, comprising seven lakes and five streams (Monteith *et al*., 2005). Much of the total variation in community composition over the period was linearly associated with time. At 12 of these, the biological trend coincided with a trend of increasing acid neutralising capacity (ANC) and an increase in at least one of pH, alkalinity and labile Al.

After a further 5 years of sampling, we have now detected linear time-trends at 16 of the 22 sites (19 with a more relaxed level of significance), eight streams and eight lakes. This increase in the net number of sites from 12 to 16 includes the marginal 'loss' of significant time-trends at two streams (Afon Gwy and Old Lodge) and one lake (Scoat Tarn), but the emergence of significant time-trends at five streams sites (Coneyglen Burn, Dargall Lane, Afon Hafren, Allt a' Mharcaidh, Narrator Brook) and two lakes (Round Loch of Glenhead and Loch Tinker). We conclude that there is a clear increase in the evidence for temporal trends in the invertebrate communities at AWMN sites. Macroinvertebrates trends in lakes and streams seem to be similar, with no difference in the responses of the two ecosystems types.

We have applied two new tools for detecting the response of invertebrates to acidity. These are the Acid Water Indicator Community (AWIC, Davy-Bowket *et al*., 2005), which was designed for streams, and Acid Waters Invertebrate Status Tool (AWIST) developed at University College London, for lakes. AWIC originally assigned 'scores' for whole families, but now a species-level scheme (AWIC*sp*) is available. These tools can be used to judge whether biological changes at sites with significant linear time-trends also indicate recovery from acidity. Time-trends without indications of recovery from acidification are likely to mean the changes in species composition are being driven by other environmental and/or stochastic mechanisms. It may be that the tools presently available could be improved, but also, even where there is evidence for recovery from acidification and a significant time-trend, there may be additional signals in the data.

Of the streams, five sites show significant evidence of recovery from acidification (Allt na Coire nan Con, Dargall Lane, River Etherow, Afon Gwy and Narrator Brook) while Allt a' Mharcaidh is close to significant and all but two others (Beagh's Burn and Coneyglen Burn) show some signs of recovery, though this is not yet significant. One site (Afon Gwy) shows significant evidence of recovery but does not have a linear time-trend (though it did in the 15 year dataset). Thus, around half the Network stream sites show clear evidence of both trends in time and recovery from acidification.

The AWIST score also suggests recovery from acidification at five of the eight lakes with significant time-trends. At Llyn Llagi, a family level AWIC score was also applied and indicated significant recovery. At the other sites (Round Loch of Glenhead, Llyn Cwm Mynach and Blue Lough), there were time-trends but no indication that this was attributable to recovery. There were no lakes where there was clear evidence of recovery from acidification without a time-trend. We still know far less about the pH tolerance of the littoral invertebrates in lakes (including many beetles and bugs) compared to the benthos of rivers and streams, and this may make detection of recovery in lakes rather more difficult than it is for streams. However, approaching half the Network lake sites show signs of change that is at least partly attributable to recovery from acidification.

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7. Salmonid Fish Populations

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7.1. Introduction

The term "acid rain" can be traced back over 100 years. However, it was not until the 1970s that the environmental impacts of acid deposition began to receive concerted scientific attention. Studies in the 1970s in Scandinavia (Wright and Snekvic, 1978) and North America (Harvey, 1975), and in the 1980s in the UK (Harriman & Morrison, 1981; 1982; Stoner *et al.,* 1984; Harriman *et al.,* 1987; Maitland *et al.,* 1987; Turnpenny *et al.,* 1987) began to identify acid deposition as the likely cause for the loss of fish populations in acid sensitive areas. Understanding the mechanisms by which acidification affected fish, the status of fish populations in acidified areas and the chemical standards required to protect fish populations are research areas that have since had, and continue to receive, considerable attention.

Acidification and associated metal toxicity (particularly aluminium) can affect the survival and performance of fish to varying degrees during their life cycle. Sayer *et al.* (1993) reviewed the substantial, but mainly laboratory, literature on the toxicity of acid waters and associated trace metals on the early life stages of fish. The review found that low pH and elevated levels of trace metals such as labile aluminium (Al^{3+}) can cause a range of problems for salmonids including reduced ova production, impaired fertilisation of ova, increased incubation time, reduced hatching success, small larvae and skeletal deformities in addition to direct mortality. The review concluded that the risk of mortality was greatest at very low pH (<5) where trace metals (including aluminium) were high. In terms of susceptibility to acid episodes, it was suggested that the early life stages could be ordered: alevins (recently hatched fish)> green eggs> eyed eggs.

In free swimming juvenile salmonids, low pH in acid waters can cause mortality through ionoregulatory disruption (Kroglund *et al.,* 2008), and high aluminium concentrations can cause mortality through respiratory disturbance (Booth *et al.,* 1988; Sparling and Lowe, 1996). The presence of both high Al and low pH represents the worst case scenario for survival. The presence of Ca^{2+} can reduce the toxic effects of low pH and high Al (Booth *et al.,* 1988; Lien, 1996; Kroglund *et al.,* 2008) and the presence of DOC has been shown to reduce the toxicity of aluminium (Peterson *et al.,* 1990; Witters *et al.,* 1990; Roy and Campbell, 1997; Karlsson-Norrgren *et al.,* 2006).

The sensitivity of juvenile salmonid fish to acid conditions varies with species, population, life stage and size. Atlantic salmon (*Salmo salar*) are more susceptible than brown trout (*Salmo trutta*) (Poleo *et al.,* 1997). Local adaptation can reduce sensitivity (Donaghy and Verspoor, 1997) and smolting fish are more sensitive than parr. In general small fish are more susceptible to low pH and large fish more susceptible to high Al (Rosseland *et al.,* 2001) within life stages. The impact of acid conditions is also heavily dependent on antecedent conditions (Allin and Wilson, 2000), and the frequency, duration, timing and magnitude of acid episodes (Kroglund *et al.,* 2008).

Given the complexity of the biological responses, the interaction between chemical controls and the difficulties in adequately characterising environmental variability, many researchers have sought alternatives to the laboratory-based ecotoxicology approach for understanding and describing the impact of acidification on fish populations. Most commonly this has involved deriving critical water quality thresholds based on data collected from regular water quality monitoring and fish sampling programmes. Several water quality criteria relating to acidification have been used to describe the quality of water for fish including Acid Neutralising Capacity (ANC), pH and various combinations of ANC, labile Aluminium (labile Al) and DOC (Harriman *et al.,* 1995; Lien *et al.,* 1996; McCartney *et al.,* 2003). This approach has the benefit of allowing the derivation of environmental standards. However, the use of single metrics (e.g. ANC) can be problematic due to complex interactions between chemical variables and the different influence that these can have on different life stages of fish (Kroglund *et al.,* 2008). Consequently analysis of fish responses to multiple chemical parameters thought to influence mortality may be useful in improving understanding of chemistry-fish relationships in the natural environment and deriving future environmental standards.

Although there have been numerous accounts of chemical recovery from acidification (e.g. Evans and Monteith, 2001; Skjelkvale *et al.,* 2001) there have been many fewer reports of biological recovery and in particular the recovery of fish populations (Monteith *et al.,* 2005). The UK AWMN represents not only a unique opportunity to improve understanding of the effects of acid waters on fish populations, but also to assess the degree of recovery in fish populations and therefore the efficacy of UK emission control policies in delivering improvements to chemical habitats for fish.

This chapter builds on previous reports and provides interpretation of the fish data collected from the AWMN. In particular, it addresses the key questions:

- to what extent do temporal trends in fish presence/absence reflect recovery from acidification across the Network between 1988 and 2006;
- have there been changes in the temporal and spatial variability of fish densities across the Network between 1988 and 2006 and
- what is the relationship between fish presence/absence and water quality across the Network.

7.2. Methods

7.2.1. Data collection

Electrofishing was carried out at three replicate reaches at each of 22 AWMN sites between 1988/89 and 2006 with a minimum of 50m separating reaches. A minimum of three passes was performed at each site, with additional passes performed if depletion in numbers was not observed between passes. Fish were processed under anaesthetic. A length and weight were taken from all fish. Scales were taken from all fish considered to be >0+ (parr). Fish were returned to the stream after fishing was complete. A wetted area (i.e. surface area of stream per reach) was obtained from each site at the time of fishing. Scales were read at a later date to assign ages to captured fish. For lakes, sampling was undertaken along stretches of the lake outflow. There was no funding from Defra for electrofishing in 2007, although the Scottish sites were fished using funding from the Scottish Government. Since 2008 electrofishing has been carried out at a reduced number of sites, with reduced effort at some sites (a reduction of 3 to 2 reaches). Given these changes in site numbers and sample design this chapter focuses on results up to and including 2006.

Hydrochemical data were collected at monthly intervals for stream sites and quarterly intervals for standing waters. Details of determinands and analyses are provided in Chapter 3.

7.2.2. Statistical analysis

Density estimates for species and age groups were based on the maximum likelihood removal method (Borchers *et al*., 2002) except in a very small number of instances (8) where depletion was not observed between passes and as such a realistic density estimate could not be obtained. In these circumstances a minimum density (total of fish caught) was reported. The density calculation used an average wetted area for each reach derived from data collected between 1998 and 2005. This avoids the illusion of fish numbers apparently varying in response to changing hydrological conditions, but allows for fair comparison between reaches and sites.

7.2.2.1. Temporal changes in fish presence/absence

In order to investigate whether there were significant temporal trends in fish presence/absence, a binomial mixed model was run for each of the sites in turn with year included as a fixed effect and reaches (pseudo-replicates) as random effects. The significance of the relationship (i.e. temporal trends) was tested using the likelihood ratio test. Significance values were adjusted using a Bonferroni correction for multiple tests.

7.2.2.2. Effects of water quality on fish presence/absence

Analyses searching for relationships between water quality and fish densities are easiest to interpret if the water quality parameters are few, and not inter-related. As the total number of potentially relevant chemical determinands for AWMN was large (19) and many of them were inherently inter-related, we first used Principal Components Analysis (PCA) to produce a smaller number of independent, but still relevant and interpretable, water-quality index metrics. The component loadings were used to assess the importance of particular water quality determinands on individual principle components (PC's). PCA scores were then extracted for sites and years and used to predict fish presence/absence. The first six components representing 89% of the total water quality variation were included in the initial analysis of fish presence.

Binomial mixed effects models were used to assess the influence of chemical controls (using principle component scores) on fish presence/absence. These result in sigmoidal response estimates. Model simplification was undertaken using a step-wise approach with an initial model being constructed containing all six explanatory variables as fixed effects and sites and reaches nested within sites as random effects. The significance of removing each of the fixed explanatory variables from the model was assessed using likelihood ratio tests and the variable with the highest *p*-value, and therefore the least influence on the model fit, removed from the model. This process was repeated until a model was produced which contained only significant explanatory variables.

7.3. Results

7.3.1. Spatial variability in fish densities: trout

Figures 7.1 and 7.2 show fish densities for trout 0+ (fry) and trout >0+ (parr), respectively. *x* and *y* axes have been standardised to show relative differences between sites. Pseudo-replicate reaches are shown as separate coloured lines. Unsurprisingly, there was substantial variability in fish density between sites across the Network. In general the ranking of sites and reaches was consistent over time in terms of both fry (Fig. 7.1) and parr (Fig.7.2) indicating consistent differences in environmental quality between sites and common temporal drivers within sites.

Trout fry densities were markedly higher at Allt a' Mharcaidh, Lochnagar, Loch Chon and Narrator Brook than other sites in the Network (densities of up to 1.5 fry m^{-2}) (Fig. 7.1). The remaining sites in the Network were characterised by low trout fry densities (generally <0.5 fry m^{-2}). Loch Grannoch has never shown fry recruitment.

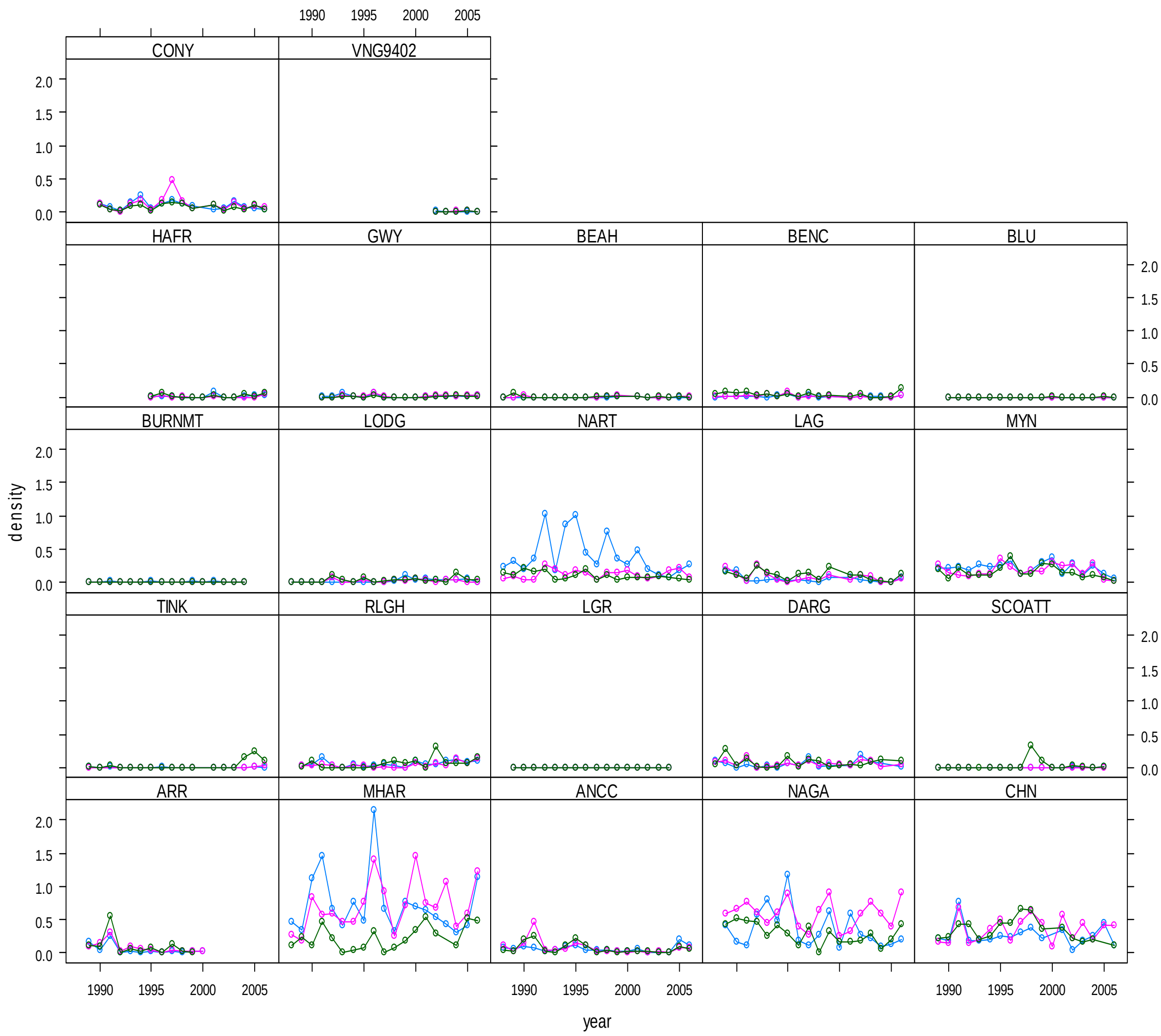

Figure 7.1. Densities of trout fry (no. fish m^{-2}) at AWMN sites (excluding the River Etherow where no fishing took place), between 1988 and 2006. x and y axes have been standardised to allow comparisons between sites. For site names see Table 1.1.

Parr densities (Fig. 7.2) were generally consistent with those for fry. The Allt a' Mharcaidh, Lochnagar and Narrator Brook were characterised by markedly higher densities than other sites in the Network. Loch Chon and the Allt a' Mharcaidh appeared to be characterised by relatively low parr densities given their generally high fry recruitment. However, this potentially reflects a number of possibilities with respect to the way that the data have been collated in this report (i.e. all age classes >1 are grouped) and the behaviour of fish at the site. For example, in the case of Allt a' Mharcaidh, it is probable that high fry numbers reflect the use of the site by anadromous brown trout (sea trout), in which case emigration from the site may influence standing parr densities. In the case of Loch Chon it is possible that fish emigrate into the nearby Loch Ard. Alternatively, both sites may experience high density dependent mortality or emigration of 0+ fish. While further insights could probably be obtained through a more detailed stock-recruitment (survival) analysis of these and other sites on the Network, resolving the various potential explanations would require additional effort beyond that possible under the AWMN at present.

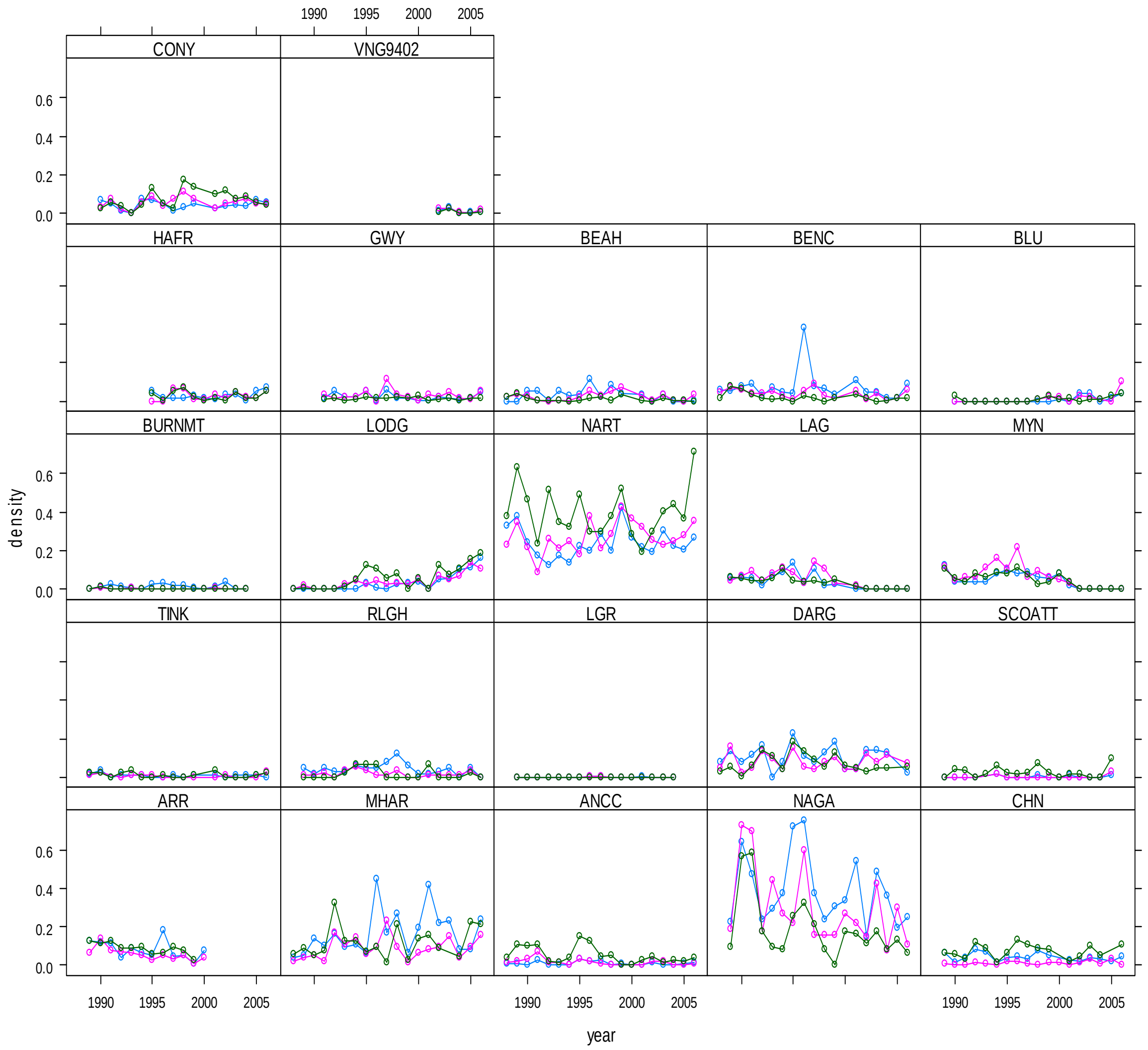

Figure 7.2. Densities of trout parr (>0+) (no. fish m^{-2}) at AWMN sites (excluding the River Etherow where no fishing took place), between 1988 and 2006. The data includes all fish >1 year old and as such may contain small numbers of adult fish. x and y axes have been standardised to allow comparisons between sites. For site names see Table 1.1.

7.3.2. Spatial variability in fish densities: salmon

Only four AWMN sites recorded salmon up to 2006. These are the Allt a' Mharcaidh, Allt na Coire nan Con, Afon Gwy and Coneyglen Burn. Salmon fry numbers (Fig. 7.3) were significantly higher at the Allt a' Mharcaidh and Allt na Coire nan Con than at the Afon Gwy which first recorded salmon fry in 2006. Coneyglen Burn has not yet shown any local recruitment.

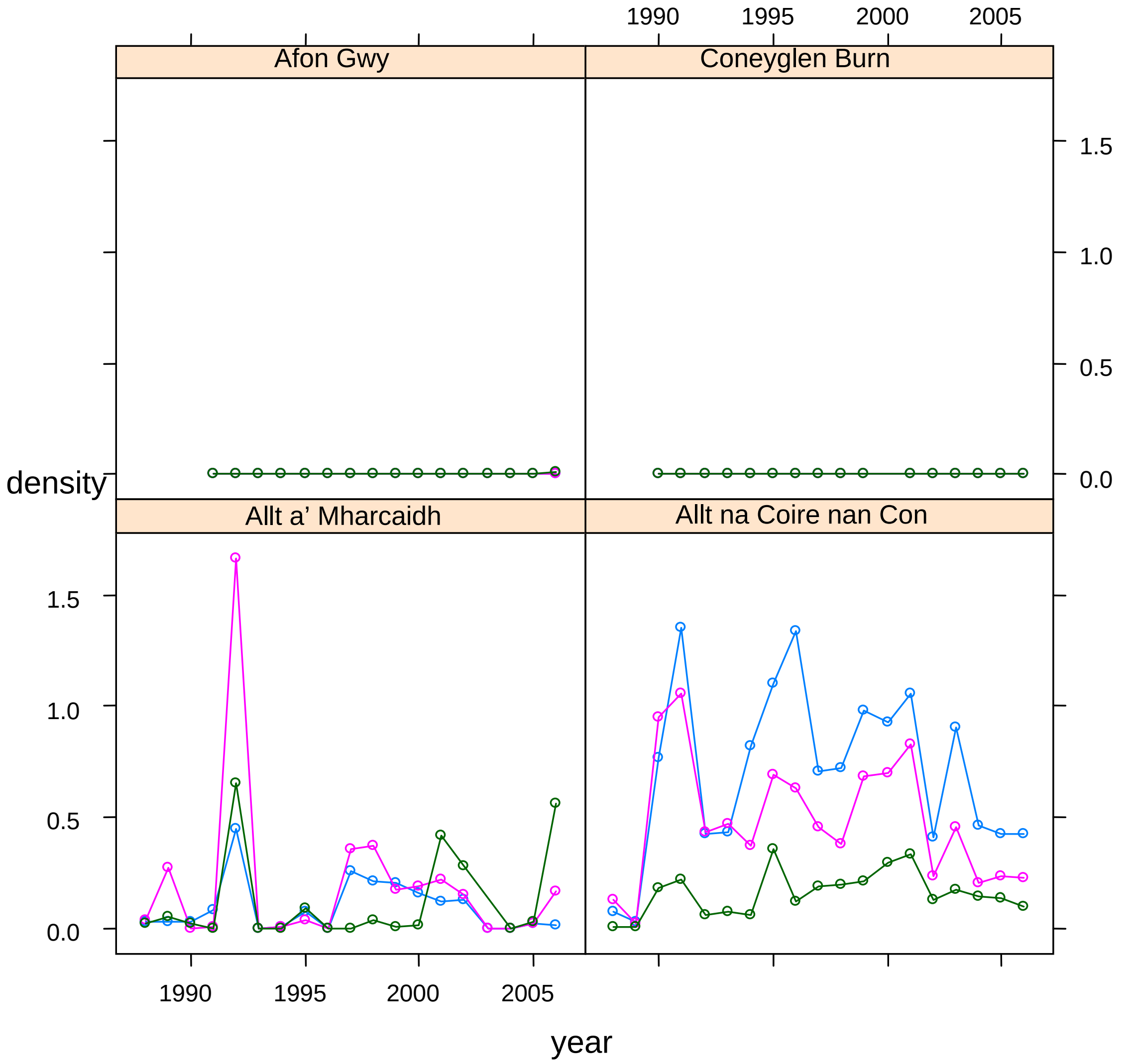

Figure 7.3. Densities of salmon fry (0+) (no. fish m^{-2}) at AWMN sites where salmon have been observed between 1988 and 2006. x and y axes have been standardised to allow comparisons between sites.

Salmon parr (>0+) densities (Fig. 7.4) at Allt a' Mharcaidh and Allt na Coire nan Con reflected fry densities, although with lower inter-annual variability. Parr were noted at low densities in the Afon Gwy and Coneyglen Burn for the first time in 2006.

7.3.3. Temporal trends in fish presence/absence

Because of the problems of assessing access possibilities for migratory salmon to the sites, analysis of presence/absence data focused on trout alone. Where trout have become locally absent as a consequence of acidification, their re-appearance (as fry or parr) can indicate recovery. However, customarily it is thought that fry provide a better indicator of acid recovery than parr. Parr are generally more resistant to acidification pressures than fry, can cover large distances and can use acidified habitats seasonally during periods of good water quality (usually the summer months). In contrast fry generally travel short distances from redds and as such are indicators of local recruitment and survival. Because of these subtle differences, data for fry (Fig. 7.5) and all age classes (Fig. 7.6) were analysed separately.

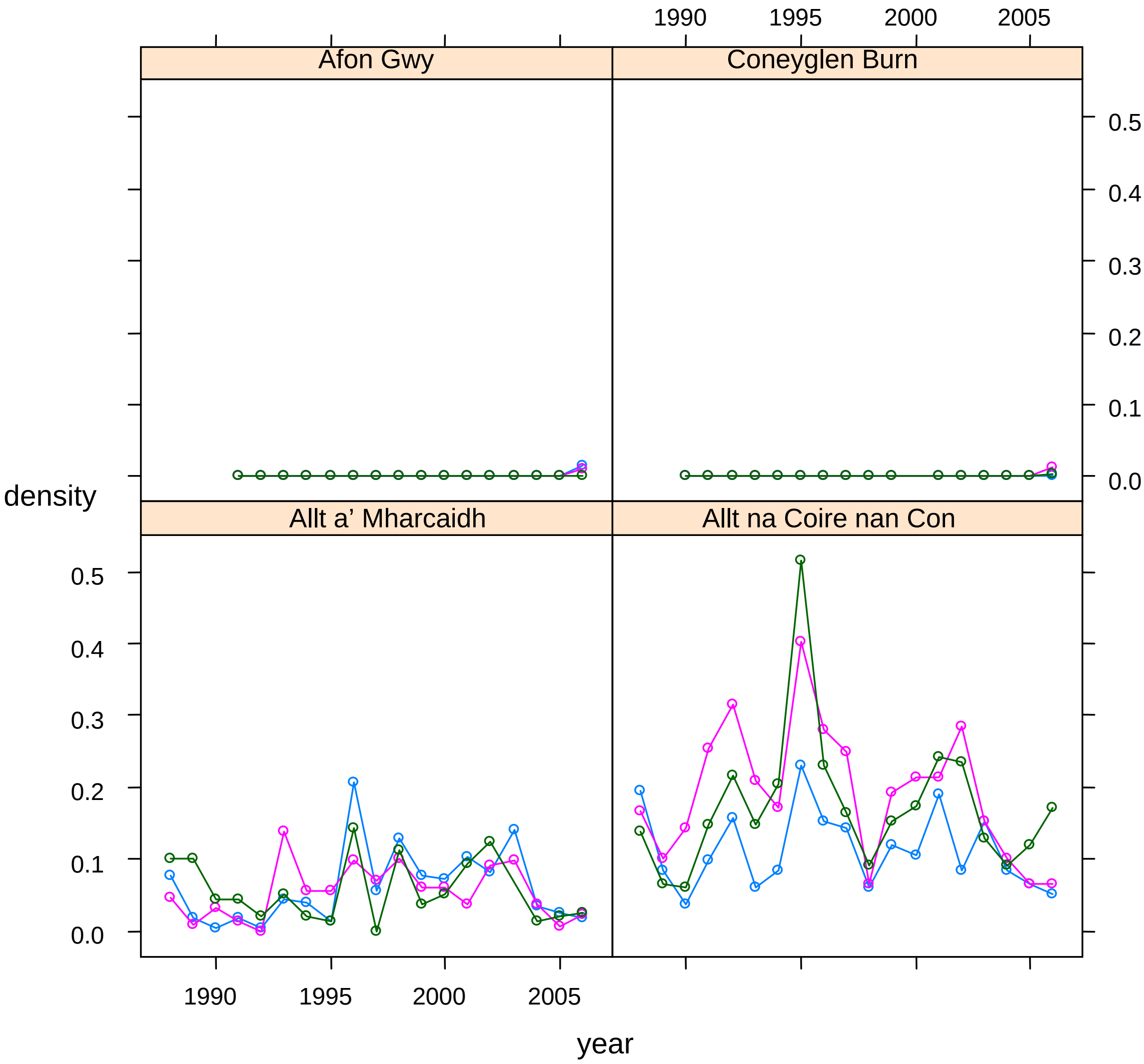

Figure 7.4. Densities of salmon parr (>0+) (no. fish m^{-2}) at AWMN sites where salmon have been observed between 1988 and 2006. x and y axes have been standardised to allow comparisons between sites.

For fry, temporal trends were seen in Dargall Lane (Likelihood Ratio, LR = 3.92, df = 1, p =0.048), Scoat Tarn (LR = 10.59, df = 1, p = 0.001), Old Lodge (LR = 19.60, df = 1, p < 0.001), Llyn Llagi (LR = 8.89, df = 1, p = 0.003), Beagh's Burn (LR = 4.10, df = 1, p = 0.043) and Blue Lough (LR = 5.09, df = 1, p = 0.024). Trends were positive except at Llyn Llagi. If a Bonferroni correction is applied for multiple tests (critical value = 0.0023) only Scoat Tarn and Old Lodge were significant. Where temporal trends were assessed for trout of all age classes, significant trends were observed at Old Lodge (LR = 24.96, df = 1, p <0.001) and Blue Lough (LR = 24.80, df = 1, p <0.001).

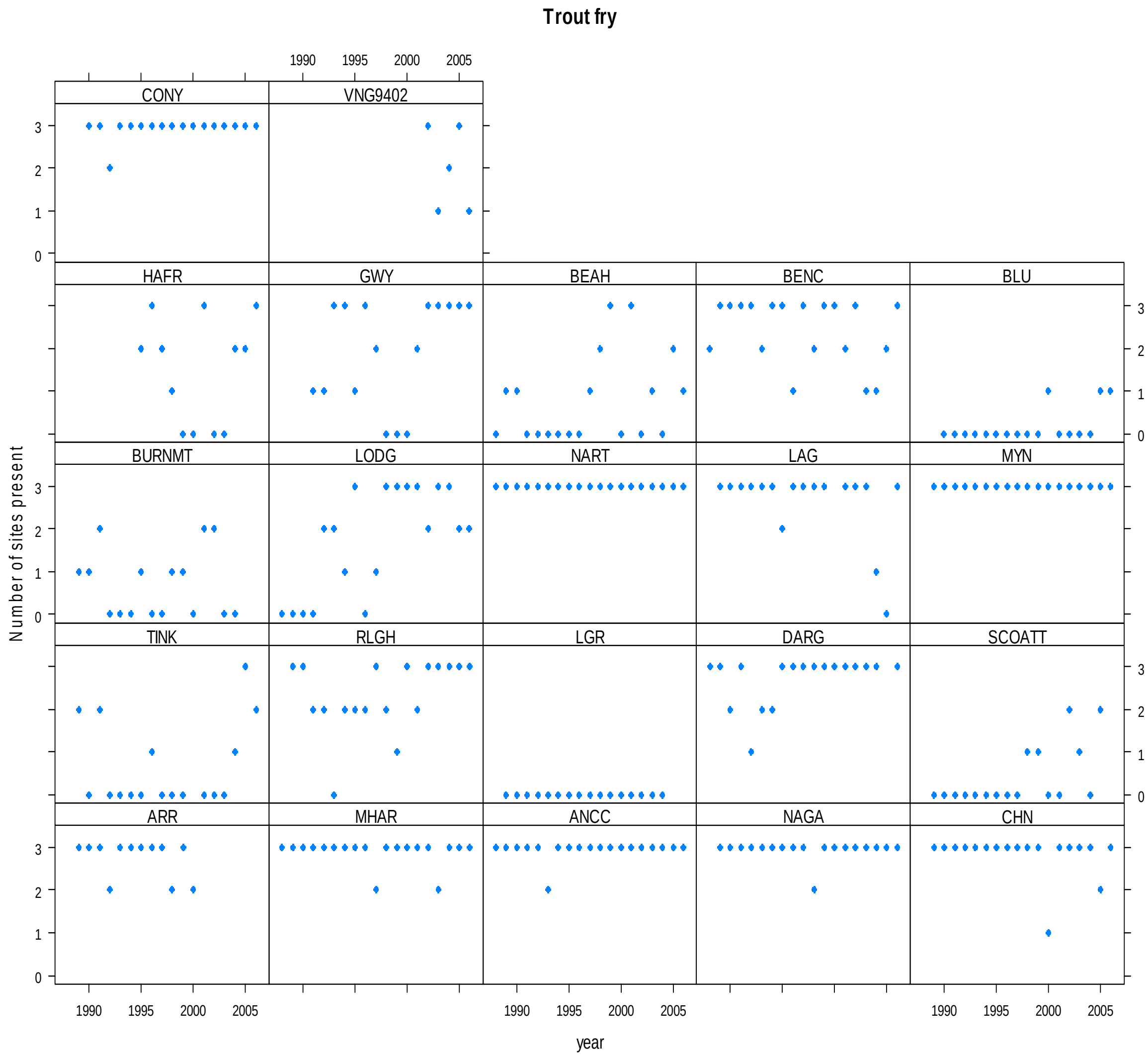

Figure 7.5. Presence/absence of trout fry at AWMN sites. Fish presence is indicated for each reach i.e. where all reaches contain fry, the site is indicated with a score of 3. If fry were not present at any sites a score of 0 would appear. For site names see Table 1.1.

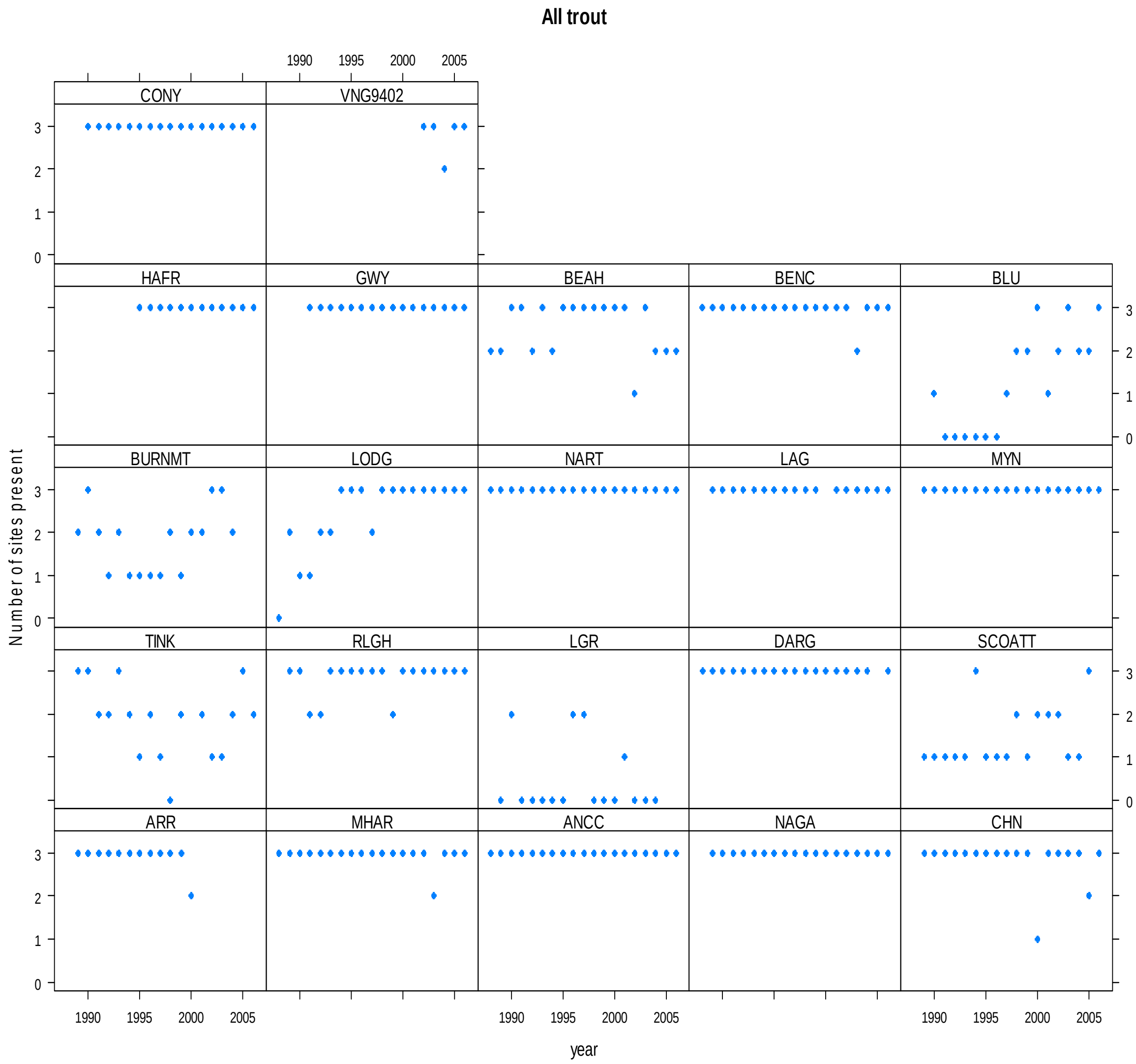

Figure 7.6. Presence/absence of trout of any age class at AWMN sites. Fish presence is indicated for each reach i.e. where all reaches contain fry, the site is indicated with a score of 3. If fry were not present at any sites a score of 0 would appear. For site names see Table 1.1.

7.3.4. Temporal variability in fish densities (1988-2006)

Previous reports on the AWMN have simply provided a site by site description of changing fish densities. For completeness and to allow comparison between previous descriptive reports, this is repeated here. Unfortunately it has not been possible to carry out robust statistical analysis of the density data at this stage. Consequently, the following section only provides a qualitative assessment of temporal changes in fish density. Figure 7.7 shows the temporal variability in trout fry (0+) densities. Figure 7.8 shows the temporal variability in trout parr densities (>0+). The *y* axes have been scaled independently to allow temporal trends to be observed within sites. Separate density data are presented for each reach (pseudo-replicate).

7.3.4.1. Northwest Scotland

Loch Coire nan Arr (Site 1) was included in the Network as a control site. It is in an acid sensitive region, but with relatively low deposition. In the late 1990s the lake was dammed, compromising the integrity of the long-term data. Prior to dam construction, the data for both fry and parr indicated a downward trend in fish density between 1988 and 2000. Loch Coire nan Arr was replaced in 2001 by a new control site **Loch Coire Fionnaraich (Site 23)** which was fished between 2000 and 2006. The run of data for this relatively new site is too short to determine if there is likely to be any long-term trends in the data, but considerable inter-annual variability in both trout fry and parr numbers are evident. **Allt na Coire nan Con (Site 3)** is a stream site in the west of Scotland. It contains both salmon and trout. Both trout fry and parr show considerable inter-annual variability in density, perhaps reflecting temporally variable habitat use by sea trout. Salmon fry first showed low levels of recruitment in 1988 and 1989, with improvements in subsequent years. Salmon parr densities increased between 1990 and 1995 and have been declining since, although 2006 showed slightly higher densities in one of the reaches.

7.3.4.2. Northeast Scotland (Cairngorms and Grampians)

The **Allt a' Mharcaidh (Site 2)** is a tributary of the River Spey in the Cairngorms. It contains both salmon and trout. Salmon fry densities have been have been highly variable over the years, but do not appear to show any particular temporal trends. Salmon parr densities show less temporal variability, again with no obvious temporal trends. Trout and fry densities also show substantial temporal variability although with no obvious long-term trends. It is possible that trout production at the Allt a' Mharcaidh is at least partially driven by sea trout.

The electrofishing sites for **Lochnagar (Site 4)** are situated in the outflow ca. 2 km downstream from the loch. This was necessary as the outflow passes underground for some distance before emerging further down the hillside. Historically it has been suggested that the water chemistry of outflow samples may not accurately reflect conditions at the electrofishing site. This was largely due to the high densities of fish and the apparently unfavourable water chemistry. Both trout fry and parr densities at Lochnagar appear to be showing downward trends between 1988 and 2006.

7.3.4.3. Trossachs

Loch Chon (Site 5) currently contains only trout, although the lower reaches below the electrofishing sites historically contained salmon. Trout fry show substantial inter-annual variability and there is a slight indication of declining numbers in recent years. Parr numbers also show substantial temporal variability, but there is no indication of any long-term trends. **Loch Tinker (Site 6)** is a site with a similar base cation chemistry to Loch Chon but at a higher altitude. There were no records of trout fry until 2004. Since then densities have increased, although they remain at very low levels. Trout parr densities are exceptionally low at the site and often no fish are recorded.

7.3.4.4. *Galloway*

At **Round Loch of Glenhead (Site 7)** trout fry densities appear to show an increasing trend between 1997 and 2006. However, parr densities appeared to increase until ca. 1995 after which numbers have declined, with reaches sometimes recording no parr.

The electrofishing sites at **Loch Grannoch (Site 8)** have rarely contained any fish. Recruitment to the loch is known to occur from tributary inflows with better water quality (unpublished data). However, it is possible that water quality in the loch and the outflow is not sufficient to allow recruitment locally and consistently. **Dargall Lane** is a tributary inflow to Loch Dee, and both trout fry and parr are found at the site. There is substantial inter-annual variability in fish densities but no obvious overall trends.

7.3.4.5. *Northern Ireland*

The four sites in Northern Ireland differ in their sensitivity to acidification. **Coneyglen Burn (Site 22)** is the least sensitive in the Network and occurs in a relatively low acid deposition region. It contains both trout fry and parr and has done so since the onset of monitoring. Salmon parr were first recorded at the site in 2006 in low densities. The site has not yet recorded any local recruitment of salmon fry. Recruitment of trout fry to the **Beagh's Burn (Site 19)** is sporadic, there are often no fry, or low densities. Trout densities are also very low and temporally variable. **Bencrom River (Site 20)** is situated in the Mourne Mountains. Trout fry densities at the site appear to have declined over time, although this pattern is largely driven by one reach, with the remaining reaches characterised by generally low fry recruitment throughout. Trout parr densities do not show any obvious trends over time. **Blue Lough (Site 21)** is one of the most acidic sites in the Network. In general there is only very sporadic trout fry recruitment at the site and that is only at a single reach. Trout parr densities appear to have increased between ca. 1997 and 2006.

7.3.4.6. *Lake District*

Scoat Tarn (Site 10) rarely shows any trout fry recruitment. Where fry are present they come from a single reach. Trout parr densities show a high degree of inter-annual variability, with the higher densities consistently coming from the same reach as the sporadic fry recruitment**.** Given the large inter-annual variability temporal patterns are not evident. **Burnmoor Tarn (Site 11)** is one of the most alkaline sites in the Network. However fry recruitment is still sporadic, from 2 of the 3 fished reaches. Parr densities are also very low, with fish generally associated with a single reach. Previous AWMN reports have suggested that continued acid episodes may be possible when a stream draining Scafell spills into the loch during periods of high rainfall. However, suitable physical habitat may also limit recruitment. The site was not fished between 2004 and 2006.

7.3.4.7. *Pennines*

During sampling between 1989 and 1993 the **River Etherow** 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.

7.3.4.8. North Wales

Llyn Llagi (Site 15) shows no obvious temporal trends in the fry data. Accurate parr density data, available up until 2002, appeared to show declining densities. Data since 2002 are not shown in this report due to a lack of accurately defined age data since fishing was carried out by the Environment Agency. **Llyn Cwm Mynach (Site 16)** is one of the heavily afforested sites in the Network. Fry densities appear to have declined since the mid-1990s. Parr data show no obvious trends although recent data are not presented due to the same ageing problems as for Llyn Llagi.

7.3.4.9. Mid Wales

Electrofishing of the **Afon Hafren (Site 17)**, a stream with a partially afforested catchment, only commenced in 1995. Fry recruitment is sporadic and densities variable. There is some indication that trout parr densities are increasing. However there is considerable inter-annual and inter-reach variability. **Afon Gwy (Site 18)** is a stream site close to the Afon Hafren with a moorland catchment. Brown trout recruitment is again sporadic, although regular recruitment has occurred in recent years. Trout parr densities do not appear to show any long-term trend. A few juvenile Atlantic salmon (a highly acid-sensitive species) were recorded in 2006. However, it is important to determine whether the appearance of salmon could be linked to recent changes in stocking practice immediately downstream before any conclusions can be drawn with respect to possible recovery.

7.3.4.10. Southern England

Old Lodge (Site 13) is a stream site in south-east England. It shows increasing trout fry recruitment and increasing trout parr densities. In south-west England, the **Narrator Brook (14)** shows declining trout fry densities in one reach and stable densities in the other two. Trout parr densities appear stable over the period of monitoring.

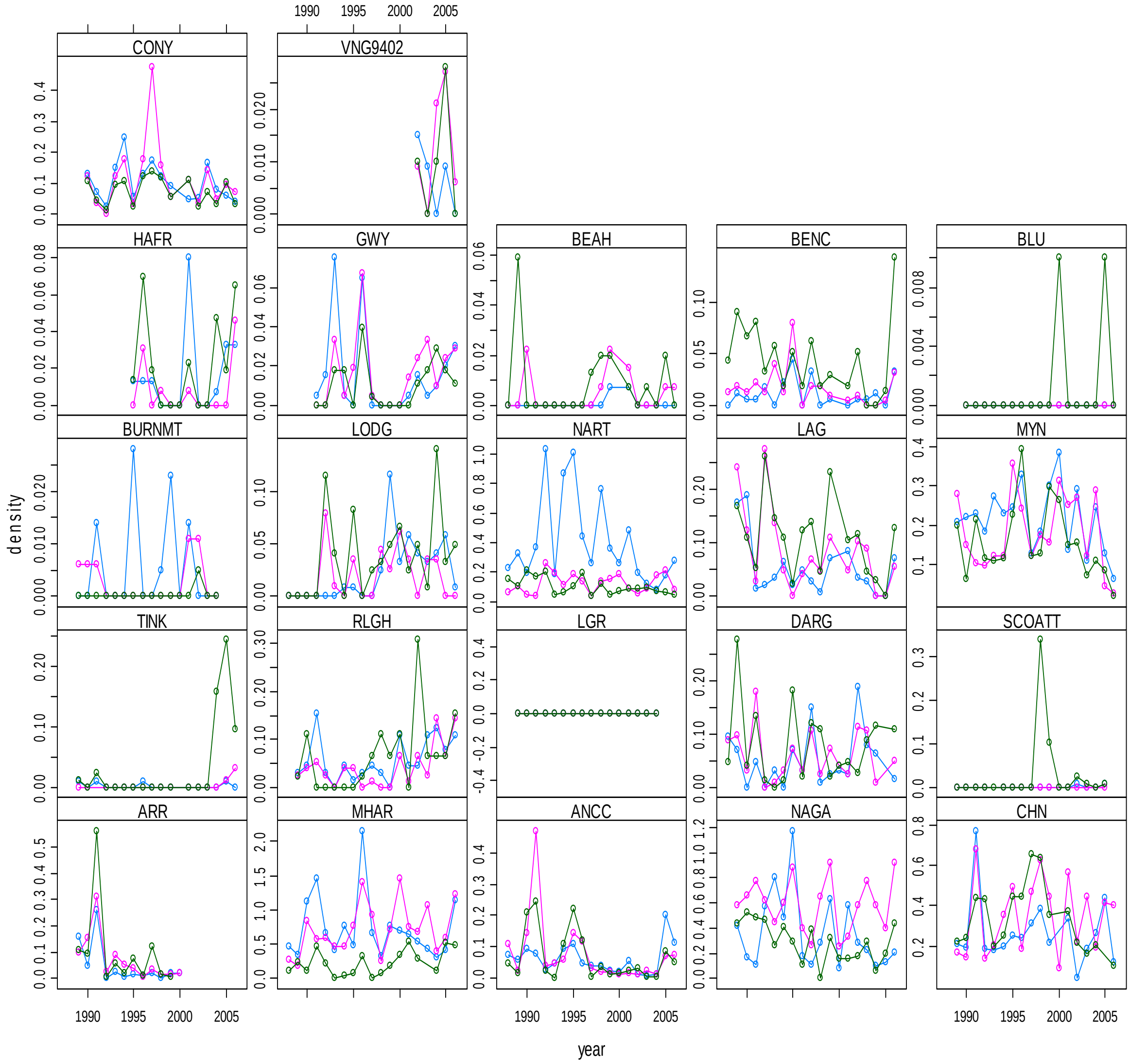

Figure 7.7. Densities of trout fry (0+) (no. fish m^{-2}) at AWMN sites between 1988 and 2006. y axes vary independently by site to allow temporal trends to be observed within sites. For site names see Table 1.1.

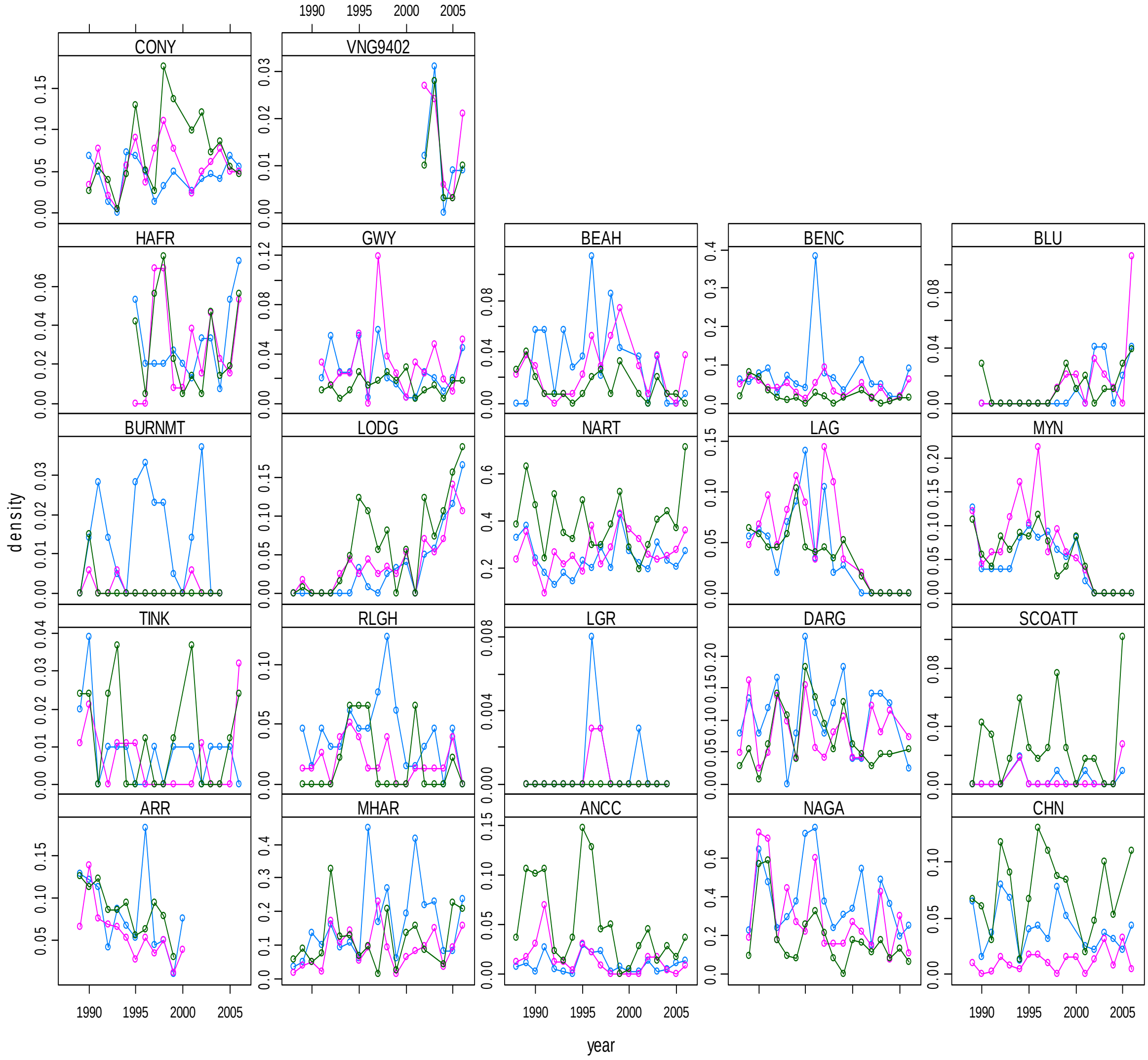

Figure 7.8. Densities of trout parr (>0+) (no. fish m^{-2}) at AWMN sites between 1988 and 2006. y axes vary independently by site to allow temporal trends to be observed within sites. For site names see Table 1.1.

7.3.5. The influence of water quality on fish presence

7.3.5.1. PCA analysis of hydrochemistry

Principal Component Analysis (PCA) was carried out using mean annual summaries of hydrochemical parameters that had been reliably collected over the entire study period (see Chapter 3). From these primary data, ANC was also calculated using two different methods (the ion balance method and the method reported by Davies *et al.*, 2005) and included in the PCA analysis. A scree plot was created to determine the number of components to be used in the analysis of fish presence/absence and eigenvalues examined to see if the axis contained more signal (information) than noise. The first six axes were judged to be informative, and their component scores extracted for use in the mixed model analysis. As only components 1, 2 and 4 (PC1, PC2 and PC4, respectively) were found to be significant in subsequent predictive analysis, the following discussion is restricted to these components.

Component loadings were examined from the PCA analysis to determine the importance of particular chemical determinands and to provide interpretation of the component axes. The component loadings and the variance in the chemical data explained by each of the components is shown in Table 7.1.

Table 7.1. Principal Component loading and variance explained in the hydrochemical data by Principal Components 1, 2 and 4.

	PC1	PC2	PC4
Variance explained	0.40	0.26	0.06
pH	0.28	-0.16	0.03
H+	-0.30	0.12	0.03
Alkalinity	0.16	-0.36	-0.13
Conductivity	-0.29	-0.22	0.21
NO_3	-0.24	0.07	-0.41
PO4	-0.06	-0.04	-0.64
Total monomeric Al	-0.28	0.18	-0.02
Non Labile Al	-0.23	0.05	-0.23
Labile Al (Al^{3+})	-0.25	0.20	0.07
DOC	-0.07	-0.29	0.03
Na	-0.25	-0.20	0.32
K	-0.21	-0.20	0.23
Ca	-0.14	-0.38	0.00
Mg	-0.22	-0.34	0.03
Si	-0.16	-0.15	-0.33
SO_4	-0.31	-0.11	0.00
xSO_4	-0.30	-0.08	-0.10
ANC (Davies, 2005)	0.14	-0.39	-0.10
ANC (Ion balance)	0.24	-0.27	-0.13

PC1 was positively influenced by pH and ANC (ion balance) and negatively influenced by H^+, conductivity, total monomeric aluminium, labile and non labile aluminium, SO_4^{2-} and xSO_4^{2-}(excess sulphate or non-marine sulphate), Na^+, K^+ and Mg^{2+}. Taken together, this suggests that PC1 primarily reflects differences between low and high acid deposition areas, with associated consequences for H^+ and Al^{3+} concentrations.

PC2 was negatively influenced by Ca^{2+}, Mg^{2+}, Alkalinity, ANC (primarily the method of Davies *et al*., 2005) and DOC. These were contrasted with positive scores for total monomeric Al and labile Al (Al^{3+}). Taken together, this suggests that this component primarily reflects differences in geology and soils, and separates more acid sensitive sites from less sensitive sites.

PC4 was dominated by the influence of PO_4^{3-} and NO_3^- which were negatively associated with the component. However, moderate associations also occurred with Si (negative) and

Na and K (positive). It would appear that this component primarily reflects nutrient inputs as a consequence of land-use including low intensity grazing, improved pasture and forestry activities.

The temporal trends in water chemistry across the AWMN are dealt with in detail elsewhere (Chapter 3). However, an understanding of fish status requires information on spatial as well as temporal variability in hydrochemistry. Figure 7.9 plots mean annual chemistry data from the AWMN (sites and years) in ordination space in relation to components 1 and 2. Detailed examination shows that sites such as Loch Grannoch and Blue Lough are characterised by moderate PC1 scores indicative of relatively low pH, ANC and alkalinity, and high SO_4^{2-} and aluminium concentrations. However, they are also characterised by high component 2 scores indicative of low base cation and DOC concentrations. Old Lodge and the River Etherow are characterised by the lowest PC1 scores, but moderate PC2 scores indicating higher base cation and DOC concentrations than seen at Grannoch and Blue Lough. Beagh's Burn and Coneyglen Burn were characterised by the highest component 1 scores and lowest component 2 scores. These sites are the least acid sites.

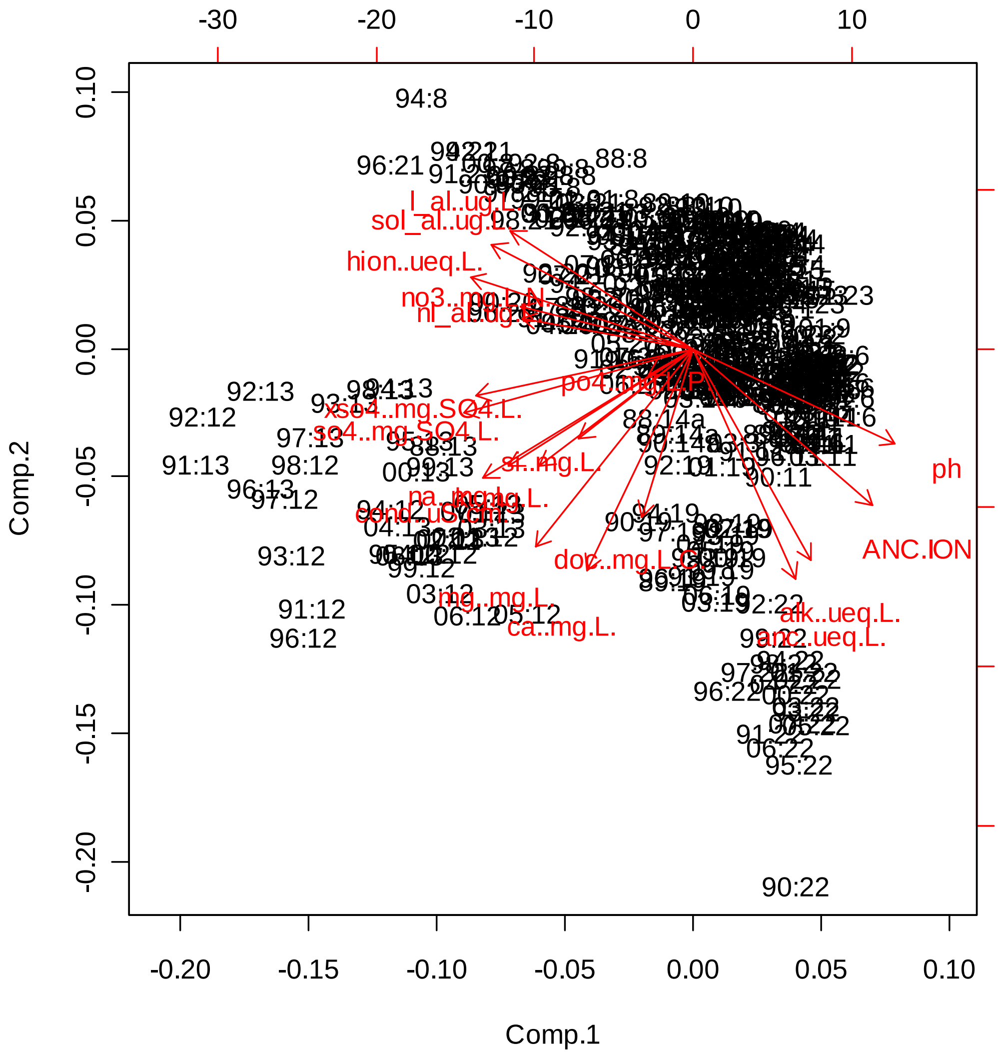

Figure 7.9. Bi-plot showing the influence of chemical determinands on principle components 1 and 2, and the distribution of samples in relation to these components. The strength of the determinands in influencing components is shown by the length of arrows. Numbers represent years and sites e.g. 96:12 = site 12 in 1996.

7.3.5.2. Effects of water quality on presence/absence of trout

A mixed model was used to investigate the relationship between water quality and the presence of fry. Site and reach (nested within sites) were included as random effects. Each of the PCs were included as fixed effects. Of the 6 PCs included in the mixed model analysis only PC1 and PC2 were significant in explaining the presence of fry (Table 7.2). Figure 7.10 shows the fitted model, and suggests that the probability of finding fry increases with increasing PC1 scores and increases with decreasing PC2 scores. This suggests that probability of finding fry is greater where acid deposition and associated detrimental effects are lower (high PC1 scores) and where base cation concentrations and DOC are higher (low PC2 scores).

Table 7.2. Results of mixed model analysis of the relationship between water quality Principal Components and fry presence.

Variable	Parameter (SE)	Likelihood ratio	P value
Removed from model			
Intercept		3.73	0.054
Component 3		0.22	0.642
Component 4		0.24	0.627
Component 5		2.20	0.138
Retained in Model			
Component 1	0.41 (0.11)	14.62	< 0.001
Component 2	-0.38 (0.16)	5.35	0.021

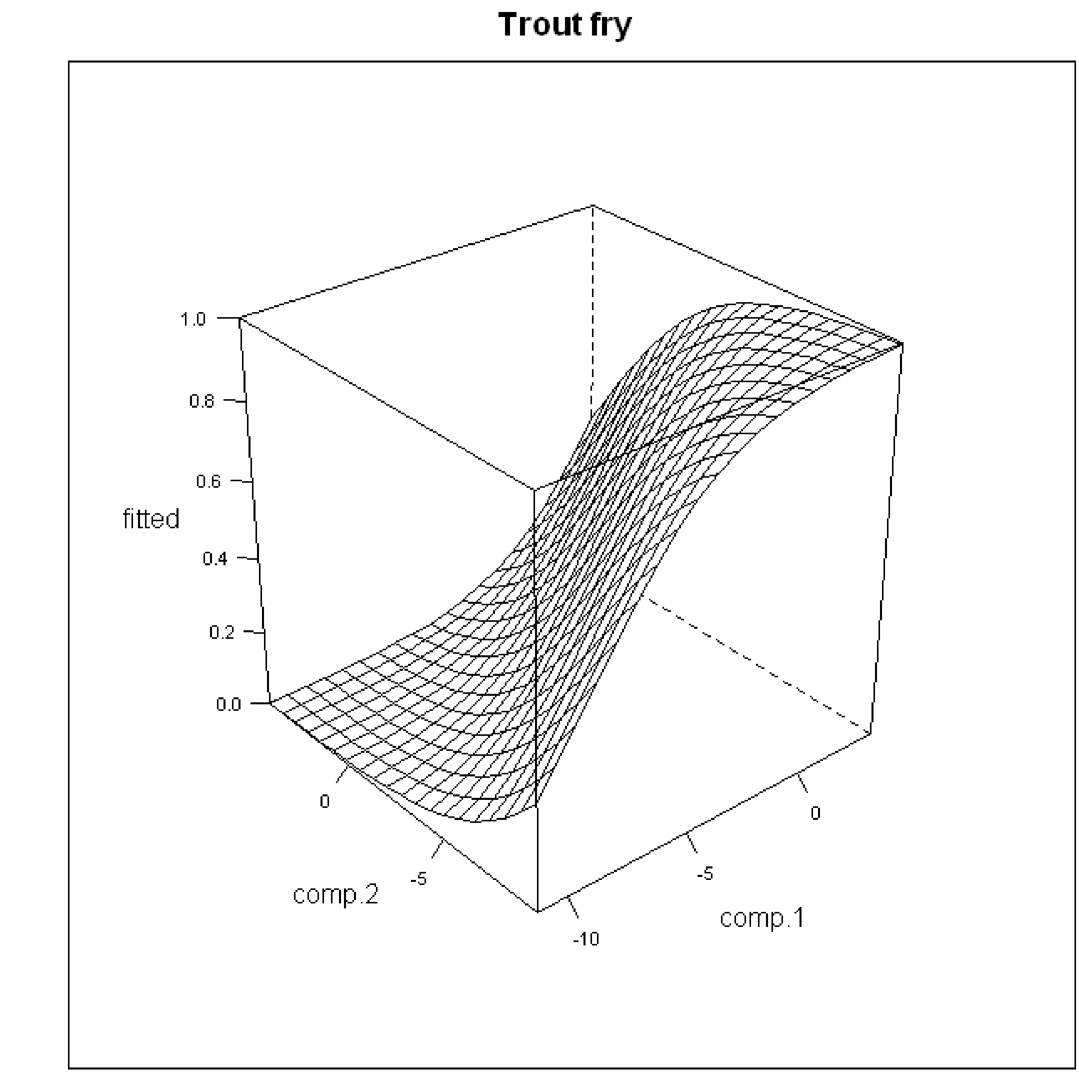

Figure 7.10. Fitted model showing relationship between WQ Principal Components and the probability of finding fry.

The mixed modelling process was repeated for trout of any age class. The results of the analysis are shown in Table 7.3. PCs 1, 2 and 4 were significant in explaining the presence of trout (regardless of age group). Fitted model output is shown in Figures 7.11-7.13. In each of the figures the predictions are illustrated by varying two of the three PCs while the remaining PC is held at its median value.

Figure 7.11 shows that the probability of finding fish declines with increasing PC2 scores: in other words trout presence is less likely where base cations and DOC are low. It also shows that the probability of fish presence also decreases with decreasing PC1 score (i.e. at sites with high SO_4^{2-} deposition and associated low pH and high Al^{3+}). However, PC1 only has an effect at higher PC2 scores (and vice versa), suggesting that the beneficial effects of high base cation and DOC concentrations can mitigate against the effects of low pH and high labile Al. Figure 7.12 shows that as PC4 scores increase so too does the probability of finding fish, indicating that the probability of finding fish decreases with increasing nutrient concentration. However, it is possible that this reflects the impact of other land-use practices rather than the impact of the nutrients *per se*. Figure 7.13 indicates that PC4 only influences fish presence where PC2 scores are very low. In other words, the influence of nutrients on survival is only important where base cation and DOC concentrations are high. This perhaps reflects the distribution of AWMN sites and their characteristics. However, it could also suggest that within the AWMN, acidity problems override other limiting factors, but that where acidity is no longer limiting other influences become increasingly apparent.

When considered together, Figures 7.10 and 7.11 (for fry and all fish respectively) indicate that trout fry presence is more sensitive to both PC1 and PC2 scores than the presence of any trout. This is consistent with the findings of previous studies.

Table 7.3. Results of mixed modelling analysis of the relationship between water quality Principal Components and trout of any age group.

Variable	Parameter (SE)	Likelihood ratio	P value
Removed from model			
Component 3		0.17	0.682
Component 5		1.59	0.207
Retained in Model			
Intercept	5.42 (1.10)	27.79	< 0.001
Component 1	0.43 (0.14)	9.47	0.002
Component 2	-0.57 (0.23)	6.79	0.009
Component 4	0.65 (0.28)	4.82	0.028

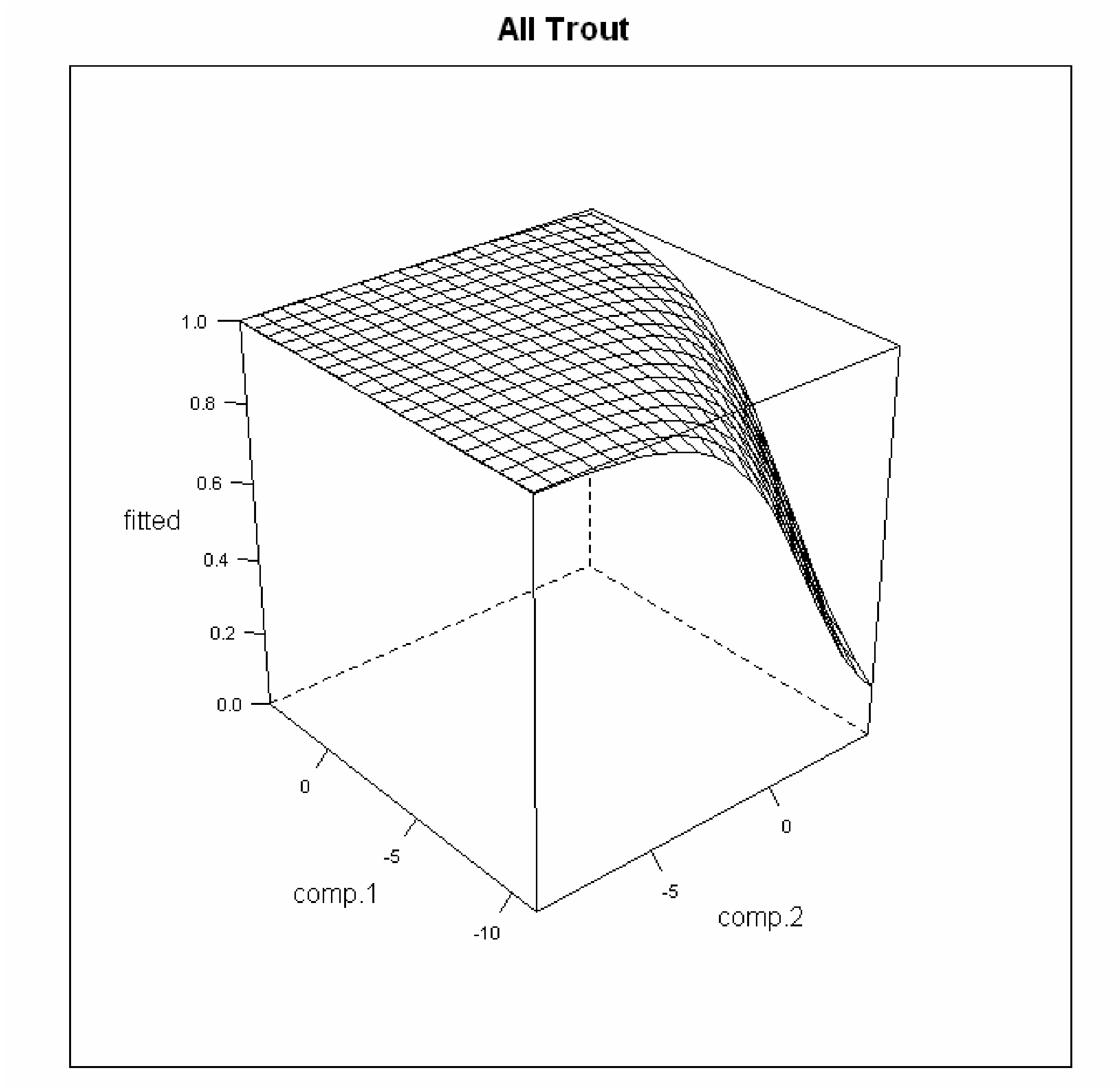

Figure 7.11. Fitted model showing relationship between PC1, PC2 and fish presence. PC4 is kept at a median level in this representation

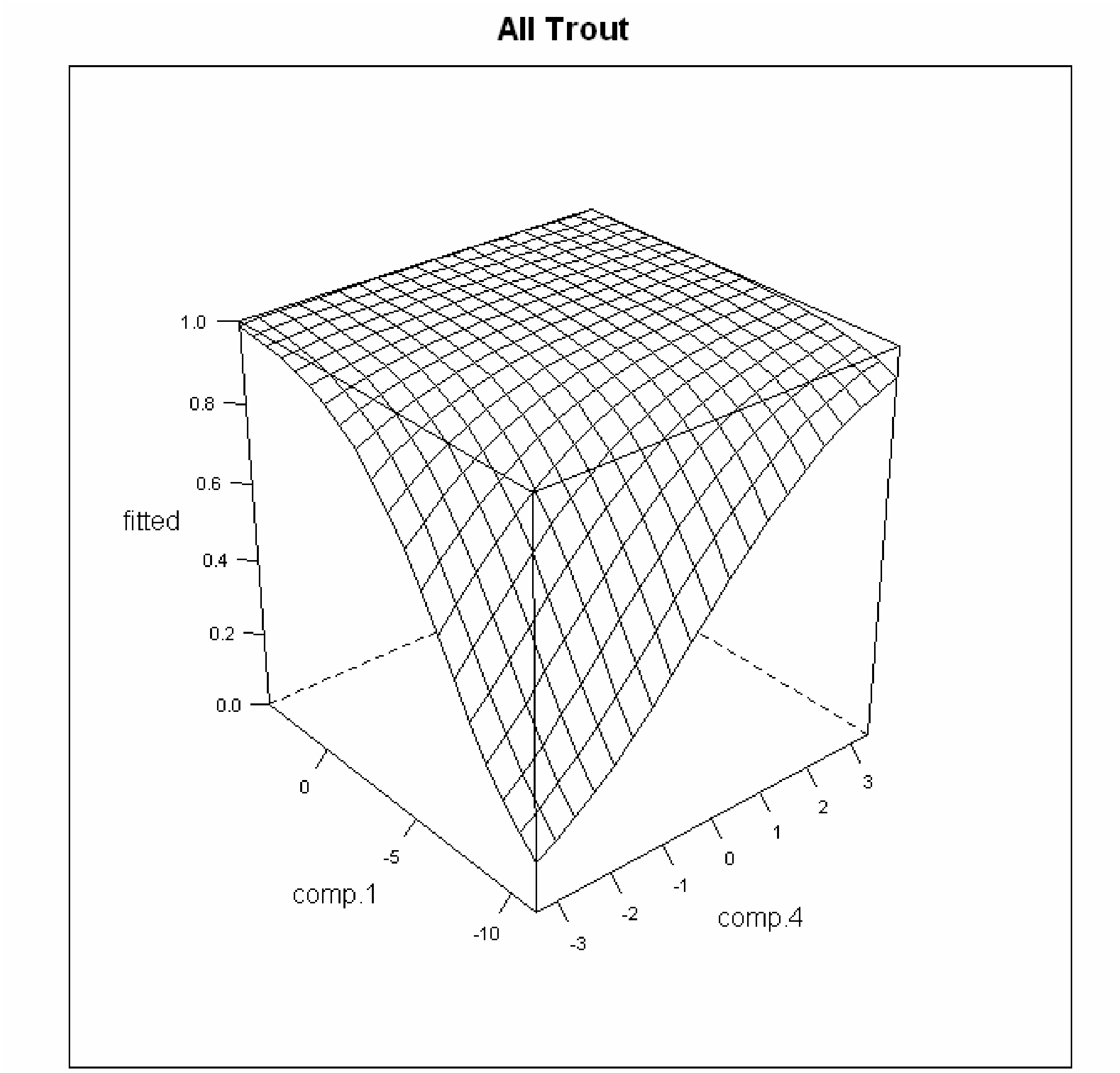

Figure 7.12. Fitted model showing relationship between Principal Component 1, Principal Component 4 and fish presence. Principal Component 2 is kept at a median level in this representation

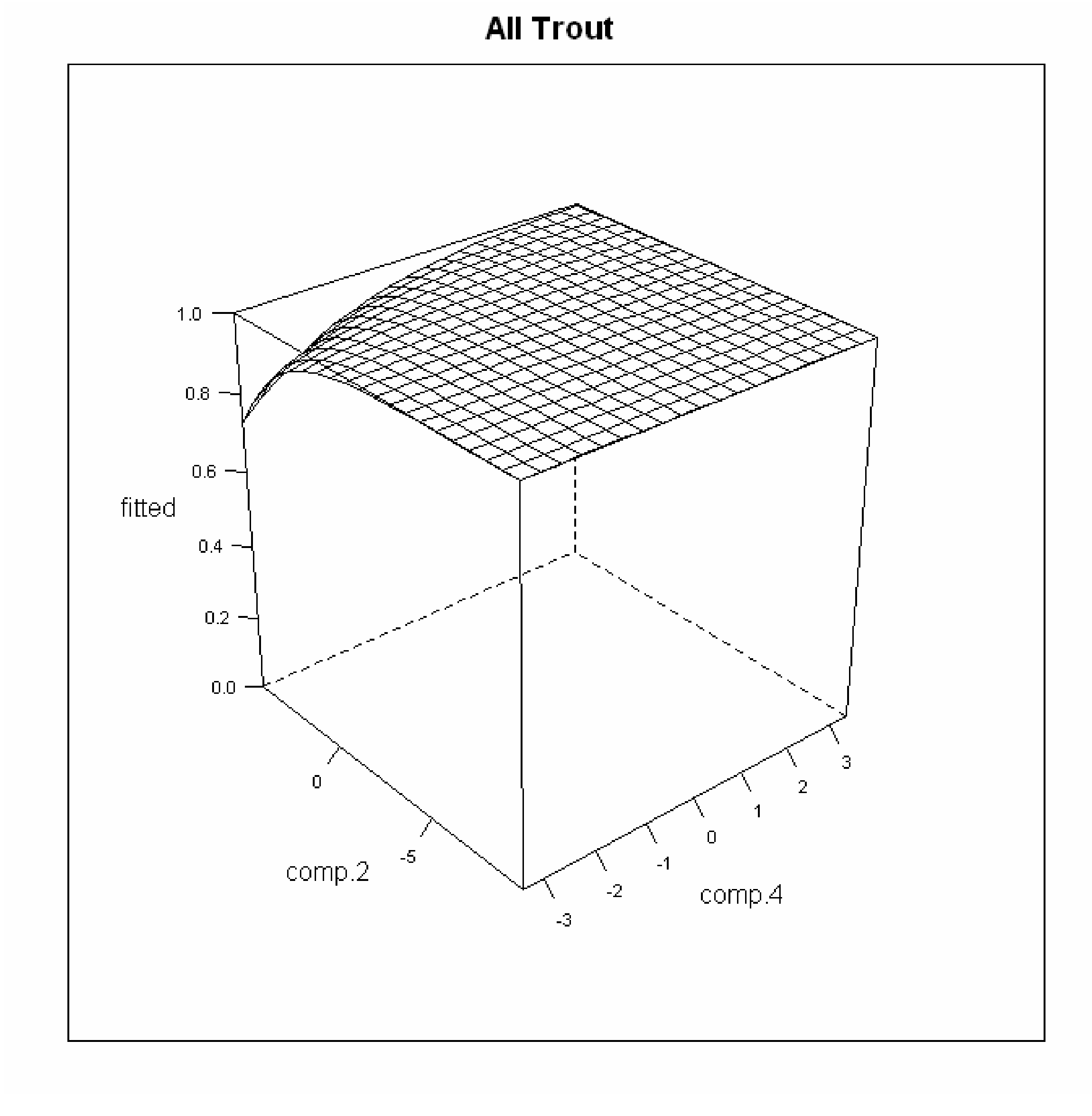

Figure 7.13. Fitted model showing relationship between Principal Component 2, Principal Component 4 and fish presence. Principal Component 1 is kept at a median level in this representation

7.4. Discussion

Previous laboratory studies have identified mechanisms whereby fish populations exhibit complex responses to changing water quality. Susceptibility to acid conditions depends on life stage, species, local adaptation, duration, frequency, magnitude and timing of exposure. It also varies with pH, Al^{3+}, Ca^{2+} and DOC, with complicated additive effects in the case of pH and Al^{3+}. Given the complexity of ecological responses, the difficulties in characterising fish populations using field sampling methods and the problems associated with characterising a temporally dynamic environment, it would not be surprising if clear and significant relationships between water quality and fish population status could not be determined. However, significant relationships were established and, importantly, the correlations discovered appear to provide intuitively reasonable explanations for observed variability in fish status (at least in terms of fish presence / absence) across the AWMN.

Complicated relationships between water quality characteristics and fish population status were identified that are generally consistent with those reported in the ecotoxicology literature. The probability of fish presence declined with principle component scores indicative of increasing Al^{3+}, decreasing pH, ANC, base cations and DOC. However, the analysis also appeared to indicate that increasing base cation and DOC concentrations could mitigate against the effects of combined acid deposition, low pH and ANC, potentially identifying varying pH / ANC thresholds between sites.

In terms of acid recovery it was not possible to undertake statistical analysis of the density data within the available resource and time constraints. However, a robust statistical analysis of trends in presence / absence of trout of different age classes was possible. This revealed significant positive trends in trout presence at five sites: Dargall Lane, Scoat Tarn, Old lodge, Beagh's Burn and Blue Lough. With Bonferroni correction for multiple tests, this is reduced to genuine trends at two sites, Scoat Tarn and Old Lodge. When the presence/absence of any age class was considered, only two sites showed significant trends over time, Old Lodge and Blue Lough. All sites showing recovery have exhibited marked increases in pH and ANC and reductions in toxic labile aluminium over the course of monitoring (see Chapter 3) and it is likely that these changes have now resulted in a hydrochemical combination that is now sufficient to allow the recovery of trout populations.

This chapter comprises the most detailed analysis of the AWMN fish data to date, providing detailed information on the water quality – fish relationships and temporal changes in fish population status. However, there are major challenges ahead for the AWMN associated with a substantially reduced Network of sites across the UK. As these sites will necessarily cover a reduced environmental gradient, it is not clear that the Network will be able to detect improvements in fish populations at acidified sites or provide further understanding of the controls on fish populations and critical thresholds. For 2010 electrofishing is planned for Loch Coire nan Arr, Allt a' Mharcaidh, Allt na Coire nan Con, Lochnagar, Loch Chon, Round Loch of Glenhead, Dargall Lane, Scoat Tarn, Old Lodge, Llyn Llagi, Llyn Cwm Mynach, Afon Hafren and Afon Gwy. It is uncertain if anything can be done at remaining sites. However, the power of this dataset lies in the number of sites and the environmental gradient covered. Clearly a reduction of 21 to 13 sites has major implications for the value of the Network, particularly if recovering sites such as Blue Lough are lost.

Future analysis of the AWMN fish data should seek to test the explanatory power of the PCA analysis presented here against traditional acid water descriptors in predicting fish presence and fish densities. In addition existing environmental standards should be assessed against these WQ models to ensure that current environmental standards are adequate to protect fish populations.

Finally, one should note that the AWMN is a valuable resource not only for assessing the impacts of acidification, but also climate change. Studies elsewhere in the UK (Gurney *et al.,* 2008) have shown that salmonid growth and smolt age-ratios have changed, partly as a consequence of changing temperatures. Temperature monitoring across the AWMN, combined with the detailed water quality and fish data collected, potentially allows for analysis of climate change effects to be carried out at a broad range of sites across the UK.

7.5. Key Points

Salmonid populations have been monitored in all but one site across the Network over the last twenty years on an annual basis, although, as a result of resourcing changes fish surveys at some sites have now stopped. In Scotland, the AWMN sites continue to be monitored with funding from the Scottish Government.

Density estimates of salmonids (brown trout, *Salmo trutta*, and salmon, *Salmo salar*) in AWMN streams and lake outflows are based on electrofishing catch data from standard reaches at each site. Populations are divided between species and age classes (0+ (fry) and >0+ (parr)) on the principle that different species and age classes have differing chemical requirements and that 0+ fish are better indicators of local conditions than older fish.

Positive changes in the presence of 0+ brown trout were observed at five sites, but significant positive trends (after accounting for multiple statistical tests using Bonferroni correction) were evident at only two of these; Scoat Tarn and Old Lodge. Analysis was also carried out on the presence of trout of all age classes (0+ and >0+), revealing significant positive trends at two sites; Old Lodge and Blue Lough consistent with recovery from acidification

There has been brown trout recruitment for the first time since monitoring began (as indicated by the detection of 0+ group fish) in the later part of the record at three sites, Old Lodge (since 1992), Scoat Tarn (1998) and Blue Lough (2000). These observations are important as they indicate that recruitment is beginning to occur at some of the most acidified sites in the Network.

There were significant relationships between water quality and the presence of trout of both age classes across the Network. Fish presence was significantly associated with a multivariate metric indicative of acidity (pH, ANC etc.). However, complicated interactions were also observed with multivariate indicators of cation concentrations and DOC. Furthermore, weak, but significant negative correlations were also observed between a multivariate metric indicative of nutrient concentrations and fish presence. This was interpreted as a land-use influence, though N deposition may also be a factor, and indicates the multi-factorial controls on fish populations.

Despite positive signs of recovery, salmonid fish populations remain severely impaired at many sites on the Network. Assessing future recovery and the chemical standards required for recovery and protection of fish populations is likely to become increasingly difficult given a reduced environmental range across the Network following recent site losses.

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8. Trace Metals

Neil Rose and Handong Yang.

8.1. Introduction

Shortly after the inception of the UK Acid Waters Monitoring Network in 1988, sediment cores taken for diatom analysis from the AWMN lakes were also analysed for a suite of pollutants including trace metals and spheroidal carbonaceous particles (SCPs). These additional determinands helped provide evidence that the acidification of the AWMN lakes was a result of acid deposition rather than the competing hypotheses that were being proposed at that time (Battarbee 1990). The concentrations of the trace metals, lead (Pb), zinc (Zn), copper (Cu) and nickel (Ni) were determined on cores that were also radiometrically dated by ^{210}Pb, ^{137}Cs and ^{241}Am (Appleby, 2001), providing a robust chronology against which to determine temporal changes in metal concentration. These were reported in AWMN annual reports at the time (Juggins *et al*., 1991; 1992; 1993) and more recently have been used in the development of regional scale Pb reconstructions for the UK and Ireland (Rippey & Douglas, 2004).

The radiometric chronologies and derived sediment accumulation rates can be used in combination with the metal concentration data to generate metal fluxes to the sediment basin and these take into account changes to concentrations that may be driven by accumulation rate variability (i.e. dilution of metal concentrations by an acceleration in sediment accumulation). Figures 8.1 and 8.2 show the Pb and Zn flux profiles, respectively, for these early AWMN sediment cores. While there was considerable variability between sites, most showed increases in Pb fluxes from the start of the period covered by the radiometric chronology to peaks from mid-20th century through to the 1980s followed by a reduction through to the sediment surface. Zinc trends also followed this general pattern, as would be expected from atmospherically deposited contaminants from similar sources. The decline in inputs to these upland lakes observed towards the top of the cores was probably due to emissions reductions resulting from changes to policy, the decline of heavy industry across the UK and, for Pb, removal from vehicle fuel. Exceptions to this are the profiles from Burnmoor Tarn and Llyn Cwm Mynach where no decline was observed and this may be due to additional catchment-derived inputs. In terms of absolute fluxes, it is apparent that northernmost sites in Scotland had lowest fluxes (cores in Figs. 8.1. and 8.2 are plotted in approximate north to south order) while highest fluxes occurred in southern Scotland and northern England. Metal fluxes in Northern Ireland were also generally low.

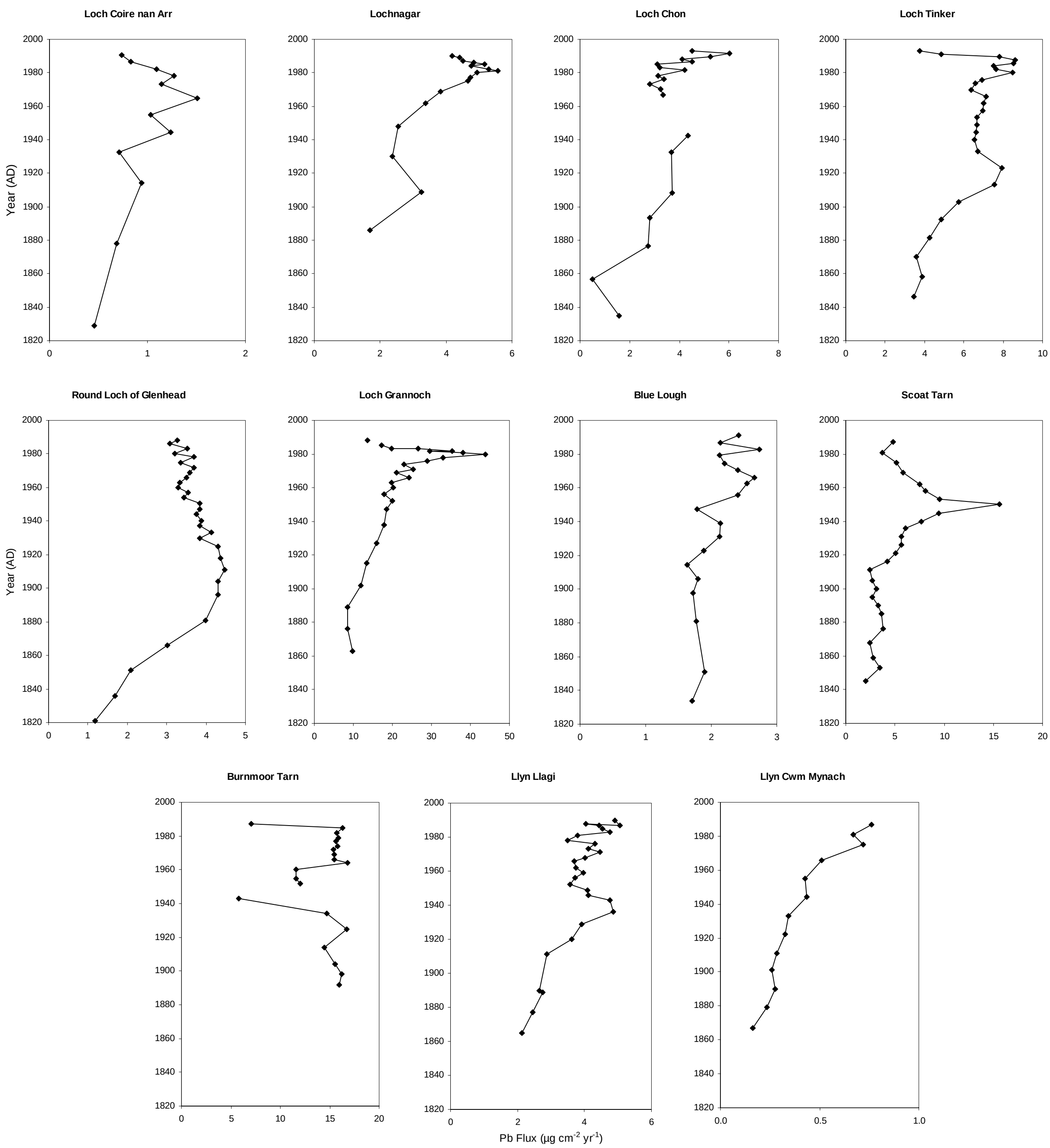


Figure 8.1.: Lead fluxes from AWMN sediment cores shown on a radiometrically-derived chronology axis.

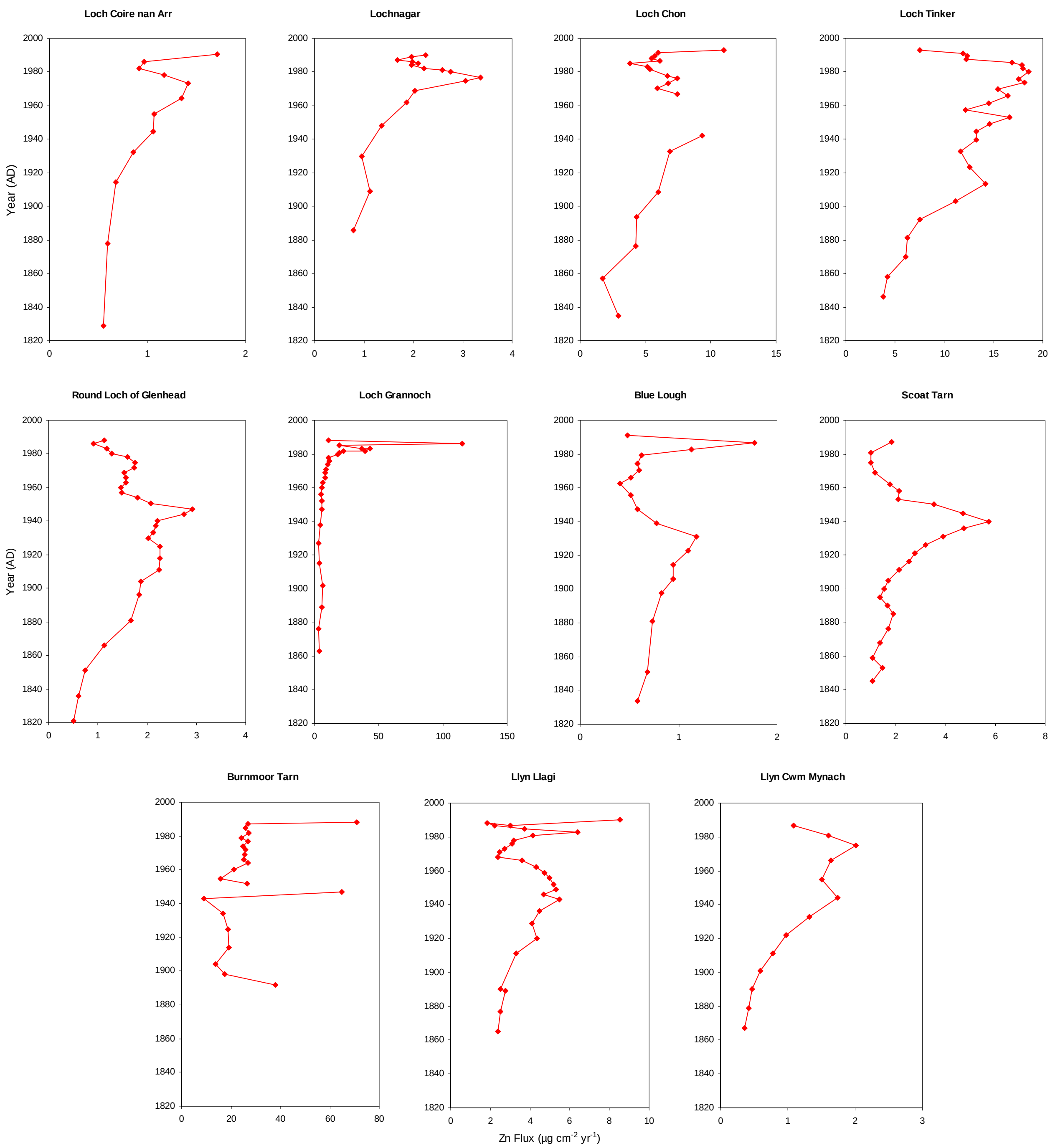


Figure 8.2 Zinc fluxes from AWMN sediment cores shown against a radiometrically-derived time-scale.

Little more work on trace metals within the AWMN was undertaken until Lochnagar was included as one of the flagship sites in the EU-funded European mountain lakes research programmes AL:PE and AL:PE II (1991 – 1996), MOLAR (1997 – 1999), EMERGE (2000 – 2003) and more recently, the EU 6th Framework European freshwaters research project Euro-limpacs. Monitoring of trace metals at Lochnagar began in 1996, with a sampling programme established for the EU MOLAR project and an associated PhD study by Handong Yang (Yang, 2000). The combined aims of these studies were to link depositional fluxes of metals at Lochnagar to the lake sediment record in such a way that historical deposition could more accurately and quantitatively be determined. Further, sampling of many ecological compartments including not only atmospheric deposition and lake waters, but also lake sediments, suspended sediments, catchment soils, various terrestrial plant and aquatic macrophyte species, epilithic diatoms and zooplankton were undertaken and analysed for a range of metals in order that a mass balance for the lake system could be obtained (Yang *et al.,* 2002). This study also showed, for the first time, the major input of metals from the catchment of an upland UK lake thought to be mainly the result of increased peat erosion.

After MOLAR, the monitoring of trace metals in bulk deposition, lake waters, sediment traps and aquatic and catchment biota continued with support from DETR under the 'Critical Loads of Acidity and Metals' (CLAM) project and the subsequent CLAM2 and 'Freshwater Umbrella' projects funded by Defra. From a metals perspective, the combined aims of these projects were:

- to continue to monitor cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu) and nickel (Ni) in a range of aquatic and terrestrial biota, sediment traps, bulk deposition and lake water at Lochnagar and to begin monitoring Hg in these ecological compartments as these data were (and remain) particularly rare in the UK.
- to assess the role that catchment and lake biota and sediment trapping could play in the monitoring of metal deposition and/or lake water metal concentrations and to modify the monitoring programme accordingly i.e. include new species or groups and remove those which proved to be ineffective;
- to identify any trends in depositional fluxes and how these relate to measured lake water, catchment and aquatic biota concentrations;
- to provide recommendations for the extension of similar monitoring to other upland sites under the auspices of the AWMN.

Analysis of lake water and deposition samples for trace metals, other than Hg, caused some problems during the CLAM project. High and erratic values were observed in a number of samples and, after a number of 'blank' test analyses, were attributed to sample filters used in one of the laboratories. Consequently, data prior to May 1999 are considered of doubtful quality. All other analyses were completed without problems producing a dataset, especially for Hg, unique within the UK and possibly within Europe. Metal concentrations for most of the terrestrial plant species at Lochnagar appeared to show a reasonable agreement with depositional trends whilst data from some reed and grass species (e.g. *Nardus stricta* and *Juncus sp.*) were considered of little monitoring value. This was also found to be the case for epilithic diatoms on artificial substrates, but only because the low productivity of the loch meant that insufficient sample was obtained in this way. In a more productive lake epilithic diatoms may yet prove to be a useful biomonitoring tool for trace metals.

At the conclusion of the final project more than ten years of metals data from Lochnagar were available. Unfortunately this could not be continued and the aim of extending the work to other sites was also not possible although the establishment of a metals monitoring Network remains a key priority. However, further monitoring of metals in biota and sediments were undertaken on an *ad hoc* and unfunded basis and this work provides significant 'added value' to the Lochnagar dataset.

Key questions to address are:

- What temporal trends can be identified from the ten year trace metal and SCP deposition and lake water dataset for Lochnagar?
- Do trace metal data from biotic and sediment trap samples from Lochnagar support any identified deposition and / or lake water trends?
- Can the trace metal data from AWMN sites be used to identify spatial patterns of contamination?
- Do the annual sediment trap trace metal concentration data from AWMN lakes provide any evidence for exceedence over effects level concentrations?

As metals monitoring in upland lakes in the UK has now ceased, this chapter describes the complete metals dataset compiled from AWMN sites. The chapter is divided into four sections dealing with: (i) bulk deposition and lake water trends at Lochnagar; (ii) data from the terrestrial and aquatic biota at Lochnagar; (iii) sediment trap data from the AWMN lakes; and finally (iv) data from terrestrial and aquatic biota at the other AWMN lakes and streams.

8.2. Bulk Deposition and Lake-Water Trends at Lochnagar

Sampling for trace metals (Cd, Pb, Zn, Cu and Ni) in lake water and bulk deposition at Lochnagar commenced in August 1996 and continued uninterrupted until March 2008. Sample collection frequency was weekly for the first 18 months as it formed part of the EU funded MOLAR project, but then became fortnightly for the remainder of the sampling period. Spheroidal carbonaceous particles (SCPs) were also analysed in the same samples in order to provide a further measure of anthropogenic contamination. Sampling for Hg in lake water and bulk deposition began in July 1997 and continued at a monthly frequency through to March 2008. While sampling was continuous, sample collection was occasionally irregular in the winter when bad weather prevented access to the site and/or sample retrieval.

8.2.1. Sampling

Bulk deposition for trace metals and SCPs was collected in a NILU-type (Norwegian Institute of Air Research) bulk deposition collector (P.no. 9713, RS1) deployed about 50 m from the north-east loch shore close to the automatic weather station (AWS) (Thompson *et al.,* 2007). Samples for trace metal analysis were acidified to 1% Aristar HNO_3. Bulk deposition samples for Hg analysis were taken using an IVL-type (Institutet för Vatten-och Luftvårdsforskning – Swedish Environmental Research Institute) sampler (Lindqvist *et al*., 1991; Jensen & Iverfeldt, 1994). Five ml concentrated Aristar HCl was placed in the sample collection bottle before fitting to the collector in order that the collected deposition was immediately acidified.

Lake-water samples for all trace metals (including Hg) were collected by submerging a rigorously acid leached 250 ml Teflon bottle approximately 20 cm beneath the surface of the water near the outflow where the lake water is well mixed. The bottles were completely filled, the lids tightened by gloved hands underwater and then the bottles double bagged. Sample treatment was the same as for the deposition samples.

8.2.2. Analytical methods

Cadmium, Pb, Zn, Cu and Ni were measured by inductively coupled plasma mass spectrometry (ICP-MS) at the (former) NERC ICP-MS Facility in Kingston University. A standard reference for trace elements in natural water, e.g. Standard Reference Material® 1640, was analysed after every fifth sample whilst acidified water (1% Aristar HNO_3 acid) blanks were run to calibrate the system. Detection limits for these analyses were as follows in Table 8.1 (all values in μg L^{-1}):

Table 8.1. Detection Limits at the NERC ICP-MS Facility in Kingston University

Cd	Pb	Zn	Cu	Ni
0.02	0.01	0.20	0.18	0.11

All Hg analyses on water and bulk deposition samples were undertaken at NILU. Before analysis the samples were oxidised with BrCl, converting stable Hg forms to water soluble species, which in turn were reduced to Hg^0 with $SnCl_2$. Samples prior to 4th June 2003 were analysed using a PS-Analytical Cold Vapour Atomic Fluorescence Spectrometer (CV-AFS) where Hg^0 is passed through a drying column before being detected in the AFS detector. The detection limit using this system was about 5 ng Hg L^{-1}. After June 2003, samples were analysed with a Tekran 2600. This significantly improved the limits of detection for the Hg analysis. Here, the Hg^0 is concentrated on a gold trap before being detected in the AFS detector and detection limits are 0.5 ng Hg L^{-1}. Analysis of SCPs from bulk deposition samples followed Rose *et al.* (2001) and involved filtering a known volume of deposition through a glass-fibre filter followed by dissolution of the filter using hydrofluoric acid.

8.2.3. Results

Figure 8.3 shows concentrations of trace metals in Lochnagar lake water since 1997. Data prior to May 1999 may have been affected by the leaching of metals during filtration but measurements after this time are considered accurate and reliable. Whilst the elevated levels resulting from this leaching are obvious in elements such as Cd, Ni and possibly Cu, the other elements do not appear to have been so affected. Since 1999, concentrations of all trace metals appear to show a general declining trend with the final year of sampling often showing the lowest concentrations of the whole sampling period. In general, periods of elevated concentration occurred in 2002 – 2003 for Pb, Cd, Zn and Cu and this led to an interpretation of increasing metal concentrations in a previous report (Shilland & Monteith, 2008). However, this has subsequently been shown to have been a temporary elevation in concentration and demonstrates the value of long-term monitoring. A period of high Hg concentrations in 2005 – 2006 was also observed. At the time it was assumed that this was due to contamination, but exhaustive investigation has shown no evidence for this. Similar patterns in the Hg bulk deposition data (see below) suggest that this may have been a 'real' event but, if so, it is unclear what the source of this additional Hg was. Concentrations after this 'episode' reduced once again to lower levels.

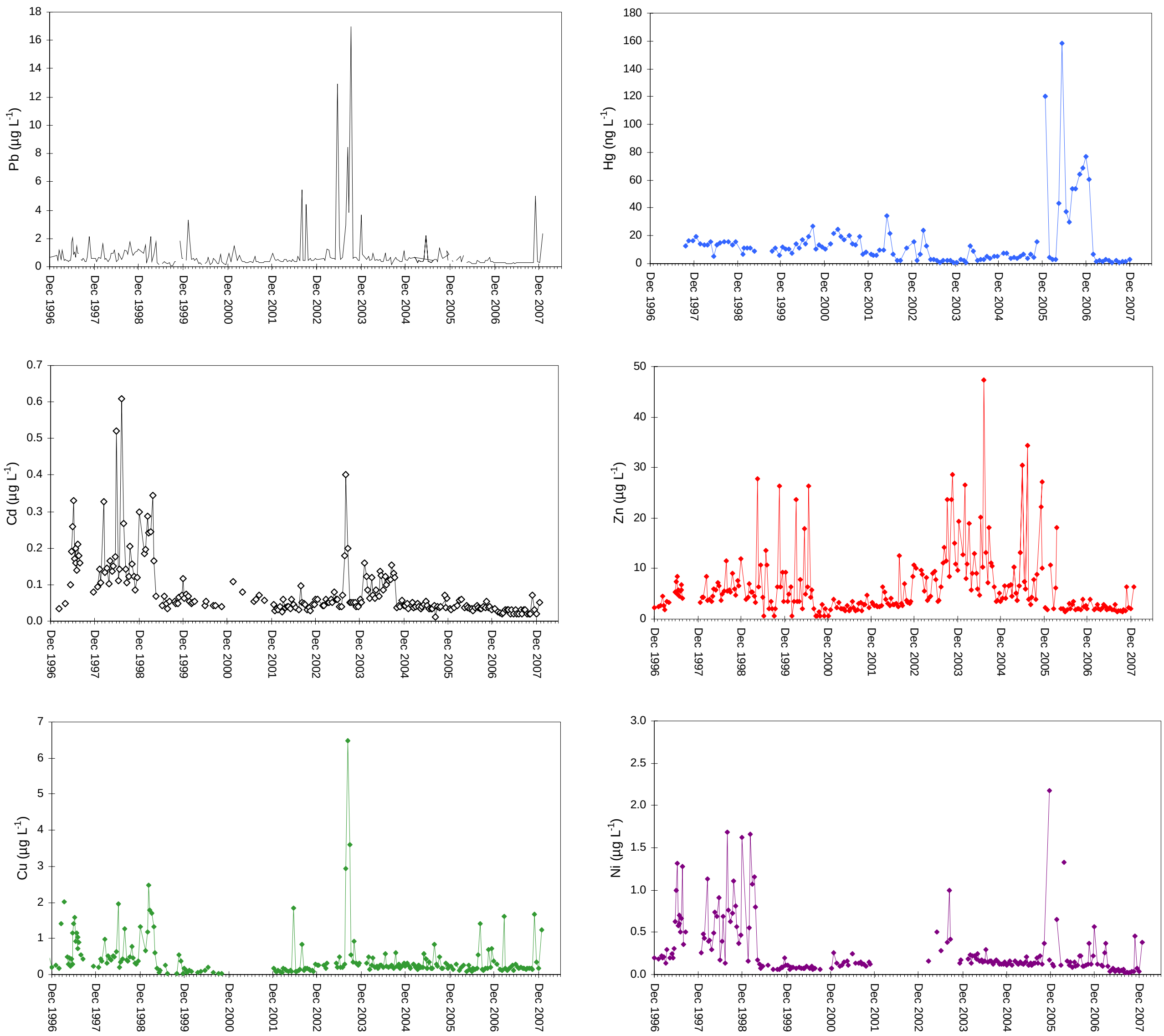


Figure 8.3: Trace metal concentrations for Lochnagar lake water 1997 – 2008.

Lake-water data are shown as annual mean concentrations in Figure 8.4 and these emphasise the periods of high concentration observed within the primary data. However, the longer-term record is now more clearly observable and shows that there has been little pattern to lake-water concentrations over the period. The exception to this would appear to be Hg where, with the exception of 2006, there appears to be a steady decline in lake water concentration over the 11 year period. Longer monitoring is required to ascertain trends in the other metals using robust statistical techniques.

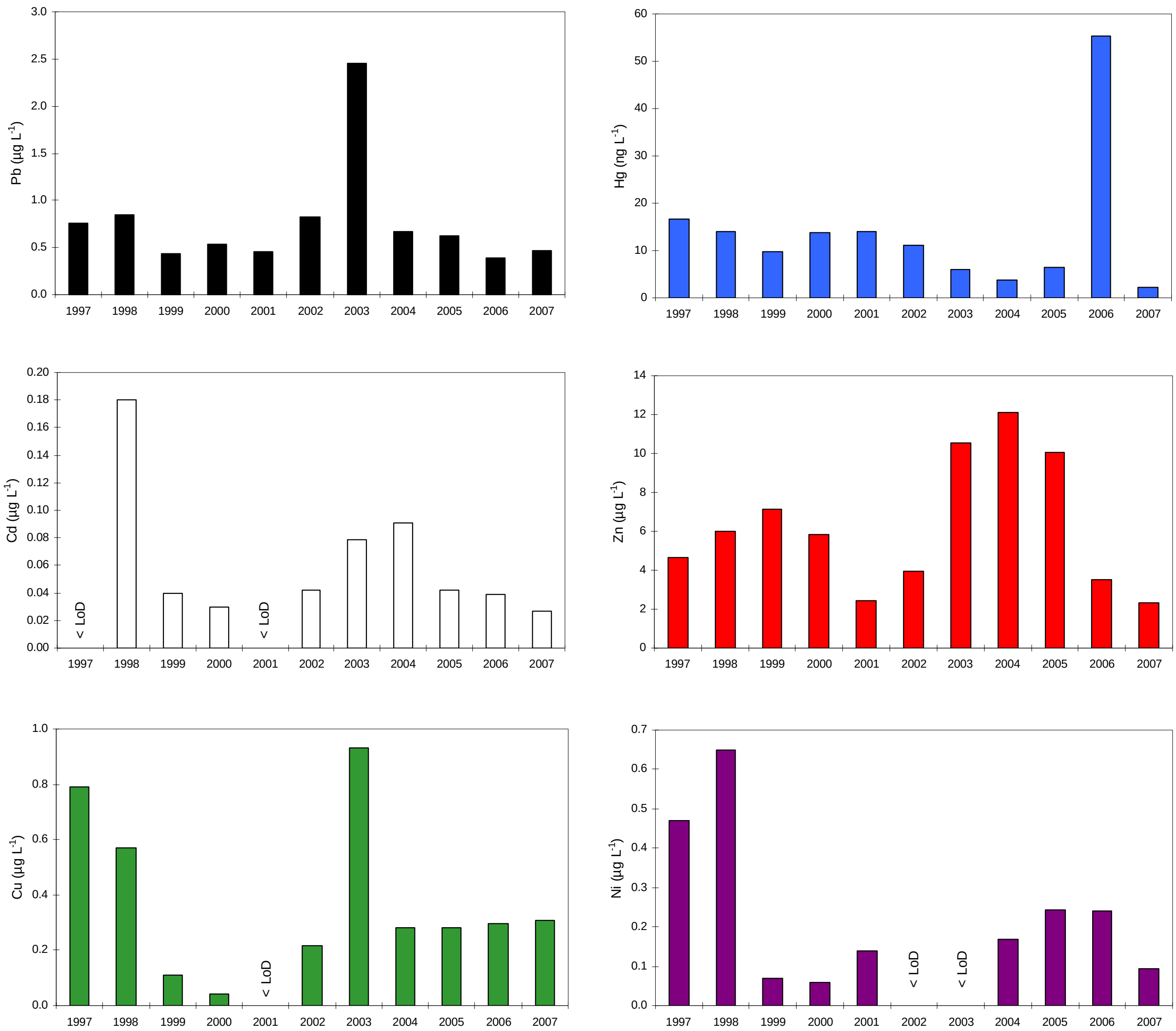


Figure 8.4: Mean annual (calendar year) trace metal concentrations for Lochnagar lake water 1997 – 2007 (<LoD indicates where more than half of the measurements were below the limit of detection for that year).

Figure 8.5 shows the trace metal concentrations in Lochnagar bulk deposition over the full monitoring period. Whilst the pre-May 1999 samples affected by the leaching from filters appear to be more obvious in these bulk deposition samples, the trends observed in the lake water data are also apparent here, i.e. elevated concentrations in 2002 – 2003 for Pb, Cd and Zn, occasional isolated 'high' values for all metals and elevated concentrations of Hg in 2005 – 2006 set against an overall declining trend. Bulk deposition concentrations may be combined with rainfall data from the AWS at Lochnagar to produce annual volume weighted depositional fluxes and these are presented in Table 8.1. Occasional power problems with the AWS during winter led to incomplete rainfall data for some years and hence some fluxes have been estimated from the total volume of rainfall collected. The combination of this and metal concentration data below the limit of analytical detection results in a higher degree of uncertainty for these depositional data than for the lake-water data, and hence no statistical analyses have yet been applied. However, it would appear that there has been little change in the depositional fluxes of Cd, Cu and Ni at Lochnagar while fluxes of Hg, Pb and Zn appear to show a decline.

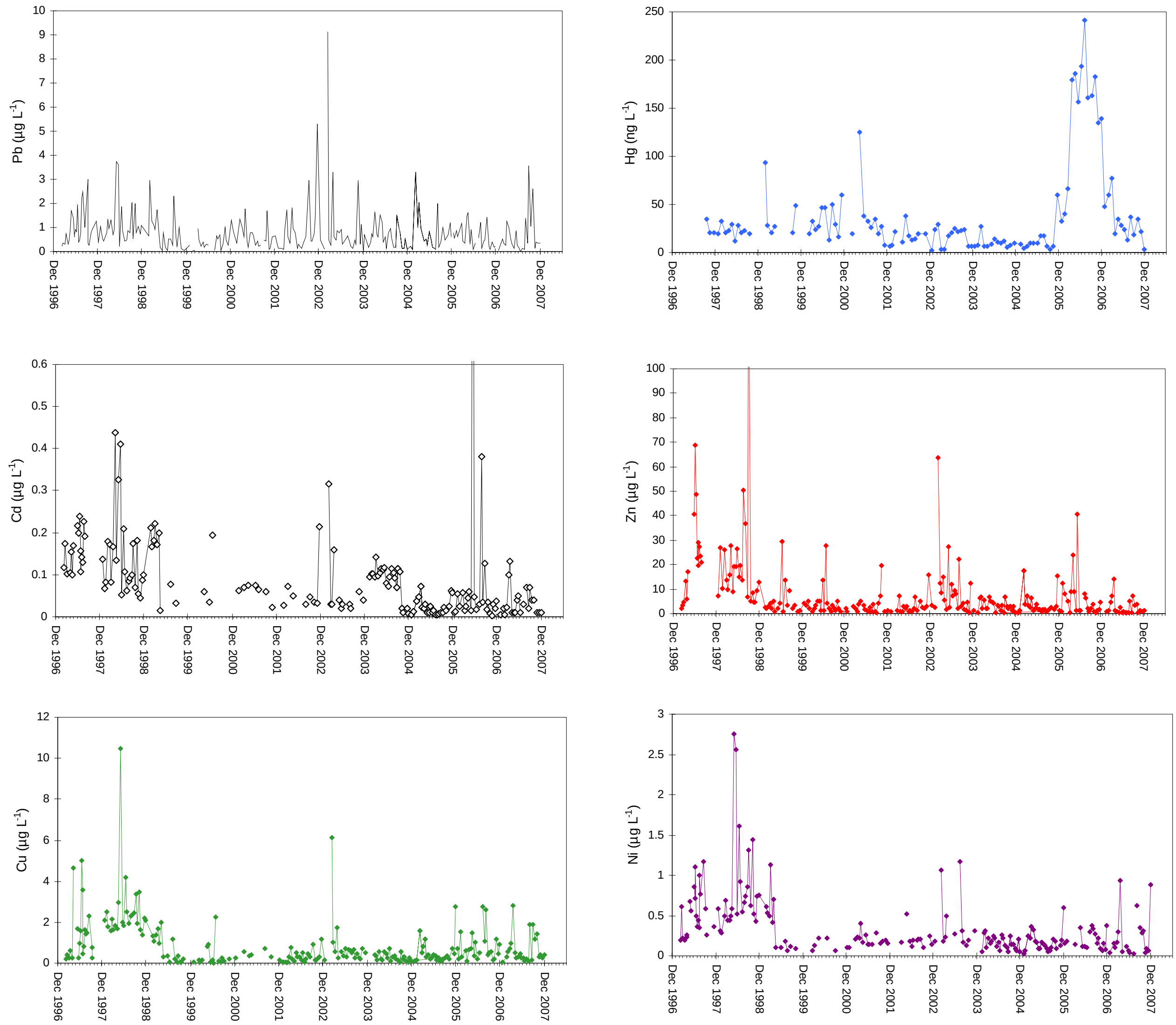
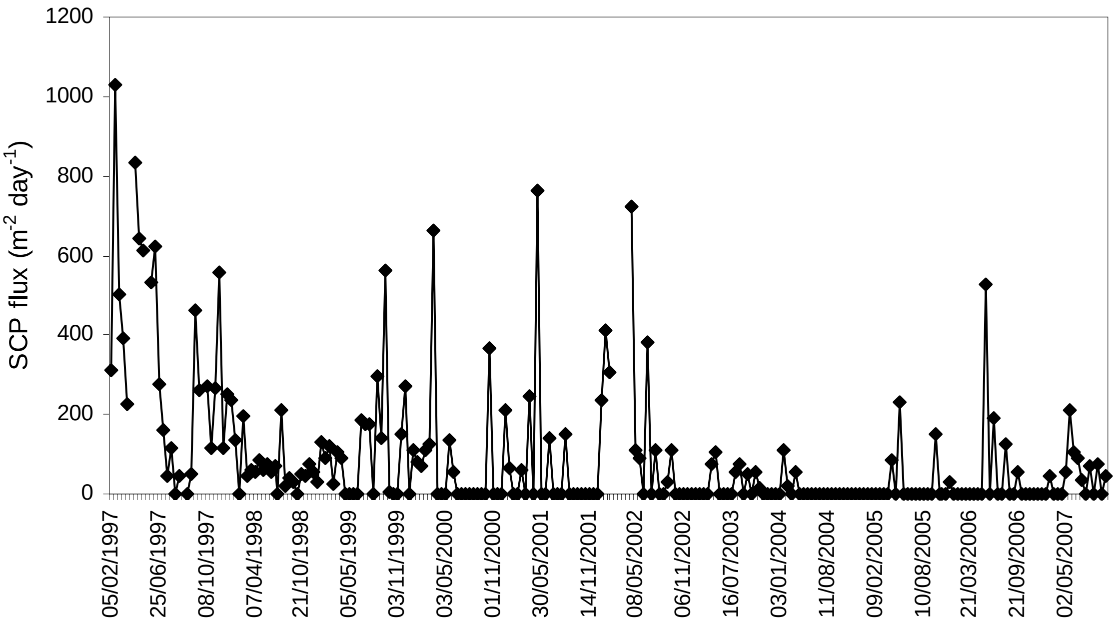


Figure 8.5: Trace metal concentrations for Lochnagar bulk deposition 1997 – 2008.

Figure 8.6 shows SCP deposition flux data for Lochnagar. SCPs are only produced from the high temperature combustion of fossil-fuels and therefore provide an unambiguous indicator of atmospherically-deposited contamination from this source. SCPs have been determined since 1997 (Fig. 8.6a) but many of the samples post-2004 show no SCPs and inputs are now much more sporadic than they were at the start of the sampling period. Conversion of these data to annual fluxes (Fig. 8.6b) shows the declining trend in SCP contamination, in good agreement with the trend in annual depositional fluxes shown by Hg, Pb and Zn. This agreement is consistent with a high-temperature coal combustion source of these contaminants and the declining trend since the late-1990s reflects a decline in emissions from these sources. However, it also raises a question over the Hg peak in 2006, as no equivalent peak was observed in either SCPs or any other metal. It therefore seems unlikely that this peak was produced by regional or national sources. The similarity between trends in both deposition and lake water show that this cannot be contamination of sampling equipment and the high values following a smooth pattern over such a period of time (Fig. 8.4) do not suggest random contamination. Furthermore, the reflection of the bulk deposition data in lower lake water concentrations, (dilution by the loch volume) is as would be expected for a 'genuine' episode. It seems most likely therefore that the 2006 Hg peak was caused by a local, as yet unknown source.

a)



b)

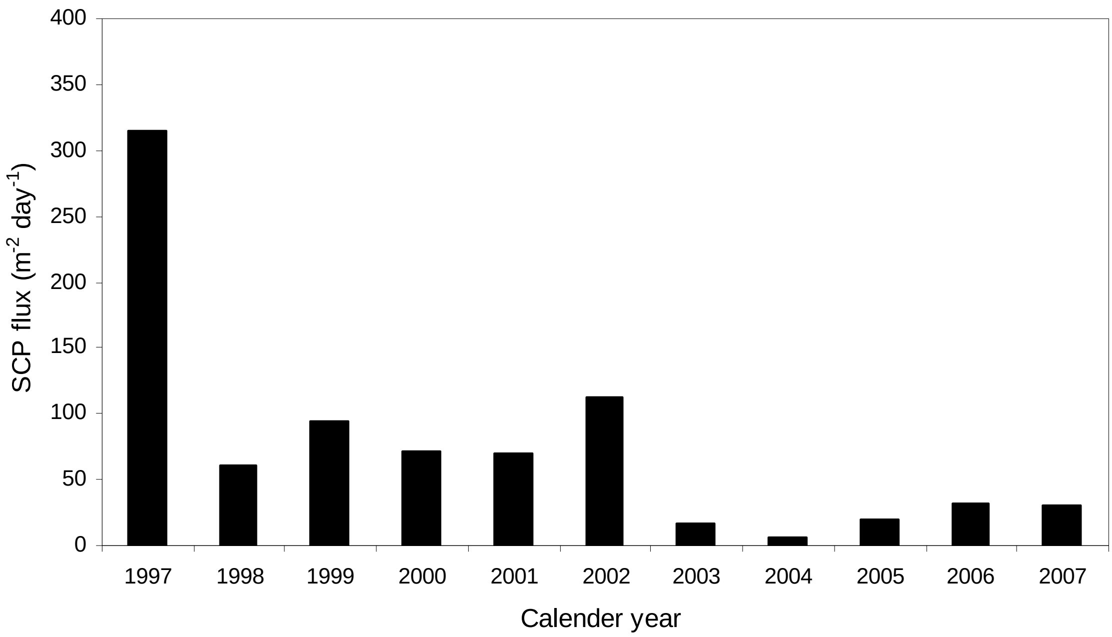


Figure 8.6: Spheroidal Carbonaceous Particle (SCP) flux data for Lochnagar 1997 – 2007 (a) fortnightly data; and (b) annual means.

8.3. Metals in Biota at Lochnagar

A wide range of aquatic and terrestrial biota from Lochnagar have been analysed for trace metals since sampling began in 1997. Over the monitoring period it became apparent that some species or classes were better suited than others and the sampling strategy has been revised accordingly. Hence, data for some species are more extensive than for others. Sampling of all biota for metals analysis ended in 2006.

8.3.1. Sampling

8.3.1.1. Terrestrial and aquatic plants

Samples of the main terrestrial plant species were collected annually in late summer. These included mosses: *Pleurozium schreberi* and *Hylocomium splendens* and ericaceous species: *Calluna vulgaris, Vaccinium myrtillus* and *Vaccinium vitis-idaea.* Leaf and shoot samples for each species were collected at various locations around the catchment and then combined to form a single sample. Plastic gloves were worn during collection and the samples stored in re-sealable plastic bags. The sampled vegetation was rinsed with deionised water and stored cool until being freeze-dried prior to analysis. Aquatic plants were collected using an Ekman grab operated from an inflatable boat, again during late summer. This grab sampling technique could not guarantee collection of species especially as many are not growing extensively within the loch. For this reason sampling of all selected species was not always possible in every year and this discontinuous dataset has therefore not been subject to statistical analysis. Intensive annual sampling of these species was avoided in order that data on macrophyte distribution in the biennial UK AWMN surveys was not affected. The species collected included the following: liverworts, *Nardia compressa* and *Scapania undulata*; aquatic mosses, *Fontinalis antipyretica* and *Sphagnum auriculatum* and the aquatic macrophyte, *Isoetes lacustris.* Once sampled, the entire aquatic growth (whole plant excluding root) was collected, washed, freeze-dried and treated as for the terrestrial species.

8.3.1.2. Zooplankton

Zooplankton samples were collected annually in late summer by using horizontal and vertical hauls of a 200 µm mesh net from an inflatable boat in the deepwater area of the loch. The zooplankton were stored in a polyethylene bottle. The sample was filtered immediately in the field using a Whatman GF/A filter paper and washed using deionised water. It was then frozen as soon as possible and freeze-dried prior to analysis.

8.3.1.3. Macro-invertebrates

Macro-invertebrate samples were taken using kick-sample techniques in a variety of littoral areas around Lochnagar. Suspended material was collected in a net and emptied into a sorting tray where the macro-invertebrates were picked out using stainless-steel tweezers and transferred to a plastic bag. Samples were then frozen as soon as possible, and freeze-dried prior to analysis.

8.3.2. Analysis

In order to measure trace metals in biological material, samples (c. 0.2 g) were extracted using 8 ml concentrated Aristar HNO_3 at 100°C for 1 hour in rigorously acid leached 50 ml Teflon beakers. For Hg measurements, after digestion, the supernates were carefully transferred into polyethylene tubes. The residue in the beakers was then washed with deionised distilled water and the supernates transferred into the same tubes. Lead, Cd, Zn, Cu and Ni were measured using atomic absorption spectroscopy (AAS) whilst Hg was measured by cold vapour atomic absorption spectrometry (CV-AAS) following reduction of Hg in the digested sample to its elemental state by 2 ml fresh $SnCl_2$ (10% in 20% (v/v) HCl). Major elements, Fe, manganese (Mn), aluminium (Al), silicon (Si), titanium (Ti) and calcium (Ca) in sediment trap samples were measured using Metorex Xmet920 X-ray fluorescence (XRF) spectrometer. Certified standard reference materials (Buffalo River sediment SRM2704 and stream sediment GBW07305) were digested and analysed during sample analysis. For AAS, reference materials and sample blanks were analysed every 20 samples. The standard solution was measured every five samples in order to monitor measurement stability. Our measured mean concentrations of Hg were 93 ng g^{-1} in stream sediment (n = 12; relative standard deviation (RSD) = 8.6 ng g^{-1}; certified value = 100 ±10 ng g^{-1}). The coefficient of variation and precision was < 5% for Pb and Cd and <15% for Zn, Cu and Ni. For XRF, reference materials were measured every five samples. Analytical detection limits for the trap and biota samples are in Table 8.2:

Table 8.2. Detection Limits For Biota at Lochnagar

Hg (ng g^{-1})	**Zn** (μg g^{-1})	**Ni** (μg g^{-1})	**Cu** (μg g^{-1})	**Cr** (μg g^{-1})	**Cd** (μg g^{-1})	**Pb** (μg g^{-1})
2.8	0.71	0.9	0.83	0.67	0.1	0.83

8.3.3. Results

8.3.3.1. Mercury (Hg)

Mercury data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 8.7. Of the terrestrial plant species, the mosses *Pleurozium schreberi* and *Hylocomium splendens* show stable levels throughout the whole monitoring period and also show comparable concentrations between the two species. Of the other terrestrial plants, the two *Vaccinium* species, *Vaccinium vitis-idaea* and *Vaccinium myrtillus,* also show little trend across the monitoring period but *Calluna vulgaris* may be showing a decline in concentration. Of the aquatic species, *Sphagnum auriculatum* appears to be showing a decline through the period and *Isoetes lacustris* shows a decline until 2006 when Hg is again elevated. Mercury concentrations in *Scapania undulata* show little trend and sampling of this species ceased in 2003 due to its scarcity. Zooplankton Hg concentrations remain consistent throughout the period and are elevated above those of other biota, possibly as a result of their trophic level. Conversely, macro-invertebrates showed lower concentrations and an increasing trend over the period in which they were sampled, but this was curtailed in 2004 as sufficient numbers of appropriate species could not be guaranteed.

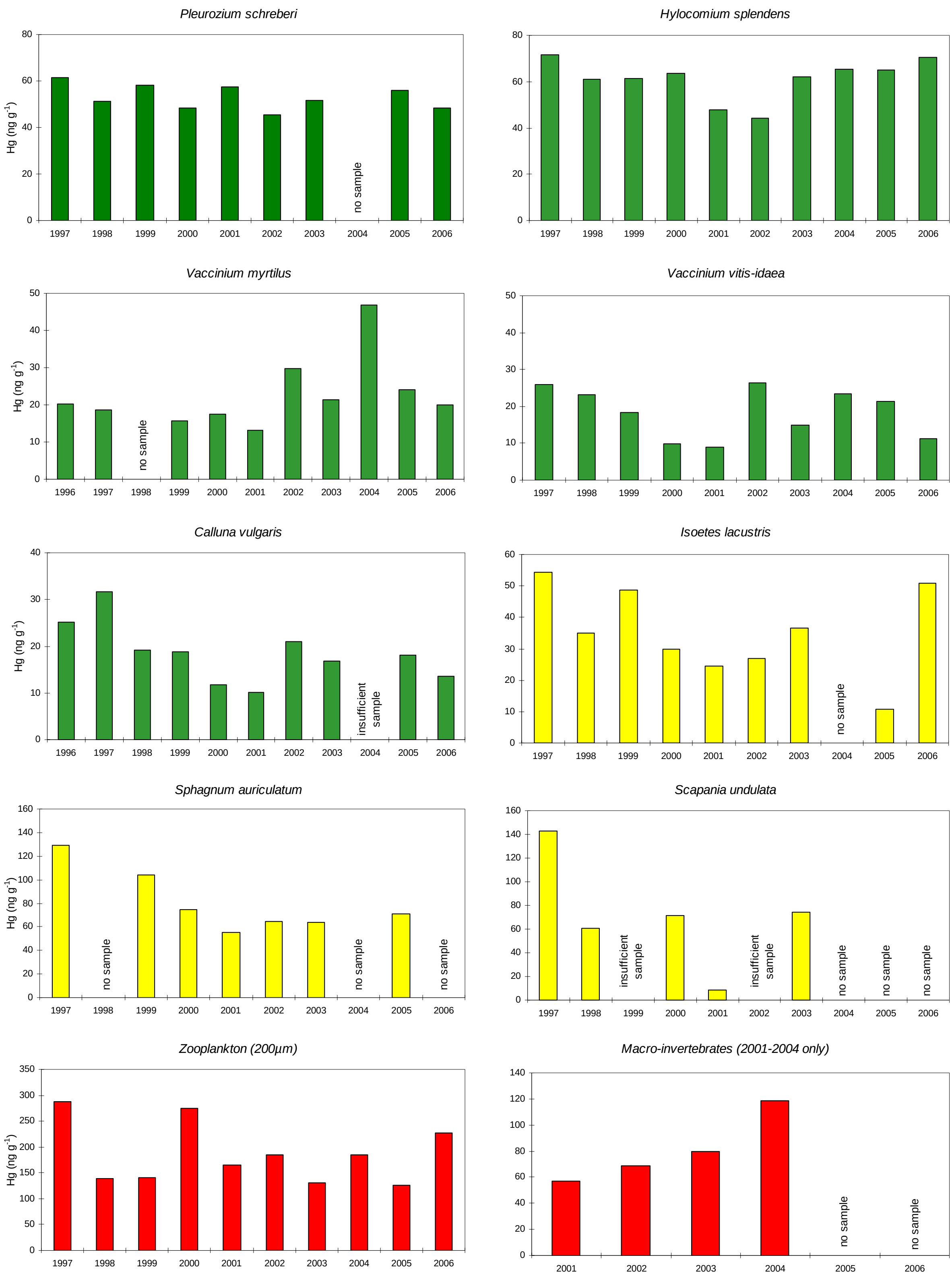


Figure 8.7: Concentrations of Hg in terrestrial and aquatic biota from Lochnagar. Terrestrial plants are shown in green, aquatic plants in yellow and aquatic fauna in red. 'no sample' indicates that the species was not collected; 'insufficient sample' indicates that available sample was used for other analyses.

8.3.3.2. Lead (Pb)

Lead data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 8.8. Many of the biota show declining trends in Pb concentration over the period of monitoring and this is in agreement with both the depositional fluxes of Pb measured at Lochnagar (Table 8.3) and with trends in emission and deposition across the UK (e.g. Playford & Baker, 2000; Rippey & Douglas 2004). All terrestrial plant species show declines, with *Vaccinium myrtillus, Vaccinium vitis-idaea* and *Calluna vulgaris* all falling below the limit of detection in the last few years. Exceptions are for 2006 in *Hylocomium splendens*, but also for 2004 in all terrestrial species when Pb concentrations either once again exceed the limit of detection (where they had fallen below it) or show an elevated Pb concentration. It is interesting to note that this increase in plant Pb concentrations follows the elevated levels in 2003 observed in both deposition and lake water. Declining trends are also generally observed in aquatic plants although limited samples were available after 2003, especially for *Scapania undulata*. The aquatic fauna show little trend although the concentrations in zooplankton do fall below detection limit in 2003 and 2005. Apart from this value, as with Hg, the zooplankton show significantly higher concentrations than the macro-invertebrates.

Table 8.3: **Volume weighted depositional fluxes of trace metals to Lochnagar 1999 – 2008. Data for 1997 and 1998 are shown for Hg only as these samples were not affected by filtration. <LoD indicates where more than half of the measurements were below the limit of detection for that year. Values in italics for 2004, 2005 and 2007 are estimates only, due to incomplete rainfall data as a result of AWS power failure. In these cases estimates of rain volume are taken from the collected bulk deposition samples.**

	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Hg	16.57	14.10	9.88	13.76	13.93	11.03	5.96	*3.88*	*6.40*	55.40	*2.13*
Pb			1.17	0.57	0.99	1.85	<LoD	*0.24*	*0.34*	0.09	*0.27*
Cd			0.02	0.01	0.05	0.06	<LoD	*0.03*	*0.01*	0.02	*0.01*
Zn			7.35	4.66	4.25	5.05	1.45	*1.20*	*1.61*	0.80	*1.06*
Cu			0.24	0.19	0.29	0.57	0.12	*0.11*	*0.22*	0.12	*0.26*
Ni			<LoD	<LoD	0.21	0.29	<LoD	*0.06*	*0.07*	2.98	*0.10*

8.3.3.3. Cadmium (Cd)

Cadmium data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 8.9. Cadmium concentrations in terrestrial plants seem to show a peak in 2003 although in general there is a shift from detectable levels of Cd to levels below the limit of detection moving through the time-series such that Cd was not detectable in any terrestrial plant sample in the last three years of sampling. This may indicate a decline in Cd concentrations through time. Trends in aquatic plants are more ambiguous due to the limitation in species availability. All species show clear increasing trends up to 2003. After this date, no further *Scapania undulata* was collected, Cd concentrations in *Isoetes lacustris* appear to decline and concentrations in *Sphagnum auriculatum* are below the limit of detection in 2005, the only year in which samples of this species were obtained after 2003. Macro-invertebrate data also show a peak in 2003 and a below detection limit value in 2004, while there is little trend in the zooplankton Cd data. Unlike Hg and Pb, Cd concentrations in zooplankton and macro-invertebrates are largely equable.

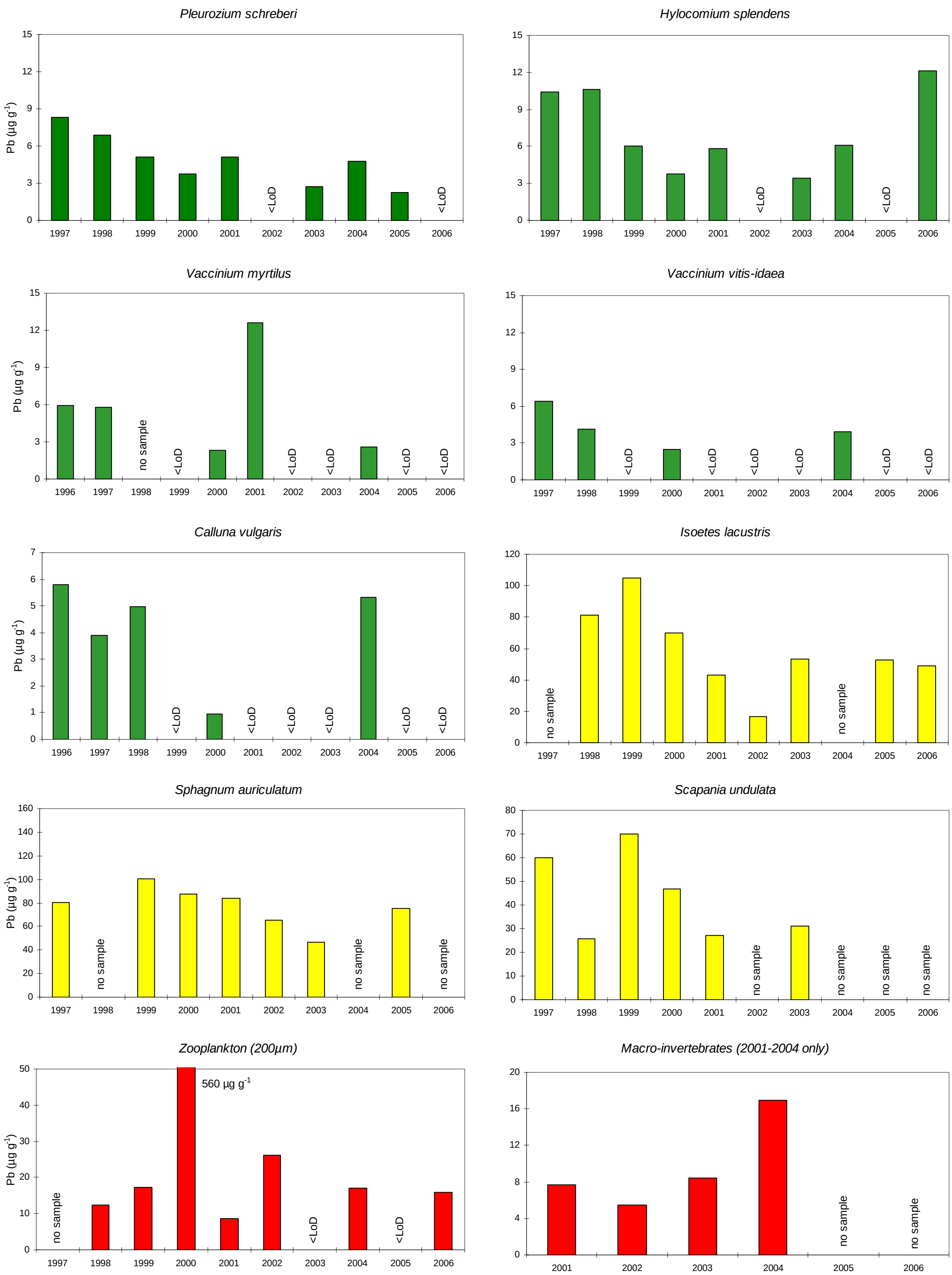


Figure 8.8: Concentrations of Pb in terrestrial and aquatic biota from Lochnagar. Terrestrial plants are shown in green, aquatic plants in yellow and aquatic fauna in red. 'no sample' indicates that the species was not collected <LoD indicates concentrations below the analytical limit of detection.

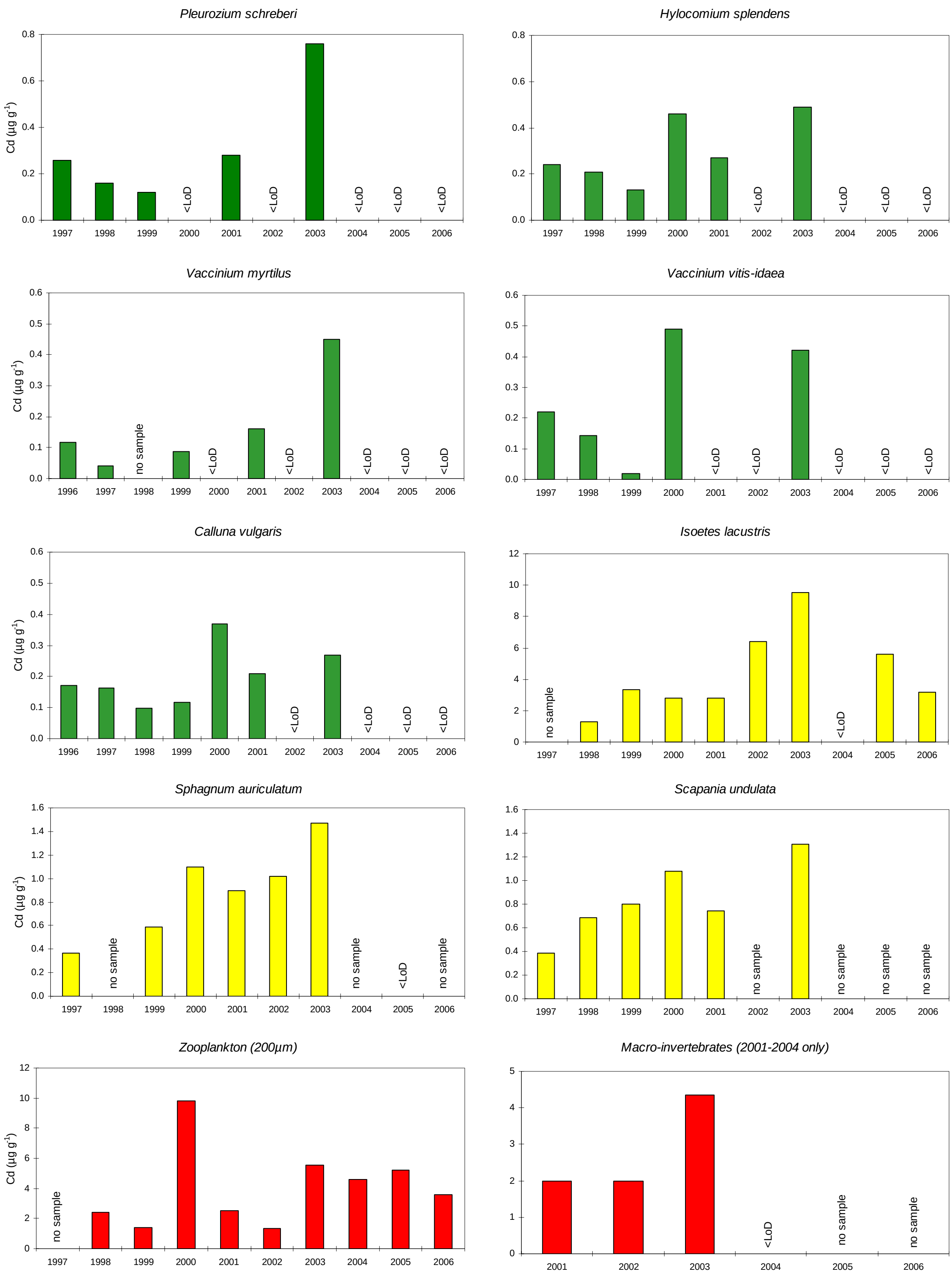


Figure 8.9: Concentrations of Cd in terrestrial and aquatic biota from Lochnagar. Terrestrial plants are shown in green, aquatic plants in yellow and aquatic fauna in red. 'no sample' indicates that the species was not collected; <LoD indicates concentrations below the analytical limit of detection.

8.3.3.4. Zinc (Zn)

Zinc data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 8.10. The terrestrial plants show very consistent trends. With the exception of *Vaccinium vitis-idaea*, which shows a concentration below the limit of detection in 2001, all other terrestrial species show high values prior to 1998, and in 2001, and low concentrations from 2002 onwards. Hence, there appears to be an observable decline in Zn concentrations in the terrestrial plant data in agreement with the trend observed in the bulk deposition (Table 8.3). By contrast, Zn concentrations in the aquatic biota show little trend although this is, in part at least, due to the sporadic nature of the sample availability. However, Zn concentrations in *Sphagnum auriculatum* do show high values in 2001 with low subsequent values in agreement with the terrestrial plant data.

8.3.3.5. Copper (Cu)

Copper data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 8.11. Terrestrial plant Cu concentrations are very similar between species and show little trend over the time-series although *Vaccinium vitis-idaea* may show declining concentrations after 1999. Aquatic flora and fauna show no clear trends although *Isoetes lacustris* may also show a decline in Cu concentration since 2000. Peak concentrations occur in different years in different species with an unusually high concentration in *Sphagnum auriculatum* in 2000, a feature that is also reflected in the zooplankton data. As with other trace metals, Cu concentrations in macro-invertebrates increase through the available sampling period.

8.3.3.6. Nickel (Ni)

Nickel data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 8.12. For all terrestrial and aquatic biota, the trends are very similar. After 1999 in all terrestrial plants and after 2000 in all aquatic species, all Ni concentrations were below the limit of detection. As with Cd and Pb, this may indicate a decline in Ni concentrations over the sampling period. For *Hylocomium splendens*, *Calluna vulgaris* and *Vaccinium vitis-idaea* a reduction to below the limit of detection continues a declining trend from the start of the time-series, while for other species, the last year of detectable Ni is also that of highest concentration (e.g. *Scapania undulata*, *Sphagnum auriculatum*, zooplankton). By contrast, Ni continued to be measurable in sediment traps up to 2004 (see below) although fell below the limit of detection after this time.

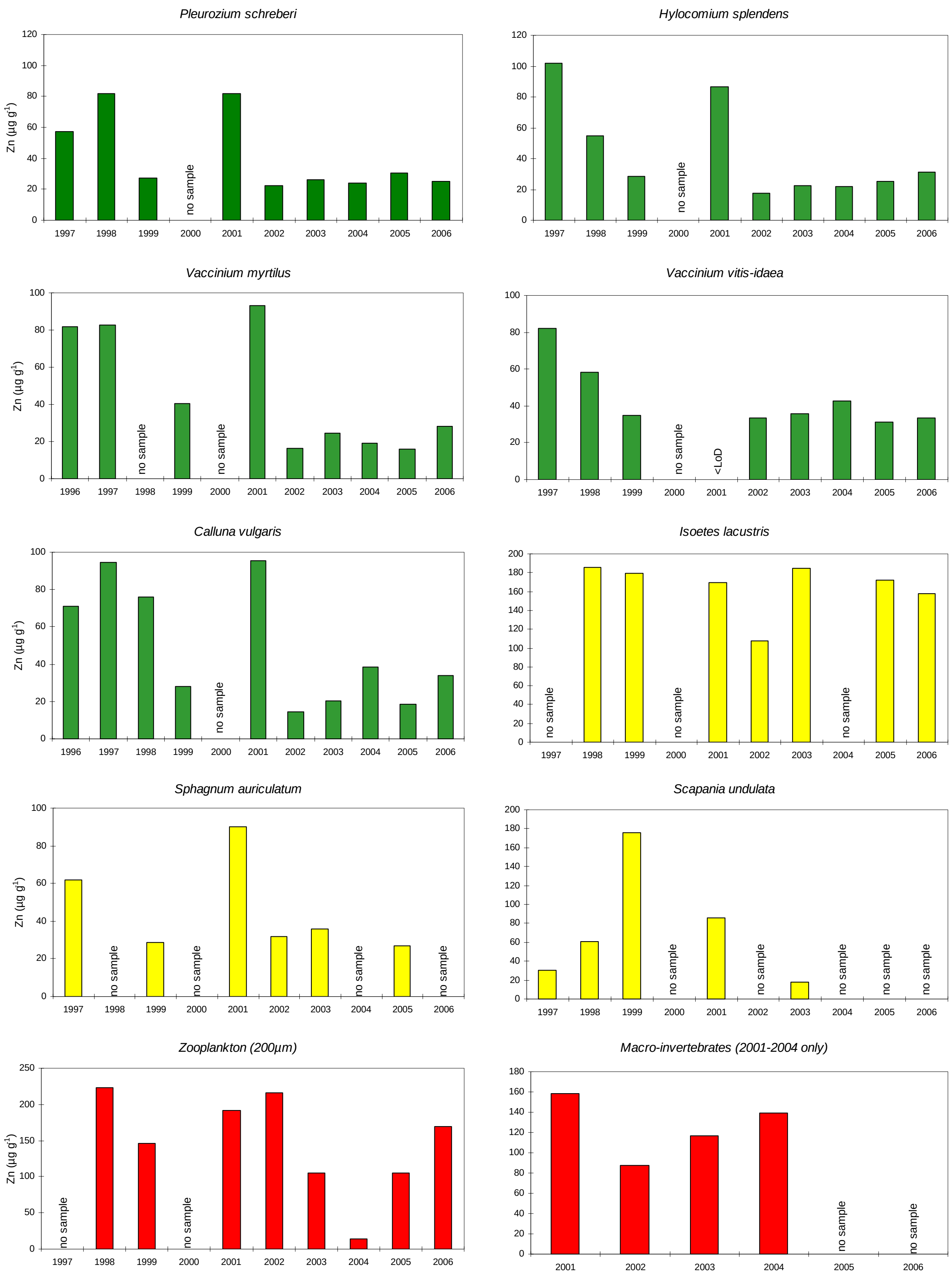


Figure 8.10: Concentrations of Zn in terrestrial and aquatic biota from Lochnagar. Terrestrial plants are shown in green, aquatic plants in yellow and aquatic fauna in red. 'no sample' indicates that the species was not collected; <LoD indicates concentrations below the analytical limit of detection.

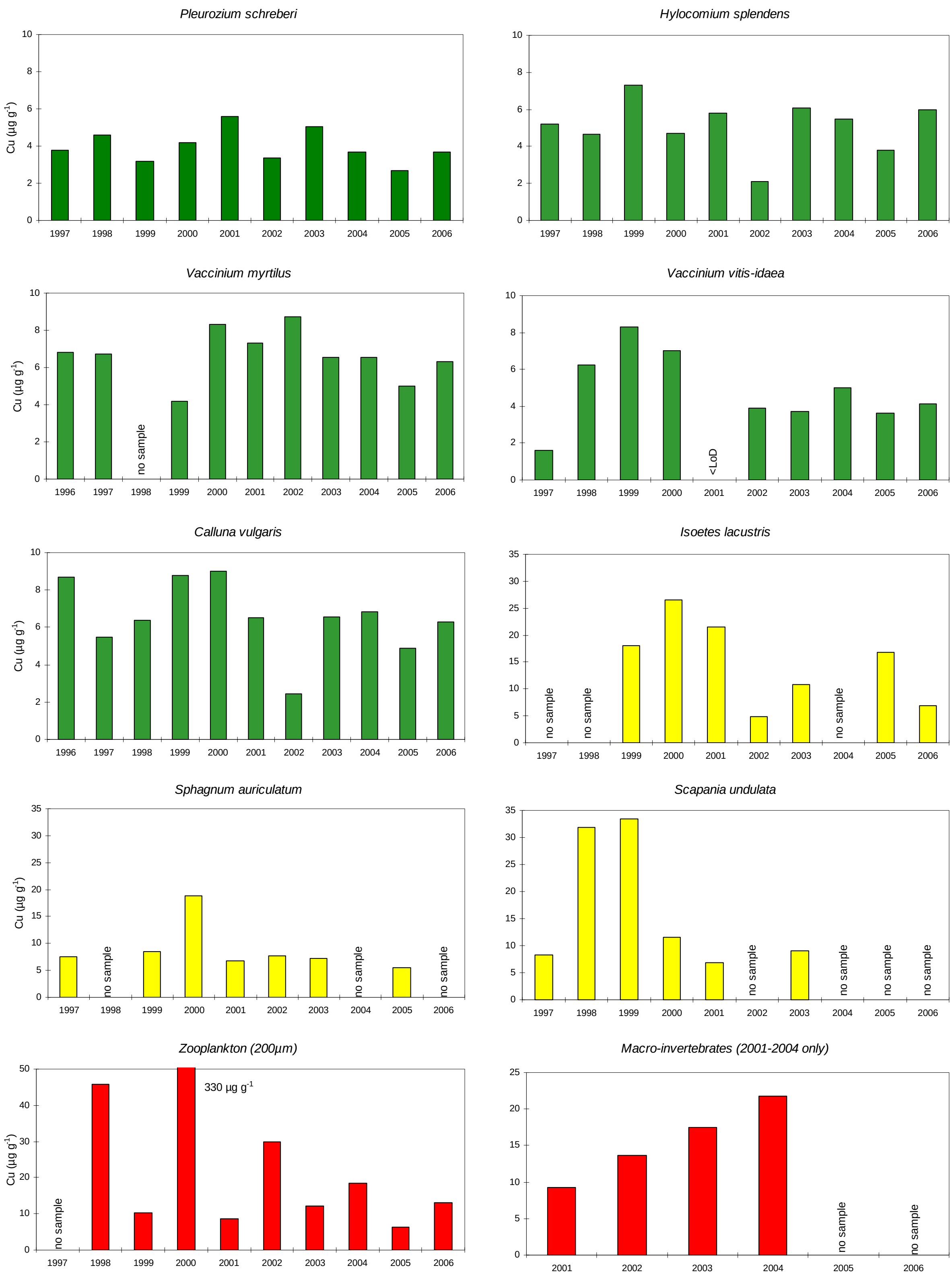


Figure 8.11: **Concentrations of Cu in terrestrial and aquatic biota from Lochnagar. Terrestrial plants are shown in green, aquatic plants in yellow and aquatic fauna in red. 'no sample' indicates that the species was not collected; <LoD indicates concentrations below the analytical limit of detection.**

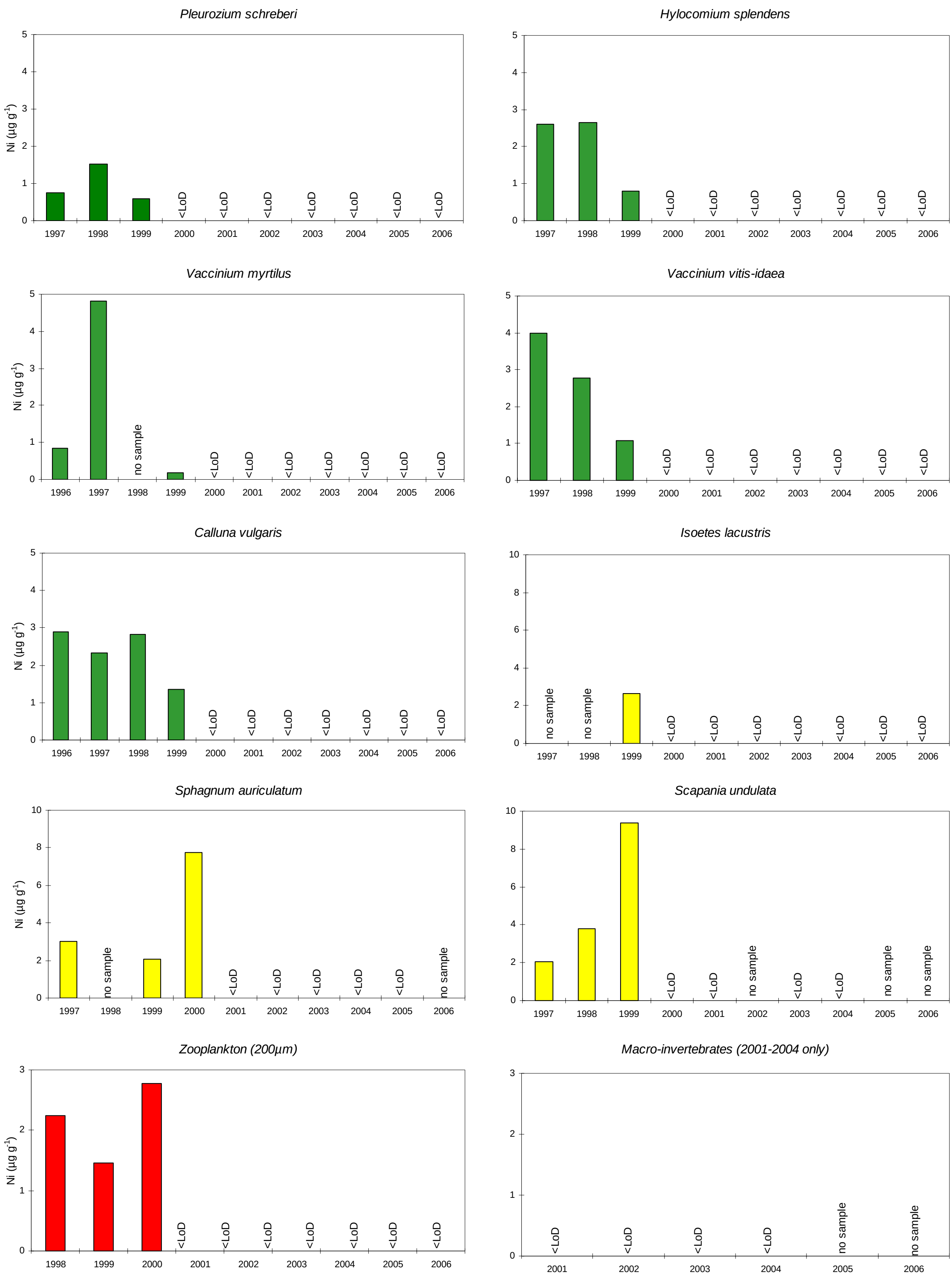


Figure 8.12: Concentrations of Ni in terrestrial and aquatic biota from Lochnagar. Terrestrial plants are shown in green, aquatic plants in yellow and aquatic fauna in red. 'no sample' indicates that the species was not collected; <LoD indicates concentrations below the analytical limit of detection.

8.4. Sediment Traps

The use of biota living *in situ* provides a valuable means by which to undertake monitoring for trace metals in upland lakes. Due to bio-concentration and, for Hg, biomagnification processes, biota elevate depositional or lake-water metal concentrations such that they become more measurable (i.e. more consistently above the limit of detection) while the natural presence of these 'monitors' within the lake or catchment means no equipment installation or maintenance is required. By contrast, the use of biota for monitoring at a network of sites ideally requires that the same species are present at all sites and that they may always be sampled at the desired monitoring frequency. Further, it is important that the sampled biota have a known growth pattern so that only samples covering a known period are taken. If these criteria cannot be met by biota, lake sediment traps can supply a reliable alternative means of monitoring.

Sediment traps may be placed in any lake so that there is no problem with presence or absence of species. Further, they have known deployment and retrieval dates such that the period covered by the sample is exactly known. Depositing sediments, particularly organic material, bind trace metals and other pollutants elevating concentrations to higher levels. However, sediment traps may also be lost (or physically removed) between sampling periods and on these occasions samples for the whole period are lost. It is also difficult to collect equivalent samples in flowing waters. In short, there are advantages and disadvantages to both biotic and trapping approaches. In the AWMN a combination of both was employed.

8.4.1. Sampling and analysis.

Sediment trapping at AWMN sites began in 1991. The sediment traps, deployed *c.*1 m above the sediment-water interface, were a simple tube design with an internal diameter of 5.5 cm and an aspect ratio (length to diameter) of 7:1. Three traps were deployed together in a triangular array and emptied annually in late summer. Samples prior to 1997 were preserved for diatom analysis using Lugol's iodine but from 1997 sediment trap samples were preserved specifically for trace metals analysis and this practice has been maintained ever since. Only post-1997 data are considered here. However, samples for trace metals analysis were available for Lochnagar from 1991 and these are discussed here. Up to 1999, all trap samples were dried by heating, making them unsuitable for Hg analysis. From 2000, samples were freeze-dried and hence Hg data are available in this and subsequent years. Trace metal analyses from sediment trap material was the same as for the biota at Lochnagar (see above). The preservation and drying of samples does not affect SCP analysis and so a record for SCPs in sediment traps is available for all AWMN sites since 1991. These have been discussed in detail in Rose & Monteith (2005).

8.4.2. Results

The annual sediment trap fluxes of Pb and Zn for the AWMN lakes are shown in Figures 8.13 and 8.14 respectively, and are presented with the original sediment core data for comparison. The data for Loch Coire nan Arr are unique within the dataset in that they show that the annual sediment trap fluxes are above those in the upper levels of the sediment core. Loch Coire nan Arr was included in the AWMN as the 'control' site in NW

Scotland but the site became very disturbed at the turn of the 21st century when controls were put on the outflow stream to regulate water flow to a fish farm below. Consequently, there was considerable disturbance in the catchment which may have led to metal remobilisation from catchment soils and elevated metal concentrations in suspended sediments. Sampling at Loch Coire nan Arr ceased in 2002 when the site was replaced by Loch Coire Fionnaraich a few kilometres away. While no core was taken for trace metals from Loch Coire Fionnaraich, annual sediment trap metal fluxes for the available period (2002 – 2006) are significantly lower than those for Loch Coire nan Arr for Pb (0.18 – 0.54 µg cm^{-2} yr^{-1}) and of a similar order or lower for Zn (0.37 – 1.84 µg cm^{-2} yr^{-1}).

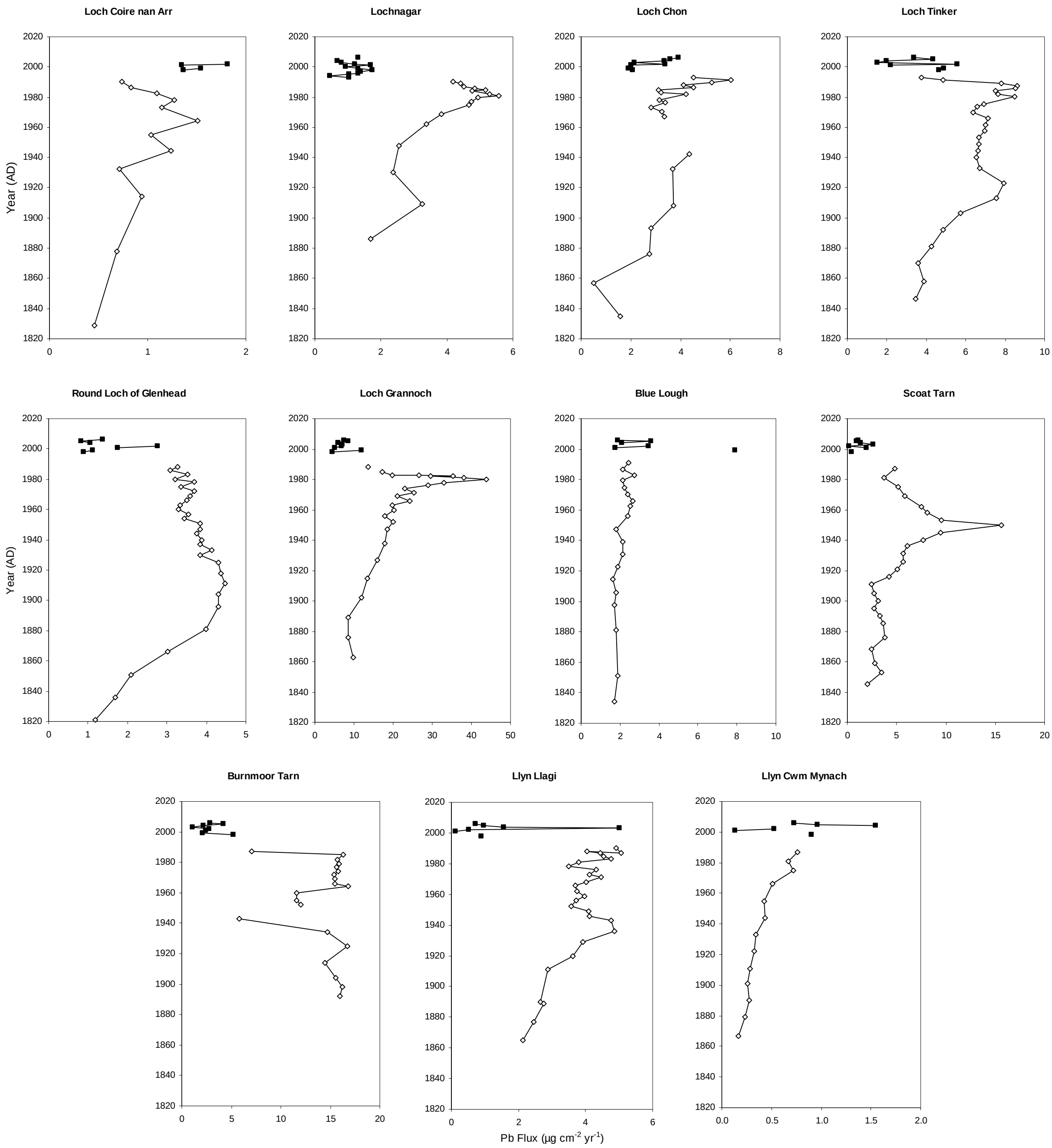


Figure 8.13: Lead fluxes from AWMN lake sediment cores and annual sediment trap Pb flux data (black symbols).

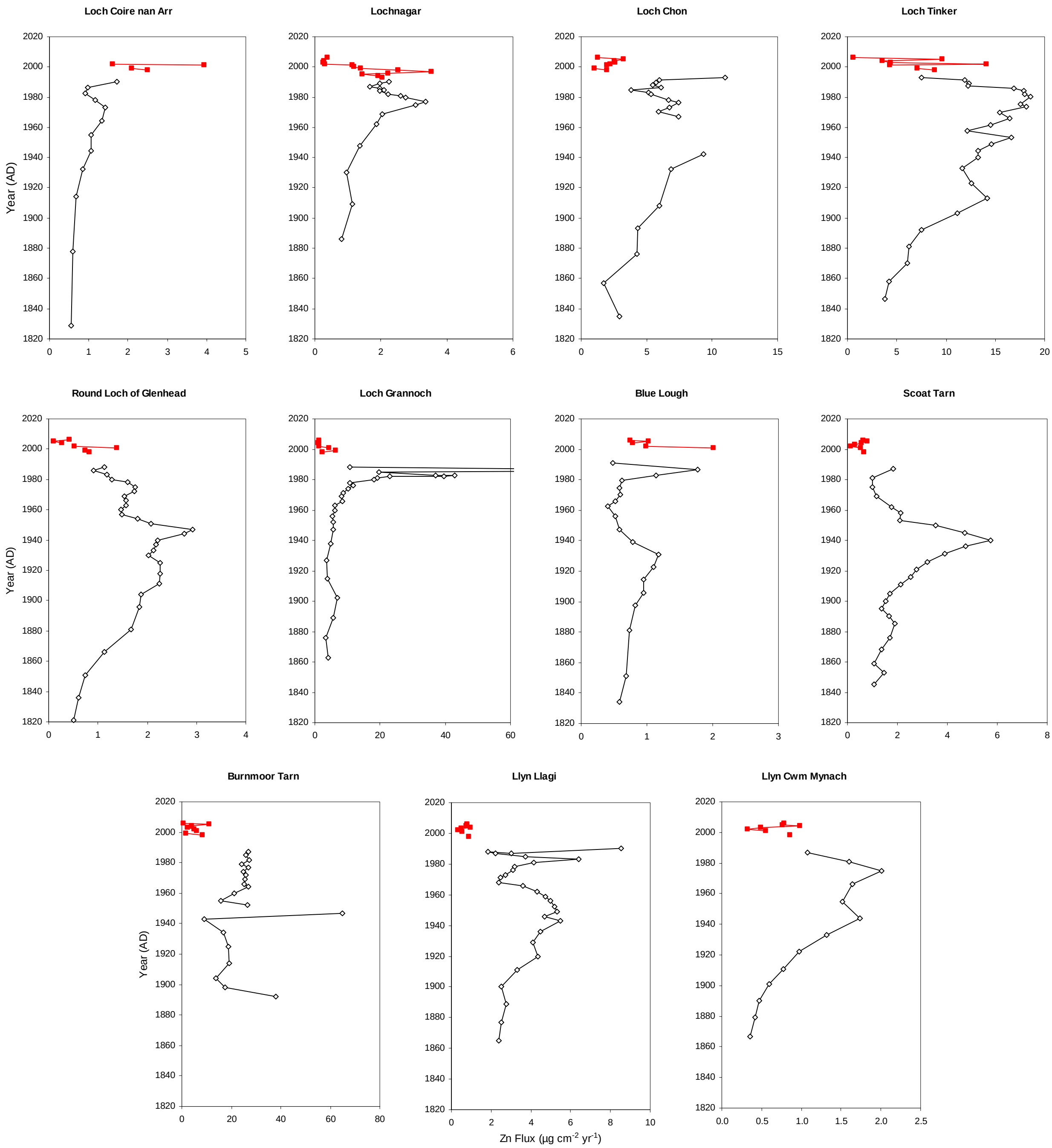


Figure 8.14: Zinc fluxes from AWMN lake sediment cores and annual sediment trap Zn flux data (red symbols).

While a few sites show annual trap metal fluxes of a similar order to that at the top of the original sediment core (Loch Chon – Pb; Llyn Cwm Mynach – Pb; Blue Lough – Pb and Zn), the annual sediment trap data from most sites show lower metals concentrations than those observed in the upper levels of the sediment cores, implying a continuation of the declines in metal inputs observed from the sediment core record. This includes Loch Tinker (Pb, Zn), Round Loch of Glenhead (Pb, Zn), Scoat Tarn (Pb, Zn), Lochnagar (Zn), Loch Grannoch and Loch Chon (both Pb and possibly Zn). By contrast, data for Llyn Llagi (Pb, Zn) and Lochnagar (Pb) appear to show a distinct mis-match with sediment trap fluxes considerably lower than the cores albeit that some of the cores were starting to show a decline in the upper levels. A similar situation is seen for Burnmoor Tarn although the trends in the core data are unusual at this site.

In many cases the sediment trap data show reduced metal inputs when compared with the upper levels of the sediment cores. The most recent data indicate metal fluxes at, or below, any observed at the sites since the mid-19th century. However, it is important to remember that the upper levels of sediments, even in upland lakes, are subject to some degree of bioturbation and hence, to a certain extent, represent a 'smoothed' record over a few years. Therefore, annual trap flux data and 'smoothed' core flux data may not be directly comparable, although a mean of annual trap data over a period of, for example, five years ought to be more so. Furthermore, sediment cores were taken from the deepest areas of the AWMN lakes and these profundal areas are generally the areas most susceptible to sediment focussing, i.e. receiving sediments resuspended and transported from other areas of the lakes. Sediment trap samples, even those suspended only 1 m above the sediment surface in deeper waters may not be subject to focussing processes in quite the same way and hence a direct comparison between trap and core data should be undertaken with some caution. Even so, recent reductions of metal inputs are still considerable and in some cases remain unprecedented within the period dateable by ^{210}Pb. A similar reduction is also observed for SCP flux data within the AWMN lakes (Rose & Monteith, 2005) whereby recent annual trap fluxes have declined to levels previously only observed in the 1930s. The combination of sediment core and trap metal and SCP flux data therefore indicates considerable reductions in fluxes of atmospherically deposited contaminants across the Network. It is interesting to note, however, that regions of higher deposition remain similar throughout the record with highest Pb fluxes in southern Scotland and northern England and lowest in northern Scotland and North Wales (cf Rippey & Douglas, 2004). Zinc patterns are less clear with highest fluxes in central Scotland.

The annual sediment trap flux data for Cu and Ni are shown in Table 8.4. In general, the patterns for these metals are similar to those of Pb and Zn. Declining trends in fluxes at the top of the sediment cores are reflected in lower sediment trap fluxes. For Ni, the trap data show a greater occurrence of below detection limit values in recent trap samples suggesting that declines in Ni concentration and fluxes are continuing, in agreement with the data from biota at Lochnagar (Fig. 8.12). For Cu, the trap data show little pattern although they are generally lower than the fluxes observed in the upper levels of the sediment cores.

Neither Cd nor Hg were measured in the original sediment cores but have been analysed in sediment trap samples since 1998. There is little pattern in the Cd data (Table 8.4), although again there is a greater prevalence of below detection limit values in recent samples especially in the most northerly sites (Loch Coire Fionnaraich and Lochnagar) suggesting a decline in fluxes and lower deposition in this region. The Hg trap data are shown in Figure 8.15. There are too few years of data to indicate any trend and most fluxes do not vary greatly over the sampling period. A longer dataset is required. However, it is interesting to note that the regional pattern is again apparent, with lowest annual fluxes in northern Scotland and North Wales and higher fluxes in central and southern Scotland.

Table 8.4: Annual fluxes of Ni, Cu and Cd from the AWMN lakes 1998 – 2006 and for Lochnagar 1991 – 2006.

Nickel (µg cm^{-2} yr^{-1})

	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Loch Coire nan Arr								0.19	0.14		0.20	0.28				
Loch Coire Fionnaraich												<LoD		<LoD	<LoD	<LoD
Lochnagar	0.48		0.03	0.01	0.07	0.06	0.05	0.08	0.05	0.05		0.03	<LoD	<LoD		<LoD
Loch Chon								0.24	0.16		0.35	0.70	<LoD	1.04		<LoD
Loch Tinker								0.63	0.77		0.42	1.23	<LoD	0.46		0.79
Round Loch of Glenhead								0.05	0.05		0.10	0.19		0.05		0.22
Loch Grannoch								0.19	0.45		0.21	0.40	<LoD	0.17		0.77
Blue Lough									0.07		0.10	<LoD		<LoD	<LoD	<LoD
Scoat Tarn								0.04			0.03	0.02	<LoD	0.09		0.20
Burnmoor Tarn								0.31	0.10		0.19	0.18	<LoD	0.20	<LoD	0.43
Llyn Llagi								0.17	0.10		0.32	0.27	<LoD	0.25		0.45
Llyn Cwm Mynach								0.05			0.01	<LoD	<LoD	0.13		<LoD

Copper (µg cm^{-2} yr^{-1})

	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Loch Coire nan Arr								0.22	0.21		0.23	0.50				
Loch Coire Fionnaraich												0.05		0.29	0.06	0.14
Lochnagar	0.29		0.40	5.55	0.30	0.19	0.19	0.21	0.16	0.19	0.11	0.13	0.12	0.10		0.12
Loch Chon								0.66	0.47		0.57	1.15	0.41	0.77	0.84	0.21
Loch Tinker								0.55	0.64		0.30	0.99	0.14	0.33	0.35	0.45
Round Loch of Glenhead								0.15	0.11		0.18	0.81		0.11		0.12
Loch Grannoch								0.48	1.04		0.58	0.84	0.50	0.73	0.29	0.69
Blue Lough								1.02		0.32	0.56		0.40	0.33	0.27	
Scoat Tarn								0.10			0.04	0.06	0.13	0.26	0.99	0.26
Burnmoor Tarn								0.34	0.14		0.22	0.19	<LoD	2.06	0.00	0.17
Llyn Llagi								0.48	0.32		0.69	0.37	0.16	0.44	0.19	0.36
Llyn Cwm Mynach								0.24			0.06	0.16	0.15	0.34	0.18	0.22

Cadmium (µg cm^{-2} yr^{-1})

	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Loch Coire nan Arr								0.021	0.016		0.029	0.033				
Loch Coire Fionnaraich												<LoD		<LoD	<LoD	<LoD
Lochnagar	0.011				0.001	0.002	0.049	0.017	0.012	0.013	0.006	<LoD	<LoD	<LoD		0.025
Loch Chon								0.026	0.008		0.032	0.052	0.008	0.145		
Loch Tinker								0.088	0.067		0.043	0.121		0.046		
Round Loch of Glenhead								0.006	0.002		0.005	0.013		<LoD		
Loch Grannoch								0.012	0.023		0.012	<LoD		<LoD		
Blue Lough									0.039		0.009	0.041				
Scoat Tarn								0.012			0.003	0.003	0.004	<LoD		
Burnmoor Tarn								0.209	0.025		0.141	0.139	0.004	0.168	<LoD	
Llyn Llagi								0.014	0.009		0.028	0.016		<LoD		
Llyn Cwm Mynach								0.008			0.002	0.003		0.041		

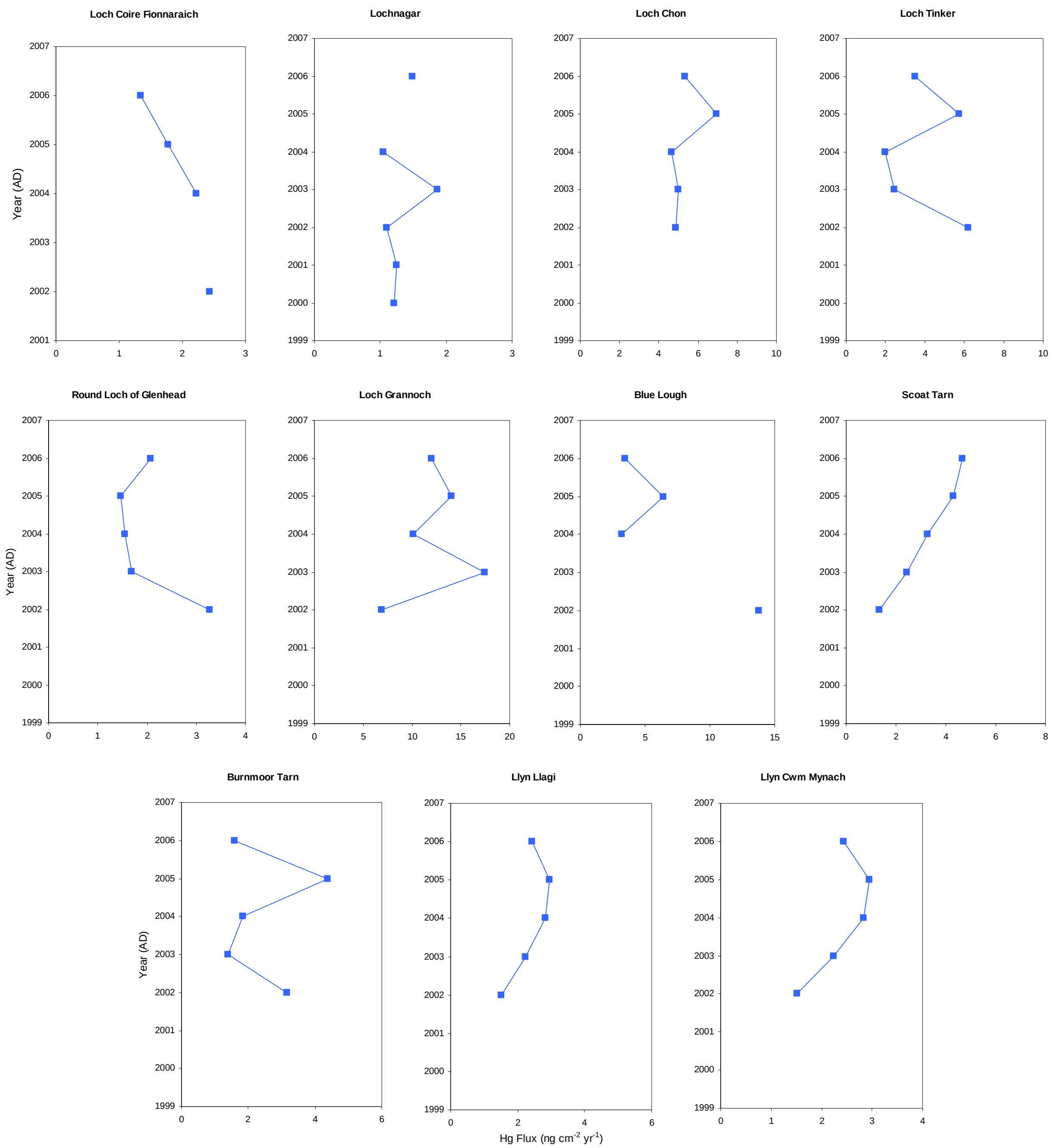


Figure 8.15: Annual Hg fluxes from AWMN lake sediment traps.

8.5. Metals in Biota at other AWMN Sites

While detailed monitoring of trace metals in biota within the AWMN has focussed on Lochnagar, other sampling has also been undertaken at other AWMN sites. This involved regular sampling of the terrestrial mosses *Hylocomium splendens* and/or *Pleurozium schreberi* where present, plus additional aquatic species in both lakes and streams. This sampling and analysis was unfunded and hence, although sampling and analytical measurements have gaps they represent considerable added value to the work undertaken at Lochnagar. However, while they are not suitable for statistical analyses they allow some preliminary consideration of spatial distributions.

8.5.1. Sampling and analysis

The two terrestrial mosses and a selection of aquatic macrophytes (including *Isoetes lacustris*, *Lobelia dortmanna*, *Scapania undulata*, *Fontinalis* sp.) were sampled from the AWMN lakes mainly between the years 2001 – 2006, while zooplankton samples taken by trawling with a 200 μm net were also obtained in some years. For the AWMN streams, sampling was mainly the same terrestrial moss species and the aquatic liverwort *Scapania undulata*. Sampling procedures, sample treatment and metals analyses were as for Lochnagar (see above).

8.5.2. Results

It is beyond the scope of this report to present all data from all sites but here we include a summary for Hg, Pb and Zn for selected species from the lakes and streams and in addition, all Pb data for 2001 as this represents the largest annual dataset across the AWMN sites. The former may be used to provide an assessment of inter-annual variation while the latter can provide a 'snapshot' of Pb contamination across the UK. Data from Lochnagar are included for comparison.

8.5.2.1. Terrestrial mosses

Tables 8.5 and 8.6 show the Hg, Pb and Zn concentrations in *Hylocomium splendens* and *Pleurozium schreberi* samples, respectively. The sites are listed in approximately north to south order. A longer dataset is available for Lochnagar, but data prior to 2001 are not included to enable a comparison with the other sites. No *Hylocomium splendens* and *Pleurozium schreberi* samples were collected from Old Lodge in south-east England and no *Hylocomium splendens* samples were obtained from the Round Loch of Glenhead in Galloway.

No trends are apparent in the Hg concentration data for either *Hylocomium splendens* or *Pleurozium schreberi* although this is not surprising given the short dataset. Concentrations in all areas of the UK are remarkably similar. The highest Hg concentrations occur in Northern Ireland *Pleurozium schreberi* samples but few samples have been collected from these sites and it is unclear how representative the results are.

For Pb, there are many concentrations below the detection limit especially in recent years, and, for 2002, at a number of sites. This is particularly apparent in the sites furthest to the north and may be indicative of a declining Pb deposition gradient from south to north. As with the Lochnagar data, the increasing prevalence of 'below detection limit' values in recent years may also indicate a decline in Pb deposition. However, for both moss species, Pb concentrations remain above detection limit values in northern England and North Wales throughout the dataset indicating that this is an area of elevated Pb deposition with respect to areas to the north and south in the UK.

Table 8.5: Hg, Pb and Zn concentrations in the terrestrial moss *Hylocomium splendens* from the catchments of AWMN lakes and streams. <LoD indicates concentrations below the analytical limit of detection. This species has not been sampled at Round Loch of Glenhead or Old Lodge.

	SAMPLE YEAR						
Mercury (ng g^{-1})	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Mean 2001 - 2006**
Loch Coire nan Arr		61.32			66.97		64.15
Loch Coire Fionnaraich	49.60	52.85		37.81	53.72		48.50
Allt a' Mharcaidh		37.39	38.40	29.91	32.35	33.87	34.38
Lochnagar	48.00	44.20	62.18	65.22	65.12	70.67	59.23
Allt na Coire nan Con		47.41	32.04	41.64	46.74	33.58	40.28
Loch Chon		33.04				39.38	36.21
Loch Tinker		38.37	38.80		41.76		39.64
Round Loch of Glenhead							
Loch Grannoch		46.71					46.71
Dargall Lane				33.16	43.13	57.45	44.58
Beagh's Burn		35.29		35.23	32.78		34.43
Coneyglen Burn		40.55		42.83	38.08	37.93	39.85
Bencrom River				59.40	62.20		60.80
Blue Lough					40.04		40.04
Scoat Tarn			58.09		60.23	76.07	64.80
Burnmoor Tarn			47.86		58.12	51.44	52.47
River Etherow						36.03	36.03
Llyn Llagi			54.06	49.11	56.85	50.91	52.73
Llyn Cwm Mynach			45.72	38.68	48.20	46.76	44.84
Afon Hafren		47.96	48.75	47.82	50.71	43.66	47.78
Afon Gwy		53.00	63.48	94.08	54.77	55.15	64.10
Narrator Brook		43.59	34.72	53.54	65.98	65.69	52.70
Old Lodge							
Lead (µg g^{-1})							
Loch Coire nan Arr	1.24	<LoD			5.58		
Loch Coire Fionnaraich	3.40	<LoD		8.75	<LoD		
Allt a' Mharcaidh	<LoD	<LoD	<LoD	4.98	<LoD	<LoD	
Lochnagar	5.80	<LoD	3.42	6.11	<LoD	12.11	
Allt na Coire nan Con	5.91	<LoD	1.88	6.17	<LoD	<LoD	
Loch Chon	8.13	2.82				<LoD	
Loch Tinker	6.21	<LoD	2.56		<LoD		
Round Loch of Glenhead							
Loch Grannoch	10.31	2.84					
Dargall Lane				5.82	2.29	<LoD	
Beagh's Burn	2.63	<LoD		4.89	<LoD		
Coneyglen Burn	3.33	<LoD		6.35	0.79	<LoD	
Bencrom River	4.62			8.25	<LoD		
Blue Lough					1.29		
Scoat Tarn	3.12		5.32		<LoD	10.68	
Burnmoor Tarn	10.44		8.21		<LoD	8.29	
River Etherow						6.38	
Llyn Llagi	11.66		3.73	6.55	<LoD	5.66	
Llyn Cwm Mynach	2.75		1.01	4.84	<LoD	<LoD	
Afon Hafren	3.53	3.79	6.19	7.97	0.98	<LoD	
Afon Gwy	53.00	63.48	94.08	54.77	55.15	<LoD	
Narrator Brook	7.25	<LoD	5.04	4.80	23.17	3.50	
Old Lodge							
Zinc (µg g^{-1})							
Loch Coire nan Arr	53.85	14.51			17.82		28.73
Loch Coire Fionnaraich	57.84	11.10		11.75	10.94		22.91
Allt a' Mharcaidh	45.27	11.59	13.10	16.55	15.07	12.78	19.06
Lochnagar	86.70	17.48	22.27	21.72	25.12	31.41	34.12
Allt na Coire nan Con	90.31	10.83	14.21	14.83	19.74	13.27	27.20
Loch Chon	47.93	24.55				33.96	35.48
Loch Tinker	65.20	17.88	30.77		27.89		35.44
Round Loch of Glenhead							
Loch Grannoch	52.21	21.24					36.73
Dargall Lane				18.38	20.53	26.02	21.64
Beagh's Burn	91.78	18.13		19.42	29.63		39.74
Coneyglen Burn	70.51	20.96		19.70	30.52	35.78	35.49
Bencrom River	64.15			36.00	42.57		47.57
Blue Lough					27.04		27.04
Scoat Tarn	82.12		44.58		22.31	33.09	45.53
Burnmoor Tarn	63.83		35.51		32.53	31.93	40.95
River Etherow						56.41	56.41
Llyn Llagi	56.87		25.49	24.40	23.60	34.58	32.99
Llyn Cwm Mynach	70.21		30.42	25.24	17.54	24.43	33.57
Afon Hafren	59.69	21.69	21.06	30.85	27.58	20.59	30.24
Afon Gwy	55.15	23.40	25.74	26.38	26.49	37.45	32.44
Narrator Brook	51.30	37.36	25.58	22.98	28.38	22.31	31.32
Old Lodge							

Table 8.6: Hg, Pb and Zn concentrations in the terrestrial moss *Pleurozium schreberi* from the catchments of AWMN lakes and streams. <LoD indicates concentrations below the analytical limit of detection. This species has not been sampled at Old Lodge.

	SAMPLE YEAR						
Mercury (ng g^{-1})	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Mean 2001 - 2006**
Loch Coire nan Arr		51.33			44.56		47.95
Loch Coire Fionnaraich	39.10	55.68		37.35	32.32	56.74	44.24
Allt a' Mharcaidh		47.00	30.57	23.43	37.75	36.87	35.12
Lochnagar	57.38	45.40	51.48		55.87	48.46	51.72
Allt na Coire nan Con		40.64	33.05	39.36	46.26	41.24	40.11
Loch Chon		41.65	42.22			37.57	40.48
Loch Tinker		25.76	45.77		37.68	52.84	40.51
Round Loch of Glenhead		40.85	39.58				40.22
Loch Grannoch		48.81					48.81
Dargall Lane			36.51	44.23	53.08	53.68	46.88
Beagh's Burn		58.96		27.48	25.87	51.71	41.01
Coneyglen Burn		36.63		40.45	30.05	35.52	35.66
Bencrom River				59.40	62.20		60.80
Blue Lough				73.54			73.54
Scoat Tarn		52.04	46.10	55.48	48.43	51.98	50.81
Burnmoor Tarn		46.59	51.03		45.47	58.01	50.28
River Etherow					40.76	49.83	45.30
Llyn Llagi			52.51	54.58	46.19	44.63	49.48
Llyn Cwm Mynach		41.91	43.54	41.94	44.91	81.75	50.81
Afon Hafren		24.46	42.34	43.40	22.53	52.03	36.95
Afon Gwy		61.05	56.48	60.15	39.61	56.85	54.83
Narrator Brook		37.56	49.44		37.88	43.73	42.15
Old Lodge							
Lead (µg g^{-1})							
Loch Coire nan Arr	5.69	<LoD			<LoD		
Loch Coire Fionnaraich	<LoD	<LoD		5.19	<LoD	<LoD	
Allt a' Mharcaidh	2.06	<LoD	<LoD	7.81	<LoD	<LoD	
Lochnagar	5.10	<LoD	2.70	4.75	2.23	<LoD	
Allt na Coire nan Con	1.08	<LoD	1.87	6.91	0.84	<LoD	
Loch Chon	8.82	5.65	1.37			<LoD	
Loch Tinker	4.38	<LoD	29.29		<LoD	<LoD	
Round Loch of Glenhead		<LoD	3.92				
Loch Grannoch	4.44	<LoD					
Dargall Lane	5.36		<LoD	7.84	3.00	<LoD	
Beagh's Burn	6.83	<LoD		6.54	<LoD	<LoD	
Coneyglen Burn	1.50	<LoD		10.53	<LoD	<LoD	
Bencrom River	4.62			8.25	<LoD		
Blue Lough	9.97			18.39			
Scoat Tarn	1.57	<LoD	4.59	7.71	<LoD	7.64	
Burnmoor Tarn	4.45	12.83	2.69		<LoD	5.90	
River Etherow	21.04			11.89	6.20		
Llyn Llagi	6.44		4.95	10.30	<LoD	5.90	
Llyn Cwm Mynach	7.74	<LoD	216.81	5.72	<LoD	5.92	
Afon Hafren	2.08	1.93	4.86	9.95	1.78	5.34	
Afon Gwy	9.62	6.51	9.64	3.46	4.34	<LoD	
Narrator Brook	2.97	<LoD	687.35		<LoD	<LoD	
Old Lodge							
Zinc (µg g^{-1})							
Loch Coire nan Arr	60.68	43.18			21.69		41.85
Loch Coire Fionnaraich	46.01	13.75		23.21	11.64	16.70	22.26
Allt a' Mharcaidh	54.17	14.75	16.98	13.36	15.37	17.63	22.04
Lochnagar	81.80	22.28	26.34	23.95	30.36	25.14	34.98
Allt na Coire nan Con	70.83	16.43	19.64	15.66	15.46	22.94	26.83
Loch Chon	53.79	20.46	30.40			25.38	32.51
Loch Tinker	96.03	29.66	26.40		19.50	31.19	40.56
Round Loch of Glenhead		17.24	20.25				18.75
Loch Grannoch	92.73	19.10					55.92
Dargall Lane	65.38		21.35	31.85	28.24	25.85	34.53
Beagh's Burn	108.92	24.14		25.15	21.63	25.09	40.99
Coneyglen Burn	94.11	25.11		21.62	24.33	47.74	42.58
Bencrom River	64.15			36.00	42.57		47.57
Blue Lough	86.94			44.68			65.81
Scoat Tarn	66.29	30.46	33.82	33.29	23.21	24.92	35.33
Burnmoor Tarn	49.32	20.16	37.60		28.03	35.64	34.15
River Etherow	150.95			28.06	29.55		69.52
Llyn Llagi	80.73		31.98	30.95	18.30	32.08	38.81
Llyn Cwm Mynach	75.47	30.09	25.21	27.73	30.80	21.32	35.10
Afon Hafren	70.46	23.24	18.83	33.79	32.00	28.09	34.40
Afon Gwy	73.16	28.46	28.47	40.14	35.94	27.89	39.01
Narrator Brook	49.02	36.82	14.16		24.54	21.73	29.25
Old Lodge							

An apparent declining trend in Zn concentrations for both species is influenced by particularly high concentrations in 2001. In many cases, Zn concentrations after this time are quite similar suggesting that the decline is not sustained. Data from Lochnagar also show this tendency from 2001 onwards (Fig. 8.9) but data prior to 2001 also indicate elevated concentrations in earlier years (e.g. 1997 and 1998). Given that Zn concentrations are significantly above the analytical limit of detection (cf. other metals such as Pb, Cd, Cu), a re-instatement of monitoring according to these protocols would be sufficient for this trend to be tracked and quantified. The highest Zn concentrations occur for both moss species in northern England and Northern Ireland. Zinc concentrations decline from these regions to both the north and south, with the possible exception of *Pleurozium schreberi* at Loch Coire nan Arr.

8.5.2.2. Zooplankton

Table 8.7 shows the Hg, Pb and Zn concentrations in zooplankton samples from the AWMN lakes. Concentrations of all metals in zooplankton are elevated above aquatic plants and this is likely to be due to their higher trophic level. Further data from across the aquatic food-web in more of these sites would better help interpret the data distribution in this class with respect to other biota. No spatial trends are identifiable in these data due to the limited availability.

8.5.2.3. Aquatic Liverworts

Table 8.8 shows the Hg, Pb and Zn concentrations in *Scapania undulata* samples from the AWMN streams. No samples were obtained after 2003 from any site and hence no trends in the data are identifiable. The highest metal concentrations vary across the UK. The highest Zn concentrations were identified in the Old Lodge (southeast England) sample, but further samples would be necessary to determine the significance of this single observation. *Scapania undulata* is one of the more common species in the AWMN streams and hence these data provide a useful baseline for future measurements.

Table 8.7: Hg, Pb and Zn concentrations in zooplankton from AWMN lakes. <LoD indicates concentrations below the analytical limit of detection.

			SAMPLE YEAR				
Mercury (ng g^{-1})	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Mean 2001 - 2006**
Loch Coire nan Arr							
Loch Coire Fionnaraich	153.00						153.00
Lochnagar	165.54	184.00	130.71	184.28	126.39	227.49	169.74
Loch Chon		223.17					223.17
Loch Tinker			119.67				119.67
Round Loch of Glenhead		176.97		161.90			169.44
Loch Grannoch		109.11					109.11
Blue Lough							
Scoat Tarn		164.52					164.52
Burnmoor Tarn			54.58	94.16			74.37
Llyn Llagi		327.58	138.96	205.03			223.86
Llyn Cwm Mynach		146.47	258.47	184.61			196.52
Lead (µg g^{-1})							
Loch Coire nan Arr	<LoD						
Loch Coire Fionnaraich	<LoD						
Lochnagar	8.60	26.20	<LoD	17.06	<LoD	15.96	
Loch Chon		<LoD					
Loch Tinker	17.36		2.29				
Round Loch of Glenhead		12.18		15.24			
Loch Grannoch	10.49	9.59					
Blue Lough							
Scoat Tarn	9.07	50.30					
Burnmoor Tarn	4.28		<LoD	15.69			
Llyn Llagi	7.78	<LoD	2.04	3.94			
Llyn Cwm Mynach	8.78	17.39	<LoD	12.80			
Zinc (µg g^{-1})							
Loch Coire nan Arr	150.96						150.96
Loch Coire Fionnaraich	138.09						138.09
Lochnagar	191.10	216.50	104.57	14.45	104.60	169.43	133.44
Loch Chon		151.44					151.44
Loch Tinker	224.61		87.00				155.81
Round Loch of Glenhead		201.89		132.00			166.95
Loch Grannoch	236.03	74.59					155.31
Blue Lough							
Scoat Tarn	161.64	98.55					130.10
Burnmoor Tarn	128.64		96.05	110.17			111.62
Llyn Llagi	163.98	177.83	63.18	89.43			123.61
Llyn Cwm Mynach	198.72	437.32	156.86	97.03			222.48

Table 8.8: Hg, Pb and Zn concentrations in *Scapania undulata* from AWMN streams. <LoD indicates concentrations below the analytical limit of detection. No samples of this species were taken after 2003.

	SAMPLE YEAR		
Mercury (ng g^{-1})	**2001**	**2002**	**2003**
Allt a' Mharcaidh		25.74	24.72
Allt na Coire nan Con		98.98	
Dargall Lane		51.08	42.62
Beagh's Burn		33.03	
Coneyglen Burn		48.13	
Bencrom River			
River Etherow			42.01
Afon Hafren		64.01	43.35
Afon Gwy		82.89	
Narrator Brook		46.78	
Old Lodge			
Lead (μg g^{-1})			
Allt a' Mharcaidh	6.93	8.15	5.43
Allt na Coire nan Con	42.20	34.72	
Dargall Lane	153.78	128.91	88.93
Beagh's Burn	29.82	26.15	
Coneyglen Burn	15.75	18.29	
Bencrom River			
River Etherow			94.47
Afon Hafren	51.89	52.36	139.89
Afon Gwy	83.65	91.67	
Narrator Brook	12.56	13.88	
Old Lodge	111.11		
Zinc (μg g^{-1})			
Allt a' Mharcaidh	74.29	27.95	32.88
Allt na Coire nan Con	80.15	39.68	
Dargall Lane	115.80	55.80	52.33
Beagh's Burn	75.90	53.79	
Coneyglen Burn	97.47	83.23	
Bencrom River			
River Etherow			164.29
Afon Hafren	95.96	54.05	62.11
Afon Gwy	94.33	73.81	
Narrator Brook	77.47	46.29	
Old Lodge	236.11		

8.5.2.4. Lead in 2001

All Pb data for the AWMN for 2001 are shown in Table 8.9 to illustrate the extent of information available from the AWMN lakes and streams. This table also includes data from the catchments of the 'Galloway cluster' lakes (i.e. the AWMN lakes, Round Loch of the Dungeon and Loch Narroch). The table shows that terrestrial moss species and *Scapania undulata* are the most common. Their wide distribution makes them useful as biomonitors of atmospheric deposition and aquatic contamination respectively. The concentrations of Pb in 2001 in the various classes fall into two main groups with concentrations of *Isoetes*, *Scapania* and *Sphagnum* being higher than the two terrestrial mosses and *Lobelia dortmanna*. This would imply that the former group would be better biomonitors in low deposition areas as bioconcentration appears to be higher. There is, however, a balance to be struck between elevated metal concentrations and geographic ubiquity.

Table 8.9: Pb concentrations in terrestrial and aquatic plants from AWMN lakes and streams and zooplankton from AWMN lakes in 2001. <LoD indicates concentrations below the analytical limit of detection. All values in $\mu g\ g^{-1}$.

	Terrestrial		Aquatic					Fauna
	Hylocomium splendens	*Pleurozium schreberi*	*Scapania undulata*	*Isoetes lacustris*	*Lobelia dortmana*	*Fontinalis sp.*	*Sphagnum sp.*	*Zooplankton*
Loch Coire nan Arr	1.24	5.69						<LoD
Loch Coire Fionnaraich	3.40	<LoD	6.76	6.73				<LoD
Allt a' Mharcaidh	<LoD	2.06	6.93					
Lochnagar	5.80	5.10	27.10	43.00			84.00	8.60
Allt na Coire nan Con	5.91	1.08	42.20					
Loch Chon	8.13	8.82	65.03	11.73				
Loch Tinker	6.21	4.38		4.76				17.36
Round Loch of Glenhead				39.04	6.41			
Loch Grannoch	10.31	4.44		125.63			75.93	10.49
Round Loch of the Dungeon								19.73
Loch Narroch								12.48
Dargall Lane	7.97	5.36	153.78					
Beagh's Burn	2.63	6.83	29.82					
Coneyglen Burn	3.33	1.50	18.29					
Bencrom River		4.62						
Blue Lough		9.97		67.65	5.08			
Scoat Tarn	3.12	1.57		10.12				9.07
Burnmoor Tarn	10.44	4.45	29.00	<LoD	5.98	7.18		4.28
River Etherow		21.04						
Llyn Llagi	11.66	6.44	44.25					7.78
Llyn Cwm Mynach	2.75	7.74						8.78
Afon Hafren	3.53	2.08	51.89					
Afon Gwy	53.00	9.62	83.65					
Narrator Brook	7.25	2.97	12.56					
Old Lodge			111.11					

8.6. Discussion

Analysis of metals data from Lochnagar up to 2003 provided evidence for increasing concentrations within various ecological compartments. It was concluded that a longer dataset was required to confirm these trends. Although the monitoring of trace metals at Lochnagar has now ceased, the additional three years of data beyond 2003, included in this report, show that these elevated metals concentrations were only temporary. This demonstrates that the interpretation of temporal trends is highly sensitive to the length of the dataset available, and emphasises the value of longevity in any monitoring network.

The current, longer dataset shows no evidence for any increasing trends. While the dataset may still be too short for robust time-series analysis the data now appear to show either no clear trend or evidence for declining concentrations. For Hg, declines are observed in annual bulk deposition and annual mean lake water data for Lochnagar and also in samples of *Calluna vulgaris* and *Sphagnum auriculatum*. For Pb, all terrestrial plants at Lochnagar show an increased prevalence of ‘below detection limit’ values as do terrestrial mosses across the AWMN. There is a suggestion that aquatic plants at Lochnagar may also be showing a decline in Pb, although this is less clear. Terrestrial plants at Lochnagar are increasingly being found to have below detection limit values in Cd concentrations and none have shown detectable levels of Ni concentration since 1999, while for aquatic plants Ni has not been detectable in any post-2000 samples. For Zn, concentrations in terrestrial plants at Lochnagar decline post-2001 while terrestrial moss Zn concentrations across the Network also show a decline. Only Cu now appears to show no declining trends. In the 2003 report, SCP fluxes in sediment traps across the AWMN indicated a decline in atmospheric pollutant input from high temperature fossil-fuel combustion sources (Rose & Monteith, 2005). With the additional three years of data, SCP fluxes at all sites remain low.

There is evidence for declines in the concentrations of a number of metals across a range of ecological compartments at Lochnagar and across the AWMN, and comparison of sediment trap data with the upper levels of the associated sediment cores shows that sediment fluxes are also considerably lower. However even though the sediment trap metal concentrations have declined with respect to sediment core data the trap metal concentrations at many sites still exceed sediment quality guidelines. Sediment guideline values for Hg (Macdonald *et al*., 2000) and for other trace metals (Buchman, 2008) are divided into a series of effects levels from the lowest effect level (LEL) where adverse biological effects are seen in 5% of benthic species to a probable effects level (PEL) at which biological effects are frequently seen and, ultimately, an apparent effects threshold (AET) at which biological effects have always been observed. It is important to stress that these are probabilities of effects and do not indicate direct toxicity. However, they do provide an indication of the scale and frequency that sediments within the AWMN lakes exceed biologically important thresholds. It is interesting to note, therefore, that LELs for some trace metals have been exceeded at all AWMN sites over the sediment trapping period and that PEL values for at least one metal have also been exceeded at all AWMN lakes except the two in the far north (Loch Coire nan Arr and Loch Coire Fionnaraich). Lead PEL values are exceeded in all lakes apart from these northern sites (10 lakes), but exceedances for Cd (4 lakes), Ni (4 lakes), Zn (2 lakes), Cu and Hg (1 lake each) are also observed (Table 8.10). Probable effects levels are exceeded at Burnmoor Tarn for five of the analysed metals (all except Hg), for four metals in Loch Tinker and three in Loch Chon. Exceedances of PEL thresholds are exceeded for two metals in Llyn Cwm Mynach, Llyn Llagi and Scoat Tarn. The single PEL exceedance for Hg occurs at Scoat Tarn in 2002 when a concentration of 540 ng g^{-1} was recorded. This not only exceeds the PEL but approaches the AET level for Hg (560 ng g^{-1}) and is considerably higher than all other Hg values in sediment trap material at the lake. While there is no evidence to suggest contamination of this sample, there is also no suggestion that this is part of any trend in Hg at Scoat Tarn.

Table 8.10: Probable effects level (PEL) exceedances for sediment trap data from AWMN lakes. Probable effects limits for Hg, Pb, Cu, Cd, Zn and Ni are 490 ng g^{-1}, 91.3 μg g^{-1}, 197 μg g^{-1}, 3.5 μg g^{-1}, 315 μg g^{-1} and 36μg g^{-1} respectively (Macdonald *et al.* 2000; Buchman 2008).

Site	Metal	Year of PEL exceedance
Blue Lough	Pb	1999, 2002, 2004, 2006
Burnmoor Tarn	Pb	All years 1998 – 2006
	Cu	2004
	Cd	1999, 2001, 2002, 2004
	Zn	1998, 2001, 2002, 2003, 2004, 2005
Loch Chon	Pb	2002, 2003, 2004, 2005, 2006
	Cd	2004
	Ni	2002, 2004
Llyn Cwm Mynach	Pb	1998, 2002, 2003, 2004
	Cd	2004
Loch Grannoch	Pb	All years 1998 - 2006
Llyn Llagi	Pb	All years 1998 - 2006
	Ni	2006
Lochnagar	Pb	1991, 1998, 1999, 2000, 2001, 2003, 2004, 2005, 2006
Round Loch of Glenhead	Pb	1998, 1999, 2001, 2002, 2004, 2005, 2006
Scoat Tarn	Hg	2002
	Pb	2003, 2004
Loch Tinker	Pb	All years 1998 - 2006
	Cd	1998, 2001, 2002, 2004
	Zn	1998, 2001, 2002, 2003, 2004, 2005
	Ni	2002, 2004, 2006

The concentrations of trace metals in sediment trap material and the annual fluxes calculated from them are generally considerably lower than the peak fluxes recorded in the sediment cores. However, as discussed above, the trap data show considerable interannual variability and in some instances there is an indication of a move from LEL exceedance to PEL exceedance in more recent years (Table 8.8). If true, this would indicate a move towards greater impact on aquatic biota from trace metal contamination. As monitoring has now ceased it is not possible to confirm this trend but with declines in metal emissions and deposition this may indicate that elevated inputs of trace metals are being introduced to the lakes from catchment sources (Rose *et al*., under revision). This is discussed further in Chapter 10. Trace metals are toxic substances and affect aquatic biota directly by impairing their physiological function, a problem that is exacerbated in acid waters owing to their greater solubility in low pH conditions. The full recovery of lakes and streams therefore requires a reduction in trace metal concentrations in surface waters as well as a reduction in acidity. The evidence for increasing metal transfer from catchment storage to surface waters indicates that recovery could be delayed by many decades.

In terms of geographical distribution, the data from sediment traps and biota from across the AWMN indicate regions of high and low deposition which are quite consistent. For Pb, Cd and Hg in sediment traps and for Pb and Zn in terrestrial mosses there is evidence that sites in northern Scotland are receiving the lowest levels of deposition. North Wales also appears to have low sediment trap fluxes of Pb and Hg although higher levels of Pb in terrestrial moss. By contrast, regions of northern England and southern and central Scotland show elevated moss concentrations and trap fluxes of Pb, Zn, and Hg, while Zn and Pb are also higher in Northern Ireland. These spatial patterns are in agreement with previous studies (e.g. Lee *et al.,* 2001; Rippey & Douglas 2004; Tipping *et al.,* 2007; Smith *et al.,* 2005) although few data are available for the south and east of England precluding a full assessment of spatial distribution using this dataset. Rippey & Douglas (2004) suggest that the whole of the south and east of the UK is an area of 'high' Pb deposition, but without a more extensive network of measurements we cannot confirm this.

In summary, although the data presented here provide some evidence for declining trends over the last decade, the fact that this is not clearer may indicate the influence of additional sources, perhaps as a result of remobilisation of previously deposited pollutants from catchment soils. There is some evidence that climate change is already affecting inputs of trace metals to upland waters by this process and these impacts are likely to increase over coming decades (see Chapter 10). Metals inputs to sedimentary basins are therefore likely to increase. However, there is currently no means by which to track these impacts. If the aims of the WFD are to be met, a metals monitoring network in the UK will be required. Such a network should fulfil certain criteria:

i) Sampling in all ecological compartments

A range of aquatic and terrestrial species provide the most appropriate monitoring tools in upland waters and should include species from various trophic levels. This allows a means by which to assess metals uptake from waters and deposition to biota at low trophic levels and determine how these pass through to fish and piscivorous animals and birds. With the threat of elevated metals inputs from remobilised catchment sources it is essential that all aspects of aquatic biota and those dependent upon them are monitored. A sediment trapping programme would also be beneficial to assess the role of increased catchment inputs.

ii) Fully cover depositional gradients

It is essential that a monitoring programme covers the key depositional gradients and our data suggest that these should centre on the region of elevated metal concentrations in northern England, southern Scotland and Northern Ireland. The AWMN generally provides a good site distribution although including additional sites in the south and east of England would be beneficial as data for these regions are particularly scarce.

iii) Include key trace metals

The trace metals Hg, Pb, Cd and Zn should be considered a minimum. They include the metals considered 'priority hazardous substances' under the WFD, those for which there is a requirement under the WFD to ensure concentrations in aquatic biota and sediments do not increase, and those included in the 1998 UNECE Aarhus Protocol on Heavy Metals. Furthermore, these metals are already known to be elevated in fish at Lochnagar (Rosseland *et al.,* 2007). The other metals included within the AWMN, Cu and Ni, are also important but their progressive move to concentrations below analytical detection limits mean that data in the longer term may be limited. However, further analyses at higher trophic levels may provide a more practical means by which to monitor these metals.

iv) Longevity

The most important criterion is longevity. Inter-annual variability and slow changes require a commitment to monitoring over the long-term. It has been shown from the main AWMN activities that 15 – 20 years is a minimum to test temporal trends reliably. Metals monitoring for freshwaters in the UK has not attained this longevity, but it is essential if we are to assess the impacts from these pollutants in upland waters. Model forecasts predict that metals concentrations in lake waters at Lochnagar are likely to remain largely unchanged (within 20%) over the next century (Tipping *et al.,* 2007) while potential for release from catchment sources of previously deposited metals, as a result of climate enhanced catchment soil erosion, is likely to result in elevated metals inputs at least until the end of the 21st century. Only a continued and long-term metals monitoring programme at upland waters across the UK will allow this potential threat to be identified and the scale of the impact assessed.

8.7. Key Points

Monitoring up to 2006 resulted in 10 years high quality data for trace metals in a range of ecological compartments. Metals monitoring focussed on Lochnagar, although additional, shorter-term data from terrestrial mosses, aquatic biota and sediment traps exist from across the AWMN. This monitoring has now ceased and concentrations and fluxes since 2006 are unknown. There is now very little contemporary metals data for UK freshwaters.

The data to 2006 suggest some evidence for declining metal concentrations and fluxes or show no clear trend.

For Hg, declines are observed in annual bulk deposition and annual mean lake water data for Lochnagar and also in some terrestrial and aquatic plant species. For Pb, all terrestrial plants at Lochnagar show an increased prevalence of 'below detection limit' values as do terrestrial moss and sediment trap Pb fluxes across the AWMN. Data for Cd and Ni also show increasing frequency of 'below detection limit' values. For Zn, concentrations in terrestrial plants at Lochnagar decline post-2001 while terrestrial moss concentrations and sediment trap fluxes across the Network also show a decline. Spheroidal carbonaceous particle (SCP) fluxes in sediment traps across the AWMN continue to show low levels.

In terms of geographical distribution, the data indicate lowest fluxes in northern Scotland and a region of elevated metal concentrations across northern England, southern Scotland and Northern Ireland.

Although sediment trap metal fluxes are considerably lower than those observed in sediment cores metal concentrations in sediment trap material still exceed probable effects levels (PEL) (the concentration at which biological effects are frequently seen) at all lakes except the two north Scotland sites. Exceedances of PEL are observed for all metals, but most frequently for Pb. There is some preliminary evidence to suggest that sediment trap PEL exceedances have become more common in recent years across the AWMN and this may indicate evidence for increased transfer of trace metals from catchment storage to surface waters. This transfer is thought to be mainly due to enhanced catchment soil erosion and there is a concern that the effects of predicted climate change may exacerbate this process and hence lead to continuing elevated metals inputs to upland surface waters despite significant reductions in emissions and deposition since the 1970s (see Chapter 10).

A metals monitoring network is required for UK upland freshwaters. This network should cover all ecological compartments and trophic levels covering key depositional gradients across the UK and include Hg, Pb, Cd and Zn as a minimum. However, the main criterion is longevity and there should be a commitment to long-term metals monitoring in order to identify and assess the impact of climate-enhanced metals inputs to UK upland waters in the 21st century.

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9. Recovery Progress: Reference Conditions and Restoration Targets

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9.1. Introduction

The data presented in preceding chapters show clearly that there has been significant change in both the chemistry and biology of acidified sites in the Acid Waters Monitoring Network (AWMN) consistent with the reduction in acid deposition that has occurred over the last 20 years. A key issue now is the extent to which improvement that has taken place meets the targets for recovery required by current legislation governing acid and acidified surface waters in the UK.

Here we briefly describe the principal legislative programmes concerned, explain how the various recovery targets are defined, describe the approaches that have been used to define recovery targets, assess progress that has been made towards the targets, and discuss reasons for the difference between the current status (2008) and the target.

Key questions to address are:

- What were the reference conditions of AWMN sites and how do these relate to recovery targets?
- How far have AWMN sites recovered towards recovery targets under the Gothenburg Protocol and the WFD and how do the approaches differ?
- What are the factors limiting or delaying recovery towards targets?

9.1.1. Legislative context

Legislation governing the restoration of acidified surface waters in the UK is set out by a number of different protocols and directives, principally:

- United Nations Economic Commission for Europe (UNECE) Oslo Protocol on Further Reduction of Sulphur Emissions (Second Sulphur Protocol) 1994;
- UNECE Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, 1999;
- EU Proposal for a National Emission Ceilings Directive (NECD) (1999);
- EU 6th Environmental Action Programme "Thematic Strategy on Air Pollution" and the "Clean Air For Europe" (CAFÉ) Programme (2001)
- EU Water Framework Directive (WFD) (2000).

The first three of these are concerned with the reduction of emissions of acidic gases in member states to decrease levels of acid deposition (S plus N) to levels below the "critical load" and the fourth (CAFÉ) is a thematic strategy for tackling the full suite of airborne pollutants. The fifth (the WFD) is concerned with maintaining aquatic ecosystems in, or restoring them to, at least 'good' ecological status.

9.1.2. UNECE protocols, the EU NECD and UK acid waters

In an attempt to tackle the 'acid rain' problem, the Convention on Long-Range Transboundary Air Pollution (CLRTAP) was set up under the auspices of the UNECE in 1979 and ratified by 24 countries in 1983. Its original focus was sulphur deposition, addressed initially through the First Sulphur Protocol formalised in Helsinki in 1985 committing signatories to reduce S deposition by 30%, from a 1980 baseline, by 1993. The lack of sound scientific underpinning for this policy was controversial and several countries refused to sign up. This led to the development of the 'critical loads' methodology, designed to provide a scientific, effects-based method for targeting emissions reductions across Europe that would reduce deposition in areas where the potential damage was greatest and therefore where abatement would be most beneficial. A formal definition of a critical load was agreed in 1988 as: "*a quantitative estimate of an exposure to one or more pollutants below which <u>significant harmful effects</u> on <u>specified sensitive elements</u> of the environment do not occur according to present knowledge*" (Nilsson & Grennfelt, 1988).

Critical loads methodology formed the basis of the Second Sulphur Protocol under the CLRTAP, formalised in Oslo in 1994, and for surface waters the recommended methodology was the Steady-State Water Chemistry (SSWC) model (Henriksen *et al.*, 1992). The SSWC model requires the specification of a critical value of acid neutralizing capacity (ANC) and the model quantifies the maximum deposition load which will not cause ANC to decline below the critical value. Most applications of the SSWC model make reference to a seminal study of fish and invertebrate populations and water quality in several hundred Norwegian lakes which provides a dose-response function linking ANC to the probability of damage to biota (Lien *et al.*, 1996). A widely used critical limit is ANC = 20 $\mu eq\ l^{-1}$ which corresponds to a probability of damaged brown trout populations of 10%. This value has been adopted in the UK, although a critical value of 0 $\mu eq\ l^{-1}$ was previously used (and is still used for a few naturally acid sites), corresponding to a 50% probability of damage to brown trout populations.

The SSWC model provided the foundation for a more sophisticated mass-balance model for sulphur (S) and nitrogen (N), the First-Order Acidity Balance Model (FAB: Posch *et al.*, 1997), developed to incorporate the increasingly recognised contribution of N deposition to acidification in surface waters. These models provided the key critical loads data for surface waters used under the subsequent Gothenburg Protocol of 1999, a "*multi-pollutant, multi-effect protocol … to abate acidification, eutrophication and ground-level ozone*". The Gothenburg Protocol is still in force and the FAB model is still the recommended method for deriving critical loads for freshwaters under the CLRTAP, although only five countries/regions currently apply it (UK, Norway, Sweden, Finland and the Swiss Canton, Ticino). The degree of critical load exceedance is then defined as the reduction in acid anion leaching flux needed to restore ANC to 20 $\mu eq\ l^{-1}$ (or 0, for naturally acidic sites), which may generally be achieved through a combination of reductions in S and N deposition.

The FAB model uses best available knowledge of long-term, sustainable sinks for deposited N to determine separate critical loads for S and N, which are combined to take into account their additive effects in causing acidification. A major uncertainty in the application of FAB lies in the prediction of future N leaching rates. These are generally far greater than current observations, indicating that in the short-term the modelled sinks for N are greatly underestimated (Curtis *et al.*, 1998; 2005). A major current research focus under the Defra Freshwater Umbrella is improving our understanding of N biogeochemistry with respect to the possibility of the 'worst-case' predictions of FAB being realised in policy-relevant time-scales. While FAB continues to be used for the official submission of UK data under the Gothenburg Protocol, model development is ongoing, and the SSWC model for total acidity, which uses measured NO_3^- concentrations in the calculation of exceedance rather than assumptions about a theoretical steady-state mass balance, may be used for comparative purposes to determine the 'best-case' critical load exceedance.

In addition to the CLRTAP of the UN-ECE, a parallel European Union initiative is the 'Directive on national emission ceilings for acidifying and ozone forming air pollutants' (2001/81/EC), commonly known as the NECD. The NECD sets binding emissions ceilings for SO_2, NO_x, NO_3^- and volatile organic compounds to be achieved by 2010 and, like the Gothenburg Protocol, utilises critical loads data to underpin these emission targets.

In May 2001 the EU launched the "The Clean Air for Europe (CAFE) Programme: Towards a Thematic Strategy for Air Quality", responsible for the development of the first thematic strategy (on "air") under the EU Sixth Environmental Action Programme. CAFÉ sets out the major medium term EU policies to tackle the detrimental effects of air pollution on human health and the environment through targeted cost-benefit analysis. CAFÉ sets the following targets (among others):

- reduction in excess acid deposition of 74% and 39% in forest areas and surface freshwater areas respectively;
- 43% reduction in areas or ecosystems exposed to eutrophication [EU, COM (2005) 446].

9.1.3. EU Water Framework Directive and UK acid waters

The main objectives of the WFD are to prevent further deterioration of surface waters, restore and provide long-term protection for them, and enhance the status of water resources (Pollard & Huxham 1998; Haunia 2002). The principal goal is to achieve ''good ecological quality'' in all relevant waters by 2015.

In contrast to many earlier water directives, and those discussed above, where chemical drivers and targets were or are of key importance, the WFD places emphasis on the ecological structure and function of aquatic ecosystems with biological elements (fish, invertebrates, macrophytes, phytobenthos and phytoplankton) at the centre of the status assessments, and hydromorphology and physico-chemistry as supporting elements.

Ecological quality is judged by the degree to which present-day conditions deviate from those prevailing in the absence of anthropogenic influence, termed reference conditions. Sites in which the various elements correspond totally or almost totally to undisturbed (reference) conditions are classed as High status. Four further categories of Good, Moderate, Poor and Bad status refer to the degree of deviation from the reference state.

While the purpose of the WFD is to establish a framework for the protection of all waters, one area of concern with respect to the effects of acidification is that many sensitive headwater streams and lakes are not designated as "separate water bodies" by UKTAG on the grounds that catchment areas or lake areas fall under 10 km^2 or 0.5 km^2 respectively. As such they are not considered under the River Basin Management Plans and have not been selected for routine WFD monitoring by the national environmental agencies. Most AWMN sites fall beneath these size thresholds, and the process by which these sites, often the most vulnerable to acidification, will be afforded protection under the WFD remains to be clarified. Nevertheless the AWMN sites provide the UK with the most representative and reliable data needed to assess progress towards the meeting of the WFD objectives for acidified waters, and data from the four English and Welsh lake sites is supplied to the EA WFD Surveillance Network whilst the Scottish Environmental Protection Agency used AWMN data for site classification purposes.

9.1.4. Importance of dynamic model output to policy formulation

Output from national scale dynamic modelling initiatives has fed directly into the development of policy within Defra by predicting the effects that atmospheric pollutants have on Britain's sensitive soils and freshwaters. Historically, sulphur (S) pollution has been the main component of 'acid rain', which has caused acidification of soils and waters, leading to biological damage (such as fish loss) in many areas. Although S pollution (mainly from fossil fuel burning) has declined considerably from its 1970s peak, many damaged ecosystems are slow to recover, and some of the most sensitive ecosystems may remain damaged even under reduced loadings. At the same time, levels of atmospheric nitrogen (N) pollution (mainly from fossil fuel burning and agriculture) increased into the 1990s and have shown only moderate declines since then. Nitrogen deposition can also contribute to acidification and, as a key nutrient for plant growth, can cause nutrient enrichment (eutrophication) of semi-natural ecosystems.

The dynamic model MAGIC has been applied to AWMN sites under the auspices of the Defra freshwater and terrestrial research programmes. This has allowed predictions of how the condition of an ecosystem will change over time, beyond the period of chemical monitoring. This builds on the critical loads approach by providing information on the timescales of damage and recovery, either by predicting how different pollution-control scenarios will affect ecosystems in future, or by calculating the change in pollution levels that would be required to achieve recovery in a damaged ecosystem by a given date (i.e. defining target loads). MAGIC can also provide hindcasts as well as forecasts, given suitable historical deposition data or scaling from measured levels. It is therefore highly useful for providing modelled estimates of reference chemical conditions for establishment of restoration targets.

Dynamic models have been continually developed to improve the way they simulate complex chemical and biological processes, and to enhance the linkages between the deposition of S and N pollutants, the chemical response of soils and waters, and the biological response of plants and aquatic biota. The results of this work directly support policy development by Defra at the national scale, and also provide a resource to support the sustainable management and environmental protection of individual sites within the UK.

The results from critical loads and dynamic modelling initiatives feed directly into the setting of European legislation through the submission of data to the UK National Focal Centre (NFC). This centre provides UK representation to the International Cooperative Programme on Mapping and Modelling (ICP M&M) and the Coordination Centre for Effects (CCE). The NFC ensures that the interests of the UK are represented, and that the UK has the opportunity to contribute to policy related discussions (such as the use of critical loads and dynamic modelling data in the review of the Gothenburg Protocol and other Directives) and to feed into the Working Group on Effects (WGE) of the CLRTAP.

9.2. Recovery Targets for Acidified UK Waters

9.2.1. The critical loads approach

Although the objectives of the different directives and protocols with respect to acid waters are the same (i.e. improvement in conditions with respect to a target) the concepts and procedures in assessing the extent of recovery are essentially different. The UNECE protocols involve targets that are derived using a chemical methodology, and a target of ANC 20 μeq l^{-1}, as noted above, is set for all sites, irrespective of the pre-acidification or reference ANC of any individual site (the exception being the naturally very acidic sites where the critical limit has been set as 0 μeq l^{-1}). In other words, the 20 μeq l^{-1} ANC target can be very undemanding for sites with significantly higher pre-acidification reference ANC values. Eliminating critical load exceedance at such sites satisfies the UNECE standards but nevertheless allows considerable remaining damage that, in the phraseology of the WFD, may maintain the site below the "good to moderate" boundary. Furthermore, the use of mean water chemistry data or targeted sampling to obtain the best estimate of the annual mean may underestimate potential impacts and deviation from targets during extreme, short duration chemical episodes, such as the acid episodes associated with high flow events in acidified streams (see below).

9.2.2. The reference condition approach

In the WFD recovery targets are defined ecologically rather than chemically and recovery is measured against the yardstick of the reference state. In theory this is more appropriate than the critical loads approach as it takes into account the extent of deviation from the pristine or high status condition. There are two problems, however. First, the WFD typology (Phillips, 2003) places all acid waters into a single class (alkalinity = < 200 μeq l^{-1}), and second, the reference state is not one that can be easily defined. The former is of great concern as the "low alkalinity" category includes a considerable diversity of waterbody types, and legislating agencies may be tempted to adopt the same standard target for all surface waters in this type. Here we consider the recovery of the AWMN lakes and streams on a site by site basis. The latter problem can be addressed using a range of approaches, including the use of space-for-time comparisons, palaeoecological analysis, and modelling.

9.2.3. The role of dynamic models in establishing chemical restoration targets

Whilst the critical loads concept is a powerful tool for assessing acidification status for specific years, critical loads and exceedances provide no indication of the time over which damage or geochemical reversibility and biological recovery will be achieved in response to reduced emissions. The critical loads concept neglects the time components of acidification, namely soil buffering, sulphate desorption, nitrogen saturation, and organic matter dynamics. Dynamic models offer the only opportunity to determine the level of deposition reduction required to achieve a given chemical restoration target, and hence a biological response, within a given time scale. Given the importance of 2015 for the implementation of both the Water Framework Directive and UNECE protocols, dynamic models provide a methodology through which to optimise the environmental consequences of both pieces of legislation in combination.

The dynamic model MAGIC (Model of Acidification of Groundwater In Catchments) has been applied to the AWMN to assess the evidence for chemical recovery in long-term water chemistry datasets. The degree of recovery is related to regional differences in catchment physico-chemical characteristics and deposition reductions, both relative and absolute.

MAGIC has been applied extensively in scientific and management studies throughout Europe and North America and used in policy related assessments leading to emissions reductions protocols or legislation. The model was developed and tested using data from long-term monitoring sites, including the AWMN, and from manipulation experiments. The version of MAGIC used here includes a conceptual model of nitrogen retention and is thus capable of simulating the acid-base responses of catchments to both sulphur and nitrogen deposition. Concentrations of water and soil variables derived from MAGIC simulations have previously been used as indices of the status of fisheries health, forest vitality, and surface water acidification or eutrophication.

MAGIC is a process-orientated model, developed to provide long-term reconstructions and predictions of soil and stream water chemistry in response to scenarios of acid deposition and land use (Cosby *et al.*, 1985). The model simulates soil solution and surface water chemistry to predict average concentrations of the major ions for annual time steps.

Deposition chemistry from the nearest bulk deposition collector in the UK Acid Deposition Monitoring Network (ADMN) was used to drive the model from 1988 to 2007. Because the deposition collector is not directly co-located at the monitoring site and since bulk deposition does not accurately reflect dry and occult deposition inputs, the annual bulk deposition concentrations at each site were corrected to match the observed Cl^- and SO_4^{2-} in surface water. The historical (pre-1988) deposition sequences for SO_4^{2-}, NO_3^- and NH_4^+ were estimated by scaling currently observed deposition to reconstructions of S emissions (Warren Spring Laboratory, 1983) and N emissions (Wright *et al.*, 1998) from Concentration Based Estimated Deposition (CBED), based on a 5x5 km grid for 2004-06. All other ions in deposition were assumed to remain constant throughout the simulation.

The calibration and application of MAGIC to the 22 AWMN sites (excluding Loch Coire Fionnaraich) represents the most rigorous and detailed site specific application of the model in the UK to date. Twenty years of observations for surface water quality and deposition were used in the calibration. The calibrated model successfully matched annual mean (1988-2007) major ion surface water chemistry and pH and soil base saturation at all sites. There is no systematic bias in the calibrated determinands. The MAGIC simulations indicate that the current application is broadly reliable, and supportive of policy development. However, certain assumptions in MAGIC regarding past and future soil processing of both nitrogen and carbon are as yet unproven, and predictions, as for any model, need to be treated cautiously.

Comparison with observed ANC (not calibrated) also shows broad consistency from site to site (Fig. 9.1). Inconsistencies between observed and simulated data at individual sites may in part be attributed to the method used to calculate the mean annual ANC. This is calculated from the mean annual ion concentrations rather than as a mean of the ANC of each sample taken within the year. Comparison of the model simulations against the observed annual runoff chemistry (using the observed mean annual deposition for 1988 – 2007 to drive the model) gives generally good results (Fig. 9.1). The exceptions were Scoat Tarn, Old Lodge, and Narrator Brook. At these sites, the model predicts a much greater variation in ANC than that observed. This is primarily due to the effects of the large inter-year variability in Cl^- deposition at these sites. The implication is that the deposition chemistry is not reflected in the annual mean stream chemistry. This could result from: (i) the very rapid response of runoff chemistry to deposition which is effectively 'missed' by the monthly/quarterly sampling regime; or (ii) very slow responses being 'averaged' over calendar years.

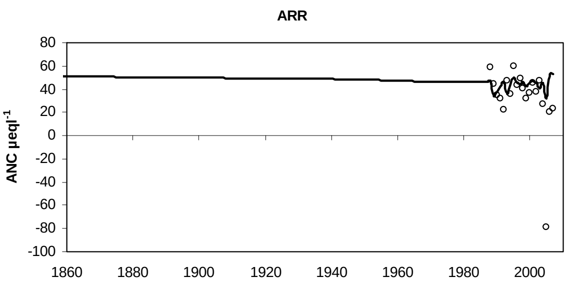
MAGIC-simulated NO_3^- replicates the broad-spectrum of responses throughout the Network in terms of overall concentrations and the general trend in NO_3^- (Fig. 9.2). The inherent temporal variability in NO_3^- observations make it notoriously difficult to model, particularly in years where climate extremes impact on biological processes. The peaks in NO_3^- during 1996 and 2003 (Allt na Coire nan Con, Loch Tinker, Round Loch of Glenhead, Old Lodge, Llyn Llagi, Blue Lough and Coneyglen Burn) were driven by climatic factors, and since MAGIC has a limited capacity to model climate-driven biogeochemical processes, these peaks were not captured in the simulation.

In general, the calibrated model successfully matches surface water chemistry pH (Fig. 9.3). At some sites, notably Allt na Coire nan Con, Dargall Lane, Burnmoor Tarn, Old Lodge and Llyn Cwm Mynach, MAGIC simulates higher surface water pH during the calibration period than those observed. For less acidified sites such as Coneyglen Burn a narrow range of pH is observed and these small changes were poorly represented by MAGIC.

Observations of soil base saturation (Heliwell *et al.*, 1998) show that the majority of soils are acid sensitive (base saturation < 20%) and therefore susceptible to the effects of acidification. With the exception of Old Lodge, there is very good agreement between MAGIC simulated soil base saturation and the observed data (r^2 = 0.98; Fig. 9.4). The calibration was less successful at Old Lodge because the high observed soil base saturation (50.4%) was not achieved through the contribution of base cations from weathering (37.4%).

Calibration issues

At two sites in particular, Llyn Cwm Mynach and to a lesser degree Old Lodge, MAGIC consistently over-predicts both ANC and pH demonstrating serious calibration problems (Figs. 9.1 and 9.3). Future predictions for these sites based on MAGIC should therefore be interpreted with caution, and future work will aim to improve these model calibrations.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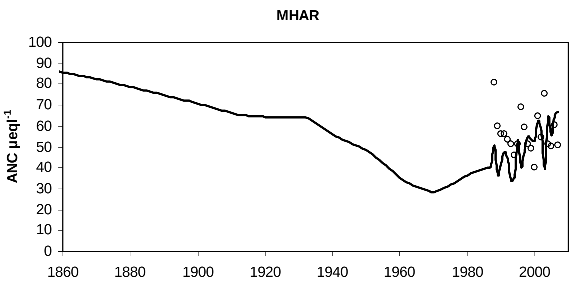
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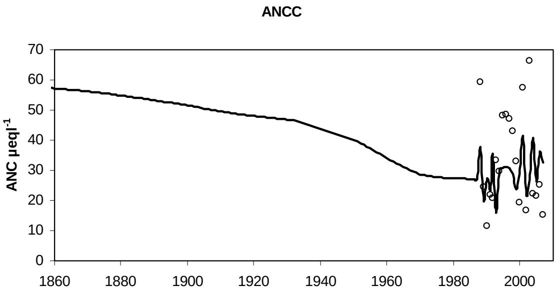
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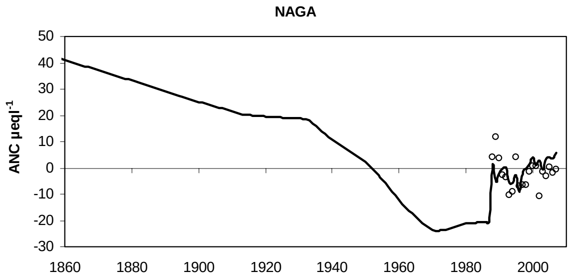
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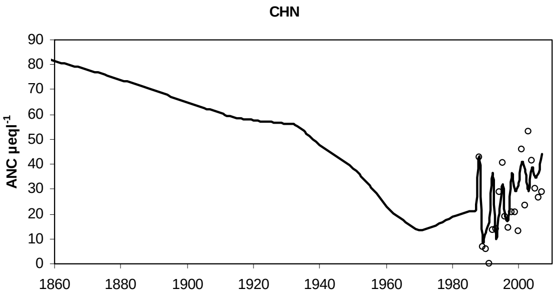
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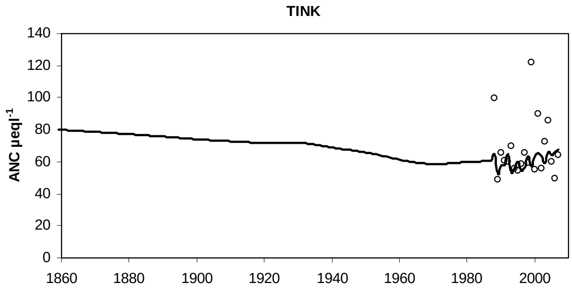
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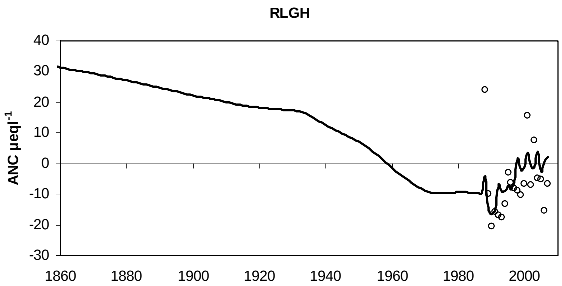
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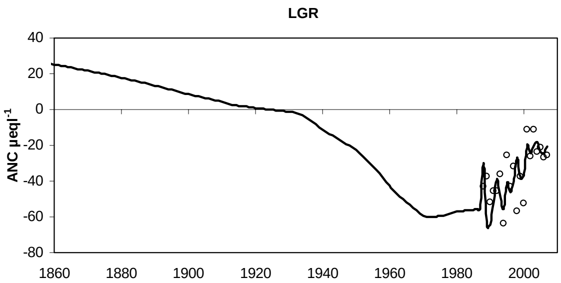
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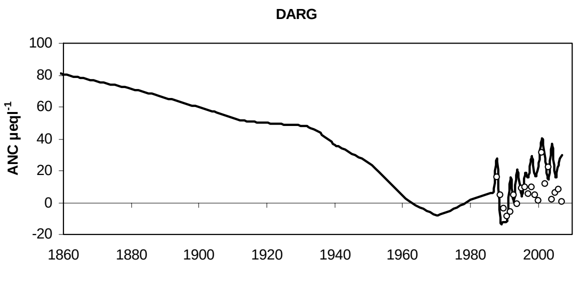
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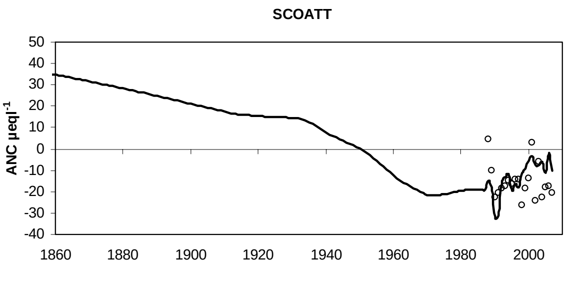
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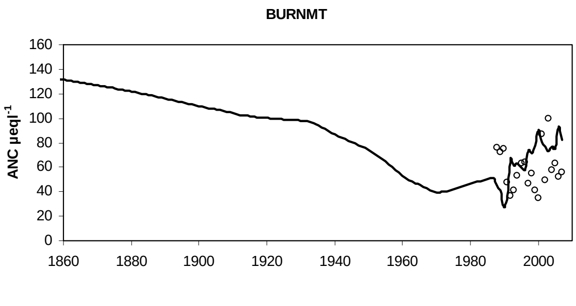
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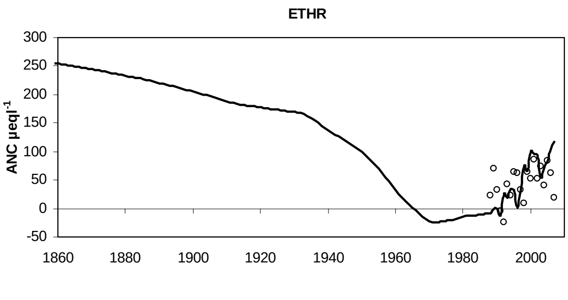
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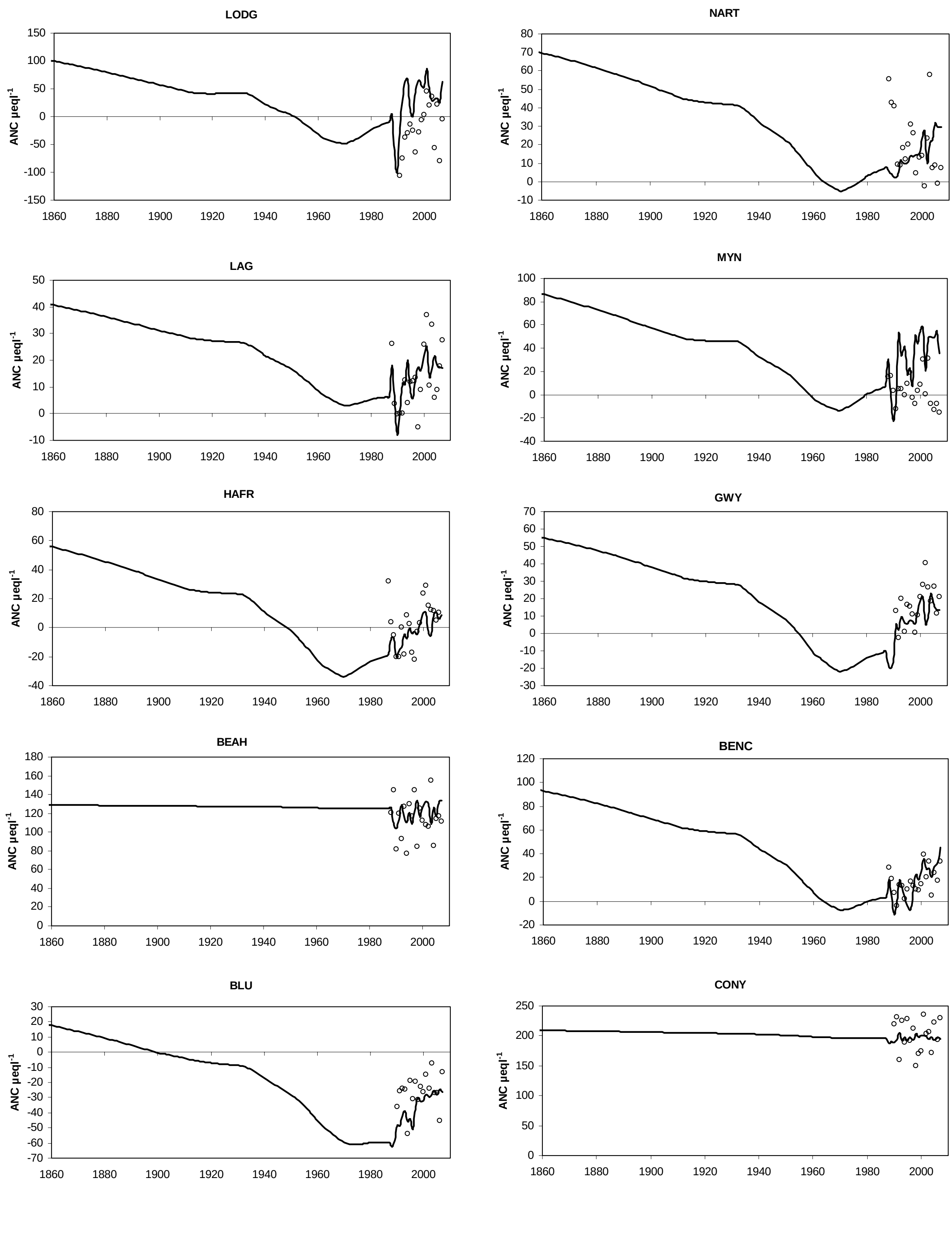
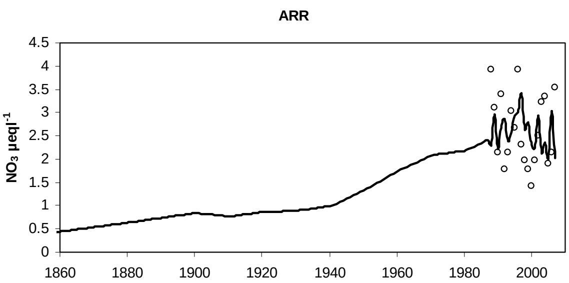


Figure 9.1: Long-term simulated surface water ANC and mean annual observed chemistry from 1988-2007 (open circles).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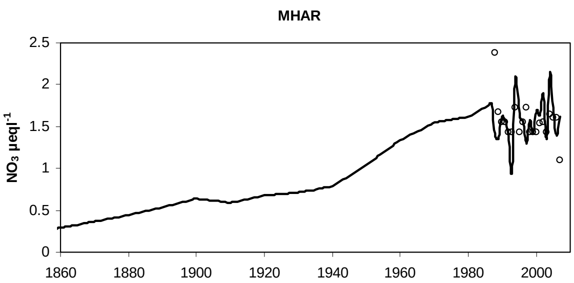
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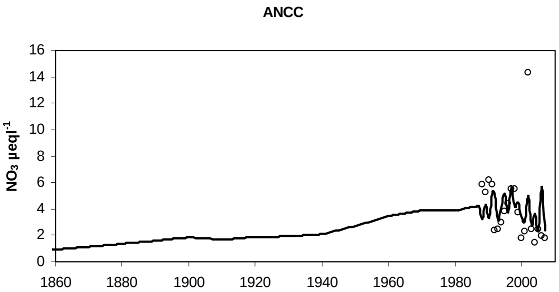
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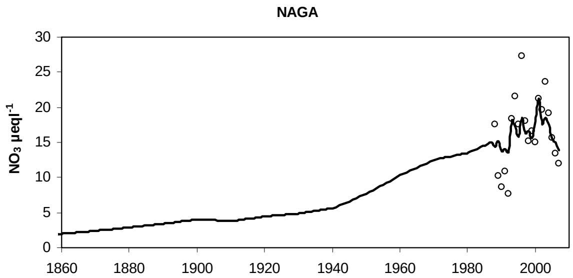
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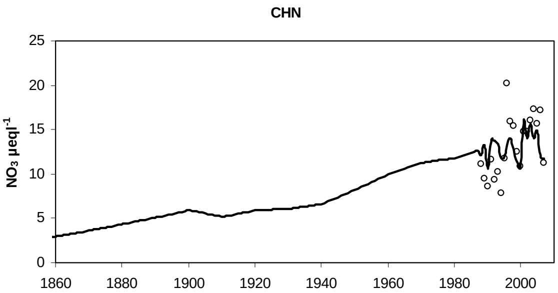
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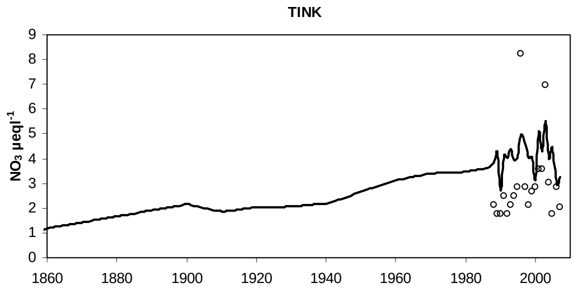
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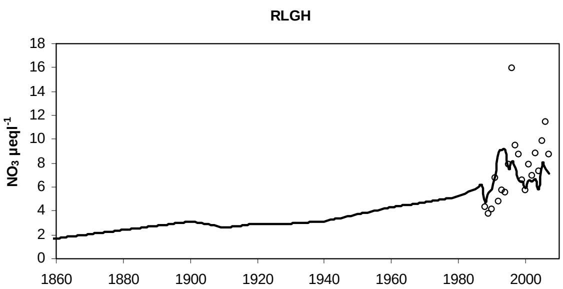
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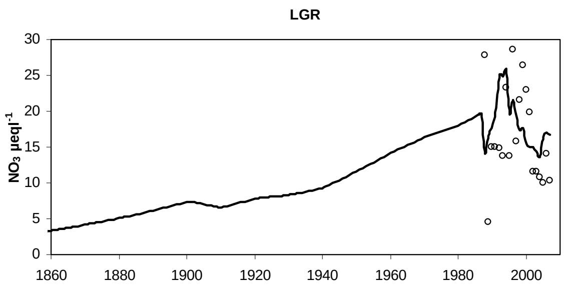
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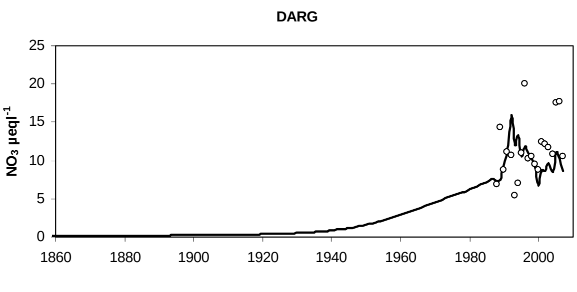
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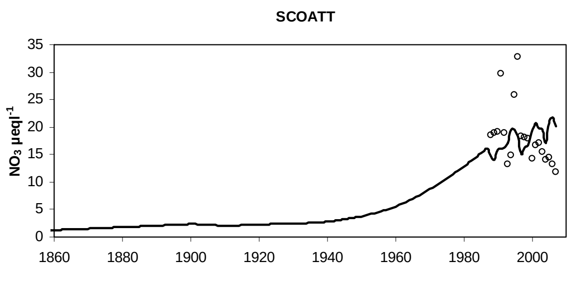
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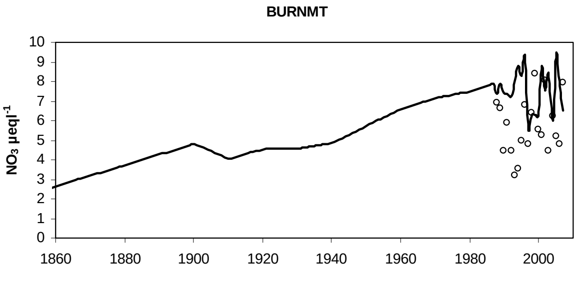
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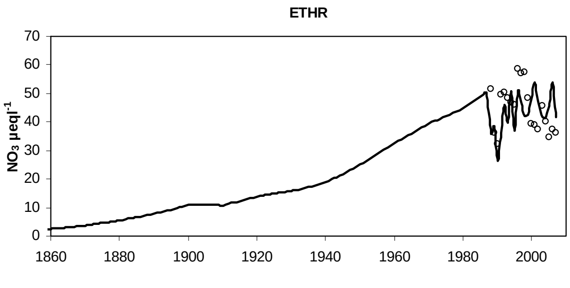
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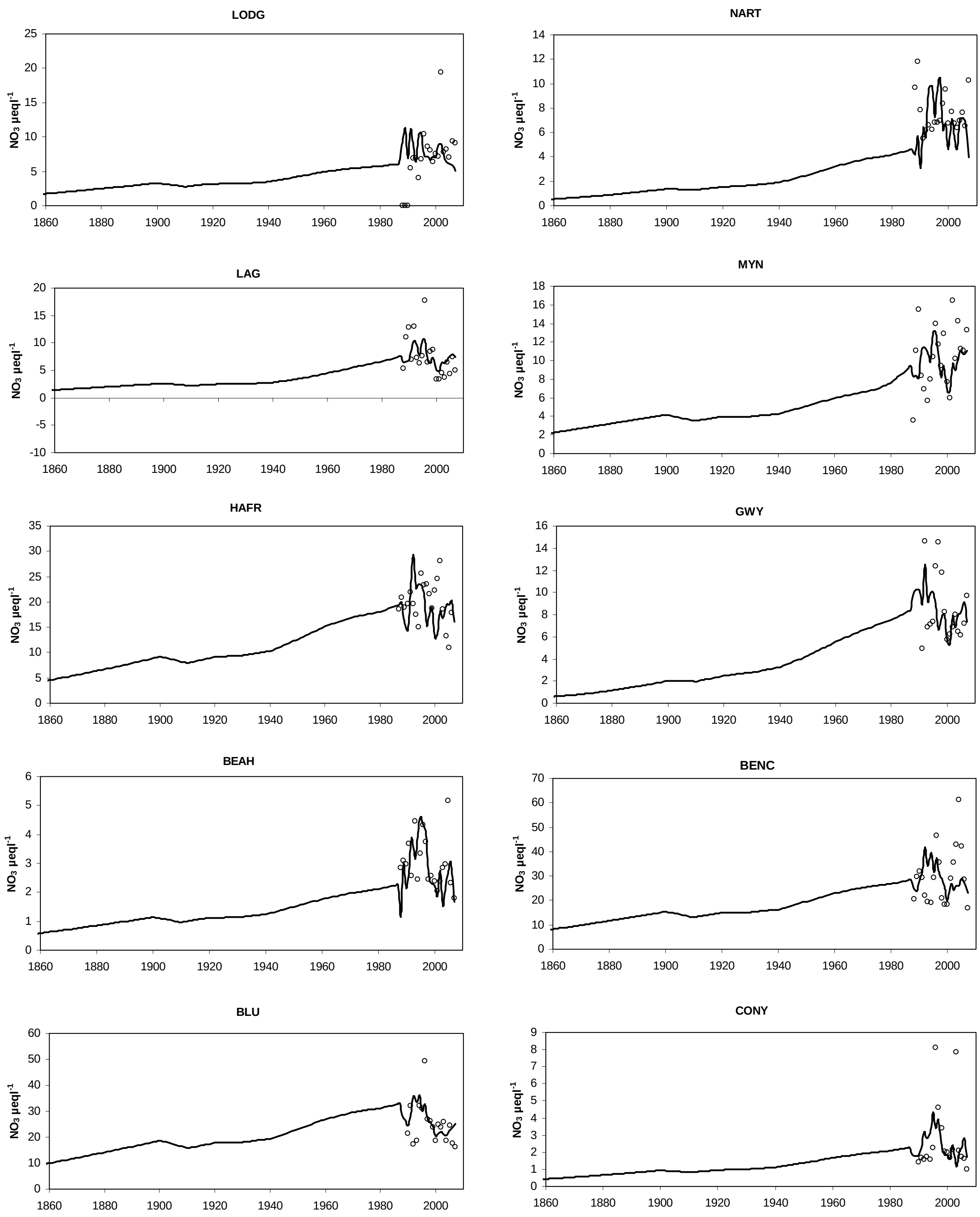
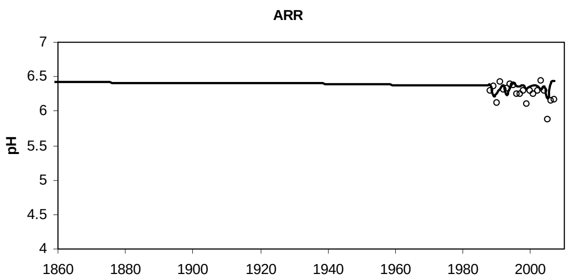


Figure 9.2: Long-term simulated surface water NO_3^- and mean annual observed chemistry from 1988-2007 (open circles).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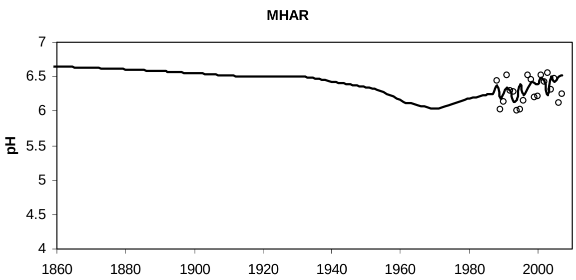
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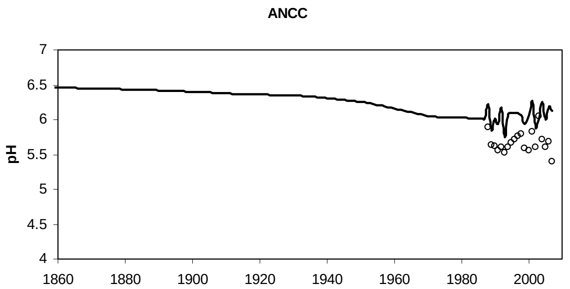
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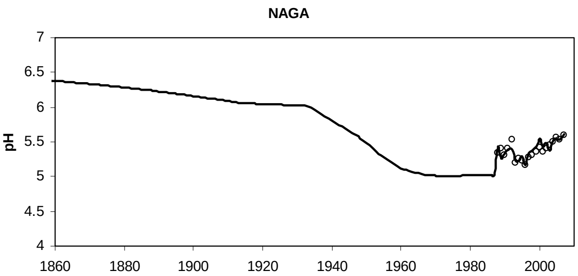
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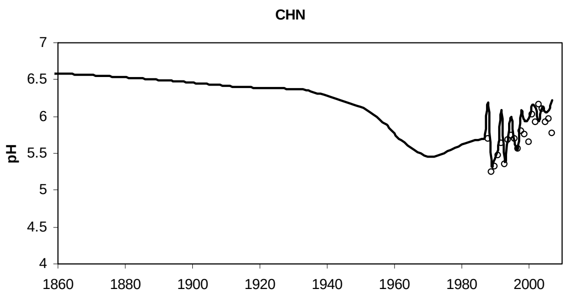
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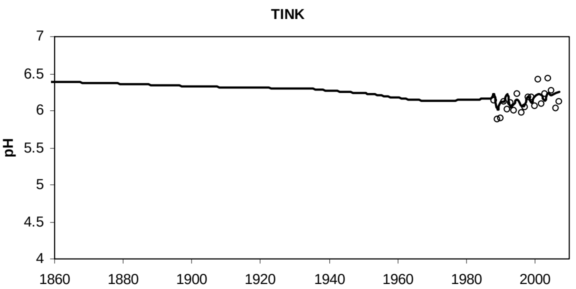
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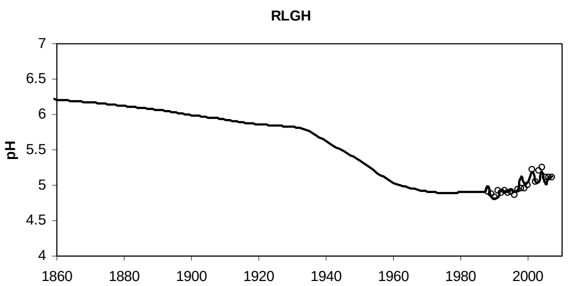
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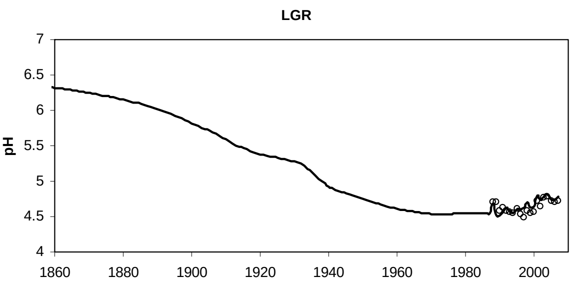
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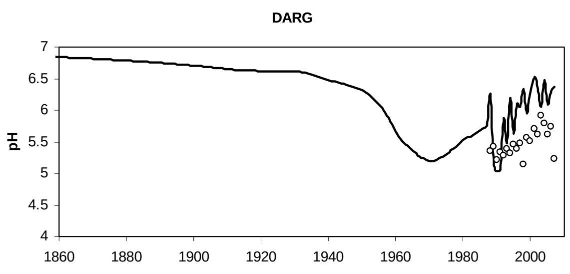
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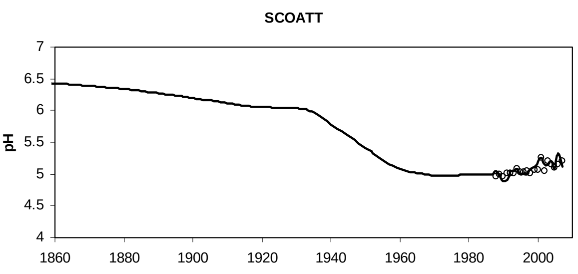
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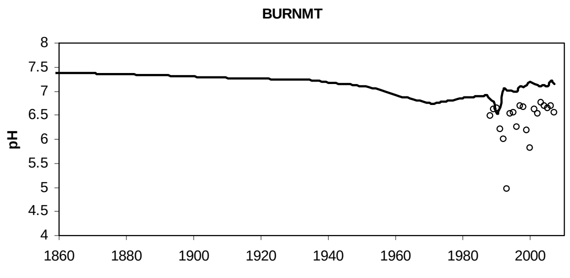
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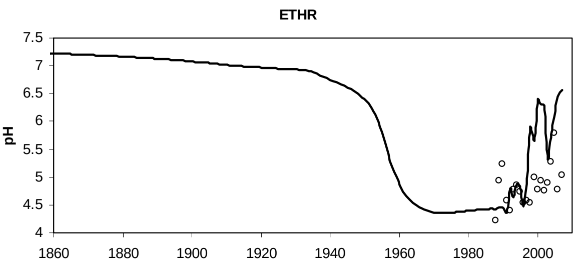
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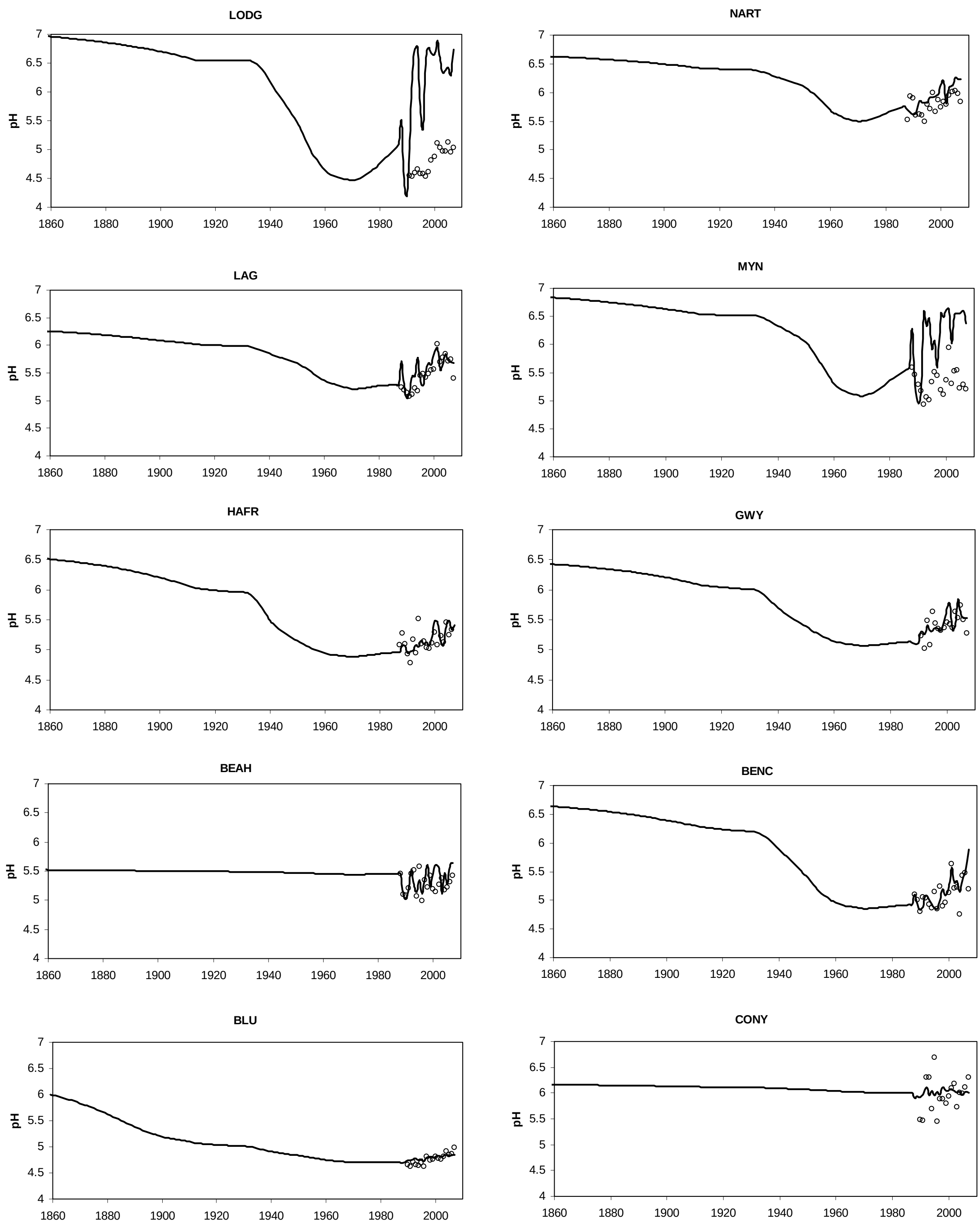


Figure 9.3: Long-term simulated surface water pH and mean annual observed chemistry from 1988-2007 (open circles).

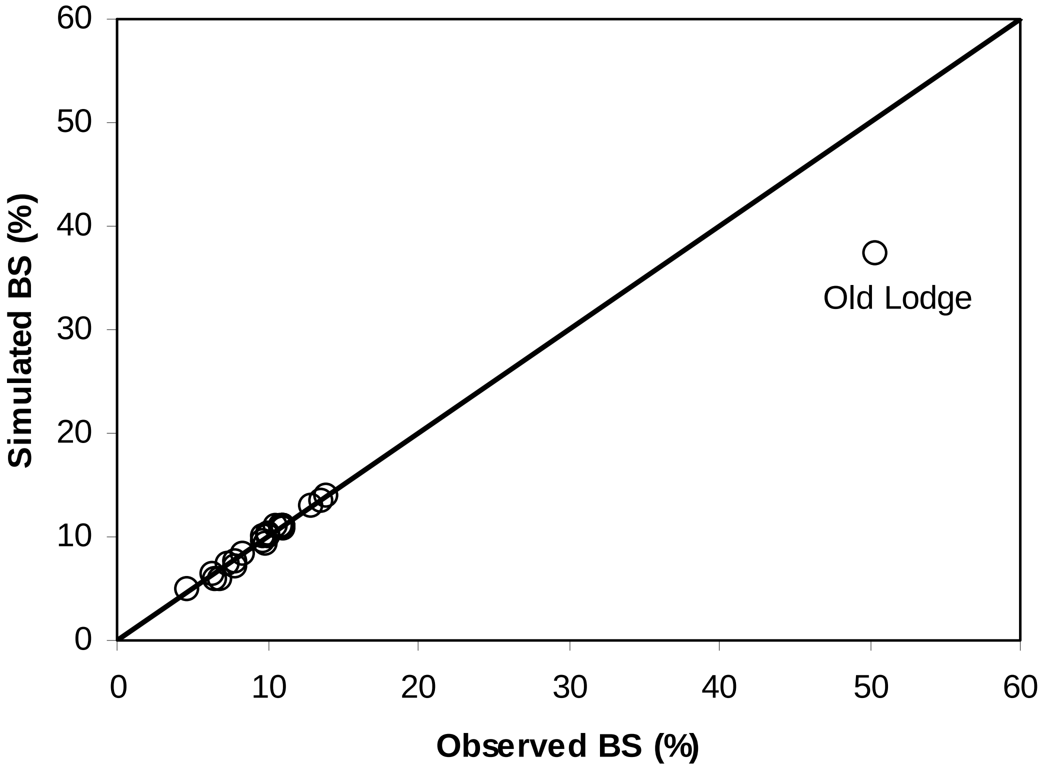


Figure 9.4: Model validation for soil base saturation based on observed and simulated data from 2002.

9.3. Recovery of UK Acidified Waters: Evidence from the AWMN

9.3.1. Progress in reducing critical load exceedance

Two complementary empirical modelling approaches have been used here, the Steady-State Water Chemistry (SSWC) model (Henriksen *et al.*, 1992) and the First-order Acidity Balance (FAB) model (Posch *et al.*, 1997; Henriksen & Posch, 2001). In the SSWC, the critical load exceedance uses measured water chemistry to calculate the critical load and measured NO_3^- concentration to provide an estimate of the leaching flux contributing to critical load exceedance. For N deposition this may be considered a "best-case" scenario where the possibility of N saturation and increased NO_3^- leaching under constant deposition is ignored. To calculate exceedance with the SSWC model, contemporary NO_3^- leaching data are required for a given deposition period because measured NO_3^- is used in lieu of N deposition data in the calculation of exceedance. For FAB the situation differs in that once the model has been applied to provide various critical load parameters (in a comparable way to the calibration of MAGIC) then in theory an exceedance for any specified period of deposition data may be calculated without the requirement for contemporary NO_3^- data.

FAB provides a measure of potential damage for any specified level of deposition, making it useful for scenario analysis, but it is open to the criticism that its N mass-balance assumptions are unrealistic, as they are based on expert judgement about (very small) long-term sustainable sinks for N deposition via soil immobilisation, denitrification and removal in biomass following biological uptake.

If the assumptions underlying both models regarding the mobility of deposition SO_4^{2-} and the use of the F-factor of Brakke *et al.* (1990) to determine soil base cation exchange are accepted, then the SSWC and FAB methods provide lower and upper limits of exceedance as an index of acidification damage (cf. Curtis *et al.*, 2005).

Critical load exceedances are calculated here for three deposition datasets, using CBED statistically interpolated from measurements across national deposition networks (1986-88, 1996-98 and 2004-06 three-year running means). Critical load exceedances are shown for both SSWC (Fig. 9.5) and FAB (Fig. 9.6) models for total acidity, while ANC trends are compared with measured changes in ANC associated with deposition reductions over the last 20 years (Table 9.1). Trend analysis has been performed on ANC values corrected for the influence of organic acids ('Cantrell method') and aluminium. For SSWC exceedances, contemporary water chemistry and deposition data are used, which for the start of monitoring means that only those sites with 1988 data are included for 1986-88 exceedances. For FAB, the official (i.e. submitted by the NFC to the CCE) dataset is used, with critical load parameters calculated using 2002 mean monitoring data and exceedances for S+N calculated for any given time period. Hence the two model applications are only comparable in a broad sense as they use different data for each set of exceedance calculations.

It is important to note that mean annual chemistry is normally used to describe ANC and set critical ANC levels. Mean annual levels of 20 μeq l^{-1} or more may be sufficient to ensure that hydrogen (H^+) and aluminium (Al^{3+}) ion toxicity is generally too low to affect most acid-sensitive species, particularly with respect to waters with relatively low levels of dissolved organic carbon (Kroglund *et al.*, 2001). However, it is also necessary to consider the effects of episodic breaches of critical levels, particularly during hydrological and sea-salt episodes, as the accompanying surge in H^+ and Al^{3+} ions may be sufficient to interfere with gill function and result in gill clogging by aluminium. Atlantic salmon are particularly sensitive to such events around the time of smolting in spring, and may suffer permanent physiological damage at this time even with exposure to elevated Al^{3+} concentration for a few hours only (Kroglund *et al.*, 2007), while brown trout are most sensitive around the time of hatching (Chapter 7).

At the start of the monitoring period, only 17 sites had sufficient contemporary chemistry to apply the SSWC model with 1986-88 mean deposition data (excluding Fionnaraich, Coneyglen Burn, Blue Lough, Afon Gwy, Old Lodge and Narrator Brook). With the best-case SSWC model, 12 out of 17 sites exceeded critical loads at the start of the monitoring period, while with FAB all sites except Coneyglen Burn exceeded critical loads. As S deposition declined, the number of exceeded sites fell through time so that by 2004-06, only 11 out of 23 sites exceed SSWC critical loads. In contrast, FAB critical loads remain exceeded at all sites except Coneyglen Burn and three in north-west Scotland (Coire nan Arr, Allt na Coire nan Con and Loch Coire Fionnaraich). Several sites show exceedance for all deposition scenarios; for SSWC they are Lochnagar, all three Galloway sites, both sites in the Mourne Mountains and Scoat Tarn. With FAB, all sites except Coneyglen Burn and the three sites in north-west Scotland remain exceeded under all three deposition scenarios.

Hence ‘current’ exceedance using the most recent deposition data suggests ongoing acidification at between almost half of sites (best case SSWC) and over three quarters of sites (worst-case FAB). However, there are reductions in the number of exceeded AWMN sites predicted by 2020 according to modelled data (see Chapter 10). Furthermore, even those sites still exceeding critical loads at present may not have ANC values below the critical limits, given the steady-state assumptions of the models (compare values in Table 9.1).

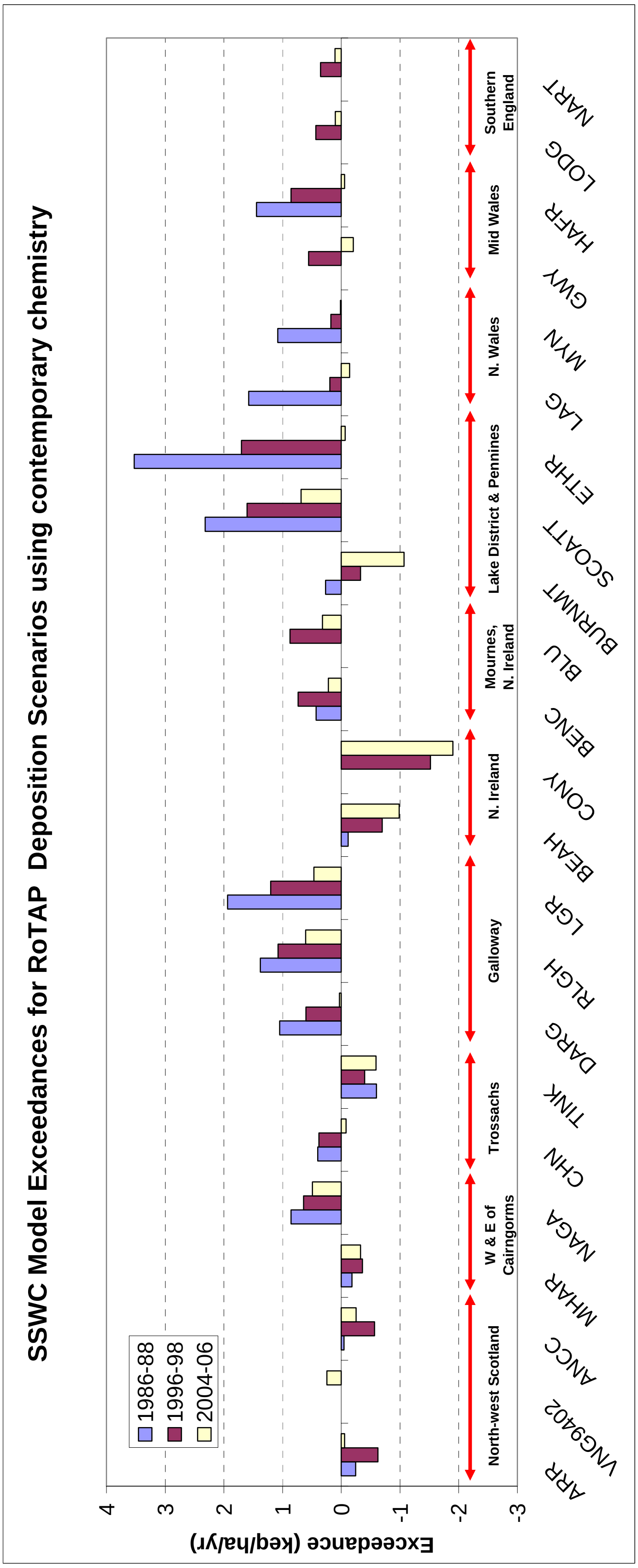


Figure 9.5: SSWC critical load exceedances using contemporary water chemistry and deposition data for three RoTAP scenarios.

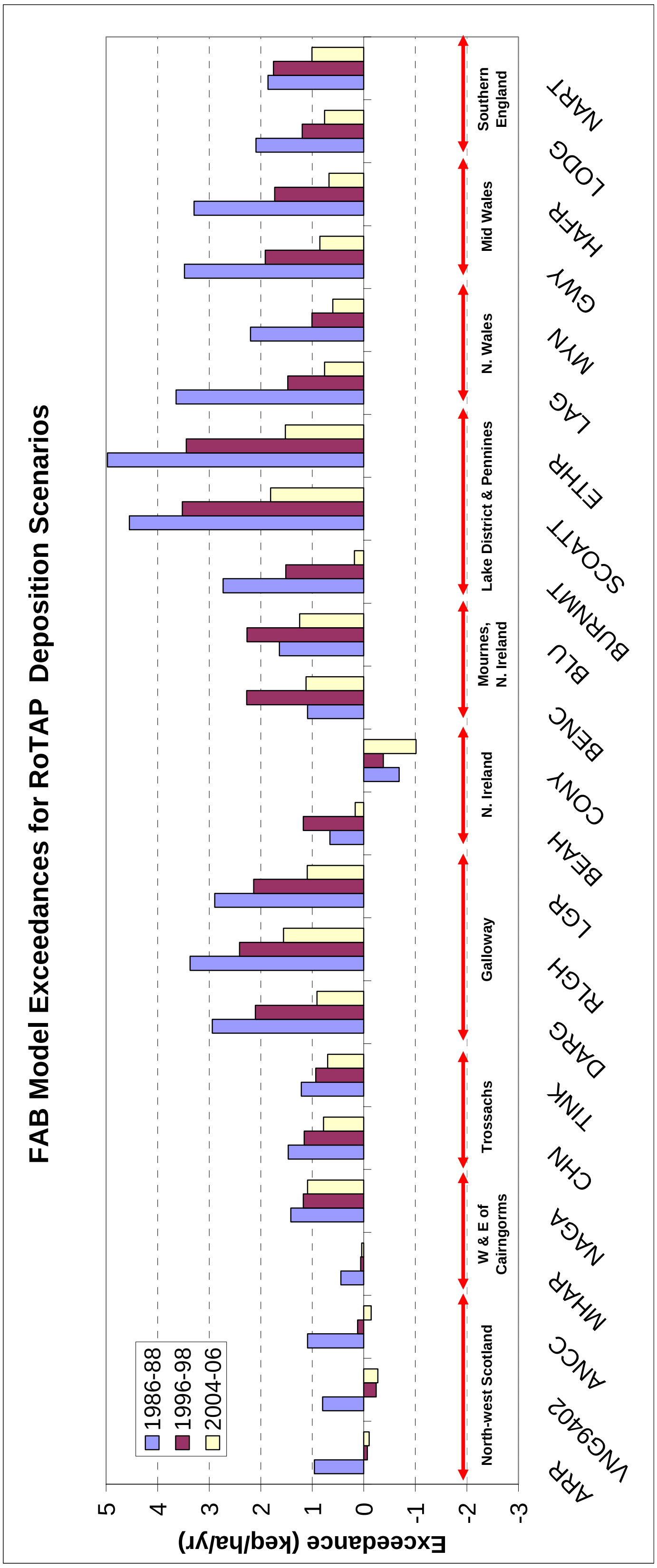


Figure 9.6: FAB Model Exceedances calculated using RoTAP deposition scenarios and official UK critical loads data (2002 mean for AWMN sites)

9.3.2. Progress towards recovery targets based on reference conditions

9.3.2.1. Acid Neutralising Capacity

The historical simulation of water chemistry is driven by sequences defined for acid deposition. MAGIC simulated ANC for 1860 illustrates that, prior to industrialisation, ANC values of all surface waters in the AWMN were above the critical limit of 20 μeq l^{-1}, with the exception of Blue Lough, which has a baseline ANC value of <20 μeq l^{-1}. The majority of sites (18 in total) have a simulated pre-industrial ANC below 100 μeq l^{-1}, indicating sensitivity to acidification; for the remaining four sites (Loch Coire Fionnaraich is excluded from the MAGIC analyses) the reference ANC is predicted to range from 129 to 254 μeq l^{-1}. These surface waters can therefore be considered relatively well buffered, and would probably have supported relatively diverse acid-sensitive plant and animal communities at this time (Fig. 9.7). It is noteworthy that the site with the highest reference ANC is the River Etherow, which nevertheless is one of the most acidified sites in the AWMN.

Despite this buffering, the significant increase in acid deposition from 1860 to its peak in the 1970s resulted in severe surface water acidification at 15 of the most acidified sites (ANC<20 μeq l^{-1}). Only the ANC of well-buffered sites in, for example, Northern Ireland (Coneyglen Burn 196.4 μeq l^{-1} and Beagh's Burn 125.2 μeq l^{-1}), Scotland (Loch Tinker 58.3 μeq l^{-1} and Loch Coire nan Arr 46.4 μeq l^{-1}, Allt na Coire nan Con 28.7 μeq l^{-1}, Allt a' Mharcaidh 28.6 μeq l^{-1}) and North west England (Burnmoor Tarn 39.5 μeq l^{-1}) maintained an ANC above the critical limit of 20 μeq l^{-1} at this time.

The ratification of several European protocols to reduce emissions of acidifying S and N compounds in the late 1980s and early 1990s (UNECE, 1999), resulted in a reversal in this acidification trend and widespread recovery of surface water chemistry throughout the UK and Europe as a whole. The number of sites with an ANC <20 μeq l^{-1} decreased from 15 sites in 1970 to 10 sites in 2005-2007, broadly corresponding with modelled critical load exceedance at present. The number of severely acidified sites (ANC < 0 μeq l^{-1}) declined from 13 sites in 1970 to 3 sites in 2005-2007.

Reference ANC values for 1860 are provided by the site-specific MAGIC model runs at the 22 AWMN sites. Chemistry data from the beginning of the monitoring period and the most recent data (both three-year mean values to iron out year-to-year variability) are then used to quantify the degree of chemical recovery towards reference conditions over the 20 year monitoring period. The difference between reference ANC and initial three-year mean ANC provides the "gap" in ANC. Note that this value does not reflect the maximum deviation from reference conditions because the inception of the AWMN occurred some years after the maximum levels of acid deposition. Progress towards reference conditions is estimated as $(ANC_{final} - ANC_{initial})/(ANC_{reference} - ANC_{initial}) \times 100\%$ (Table 9.1).

Table 9.1: Assessment of chemical recovery and 'gap closure' based on ANC trends (yellow highlighting = recovery, red = still acidified, with ANC 'gap closure' given as % relative to ANC difference between MAGIC derived baseline values and start of monitoring)

Site Code	Sitename	ANC Trend Sig.	ANC Trend Monotonic	Baseline ANC	Initial monitoring Period	Initial monitoring ANC	2005-07 ANC	Critical ANC	Recovery relative to: ANCcrit	Recovery relative to: Baseline
North-west Scotland										
ARR	Loch Coire nan Arr	ns	Mostly	51.0	1989-91	44.2	43.0	20	n/a	-18%
ANCC	Allt na Coire nan Con	***	Mostly	57.2	1989-91	33.5	44.4	20	n/a	46%
North-east Scotland										
MHAR	Allt a'Mharcaidh	***	Yes	85.8	1989-91	51.7	68.0	20	n/a	48%
NAGA	Lochnagar	***	Since 2000	41.0	1989-91	3.7	14.3	20	65%	29%
Trossachs										
CHN	Loch Chon	***	Yes	81.4	1989-91	11.1	49.5	20	yes	55%
TINK	Loch Tinker	**	Yes	79.9	1989-91	55.7	72.1	20	n/a	68%
Galloway										
DARG	Dargall Lane	***	Yes	80.4	1989-91	4.3	23.0	20	yes	25%
RLGH	Round Loch of Glenhead	***	Yes	31.3	1989-91	-9.4	14.1	20	80%	58%
LGR	Loch Grannoch	***	Yes	25.3	1989-91	-33.8	5.4	20	73%	66%
Northern Ireland										
BEAH	Beaghs Burn	**	Yes	128.9	1989-91	97.5	132.0	20	n/a	yes
CONY	Coneyglen Burn	ns	~Yes	209.1	1991-93	198.4	227.4	20	n/a	yes
BENC	Bencrom River	***	Yes	93.0	1989-91	-4.1	32.4	20	yes	38%
BLU	Blue Lough	***	Yes	17.6	1991-93	-43.6	-4.0	0	91%	65%
Lake District										
BURNMT	Burnmoor Tarn	***	~Almost	131.2	1989-91	55.5	81.6	20	n/a	34%
SCOATT	Scoat Tarn	***	Yes	34.7	1989-91	-20.3	-0.7	20	49%	36%
Pennines										
ETHR	River Etherow	***	Yes	253.9	1992-94	14.7	91.4	20	yes	32%
North Wales										
LAG	Llyn Llagi	***	Mostly	40.8	1989-91	3.6	17.5	20	85%	37%
MYN	Llyn cwm Mynach	ns	No	86.2	1989-91	10.7	7.1	20	-40%	-5%
Mid-Wales										
GWY	Afon Gwy	ns	~Yes	54.8	1992-94	9.1	19.8	20	98%	23%
HAFR	Afon Hafren	*	No	55.7	1989-91	1.7	10.4	20	48%	16%
South-east England										
LODG	Old Lodge Stream	***	No	99.6	1992-94	-28.5	31.6	20	yes	47%
South-west England										
NART	Narrator Brook	***	No	69.6	1992-94	13.5	20.0	20	99%	12%

For visual comparison the data are also presented for sites ordered by baseline (1860 reference) ANC in Figure 9.7. Although quantifiable, estimates of gap closure are approximate because within-year variability in ANC may be very large and the critical ANC threshold may be crossed for greater or lesser periods of the year in borderline cases. For this reason, three year running mean values for the start and end of the monitoring period are used in this analysis.

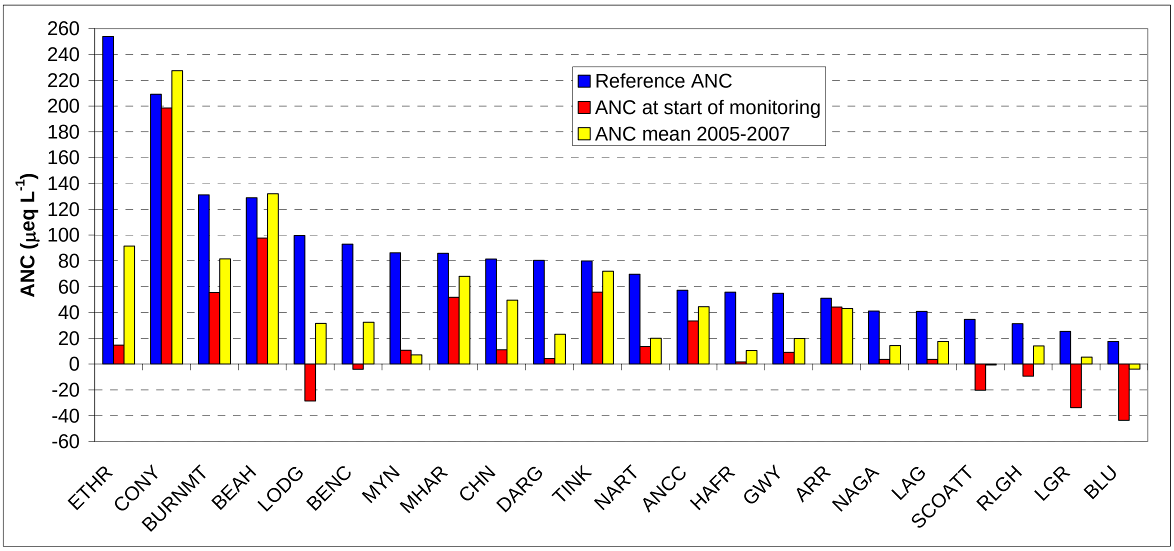


Figure 9.7: ANC values for reference conditions (using MAGIC hindcasts for 1860), at start of AWMN monitoring (3 year mean) and at present (2005-07 mean)

Consideration of ANC changes from MAGIC hindcast baseline values to the start and end of monitoring reveals three groups of sites:

(i) No recovery in ANC to either critical limit or reference conditions
Ten sites have current ANC values below both their critical limit and their reference values; Lochnagar, two Galloway sites (Round Loch of Glenhead, Loch Grannoch), Blue Lough, Scoat Tarn, all four Welsh sites (Llyn Llagi and Llyn Cwm Mynach, Afon Gwy and Afon Hafren) and Narrator Brook. These sites fail to meet the requirements for either the good ecological status (i.e. reference conditions) required by the WFD or the less stringent target of ANC = 20 μeq l^{-1} (0 μeq l^{-1} for Blue Lough) required under the Gothenburg Protocol.

(ii) Achievement of critical limit but not recovered to reference conditions
Five sites show ANC recovery to critical limits but not to reference conditions: River Etherow, Old Lodge, Loch Chon, Dargall Lane and Bencrom River. A further five sites show ANC values still below reference conditions but never below critical ANC values: Loch Coire nan Arr, Allt na Coire nan Con, Allt a' Mharcaidh, Loch Tinker and Burnmoor Tarn. In this group of sites, the low ANC limit values used for critical loads modelling have allowed a decline in ANC from reference conditions. Hence these sites meet the requirements of the Gothenburg Protocol but fall short of the Reference conditions implicit in the WFD.

(iii) Recovered to reference conditions (or no change from reference)
Two Northern Irish stream sites (Coneyglen Burn and Beagh's Burn) showed very minor acidification with only slight ANC declines below reference values, and have now fully recovered in terms of mean annual ANC relative to the MAGIC modelled reference values. Note however that this apparent decline and recovery could simply represent year to year variability within the error associated with the MAGIC hindcast. There may therefore have been no significant acidification at these sites, meaning they have remained at reference conditions with respect to acidity.

9.3.2.2. Soil acidification and recovery

There is no doubt that the main driver of acidification and recovery of surface waters is the deposition of acid anions. However the rate and magnitude of this chemical recovery is highly variable at the AWMN sites due to a number of factors, including the weathering rate of the parent materials and the soil base saturation. Generally, sites underlain by parent material with low weathering rates and soil base saturation are unable to balance the leaching demands of current acid anion deposition. This leads to the continued depletion of soil bases and to increased levels of acidity and aluminium in surface waters which will also increase the rate of acidification. Despite the significant reductions in S and to a lesser extent N deposition since 1970, the simulated soil base saturation at all sites across the Network either continued to decline or remained stable until the late 1980s, with marginal recovery detected at some sites in the past decade (Table 9.2). Although the neutralisation of acidity through exchange with soil base cations can marginally reduce acidification, at some sites the reverse process is also simulated whereby stored acidity is released from the soil and this is predicted to delay recovery. In general, this limited recovery in the soil base cation status is predicted to partially offset the rate of chemical recovery of surface waters at the AWMN sites.

Table 9.2. Soil base saturation (%) for key years at AWMN sites.

	1860	1970	1988-1990	2005-2007
Loch Coire nan Arr	12.4	11.2	10.7	10.5
Allt a' Mharcaidh	8.6	6.7	6.3	6.4
Allt na Coire nan Con	14.7	8.2	7.0	7.1
Lochnagar	33.3	14.4	10.0	9.3
Loch Chon	15.4	10.2	9.4	9.6
Loch Tinker	20.1	15.6	14.3	13.9
Round Loch of Glenhead	17.4	7.7	5.9	6.0
Loch Grannoch	20.4	8.6	6.8	7.2
Dargall Lane	7.3	5.1	4.8	4.9
Scoat Tarn	23.8	14.0	11.7	10.6
Burnmoor Tarn	19.5	11.6	10.6	11.1
River Etherow	29.4	13.1	10.5	11.2
Old Lodge	39.7	37.9	37.5	37.4
Narrator Brook	11.7	8.7	8.3	8.3
Llyn Llagi	21.9	14.9	13.3	13.2
Llyn Cwm Mynach	13.2	9.2	9.2	10.2
Afon Hafren	19.0	13.8	12.8	12.8
Afon Gwy	18.5	12.2	11.0	11.1
Beagh's Burn	10.5	10.3	10.2	10.2
Bencrom River	14.7	8.6	7.5	7.7
Blue Lough	17.1	7.8	5.9	5.8
Coneyglen Burn	12.1	10.5	10.0	10.0

9.3.2.3. Changes in pH

Reference pH values can be estimated in two ways, using a palaeoecological approach based on a diatom-pH transfer function (Birks *et al.*, 1990) and using a MAGIC-modelling approach.

MAGIC-modelled pH changes

For consistency of comparisons, MAGIC-modelled pH changes are compared with the modelled 1860 reference values rather than using measured pH data for the start and end of the monitoring period. In general, surface water pH declines steeply from 1860 to 1970, at which time the pH at 16 sites is less than 5.5, a key threshold for protecting aquatic ecology (Newcombe, 1985). With the implementation of the CLRTAP and NECD protocols to reduce acid deposition, the number of sites falling below this critical threshold is greatly reduced to 6 by 2005-2007 according to MAGIC modelled values (Loch Grannoch 4.75, Blue Lough 4.83, Round Loch of Glenhead 5.08, Scoat Tarn 5.16, Afon Hafren 5.40 and Beagh's Burn 5.47). It is also evident that these sites are currently the most acidified, having changed most from their reference condition (Fig. 9.8; Table 9.4). The current MAGIC-modelled pH values present an optimistic picture relative to measured values, though 12 sites remain below pH 5.5 over the period 2005-07.

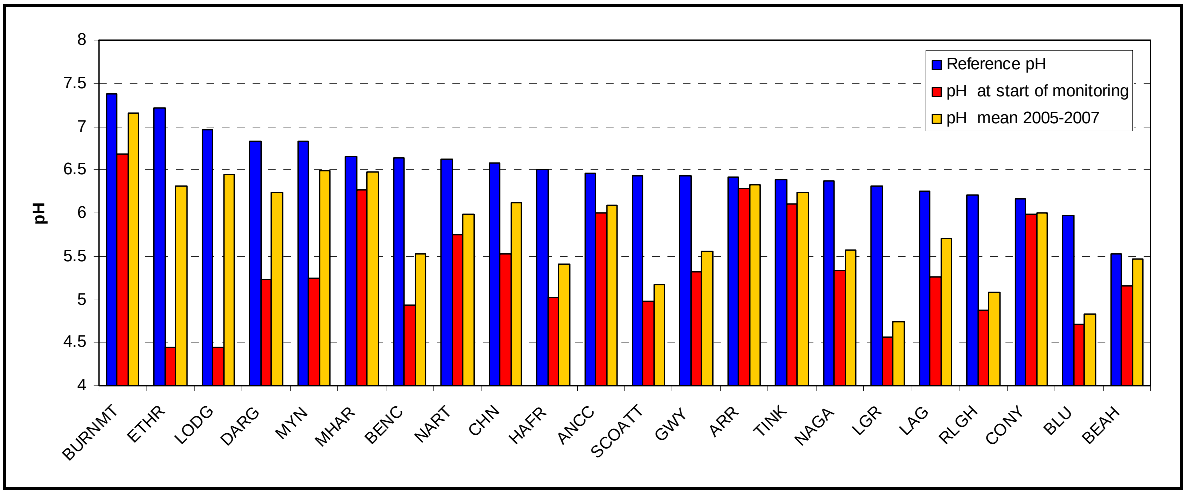


Figure 9.8: MAGIC-modelled pH values for i) reference conditions (1860), ii) at start of AWMN monitoring (3 year mean) and iii) at present (2005-07 mean)

Diatom-inferred changes in lakewater pH

We used standard methods to reconstruct lake water pH from the diatom analyses of sediment cores taken from the lake sites in the AWMN. To assess their accuracy we compared pH inferences from the diatom data collected annually in the sediment traps against the measured water column pH over an 18 year period using three different training sets (Battarbee *et al.*, 2008). Whilst the trends in pH inferred from the trap diatoms followed closely the trends in mean measured pH, there was a tendency for the diatom-inferred values to under-estimate the measured values, with the pH values generated by the SWAP training set (cf Birks *et al.*, 1990) being the most biased. However, all inference models provided a good estimate of the measured values if the standard error of the method (cf Battarbee *et al.*, 2005) of +/- ~0.3 pH units is considered. Moreover, whilst the different training sets could still be improved to provide better analogues or improve representation of some taxa (i.e. by adding more sites to correct bias in the pH gradient covered), it is unlikely that new work will make a significant difference to the results.

It is also important to allow for the inherent variability of pH in poorly buffered upland waters, on both seasonal and inter-annual time-scales. Therefore none of the estimates of pre-acidification pH generated by the different models have been rejected. Table 9.3 consequently shows reference pH values for the mean of the three different models. The diatom-inferred reference pH value for Blue Lough is 4.91. Other sites vary between 5.26 and 6.42, demonstrating the wide range of reference pH conditions between sites and illustrating the need for restoration pH (and ANC) targets to be site specific.

9.3.2.4. Comparisons between diatom and MAGIC pH

MAGIC model hindcasts to 1860 are compared with diatom-inferred pH for the reference period in Table 9.3. There is some agreement between the datasets for most sites, but on average the MAGIC hindcasts are higher than those using the palaeolimnological (diatom-inferred) method. The difference is generally most marked for the most acidified sites, although Burnmoor Tarn also shows a major discrepancy. The tendency for MAGIC to give higher values has already been highlighted (Battarbee *et al.*, 2005) and has been attributed at least in part to the way DOC is treated in MAGIC.

Table 9.3. Reference (diatom-inferred and MAGIC modelled) and present day (measured) pH and Ca ($\mu eq\ l^{-1}$) for the 11 AWMN lake sites

Site	DI-pH(1800)	MAGIC pH (1860)	pH (April 07–Mar 08)	Ca
Loch Coire nan Arr#	6.11	6.42	6.16	33.8
Lochnagar	5.61	6.38	5.49	20.9
Loch Chon	6.33	6.58	5.88	73.7
Loch Tinker	6.35	6.39	6.06	74.7
Round Loch of Glenhead	5.43	6.21	5.14	30.4
Loch Grannoch	5.26	6.32	4.68	36.1
Scoat Tarn	5.84	6.43	5.25	27.0
Burnmoor Tarn	6.42	7.39	6.71	88.1
Llyn Llagi	5.77	6.26	5.43	42.7
Llyn Cwm Mynach	5.95	6.83	5.00	60.3
Blue Lough	4.91	5.99	4.94	26.0

#Means for April 2006 – March 2007 when monitoring ceased

Uncertainties in hindcast reference pH

The known uncertainties associated with diatom-inferred pH values based on the training sets used are of the order of ±0.3 pH units. Hence the underestimated diatom-inferred reference pH values for Burnmoor Tarn and to a lesser degree Blue Lough relative to present day measured values are within the error of the method.

With MAGIC, uncertainties in reconstructing past background chemistry have generally received less attention, but are in some respects greater due to the sensitivity of background chemistry to weak acid concentrations in the absence of strong acids. Examples of probable major over-estimates of reference pH are found at Burnmoor Tarn, Blue Lough and Llyn Cwm Mynach (Table 9.3). For MAGIC, one possible explanation is that DOC concentrations in catchment soils may have been higher in the past, a condition not currently included in the model. However, not enough is known about the relationship between sulphur deposition and soil water DOC concentration for the process to be reliably incorporated at this stage. Similarly, improved information on appropriate lake pCO2 values would increase the accuracy of the model pH prediction

9.3.2.5. Summary of pH changes

Taking the datasets together the results show:

- that the most naturally acidic site is Blue Lough in the Mourne Mountains. This site has been strongly acidified but has always had a very low pH. Acidification here seems to have been marked especially by an increase in labile Al concentrations rather than a significant decrease in pH, a hypothesis supported by the decrease in labile Al that has occurred at Blue Lough over the last 20 years (see Chapter 3) as the site has started recovering;
- that some very sensitive acidified sites in areas of historically high acid deposition show only slight evidence of recovery (Round Loch of Glenhead, Scoat Tarn, Lochnagar, Loch Grannoch, Llyn Cwm Mynach);
- that one very sensitive site in an area of high acid deposition has shown significant recovery (Llyn Llagi);

that three less sensitive acidified sites (Loch Tinker, Loch Chon and Burnmoor Tarn) in areas of high deposition show evidence of some recovery; and

that one very sensitive site, Loch Coire nan Arr, used as a reference site in the Network due to its location in an area of low acid deposition has been only slightly acidified.

Overall, except for the three sites with pH values at the present day close to those during the reference period (Blue Lough, Coire nan Arr and Burnmoor Tarn) all sites exhibit very large gaps between the reference and present day values, suggesting that the recovery in pH has so far been significantly lower than expected on the basis of the reduction in acid deposition that has taken place.

9.3.2.6. Changes in diatom assemblages

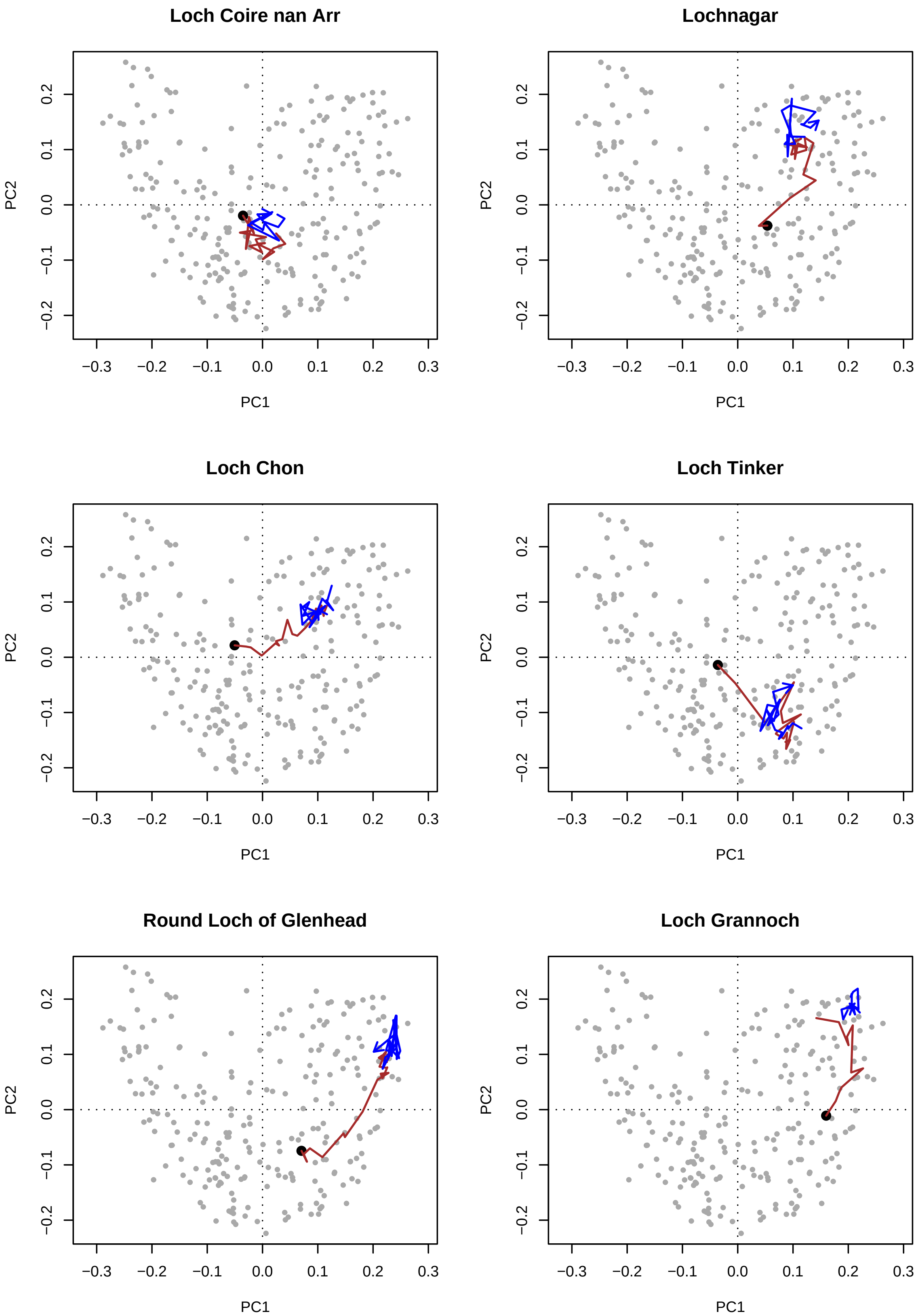
The most direct method of assessing the degree of recovery at the AWMN lake sites is a comparison between the diatom assemblages of sediment core reference samples (representing pre-acidification conditions in approximately 1800 AD), the record of diatom assemblage change through to the top of sediment cores taken in the late 1980s (representing the conditions during or slightly after the period of maximum acid deposition in the UK) and the record of diatom change from samples through to the present day (2008) taken from the sediment traps that were installed in each AWMN lake in 1991 and emptied annually since then.

By combining the data from the traps with the diatom data from sediment cores in this way it is possible to track changes in the diatom flora of each site continuously from 1800-1850 AD through to the present day using, with the exception of the switch from core sediment to trap sediment, an identical standard methodology. It has already been shown, from a study of Loch Fleet in Galloway that simple open traps, similar to those used in the AWMN, are very effective at integrating populations from contemporary living diatom communities (Cameron, 1995). This is illustrated in Figure 9.9 where in almost all cases the upper core samples plot extremely closely to the earliest trap samples in ordination space at each site.

To follow the changes in the diatom assemblages at each site we have entered the core and trap data passively into a Principal Components Analysis (PCA) of diatom assemblage data from a large dataset of 121 low alkalinity lakes from across the UK. The sites represent the full range of low alkalinity lake types found in the UK (Battarbee *et al.* in press) varying in degree of acidification, base cation status, DOC, altitude and distance from the coast. Each of the 121 sites is represented by two samples, one from the ca 1800 AD level in a core from that site and one from the surface sediment sample (= present day at the time of sampling). The diatom data from each AWMN site are thereby constrained by the range of variability in the overall dataset, and the time trajectory for each site shows the post-1850 changes in diatom assemblages caused by acidification and the post-1985-1990 changes that represent the response to emission reduction and the degree of recovery.

Overall the results (Fig. 9.9) show clear evidence of the acidification history of the sites, followed in most cases by recovery. The trajectories for each site are seen more clearly in Appendix 6. At two sites (Llyn Cwm Mynach and Loch Grannoch), both of which have catchments dominated by plantation forestry, the analysis shows no evidence of diatom recovery. Both sites still have diatom assemblages characteristic of very acid waters. At Coire nan Arr there is little difference between the diatom floras of the reference period, the period of maximum acidity and the present day. This is expected and reflects the status of Coire nan Arr as the control site in the Network, i.e. a sensitive site but in an area of relatively low acid deposition. All other sites show some evidence of recovery but, with the exception of Llyn Llagi, the extent of recovery over the last 20 years is quite limited. The gap between the present day diatom assemblage and the reference assemblage remains substantial in most sites.

Of special interest is the evidence provided by the analysis of the direction of the recovery arrow. In some cases (Loch Tinker, Loch Chon, Burnmoor Tarn), the data show that the diatoms are tracking back broadly in the direction of the reference assemblage, but in the case of Llyn Llagi, Lochnagar, the Round Loch of Glenhead and Blue Lough, the back-trajectory is deflected away from the reference direction, indicating that the current diatom assemblage in those lakes contains a different mixture of species, or a different relative abundance of species, compared with the compositional change that occurred in the lakes during the equivalent acidifying stages. Inspection of the diatom data indeed show that for Llyn Llagi, *Tabellaria flocculosa* (a species that has been observed to be increasing in the diatom epilithon of a number of AWMN lakes and streams) is now more abundant than in the past; for Lochnagar there has been a major increase in *Aulacoseria distans* var. *nivalis*, a taxon that was formerly rare in the lake; for the Round Loch of Glenhead, *Navicula leptostriata* is increasing strongly but was relatively rare in the past; and in Blue Lough *Semiorbis hemicyclus* has become the dominant diatom in the lake over the last 10 years, although it also was very rare in the past. The significance of these specific responses is not yet fully understood but may be related either to the influence of other external factors, such as climate change and nutrient enrichment from N deposition, or changes in within-lake community dynamics.


Loch Coire nan Arr
Lochnagar
Loch Chon
Loch Tinker
Round Loch of Glenhead
Loch Grannoch
PC1
PC2
−0.3 −0.2 −0.1 0.0 0.1 0.2 0.3
−0.2 −0.1 0.0 0.1 0.2

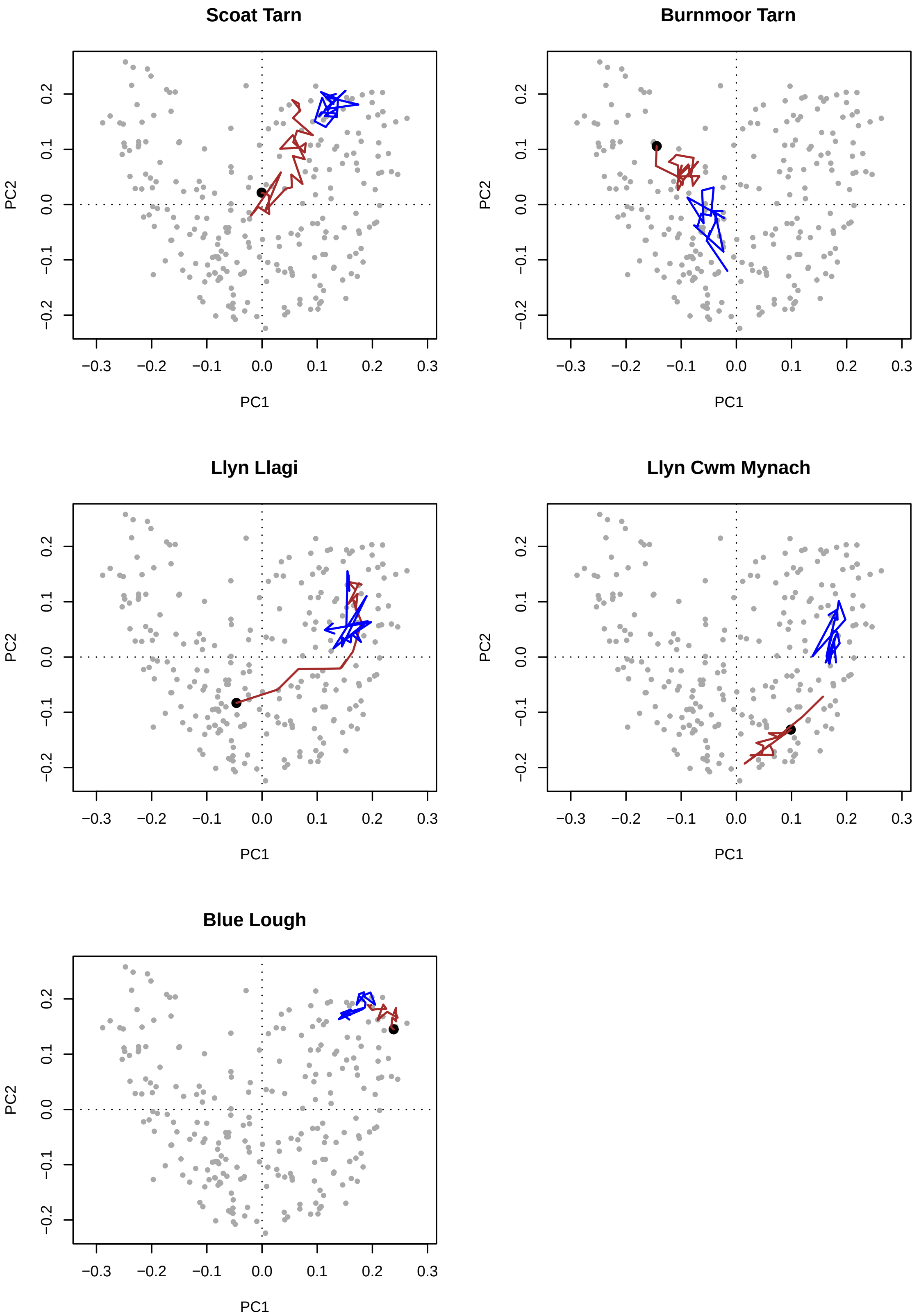


Figure 9.9: "Recovery" trajectories for diatom assemblages at 11 AWMN lakes based on differences between species composition diatom floras of the reference period through to the present day. Core data (*c.* 1800-1850 AD to *c.* 1990) are plotted in brown, sediment trap data (1990-2008) are plotted in blue. The black spot indicates the reference sample; the arrow head indicates the most recent (2008) sample.

9.4. Discussion

After 20 years of monitoring, the chemical and biological data from the AWMN are consistent in showing an improvement in water quality at all the acidified sites in the Network since the introduction of measures to reduce acid emissions in the UK in the 1980s. Here the extent of the improvement has been judged against the national critical loads target of at least 20 or 0 μeq l^{-1} ANC required to meet UNECE and EU critical loads protocols, or the more rigorous requirements of the EU WFD, related to good or high ecological status by comparison with the reference. There is a significant mismatch between the two approaches, primarily because the critical loads approach uses a fixed ANC standard across all sites rather than one site-specific reference value. Consequently for sites with relatively high natural alkalinity, e.g. Loch Chon, the 20 μeq l^{-1} target is reached easily and the site is registered as no longer exceeding the critical load, despite our evidence that biological recovery (diatoms and macroinvertebrates) is still ongoing. For sites with relatively low natural ANC, below 20 μeq l^{-1} (e.g. Blue Lough), even the less ambitious target of 0 μeq l^{-1} is unreachable and the site is registered as permanently exceeding the critical load. Such sites require special treatment in the critical loads scheme.

When judged against the reference conditions, defined using both palaeolimnological techniques and ANC hindcasting with the MAGIC model, it is apparent that the recovery so far observed, whilst significant, is also limited. There is also evidence at some sites that the recovery pathway, as illustrated by the diatom trajectory analysis, is not identical to the acidification pathway.

There are many possible reasons for the limited scale of recovery. The precise mixture probably varies significantly on a site by site basis. They include:

(i) *Inadequate reduction in acid deposition.* Although S deposition has declined to very low levels in comparison with the ca. 1980 maximum, N deposition is still relatively high and contributes a small but significant fraction of the total acid anion concentration at some sites. However, this cannot account for the limited recovery overall as the reduction in S deposition since 1987, accounting for the major proportion of acidifying anions, has been greater than 80%, while nitrate leaching is still a very small proportion of deposited N in most catchments.

(ii) *Limited or no recovery of soil base saturation.* According to MAGIC model simulations, limited recovery in the soil base cation status (base saturation) is predicted to partially offset the rate of chemical recovery of surface waters at the AWMN sites. Some sites show small increases in response to declining acid deposition while others show a continuing decline to the present day, restricting the ability of ion-exchange in catchment soils to buffer deposition inputs of acidity.

(iii) *Continued release of S from catchment soils*. Although many studies have shown that S acts conservatively in catchment soils and that reductions in deposition are rapidly followed by concomitant reductions in sulphate flux to surface waters (e.g. Cooper 2005; Davies *et al.* 2005), there is also evidence that stored 'legacy' S may continue to be released through time even after deposition is reduced to negligible levels, especially at sites with organic soils, through both oxidation and erosion processes (e.g. Daniels *et al.*, 2008). This is likely to be a particular problem at the River Etherow, where extremely high historical loads of S combine with the thick peat soils of its catchment. However, sulphate levels at many of the other AWMN sites also remain high compared to expected background values typical of those at the AWMN control sites in the North-west of Scotland (see Chapter 3).

(iv) *An offsetting increase in the release of nitrate from catchment soils*. Not only has the reduction in N deposition been small in comparison to S deposition, but at a small number of sites in the Network (e.g. Round Loch of Glenhead, Loch Chon) NO_3^- concentrations have risen, offsetting some of the effects of reduced sulphate concentrations. At many other sites (e.g. River Etherow, Scoat Tarn) NO_3^- levels remain at much higher levels than the expected background values of <5 μeq l^{-1} found in the control sites, as a result of sustained historic N deposition and soil saturation by N, leading to seasonal or all year round N leaching (cf Stoddard, 1994; Curtis *et al.*, 1998; 2005).

(v) *pH has not responded as rapidly to declining acid deposition as initially expected.* The reduction in acid anion concentrations across the Network has been balanced by a reduction in Ca^{2+} concentration, an increase in DOC, and at a number of the most acidified sites, a reduction in labile Al, and relatively little of the change in ANC to date has been expressed by pH increase. It is also now clear that the increase in DOC, once thought to be caused by climate change, is also the result of a reduction in acid deposition (Monteith *et al.,* 2007). It is possible therefore, that the overall chemical response, as indicated by the change in ANC, is indeed proportionate to the deposition reduction, but that at many sites this has not yet led to a significant increase in pH.

(vi) *The biological response has not been proportionate to the chemical change*. The biological response may be slow due to lags in re-colonisation with respect to refugial distance, dispersal strength and persistence capacity for some biological groups. This may be particularly important at stream sites where extreme acidic flow events still occur (e.g. Ormerod & Durance, 2009). However this is not borne out by the evidence presented here.

(vii) *Recovery is being confounded by other stresses.* Whereas acid deposition, especially S deposition, has been the dominant factor controlling the composition of biological communities in acidified upland surface waters, these water bodies have also have been subject to other external influences including land-use change and climate change over the last 200 years. Base cation depletion of catchment soils through acid deposition has reduced soil alkalinity, and forest growth may have contributed to this process at some sites, although the results for this effect across the network are equivocal. Small but significant changes in climate have also occurred over the last 200 years (see Chapter 10) and there appear to be small declining trends in precipitation over the monitoring period (see Chapter 2).

The future prognosis for the AWMN sites in terms of continued recovery from acidification to 2020 and beyond is discussed in Chapter 10.

9.5. Key Points

- Significant chemical and biological recovery has been observed over the period of monitoring, but most sites are still far from their reference conditions.
- There is a significant mismatch in recovery assessed relative to either the Gothenburg Protocol or more stringent WFD.
- Some sites achieving critical loads (and hence requirements of Gothenburg Protocol) may still continue to experience departures from chemical and biological reference conditions into the future.
- Recovery at some sites may be restricted by a variety of potential confounding factors, including insufficient reductions in deposition, soil base cation depletion, chemical and biological hysteresis, nitrogen saturation, climatic change and land-use changes.

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10. Recovery: the Future, Confounding Factors and Threats

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10.1. Introduction

Data from the Acid Waters Monitoring Network (AWMN) show that both chemical and biological recovery is underway at most sites. However, when judged against reference conditions for low alkalinity waters, the degree of improvement for most sites is still very modest, particularly in the context of the large reductions in S deposition in the atmosphere or SO_4^{2-} concentration in the water over the same period. The reasons for this have been discussed in Chapter 9.

In this chapter we look to the future and ask:

- Will the improvement be sustained under current legislative schemes for the reduction in acid emissions? and
- To what extent might a full recovery be prevented by other factors, such as land-use change, eutrophication from Nitrogen deposition, toxic substance contamination and climate change?

10.2. Future Trends in Acid Deposition

In this section we focus on recovery projections for the future using both the steady-state models SSWC and FAB and the dynamic model MAGIC. For the SSWC and FAB models we include all sites, both moorland and afforested, but in the case of MAGIC we only present results for the moorland sites here with the results for the afforested sites being presented in the next section, on land-use change. Comparisons between models presented in this section, however, include all sites.

10.2.1. Scenarios for S and N deposition

Reductions in sulphur (S) and nitrogen (N) emissions and deposition in the UK have been described in detail by RoTAP (in press), and Chapter 2 of this report describes the trends in bulk deposition from sites in the Acid Deposition Monitoring Network (ADMN) closest to the AWMN sites. According to RoTAP, further major reductions in deposition of S (47%) and oxidised N species (32%) will be achieved by 2020 relative to 2005, but the reduction will be much less for reduced N emissions (16%), so that reduced N will dominate total N deposition.

In looking to the future we have used deposition estimates from the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model (Singles *et al.,* 1998). Site specific deposition scenarios were used to assess the response of soils and waters to emission reductions under the current legislation (Gothenburg Protocol: Table 10.1). For the longer term projections with the MAGIC model, deposition is ramped down from present levels to the projected reductions in 2020 and held constant to 2100.

Table 10.1: Catchment area-weighted deposition (keq ha^{-1} yr^{-1}) generated from Concentration-Based Estimates of Deposition (CBED) 5x5 km data for 2004-6 and predicted by FRAME for 2020. NB Moorland deposition field includes a dry deposition correction for proportion of forest cover in catchments

	xSO_4		NOx		NHy	
	2004-06	2020	2004-06	2020	2004-06	2020
Loch Coire nan Arr	0.35	0.14	0.32	0.24	0.29	0.25
Allt a' Mharcaidh	0.25	0.12	0.34	0.24	0.27	0.25
Allt na Coire nan Con	0.39	0.16	0.38	0.28	0.35	0.29
Lochnagar	0.56	0.29	0.74	0.53	0.57	0.50
Loch Chon	0.72	0.35	0.76	0.54	0.75	0.62
Loch Tinker	0.77	0.38	0.81	0.58	0.79	0.65
Round Loch of Glenhead	0.58	0.30	0.58	0.41	0.84	0.65
Loch Grannoch	0.40	0.21	0.43	0.31	0.69	0.55
Dargall Lane	0.42	0.22	0.45	0.32	0.67	0.53
Scoat Tarn	0.53	0.30	0.66	0.47	0.91	0.73
Burnmoor Tarn	0.46	0.26	0.56	0.40	0.84	0.69
River Etherow	0.81	0.51	1.00	0.68	1.13	0.93
Old Lodge Stream	0.37	0.27	0.52	0.38	0.54	0.50
Narrator Brook	0.43	0.32	0.64	0.50	0.87	0.71
Llyn Llagi	0.45	0.29	0.52	0.38	0.68	0.58
Llyn cwm Mynach	0.38	0.22	0.44	0.33	0.60	0.51
Afon Hafren	0.45	0.27	0.54	0.40	0.72	0.61
Afon Gwy	0.45	0.27	0.54	0.40	0.72	0.61
Beaghs Burn	0.32	0.18	0.31	0.23	0.80	0.67
Bencrom River	0.45	0.25	0.50	0.37	1.29	1.13
Blue Lough	0.41	0.23	0.46	0.34	1.17	1.02
Coneyglen Burn	0.30	0.16	0.31	0.23	0.81	0.70

10.2.1.1. Steady-state model projections

Surface water SO_4^{2-} concentrations are expected to continue to decline in future in line with the reductions in S deposition that are predicted in Table 10.1. What is less certain is the extent to which surface water NO_3^- concentrations will respond to changes in N deposition. Throughout the UK there has been no clear long-term trend in N deposition while surface water NO_3^- trends appear to differ even for sites which are likely to have experienced similar deposition regimes. Because of these strong non-linearities, it is not known whether future trends in concentration will be proportionate to N deposition, either as NO_x or total N. In any case, they are likely to be smaller than reductions in xSO_4^{2-} concentrations, ensuring that NO_3^- relative to xSO_4^{2-} becomes a progressively more important potential acidifier.

Current studies under the Defra Freshwater Umbrella research programme using the dual isotope approach to determine sources of leached NO_3^- indicate that a major proportion of deposited N detected in runoff has been biologically cycled. A key, but as yet unanswered, question is whether the original N source included both oxidised and reduced N deposition, with rapid microbial turnover in soils and waters, or mostly oxidised N species which were less strongly retained in terrestrial ecosystems but still rapidly turned over in surface waters. In either case, biological cycling clearly fails to prevent NO_3^- leakage into surface waters particularly in areas of high N deposition where the soils are relatively thin, with a small carbon pool or dominated by bare rock.

Added to this is the uncertainty regarding our understanding of N saturation, exemplified by the difference between the Steady State Water Chemistry (SSWC; Henriksen *et al.*, 1992) and First Order Acidity Balance (FAB; Posch *et al.*, 1997) model exceedances for a given site. Current thinking, based partly on the stable isotope work noted above, is that NO_3^- leaching is dictated by the relative size of labile and stable N pools and is inextricably linked to the carbon cycle, and indeed to climatic fluctuations. If observed NO_3^- is all derived from the labile N pool, it may be that immobilisation in the stable pool provides a very long-term sink and may be disregarded in critical loads, suggesting that the FAB model predictions may be overly pessimistic in terms of N. Another possibility is that reduced N deposition could enter terrestrial N pools with slow turnover while oxidised N deposition more easily reaches the labile and rapidly cycled N pools in surface and groundwaters. Until these scientific problems are resolved, the SSWC and FAB models will continue to be used to provide lower and upper bounds on surface water acidification and ANC recovery (or decline).

Based on FRAME-modelled data for 2020 that uses catchment-weighted average deposition values for moorland and forest (RoTAP, in press), critical load exceedances have been calculated using two models (Fig. 10.1). FAB model exceedance indicates the worst-case where an increasing proportion of N inputs are leached. The SSWC model provides a 'best-case' exceedance as it makes no assumption that NO_3^- leaching could increase under constant N deposition, but it is not well equipped to account for changes in NO_3^- leaching in response to changing N deposition loads because it contains no mass balance for N. Hence we present two SSWC exceedance figures based on: (i) no change in NO_3^- from measured values used in critical load calculations (2004-06 mean values; see Chapter 9); and (ii) NO_3^- concentrations scaled to changes in total N deposition from 2004-06 to 2020. The latter figure allows NO_3^- to change in proportion to N deposition and hence presents the best case with respect to N of the three scenarios for most sites, where N deposition is expected to decline. Exceedance calculated for no change in NO_3^- is generally intermediate between the other scenarios.

By 2020, none of the sites in north-west Scotland shows exceedance under any scenario. The Allt a' Mharcaidh to the west of the Cairngorms also shows no exceedance, but Lochnagar in the Grampians still exceeds critical loads under all scenarios (Fig. 10.1). In the Trossachs, Loch Chon just exceeds its critical load in 2020 according to the worst-case FAB model but not the SSWC model formulations, while Loch Tinker is protected under even the worst-case FAB model. The two loch sites in Galloway (Round Loch of Glenhead and Loch Grannoch) are exceeded under all scenarios, while the stream site, Dargall Lane, is exceeded only under the worst-case FAB scenario. Of the 10 sites in Scotland (including both Coire nan Arr and its replacement Loch Coire Fionnaraich), three remain exceeded under all scenarios, while two more (Loch Chon and Dargall Lane) will be exceeded if NO_3^- leaching increases in line with FAB model predictions. Loch Chon is one of the two sites which show an increasing NO_3^- trend at present.

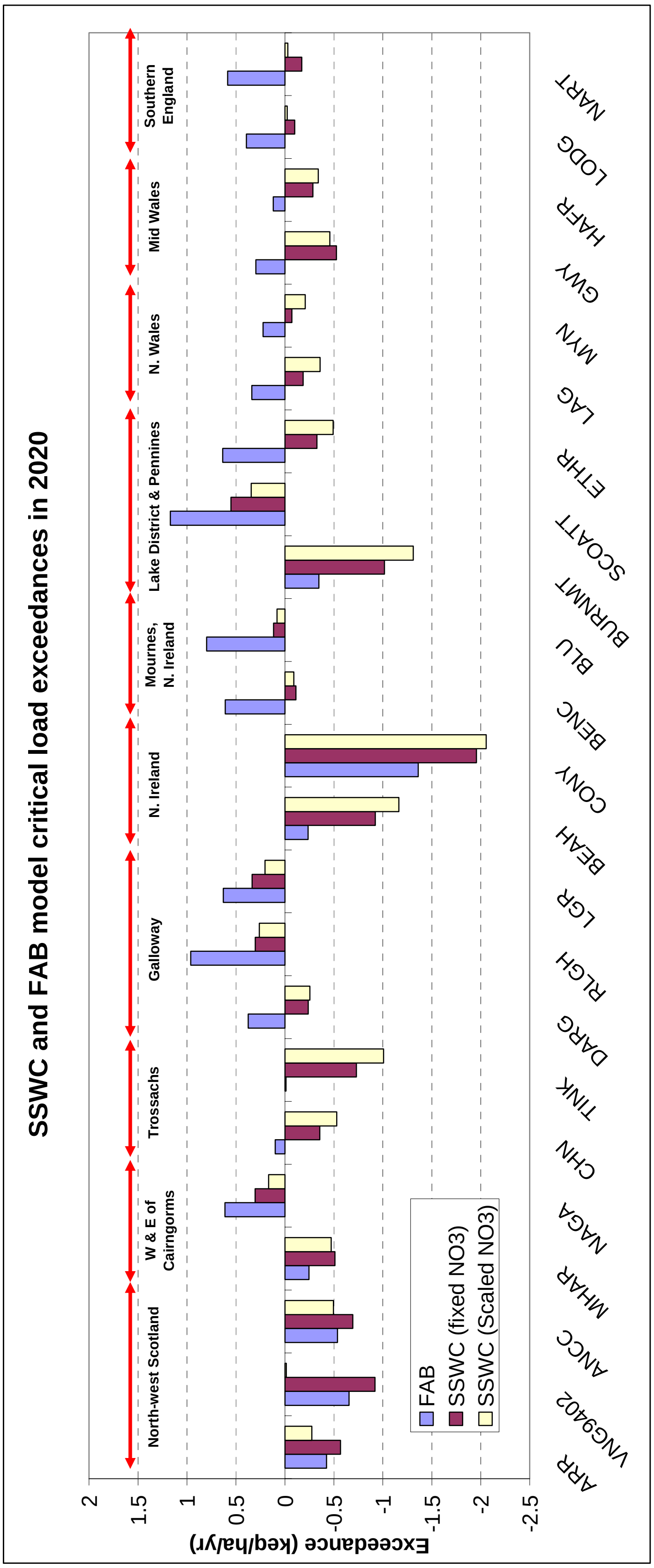

Figure 10.1: Critical load exceedances at AWMN sites in 2020 according to worst (FAB), intermediate (SSWC no change in NO_3 leaching) and best case (SSWC with NO_3^- scaled to deposition) models. For site codes see Table 1.1.

In Northern Ireland, neither Beagh's Burn nor Coneyglen Burn are exceeded under any scenario but the more sensitive sites in the Mourne Mountains are both exceeded in 2020 under the worst-case FAB model scenario. Blue Lough remains exceeded even under the best-case SSWC scenario with reduced NO_3^- leaching. In the Lake District, Scoat Tarn is exceeded under all scenarios while Burnmoor Tarn is not exceeded under even the worst case. All remaining sites in England and Wales show exceedance, but only under the worst-case FAB model.

Overall, five sites (Lochnagar, Round Loch of Glenhead, Loch Grannoch, Blue Lough, Scoat Tarn) will exceed critical loads in 2020 even under the best case critical load model assumptions. A further 10 sites will exceed critical loads if NO_3^- leaching increases to levels predicted by the FAB model. Only eight sites achieve critical loads under all scenarios.

10.2.1.2. MAGIC model projections

In contrast to steady-state models such as FAB and SSWC, MAGIC is a dynamic, process-based model that simulates soil and surface water chemistry through time. The MAGIC model embraces the N saturation concept through the inclusion of dynamic equations for N cycling and the introduction of a soil organic matter compartment that controls NO_3^- leakage from the terrestrial ecosystem to surface waters and is based conceptually on an empirical model described by Gundersen *et al.* (1998). The dynamic representation of nitrogen saturation stems from the basic concept that, through time, soil is enriched with accumulated nitrogen deposition and, in response, the soil C:N declines until a threshold is exceeded and N leaches to surface waters. The rate of nitrogen leaching depends mainly on the rate of net N input to the soil, the soil C/N ratio and the size of the soil carbon pool (Evans *et al.*, 2006). This concept has been widely tested and provides an effective indicator of soil susceptibility to N leaching. Provision is also made in the model for major processes affecting NO_3^- and NH_4^+ in soils and waters and these are incorporated either explicitly or implicitly into the model. They include atmospheric deposition, nitrification, denitrification, mineralisation, uptake by trees (and removal of biomass in managed systems), litter production, decomposition, and immobilisation into soil organic matter. In essence, MAGIC models a slow transition from the current (~SSWC) level of N leaching to the nitrogen-saturated state predicted by FAB.

MAGIC predictions for moorland sites

The non-afforested or moorland AWMN sites, most of which are either currently acidified or are sensitive to acidification, represent a consistent dataset with which to assess the likely impacts of the current legislation (Gothenburg Protocol) across the UK. Here we assess the direct effects of emission reductions on them to circumvent any potentially confounding influences of forestry on water quality. Model predictions indicate that, in general, surface water acidity will continue to improve in the next decade and beyond under the Gothenburg Protocol (Fig. 10.2). Recovery is primarily attributed to the significant decline in SO_4^{2-} concentrations from a mean of 53.9 μeq l^{-1} ($_{x}SO_4^{2-}$ 35.3 μeq l^{-1}) present day to 43.7 μeq l^{-1} ($_{x}SO_4^{2-}$ 20.6 μeq l^{-1}) in 2020, a change of 33.6% (note all sites are below the 1:1 line in Fig. 10.2a). Since most UK soils are relatively young, they have little capacity to absorb SO_4^{2-}. This effectively causes SO_4^{2-} to be in steady state with respect to the balance between input and output. Therefore projections for SO_4^{2-} in 2020 and 2100 are similar, as the S deposition scale factors were held constant between these dates. The greatest simulated absolute reductions in SO_4^{2-} concentration was at Old Lodge (35.7 μeq l^{-1}) and the River Etherow (36.3 μeq l^{-1}), the latter being in close proximity to emission sources, while the least change was predicted at more remote sites in the north-west of Scotland (Loch Coire nan Arr; 4.76 μeq l^{-1}) and in Northern Ireland' (Beagh's Burn 0.24 μeq l^{-1}). Due to the negligible xSO_4^{2-} (anthropogenic S) concentrations observed at Beagh's Burn in 2007, the long-term simulation indicates no recovery at this site. Beagh's Burn is one of the most peat-dominated sites in the Network, and deposited xSO_4^{2-} is retained by reduction and storage in organic matter. This store is however likely to be sensitive to periodic release during droughts, leading to acidic episodes, as has been observed at the Moor House Environmental Change Network (ECN) site (Adamson *et al.,* 2000).

It is clear that xSO_4^{2-} remains the dominant anion throughout the forecast simulation. This result emphasises the importance of achieving the agreed S emission reductions to promote chemical recovery from acidification in the next decade. In general, reductions in xSO_4^{2-} led to an improvement in Acid Neutralising Capacity (ANC) which, as expected, is most marked at sites with the lowest ANC (<50 μeq l^{-1}; Fig. 10.2b). There are two underlying factors responsible for the differences between predicted ANC in 2020 and 2100, enhanced NO_3^- leaching (Fig. 10.2c) and the significant differences in the weathering rate of parent material between sites which contribute base cations to surface waters. Overall ANC recovery is projected to continue along the same trajectory from 2007 to 2020, with a clear increase at all non-afforested sites. The projected change in pH from 2007 to 2020 also reflects varying degrees of recovery across the sites. With the exception of Blue Lough, which shows no improvement in surface water acidity, all non-afforested sites with a present day pH <6 demonstrate significant recovery from acidification (specifically Scoat Tarn, Afon Gwy, Lochnagar, and Bencrom River). These are also the sites that show the greatest longer term simulated increase in pH by 2100 (Fig. 10.2d).

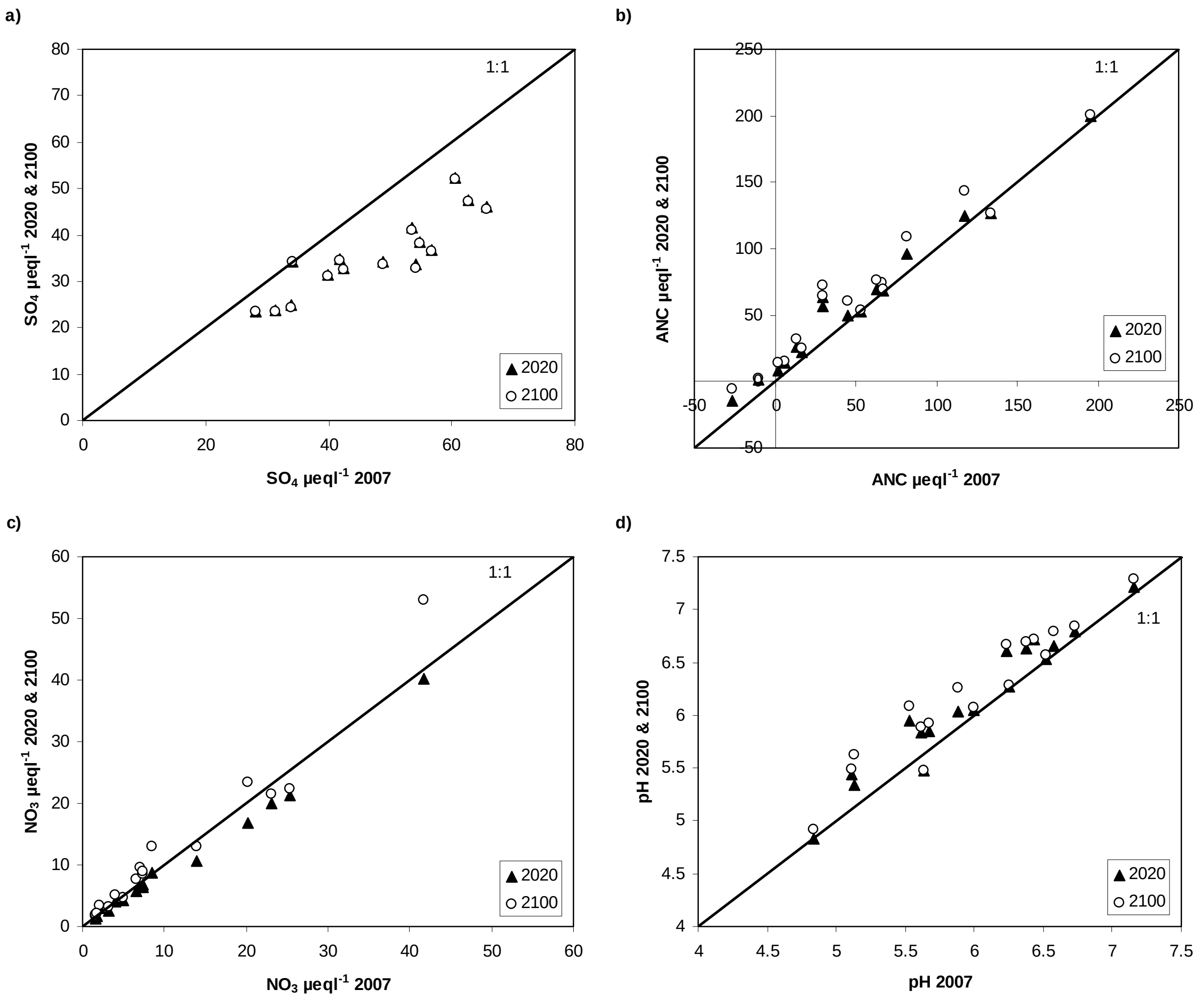

Figure 10.2. MAGIC-predicted change at the non-afforested sites for 2007-2020 (closed triangles) and 2007-2100 (open circles) in surface water a) SO_4^{2-}, b) ANC, c) NO_3^- and d) pH.

The speed of change in surface water ANC, both in terms of acidification and recovery, lies not only in the magnitude of change in S and N deposition, but also in the magnitude of change in soil characteristics and weathering rates. The key process for neutralising acid inputs is the exchange of base cations from soils. This store of exchangeable cations is, in turn, mainly replenished by base cations supplied by weathering of soil minerals. The pool of exchangeable base cations can therefore only start to recover when the S and N deposition decreases to below the weathering rate. A negligible improvement in soil base saturation is predicted between 2007 and 2020, despite emission reductions (Fig. 10.3). Over such a short period this result is expected as soils respond slowly to changes in acid deposition. In the longer term (2007-2100), soil base saturation across the non-afforested sites is predicted to increase by an average of 1.2% (from 11.1% saturation in 2007 to 12.3% saturation in 2100). This implies that acid deposition inputs at this time have decreased below the rate of base cation supply from weathering.

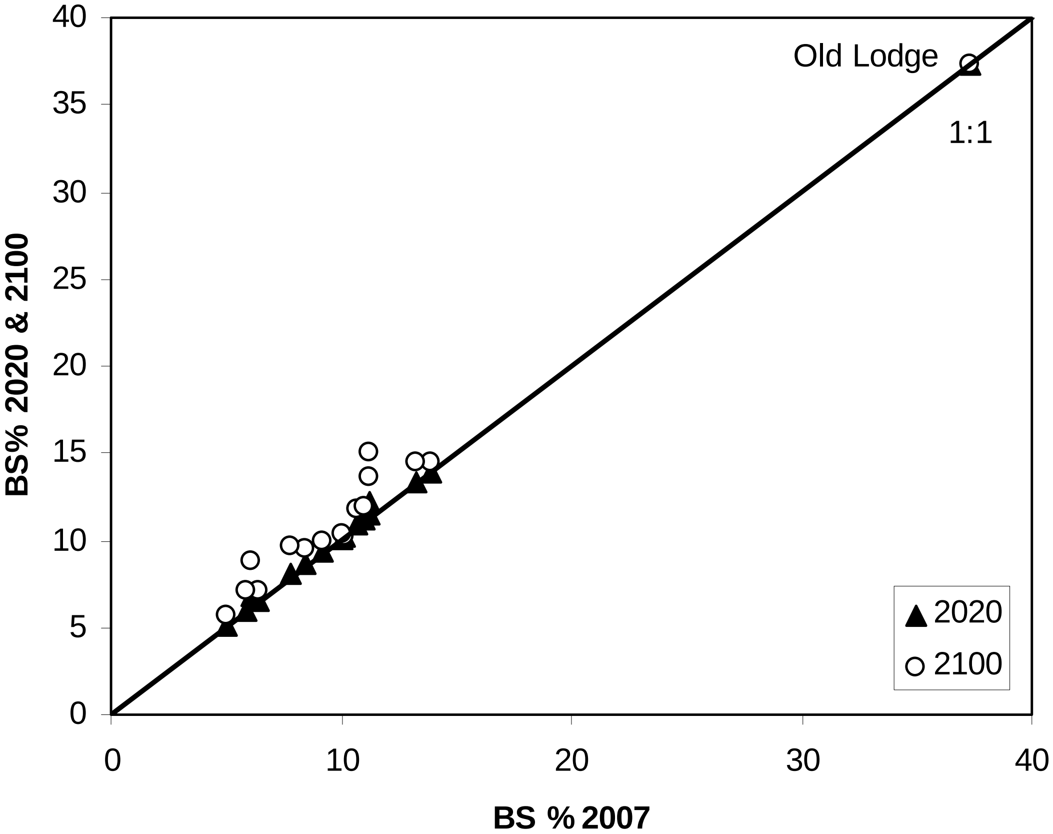

Figure 10.3. MAGIC-predicted change at the non-afforested sites for 2007-2020 (closed triangles) and 2007-2100 (open circles) for soil base saturation.

10.2.1.3. Model comparisons – all sites

While the focus of the MAGIC modelling above is on non-afforested sites, to allow a full comparison of modelled output from the FAB and SSWC models, the following section includes simulated results from both afforested and non-afforested sites. Details of the impact of forestry on soil and water quality are described in detail in the next section. The extent to which MAGIC predicts a reduction in the number of sites exceeding the critical ANC threshold of 20 μeq l^{-1} is shown in Table 10.2, in comparison with output from the SSWC and FAB models. Note that while this is a useful exercise in comparing independent model outputs, the static and dynamic models are not strictly comparable because critical loads are not associated with a timescale, whereas MAGIC predicts ANC for any specified year. Hence it is most instructive to compare critical load exceedances (using SSWC or FAB) with MAGIC predictions where the critical ANC limit (generally 20 μeq l^{-1}), used in critical load models, is not reached.

The eight sites that currently have an ANC <20 μeq l^{-1} are widely distributed throughout the UK and include Blue Lough (-26 μeq l^{-1}), Loch Grannoch (-32 μeq l^{-1}), Scoat Tarn (-10 μeq l^{-1}), Round Loch of Glenhead (2 μeq l^{-1}), Lochnagar (6 μeq l^{-1}), Afon Hafren (10 μeq l^{-1}), Afon Gwy (13 μeq l^{-1}) and Llyn Llagi (17 μeq l^{-1}). According to MAGIC, by 2020 five sites will still remain below the threshold: Loch Grannoch (-17 μeq l^{-1}), Blue Lough (-15 μeq l^{-1}), Scoat Tarn (2 μeq l^{-1}), Round Loch of Glenhead (8 μeq l^{-1}) and Lochnagar (14 μeq l^{-1}). Simulations to 2100 show a marginal recovery in water quality from 2020. However, in 2100 emission reductions are predicted to be insufficient to protect Blue Lough (-5 μeq l^{-1}), Loch Grannoch (-3 μeq l^{-1}), Scoat Tarn (2 μeq l^{-1}), Round Loch of Glenhead (14 μeq l^{-1}) and Lochnagar (15 μeq l^{-1}) from exceeding their critical limit. These results suggest that under current and predicted reductions in acid deposition, some sites will fail to reach the required critical limit for ANC considered necessary to protect aquatic ecosystems.

The release of NO_3^- from soils to surface waters is predicted by MAGIC to confound the rate of chemical recovery at the non-afforested AWMN sites. As N deposition continues in the future and the soil pool of N becomes enriched relative to available carbon (C), the model predicts that immobilisation of atmospheric N will continue to 2020 with a reduction in NO_3^- in runoff from a present day mean of 10.6 μeq l^{-1} to 9.5 μeq l^{-1} by 2020. However, in the longer term (2100) NO_3^- leaching is forecast to increase from current concentrations to reach 11.9 μeq l^{-1} (Fig. 10.2c). Figure 10.4 demonstrates the important contribution of NO_3^- to the total acid status of surface waters from the 1970s to 2100. In light of reductions in S deposition during this time, the predicted increasing trend of NO_3^- confounds the rate of recovery at most AWMN sites to varying degrees. However for three sites this contribution of NO_3^- has potentially more serious implications for the recovery of water quality. Constant N deposition was simulated with MAGIC between 2007 and 2100. However, the contribution of NO_3^- to total acidity increased at 12 sites during this period. Sites where the amount of N leaching was predicted to increase in 2100 relative to 2007 include Dargall Lane (34%), Round Loch of Glenhead (26%), Narrator Brook (24%) and River Etherow (21%). In 2020 the majority of sites immobilised most of the deposited N through plant and soil uptake; two sites in Scotland (Coire nan Arr, 33% and Dargall Lane, 2%) and one site in the south west of England (Narrator Brook, 4.3%) were predicted to show signs of increased NO_3^- leaching to surface waters at this time. Since the critical ANC threshold of these sites is not exceeded, this increase in NO_3^- does not in theory pose an acidifying threat to the aquatic biology of these systems, although it may cause a nutrient loading threat (see below). This is based on the assumption in the critical loads approach that there are no harmful effects if ANC is maintained above the critical limit. However, this limit is considerably below reference values for these sites (see Chapter 9).

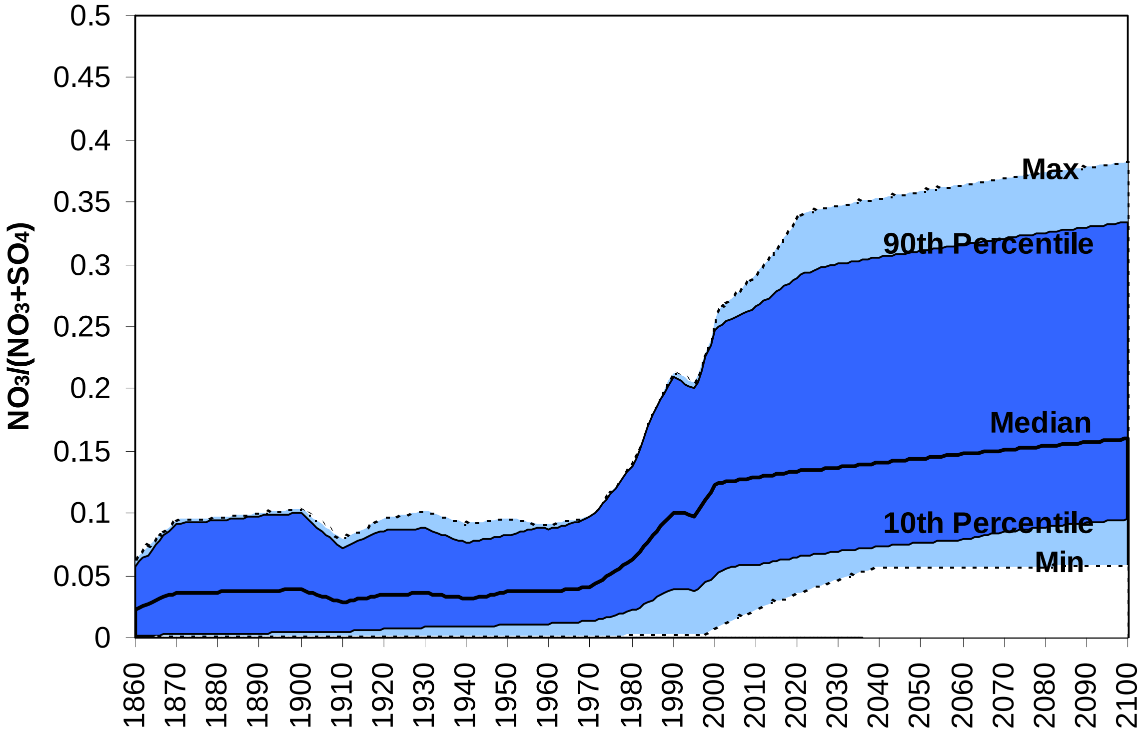

Figure 10.4. Multiplot of NO_3^- as a proportion of total acidity for all AWMN sites

Model comparison

A comparison of model results between FAB, SSWC and MAGIC (Table 10.2) shows that FAB predicts more acidic conditions compared to the SSWC and MAGIC models for 2020 deposition levels. Under the worse-case scenario, as predicted by the FAB model, 15 sites are predicted to have long-term ANC <20 µeq l^{-1}. The SSWC (fixed and scaled NO_3^-) and MAGIC model predicted significantly fewer sites exceeding the critical load, although there is commonality between models with the same five sites showing critical load exceedance in 2020 (Lochnagar, Round Loch of Glenhead, Loch Grannoch, Blue Lough, Scoat Tarn). In addition all models predict that Blue Lough will remain below the <0 µeq l^{-1} ANC threshold at 2020 deposition levels. In this context, when comparing critical load exceedance between the three approaches for 2020 deposition levels, it can be concluded that MAGIC and SSWC represents overall 'best case' predictions compared with the 'worst case' predictions from FAB. Longer term MAGIC predictions show a slight improvement in water quality to 2100 under constant 2020 deposition levels, but with the same five sites breaching the ANC < 20 µeq l^{-1} threshold. The contribution of leached NO_3^- to surface waters had a negligible acidifying effect on the ANC because a concurrent increase in the base cation concentration in surface water buffered against this increase in NO_3^- resulting in no change in the number of sites exceeding the critical load between 2020 and 2100. In this respect, increased NO_3^- leaching is delaying recovery in ANC rather than causing a re-acidification.

Table 10.2. Number of sites below ANC critical thresholds (long-term loads for SSWC and FAB critical ANC values for MAGIC) in response to the Gothenburg Protocol for present day, 2020, and 2100.

	2007	2020	2020	2020	2020	2100
	Present	MAGIC	FAB	SSWC – fixed NO_3	SSWC – scaled NO_3	MAGIC
ANC<0	3	2	10	3	1	2
ANC<20	8	5	15	5	5	5

These different outcomes reflect inherent differences in assumptions between models. Since FAB and the SSWC are steady-state models, they take no account of time lags in the response of surface water concentrations to changes in deposition load, whether for S, N, non-marine chloride or base cations. A projected critical load exceedance for a given date, e.g. 2020, does not therefore imply that damage will occur on that date. It indicates only that the forecast deposition levels are not sustainable in the long-term if ANC is to be maintained above the critical value. In this respect, hysteresis or time lags are irrelevant for FAB because the mass-balance is based on long-term steady-state conditions once they have been established. However, MAGIC explicitly accounts for the timing of changes in key chemical processes that are directly driven by acid deposition and impact on soil and surface water chemistry. For example, the dynamics of S released from the soil is an important factor that influences the rate of recovery of soils and surface waters from acidification. Desorption of SO_4^{2-} involves release of acidity in nearly stoichiometric proportion (Gustafsson, 1995). Soils with large amounts of adsorbed SO_4^{2-} might, therefore, remain acidified for years or even decades after a substantial decrease in S deposition (Beier *et al*., 1995). This release of organically bound S from the soils might potentially prolong the lag in recovery in soils and surface water for decades (Daniels *et al*., 2008).

In the projections for critical load exceedance presented in Table 10.2, the main difference between the steady-state FAB model and the dynamic MAGIC model lies in the lack of time-scale for N saturation and enhanced leaching associated with FAB. The 'worst-case' predictions of FAB are for the long time-scale over which this condition will be reached for some sites, and indeed the declining status of some sites by 2100 partly reflects this. The major differences in the role of NO_3^- predicted for 2020 and beyond by FAB and MAGIC reflect gaps in our understanding of the short-term dynamics of NO_3^- leaching. While the worst-case predictions of FAB may be overly pessimistic, at least over the next few decades, the representation of NO_3^- leaching dynamics in MAGIC does not explain very variable concentrations over the last 20 years at many sites which have been attributed to climatic and other factors. These issues are discussed below (see also Chapter 9).

10.2.2.Policy relevance and recommendations

The projections for recovery described above have several implications for policy, especially as regards their uncertainty and the difference between models.

First, it is important to be aware of the different targets for recovery used by the principal relevant United Nations Economic Commission for Europe (UNECE) protocols and EU directives. The target used in the UK under the UNECE protocols is a minimum ANC of 20 $\mu eq\ l^{-1}$. For most sites this is substantially less than their reference ANC, and we have observed biological recovery in sites where ANC was always greater than 20 $\mu eq\ l^{-1}$.the value selected, however, is deemed to provide an acceptable risk of damage to fish populations, allowing for occasional acid episodes. For a few sites, such as Blue Lough in the AWMN, the value of 20 is not attainable, as this is a naturally very acidic lake with a modelled reference ANC slightly below 20 μeq l^{-1} (Table 9.1), and for critical loads modelling a target ANC of 0 μeq l^{-1} is used. A better ecological target might be that contained in the EU Water Framework Directive (WFD) that allows only a small deviation from the reference value. On these grounds, achieving "good ecological status" under the WFD is considerably more difficult for the strongly acidified sites than achieving a reduction in critical load exceedance under the Gothenburg Protocol. Naturally acidic sites like Blue Lough are so sensitive to acid deposition that very low deposition targets would be required to prevent more than a small deviation from reference ANC.

Second, model projections do not allow for inter-annual variability. MAGIC represents biogeochemical processes on an annual time-step and time-series predictions must be interpreted with regard to the observed variation in annual mean chemistry. However, the model simulations into the future are driven by a 'smoothed' deposition trajectory and so do not reflect the variation in annual deposition that has been observed for example between 1988 and 2007, the period of monitoring. Since much of this variation in annual deposition reflects changes in rainfall totals, it is likely the future trajectory of water quality change will show similar inter-annual variability. The relationship between variability in deposition flux and variability in mean surface water chemistry is unlikely to be linear but it is not known how the variation about the long-term mean will change as the sites recover from acidification.

And third, there is a need to be aware of the differences between models and the roles of different models in addressing policy questions. So far the concept of "good ecological status" has not yet been adequately defined to enable the reduction in acid deposition needed for recovery to be quantified and modelled. The steady-state and dynamic models described above are used only to project recovery as defined by the Gothenburg Protocol. They provide an assessment of how effective current policies under the protocol might be in reducing critical load exceedances, with ANC 20 ueq l^{-1} (or 0 ueq l^{-1}) as the critical limit, at 2020 (all models) and 2100 (MAGIC) projected deposition of acidity. As discussed above, MAGIC and SSWC give a more optimistic projection of the 2020 scenario than FAB. We do not favour one of these models over the other. At steady state, the models will converge because the long-term sinks for nitrogen are the same. MAGIC, however, predicts that most sites will not reach such a steady state for more than a century. On this basis, with respect to a given ANC, MAGIC can be regarded as providing the best estimate of future water quality at a defined point in time, whereas FAB provides the best measure of the deposition reductions needed to protect water quality sustainably over the long-term. As such both models need to be used together, but with caution.

The difficulty is not with the use of different models but the extent to which the future behaviour of nitrogen in catchment soils can be predicted. MAGIC uses a relationship between N leaching and the C/N ratio in soils that has been proven mainly in experimental manipulations, while the size of the nitrogen sinks assumed in the FAB model are based on present day estimates that may not be valid for the future. Improving our understanding of nitrogen and carbon dynamics in this context, and in the context of changing land-use and climate patterns, remains the most important area of further research if the predictability of models is to be improved. As pointed out above, recent research using stable isotope techniques may lead to a revision of our concepts of reactive and stable C and N pools and hence the timescales required to reach N saturation. Critically the model uncertainties also underline the need to continue monitoring N in soil and surface waters over the long-term.

As sites begin to recover it is becoming increasingly important, especially in the context of the Water Framework Directive, to define better the extent to which the ecological status of acidified lakes will improve under current legislation. The evidence we have so far suggests that the most acidified sites will remain in "poor" condition for a very long time, despite the improvements that are taking place. An urgent research need therefore is to improve our understanding of reference conditions at all sites, using both palaeoecological and spatial analogue (i.e. using acid-sensitive sites in low deposition areas) techniques, and to develop improved methods of defining the "good/moderate" conditions and other boundaries used by national agencies in their implementation of the WFD.

10.3. Future Changes in Land-Use

Forestry is acknowledged to be a contributing factor to the acidification of surface waters in acid sensitive parts of the UK. Studies of adjacent streams with afforested and moorland catchments in the 1980s indicated that streams with afforested catchments were more acidic and had poorer fish populations than sites with moorland catchments (Harriman and Morrison 1982). Later research showed that the main mechanism was enhanced interception of acidic sulphur and nitrogen pollutants from the atmosphere by aerodynamically-rough forest canopies (Forestry Commission, 2003). An additional, but in general less important, mechanism (Department of Environment and Forestry Commission 1991) is the loss of neutralising capacity in forest soils as a result of base cation uptake and the removal of base cations by harvesting. The influence of forestry on water quality therefore depends not only on trends in acid deposition but also on the stage of the forest cycle from planting and growth to felling and re-planting.

Here we describe future planting policy in the catchments of the five sites and consider, using MAGIC model projections, how the combined effects of future forestry and acid deposition policies might influence their recovery from acidification.

10.3.1.Forestry policy

The Forestry Commission has adopted the critical loads approach (SSWC model) in the identification of freshwaters at risk of acidification in order to inform decision making with respect to forest plans. All new forest planting and restocking within, or adjacent to, exceeded areas require an assessment of the susceptibility of local waters to a forest scavenging effect before plans are approved.

The procedure for undertaking catchment-based assessments is set out in The Forestry Commission's "Forests & Water Guidelines (Fourth Edition)" (Forestry Commission, 2003). Factors considered include the nature of the underlying geology, the size and species mix of a planting scheme, the age distribution, altitude and proportion of forestry already in the catchment and the sensitivity of local water uses. Where these exceed certain conditions or defined thresholds, the principal watercourse draining the area proposed for new woodland or restocking is sampled at high flow and the freshwater critical load calculated. If the total acid deposition exceeds the critical load, approval of a planting grant or restocking plan is unlikely until there are further reductions in pollutant emissions, or in the case of restocking, the area of closed canopy, conifer forest above 300 m elevation is reduced to <30% of the catchment (altitude limit does not apply within Special Areas of Conservation).

Wider forestry policy is helping to address the acidification issue and promote recovery by driving improvements to the design and diversity of upland conifer plantations. Sustainable forest management is resulting in major restructuring of plantations, involving a shift from forests dominated by single species, even-aged stands to more diverse forests with greater open space, a higher proportion of native broadleaves, an increased variety of conifer species, and a broader range of tree age. The net effect of these changes is to reduce the area of conifer forest, usually the higher altitude stands, and lower the proportion of closed canopy forest at any given time, which can be expected to decrease the overall scavenging effect and thus the additional acidification pressure exerted by forestry. Another benefit results from the opening up of stream sides and the creation of native riparian woodland buffer zones. The removal of heavy shading cast by bank side conifers has been shown to improve freshwater and riparian habitats, and increase fish numbers where water quality is suitable (Broadmeadow & Nisbet, 2002).

Forest plans are a set of maps and documents that outline the felling, thinning and restocking work to be carried out over a period of 20 years or more. They are reviewed at regular intervals and subject to a period of consultation and application for approval by the Forestry Commission. All public sector owned forests and most large private forests are covered by a forest plan. The plans for the five sites described here are shown in Appendix 8.

10.3.2.Forestry plans for the AWMN afforested catchments

Details of the plans for five of the six afforested sites in the AWMN are described below. The forests in four of the sites are managed by the Forestry Commission while a fifth (Llyn Cwm Mynach) is now owned by the Woodland Trust. We have no forest plan available for the sixth site (Coneyglen Burn).

10.3.2.1. Allt na Coire nan Con

In 1988, approximately 48% of the catchment was covered by Glenhurich Forest, which is managed by the Forestry Commission’s Lochaber Forest District. The forest is dominated by Sitka spruce (*Picea sitchensis*) and Lodgepole pine (*Pinus contorta*) planted in the early 1920s and 1930s. Felling in recent decades reduced the proportion of conifer forest to 35% of the catchment by 2007 and the Forest Design Plan expects this trend to continue until it reaches a level of around 20% by 2050 (Table 10.3, Appendix 8 Figures 1 and 2). The reduction in conifer cover involves part conversion to open space, mainly through a lowering of the tree line to reduce pollutant scavenging and improve landscaping, and a larger scale change to broadleaved woodland. The latter is targeted to riparian buffer zones in an effort to protect water quality and enhance biological recovery. Native broadleaves will be established over 75% of the riparian corridor through natural regeneration, supplemented by planting where necessary.

Table 10.3. Forestry plans for Allt na Coire nan Con

Year	Proportion of catchment area (%)				
	Open	Felled	Broadleaved	Conifer	Immature Conifer
2007	64	0	1	35	0
2015	64	1	1	34	0
2050	58	1	21	19	1

10.3.2.2. Loch Chon

The Loch Chon catchment forms part of Loch Ard Forest, which is managed by the Forestry Commission's Cowal and Trossachs Forest District. The current Forest Design Plan was introduced in 2001 and only extends to 2011, when it will be reviewed and a longer-term plan agreed. It is expected that the focus of the new plan will be to create a riparian woodland habitat network involving the conversion of conifer stands to native broadleaves within a minimum 20 m wide buffer zone along either side of all permanent watercourses (Table 10.4, Appendix 8 Figures 3 and 4). The upper tree line will be reduced below the 300 m contour, increasing the proportion of open space from 40% in the 1980s to 57% by 2050. Overall conifer cover will decline from an initial 53% to 21%.

Table 10.4. Forestry plans for Loch Chon

Year	Proportion of catchment area (%)					
	Open	Felled	Broadleaved	Conifer	Immature Conifer	Water
2007	53	2	8	25	5	7
2050	57	1	14	21	0	7

10.3.2.3. Loch Grannoch

The Loch Grannoch catchment comprises two forests, Round Fell on the west side and Fleet Basin to the east, both of which lie within the Forestry Commission's Galloway Forest District. Each forest has its own design plan, with both seeking to lower the tree line below 300 m, partly to reduce the pollutant scavenging effect but also to improve foraging habitat for raptors. Significant areas of native broadleaved woodland will be planted to form riparian buffer zones along the main inflowing streams. The net effect of these changes will be to reduce the proportion of conifer cover from 64% in the 1980s to 29% by 2050 (Table 10.5, Appendix 8 Figures 5 and 6).

Table 10.5. Forestry plans for Loch Grannoch

Year	Proportion of catchment area (%)					
	Open	Felled	Broadleaved	Conifer	Immature Conifer	Water
2007	47	0	0	43	0	10
2015	40	12	0	33	5	10
2050	53	4	4	27	2	10

10.3.2.4. Llyn Cwm Mynach

The Llyn Cwm Mynach catchment forms part of Blaen Cwm Mynach Forest, which was privately owned until its recent purchase by the Woodland Trust. The Trust has yet to prepare a forest plan but its long-term vision is to gradually transform the present conifer forest to predominantly native broadleaf woodland. This will take many decades and in the interim, some of the conifer crop will be converted to continuous cover stands. There is also likely to be a lowering of the tree line with conversion back to former heathland. The proportion of conifer forest is expected to be reduced from 53% in the 1980s to 30% by 2050 (Table 10.6, Appendix 8 Figures 7 and 8).

Table 10.6. Forestry plans for Llyn Cwm Mynach

Year	**Proportion of catchment area (%)**			
	Open	Broadleaf	Conifer	Water
2007	48	0	47	5
2015	52	3	40	5
2050	54	11	30	5

10.3.2.5. Afon Hafren

Hafren Forest lies within the Forestry Commission's Coed y Gororau Forest District and the present design plan is due to be reviewed in 2010. The proportion of conifer cover is expected to continue to decline through time, mainly involving the creation of 100-150 m wide native riparian woodland buffer zones along the two main watercourses. This will reduce the overall conifer cover from 49% in the 1980s to 32% by 2050 (Table 10.7, Appendix 8 Figures 9 and 10).

Table 10.7. Forestry plans for Afon Hafren

Year	**Proportion of catchment area (%)**				
	Open	Felled	Broadleaf	Conifer	Immature Conifer
2007	54	0	2	35	9
2015	56	0	2	40	2
2050	59	0	9	31	1

10.3.3. Projected changes in the soil and water chemistry of the afforested AWMN sites

The combined effects of future forestry and deposition on water quality were evaluated using MAGIC. Forest re-design had already led to a reduction in conifer forest cover from that originally planted and further reductions are planned over the next 40 years at the five sites (by approximately 13% across sites); the reduction involves conversion to open land and planting of broadleaved species (with a focus on riparian zones) (Table 10.3–10.7). It is well established that decreased canopy cover will result in decreased atmospheric scavenging and consequently reduced total deposition to the forests, and increased catchment runoff (soil percolation). Furthermore, the reduction in merchantable timber will result in a decrease in the removal of base cations through forest harvesting. These processes have been incorporated in MAGIC assuming that the reduction in the proportion of coniferous species will result in a proportional reduction in dry deposition of anthropogenic air pollutants. Similarly a proportional increase in catchment runoff was assumed given the overall reduction in forest cover and the reduction in the proportion of conifer species. It was also assumed that native broadleaved species would not result in a long-term net removal of base cations as they are to be mainly planted as non-productive stands along riparian buffer zones (see Table 10.8).

Table 10.8. Reductions in coniferous forest cover (%) relative to 2007, dry deposition factors (DDF), increased catchment runoff relative to 2007 in 2015 and 2050 used to generate forecast sequences for Allt na Coire nan Con (ANCC), Loch Chon (CHN), Loch Grannoch (LGR), Llyn Cwm Mynach (MYN) and Afon Hafren (HAFR).

	Year	ANCC	CHN	LGR	MYN	HAFR
Forest cover (% red.)	2015	1	0	5	7	2
Forest cover (% red.)	2050	15	9	14	17	12
Sulphate (DDF)	2015	1.15	1.13	1.16	1.17	1.18
Sulphate (DDF)	2050	1.09	1.09	1.12	1.13	1.14
Nitrate (DDF)	2015	1.40	1.36	1.45	1.47	1.50
Nitrate (DDF)	2050	1.24	1.25	1.34	1.36	1.38
Ammonium (DDF)	2015	1.19	1.17	1.21	1.23	1.24
Ammonium (DDF)	2050	1.11	1.12	1.16	1.17	1.18
Runoff (2007 factor)	2015	1.00	1.00	1.01	1.02	1.01
Runoff (2007 factor)	2050	1.04	1.02	1.04	1.04	1.03

10.3.3.1. Comparison of modelled responses between afforested and non-afforested sites

Compared to the non-afforested sites there is no apparent evidence that afforested sites are more acid, or indeed that the combined future projections of deposition and land management will significantly alter the path to recovery. Whilst Loch Grannoch is clearly the most acidified site in the Network with a simulated present day ANC of -32.29 µeq l^{-1}, this partly reflects its more acid-sensitive status, with a lower reference ANC of 25 µeq l^{-1}. The ANC levels at the other four afforested sites are currently within the range of moorland sites in the Network. Serious calibration issues were encountered at Llyn Cwm Mynach (Fig. 9.1) and therefore all references to future simulations regarding this site should be regarded with caution.

The surface water NO_3^- signal is unclear at the afforested sites from 2007 to 2020. However a reduction at some sites was apparent in 2100. The longer term (2100) forecast at Llyn Cwm Mynach indicates increased concentrations of NO_3^- relative to 2007 and 2020. While we have little confidence in the modelled results at this site, it is likely that given the observed increasing trend in NO_3^- concentrations (Fig. 9.1), these longer term predictions for NO_3^- are credible. Due to the poor calibration at Llyn Cwm Mynach it is clear however, that other processes, possibly relating to organic acids, are not adequately represented in the current model application and further work is necessary. As with ANC, NO_3^- concentrations at the afforested sites are within the range of those simulated for moorland sites. A recovery in surface water pH was forecast for the forestry sites with the greatest projected increase at the most acid sites. These general improvements in water quality reflect changes in soil base saturation, which increases significantly by 2100.'

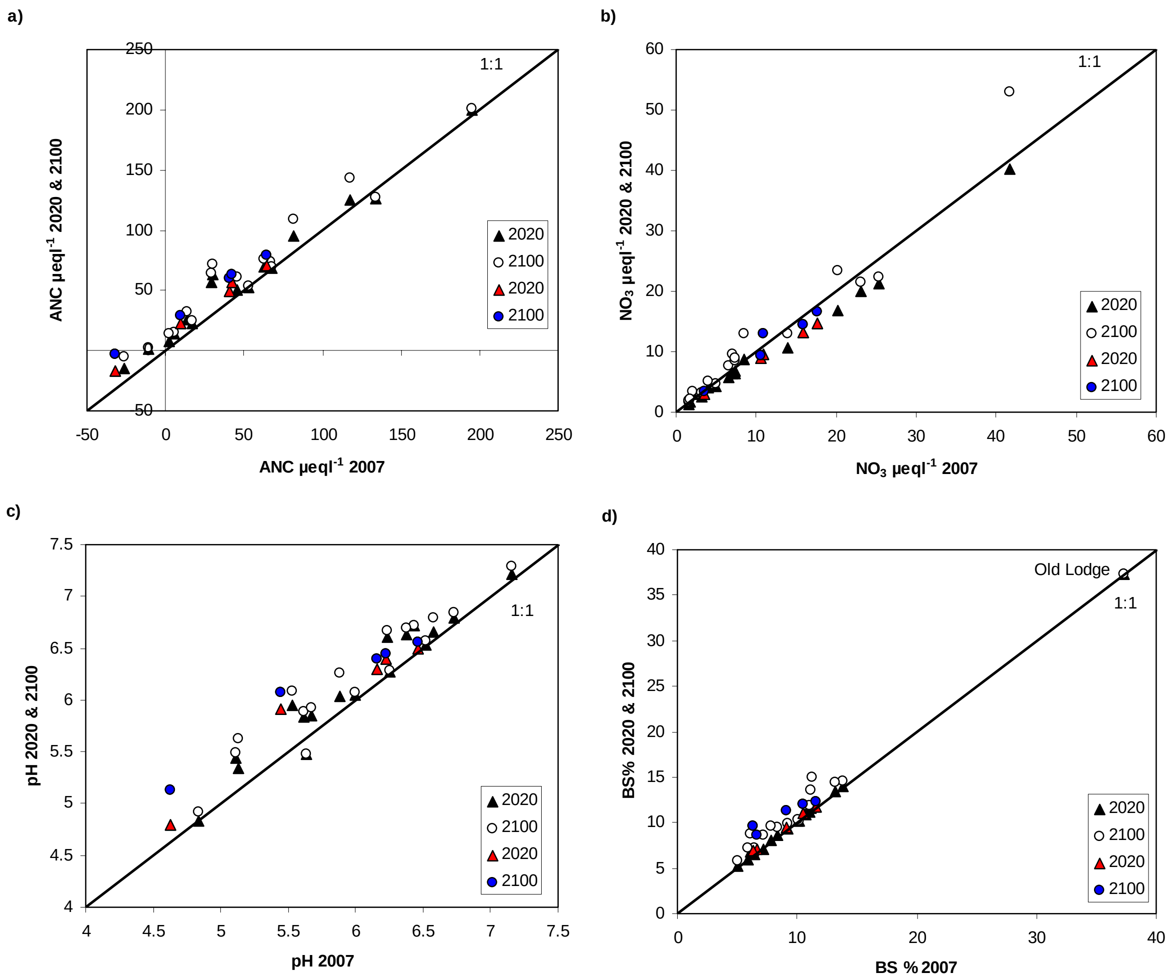

Figure 10.5. MAGIC simulated change at the non-afforested sites for 2007–2020 (black closed triangles) and 2007–2100 (black open circles)and afforested sites for 2007-2020 (red triangle)and 2007-2100 (blue circle) in surface water a) ANC, b) NO_3^- c) pH, and d) soil base saturation.

10.3.3.2. Temporal trends in soil and water quality

All afforested sites show decreased concentrations in surface water SO_4^{2-} concentration, slight changes in NO_3^-, increased pH, ANC and soil base saturation and decreased aluminum (Al^{3+}) concentrations in surface water under the combined effects of future forestry plans and acid deposition reductions (Table 10.9). The simulated decrease in SO_4^{2-} is caused by reductions in atmospheric deposition (by 2020, Table 10.9) and decreased scavenging by coniferous forests through the simulated reductions in forest cover between 2007 and 2050. Nitrate in surface waters is influenced by decreased scavenging and reduced uptake owing to reductions in coniferous forest cover resulting in little change in NO_3^- concentrations. The reductions in S deposition (and scavenging) result in an increase in pH, ANC and soil base saturation across all sites, along with decreased concentrations in labile Al. The largest improvements were simulated at Loch Grannoch and Afon Hafren, in line with the largest reductions in SO_4 (approximately 10 μeq l^{-1}).

Reducing the amount of coniferous forest by the amounts in the forest plans for the five sites results in a slight increase in ANC (Fig. 10.6) and pH (not shown) compared to simulations that assume no change in forest cover (Fig. 10.6). However, in contrast, soil base saturation at Allt na Coire nan Con, Loch Chon and Llyn Cwm Mynach is projected to decrease under planned coniferous forest reductions compared to no change, although slight increases are predicted for Loch Grannoch and Afon Hafren. The decrease in base saturation is caused by the more significant flux of base cations leaving the forest sites as a result of increased soil water percolation, offset at Loch Grannoch and Afon Hafren by the greater magnitude reduction in forest uptake. Further research into the effect of flow pathways and forest uptakes at individual afforested sites may assist interpretation of these results.

Table 10.9. Simulated surface water and soil chemistry during 2015, 2020, 2050 and 2100 in Allt na Coire nan Con (ANCC), Loch Chon (CHN), Loch Grannoch (LGR), Llyn Cwm Mynach (MYN) and Afon Hafren (HAFR) for the future forest planting scenario.

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	Year	ANCC	CHN	LGR	MYN	HAFR
SO_4^{2-} (μeq l^{-1})	2015	40.96	39.05	58.09	51.14	50.06
	2020	37.69	34.25	50.57	45.87	43.23
	2050	35.86	32.67	47.99	44.25	41.46
	2100	35.85	32.65	47.97	44.24	41.45
NO_3^- (μeq l^{-1})	2015	3.14	9.58	15.85	10.14	14.32
	2020	2.92	8.84	14.76	9.65	13.26
	2050	3.05	8.78	14.98	10.76	13.39
	2100	3.39	9.36	16.59	13.04	14.43
ANC (μeq l^{-1})	2015	67.85	46.05	-22.69	51.98	17.75
	2020	70.16	49.72	-16.51	57.00	22.68
	2050	75.69	55.91	-7.22	62.77	27.02
	2100	78.72	59.71	-2.71	62.64	28.99
pH	2015	6.48	6.24	4.72	6.35	5.76
	2020	6.5	6.29	4.79	6.40	5.91
	2050	6.54	6.37	4.98	6.44	6.01
	2100	6.56	6.40	5.13	6.45	6.07
Al^{3+} (μeq l^{-1})	2015	1.23	0.08	7.54	0.00	0.16
	2020	1.19	0.07	4.67	0.00	0.09
	2050	1.09	0.06	1.36	0.00	0.06
	2100	1.05	0.05	0.53	0.00	0.05
Soil base	2015	6.88	9.33	6.67	10.84	11.62
saturation (%)	2020	7.09	9.52	6.96	11.05	11.68
	2050	7.98	10.46	8.41	11.77	12.01
	2100	8.69	11.35	9.67	12.01	12.33

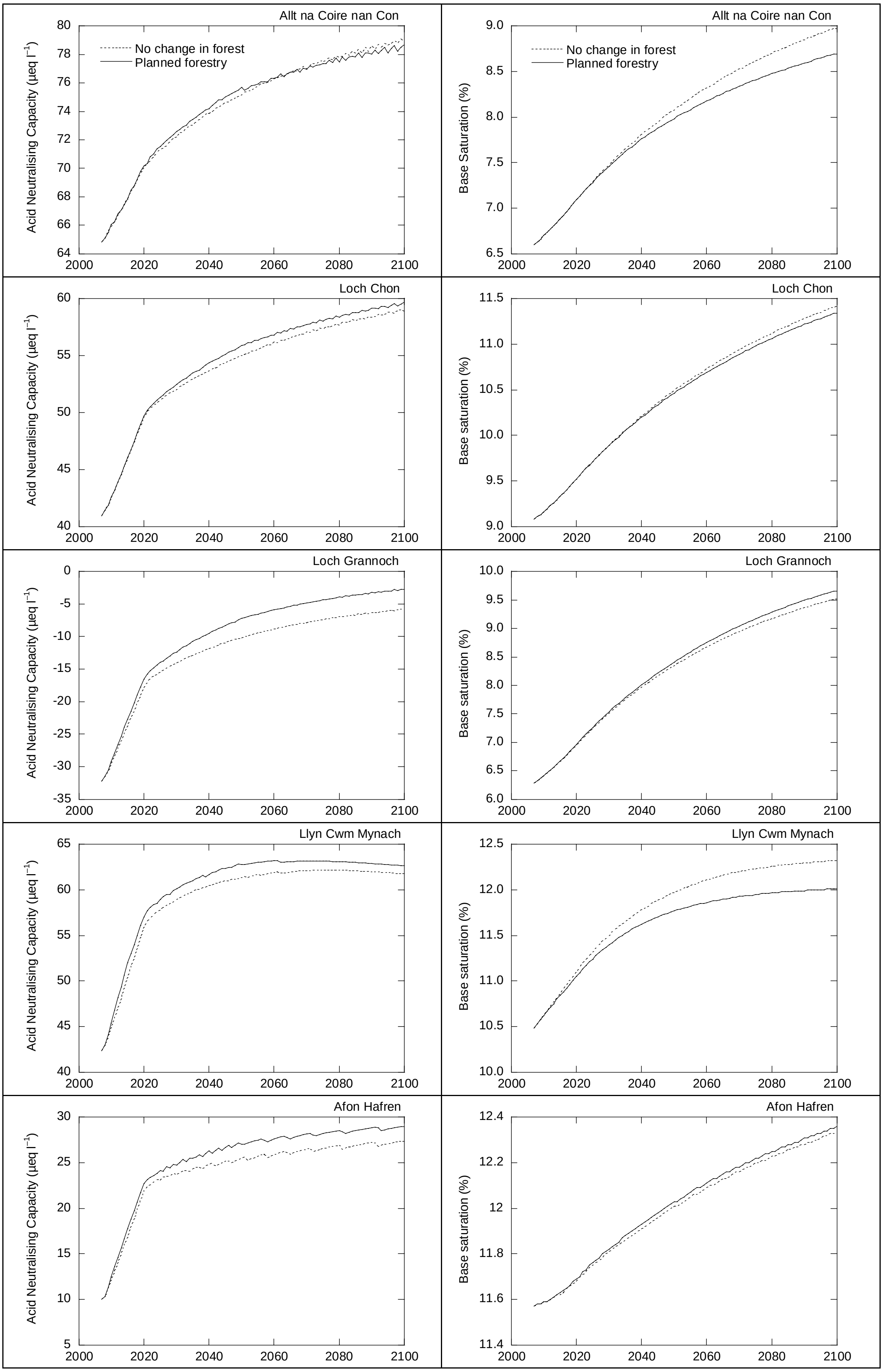


Figure 10.6. Time-series comparison of simulated acid neutralising capacity and soil base saturation under planned forestry cover and assuming no change (reduction) in coniferous forest cover.

10.3.4.Policy relevance and recommendations

Four of the five AWMN afforested sites considered here (Afon Hafren, Llyn Cwm Mynach, Loch Grannoch, Loch Chon) remain acidified, although all show increases in ANC that are proportionate to reductions in acid deposition (Chapter 3). This is manifested at the most heavily acidified sites (Afon Hafren, Llyn Cwm Mynach, Loch Grannoch) mainly by a decline in labile Al. However labile Al remains at potentially toxic concentrations and there is relatively little evidence of pH increases or biological recovery so far at these sites. The afforested sites are not significantly different from the strongly acidified moorland sites in this respect (Chapter 3).

Looking to the future, MAGIC predicts a very rapid recovery at the acidified afforested sites with all except Loch Grannoch predicted to have an ANC > 20 ueq l^{-1} by 2020. Loch Grannoch is predicted to continue to improve, but may still have high SO_4^{2-} and NO_3^- levels and a negative ANC by the end of the century. We consider the projections for Llyn Cwm Mynach to be unsafe as MAGIC is not able to simulate observed chemistry at this site accurately (see Chapter 9). The rapid improvement projected for this site is unlikely.

These MAGIC-based predictions are in line with the SSWC model but not the FAB model, which suggests that nitrogen saturation will confound recovery and eventually lead to four of the five afforested sites failing to meet the critical ANC 20 threshold. However, all three models have weaknesses, especially with respect to their assumptions about the behaviour of N. These predictions therefore need to be regarded with caution. Improving our understanding of N dynamics in upland soils remains a priority for research, as noted above.

Planned reductions in forest cover will have a small effect on the risk of critical loads exceedance and are unlikely to significantly alter the path to recovery. However, the conversion of closed canopy conifer forest to native broadleaved woodland within riparian zones can improve the quality of freshwater and riparian habitats. The establishment of native woodland riparian buffer zones may also play a role in controlling nitrate leaching

The analyses presented here have only considered the joint effect of changing acid deposition and planned changes to forest design. No analysis has yet been made of the impact of changes in land-cover that might occur at both moorland and afforested sites as a result of climate change or the potential impact of a changing climate on the biogeochemistry of afforested catchments. Understanding the role of climate change in this context is a high priority for future research.

10.4. Nitrogen Deposition and Eutrophication

In contrast to SO_4^{2-}, NO_3^- acts not only as an acid anion but also as a nutrient. It is consequently a potential cause of eutrophication in upland waters as well as a cause of acidification. So far there is little apparent biological evidence to show that AWMN sites have been enriched, but: (i) the Network is not yet designed to detect the impact of eutrophication; (ii) elevated NO_3^- may already have caused undetected biological changes in some sites; and (iii) the main impacts may lie ahead if and when surface water NO_3^- concentrations increase and if future climate change accelerates N leaching from catchment soils (Curtis *et al.* 2005). What has been demonstrated, both in the UK and in other countries, is that the productivity of some upland waters is indeed N-limited.

10.4.1.Changing perceptions of the P limitation paradigm

Until quite recently, the conventionally held view on the nutrient limitation status of surface waters was that inputs of phosphorus (P) to lakes caused eutrophication while inputs of nitrogen did not, i.e. the algal productivity of most lakes is P limited (e.g. Schindler, 1977). It was hypothesised that, over the longer term, lake ecosystems were able to adapt to obtain carbon and nitrogen from the atmosphere by fixation, while P supply is limited by catchment sources. However, several studies in recent years have challenged this view, and there have been several publications debating the relative roles of N and P in limiting lake primary productivity over differing spatial and temporal scales (Elser *et al.,* 2007; Lewis Jr & Wurtsbaugh, 2008; Sterner, 2008; Schindler *et al*., 2008; Conley *et al*., 2009). The necessity for controlling both N and P inputs to lakes, estuaries and coastal systems has been proposed (Conley *et al.* 2009) but for the large majority of upland waters the main controllable pollutant source is atmospheric N deposition.

Indirect evidence for nutrient N effects on remote lakes has come largely from palaeolimnological studies. In some alpine and Arctic lakes in North America, nitrogen deposition has been proposed as a major cause of changes in phytoplankton communities (e.g. Baron *et al*., 2000; Wolfe *et al*., 2001; Fenn *et al*., 2003; Sickman *et al*., 2003; Saros *et al*., 2005) with evidence based on diatom and isotopic analysis of lake sediment ^{15}N. Similar studies in the UK reached the same conclusions (Curtis & Simpson, 2007).

More direct evidence of the effects of inorganic N inputs on lake productivity has come from two types of study: (i) correlative studies of nutrients and productivity indicators; and (ii) bioassays using *in-situ* or laboratory incubations with nutrient addition treatments.

Analysis of lake nutrient chemistry and chlorophyll-*a* datasets from Scandinavia and North America revealed higher phytoplankton biomass relative to total phosphorus concentration where nitrogen deposition levels were elevated (Bergström *et al*., 2005; Bergström & Jansson, 2006). These studies were expanded to incorporate *in situ* phytoplankton bioassays in four regions across gradients of N deposition and climate in Sweden (Bergström *et al*., 2008) and then Norway and Colorado, USA (Elser *et al*., 2009). Overall, responses to N additions were stronger than to P additions, although higher N deposition regions showed a progressive switch from P limitation to co- and N limitation as summer depletion of dissolved inorganic nitrogen (DIN) pools progressed (Bergström *et al*., 2008). In low N deposition regions of Norway (<5 kgN ha^{-1} yr^{-1}), no lakes showed P limitation, but 12 out of 19 lakes were N limited. With high N deposition, none showed N limitation but 13 out of 18 showed P limitation (Elser *et al*., 2009).

The role of micronutrients may have been underestimated in lakes, even though it has received much attention in marine systems. For example, iron can be a key micronutrient and may also play a role in regulating NO_3^- assimilation (Sterner 2008). Furthermore, a Swedish study has shown that nutrient limitation may play a minor role in limiting whole-lake productivity in nutrient-poor lakes and that light-limitation of benthic production has a greater impact (Karlsson *et al.* 2009). While this study considered TP rather than N limitation, it suggested that increases in planktonic production are unlikely to offset decreases in benthic production as light irradiance of the benthic zone declines. This highlights the potential importance of increasing trends in DOC observed across many of these lakes in the northern hemisphere (Monteith *et al*., 2007) which, if matched by an increase in colour, would be expected to depress benthic production in these circumstances.

The debate over N versus P limitation of phytoplankton continues, however, with Schindler *et al*. (2008) arguing that control of N inputs cannot prevent growth of N-fixing cyanobacteria and may even competitively favour them. The debate may be simplified for those oligotrophic upland lakes where only N deposition may be controlled to prevent eutrophication.

10.4.2.Evidence for N limitation in UK lakes

In the UK, phytoplankton growth rate and yield limitation by N and P was tested directly in laboratory incubations and with *in situ* nutrient diffusing substrata for periphyton by Maberly *et al*. (2002). The 30 lakes studied were subsequently supplemented by an additional 13 lakes where similar phytoplankton bioassays were carried out (Curtis & Simpson, 2007). Across the 43 upland lakes, growth and productivity were limited almost as frequently by N availability as by P, but joint- or co-limitation of growth by both N and P together was the most common status. Furthermore, the bioassay studies support the assertions of Bergström & Jansson (2006) that N limitation is widespread in upland lakes and that even P-limited sites may once have been N-limited but are now so modified by anthropogenic N deposition their nutrient status has changed (see also Liess *et al.* 2009). The UK AWMN site Scoat Tarn is an example of a lake which shows P limitation of phytoplankton growth, which may have been induced by high levels of NO_3^- leaching resulting from large deposition loads of total N (Curtis & Simpson, 2007). This site may have historically been N limited but now it has an excess of inorganic N. In a global synthesis across several ecosystems, Elser *et al.* (2007) concluded that limitation by N or P was equally common for terrestrial and freshwater systems, while all responded to inputs of both N and P together.

10.4.3.Nutrient N bioassays at AWMN lakes

Most of the AWMN lakes have been bioassayed as part of the studies of Maberly *et al.* (2002), the Defra Freshwater Umbrella studies of Curtis & Simpson (2007) and more recently, Bromley (2009). In the study of Maberly *et al.* (2002), four AWMN sites (Coire nan Arr, Blue Lough, Llyn Llagi and Round Loch of Glenhead) were included in a wider study, with phytoplankton bioassays carried out in April-May (spring or early summer), June-July (mid-summer) and August (late summer) 2000. In addition, nutrient diffusing substrata were used for *in situ* periphyton bioassays in early to mid- summer and mid- to late summer 2000 (Table 10.10). The later study, reported in Curtis & Simpson (2007), entailed phytoplankton bioassays in June, July and September 2005 (early, mid and late summer) at a further four AWMN sites (Scoat Tarn, Lochnagar, Burnmoor Tarn, Loch Coire Fionnaraich; Table 10.10). Finally, one-off phytoplankton bioassays were carried out at 10 AWMN lakes in late May/early June 2009 (Bromley, 2009). Over the three studies, 11 AWMN sites have been bioassayed with the only lake site excluded being Llyn Cwm Mynach.

Of the eight sites studied by Maberly *et al*. (2002) or Curtis & Simpson (2007), three were primarily P-limited (Scoat Tarn, Blue Lough and Lochnagar) and these are all located in high N deposition areas with high lake water NO_3^- concentrations. 2005-07 mean concentrations for the three sites were 14, 20 and 16 μeq l^{-1}, respectively, as compared with reference values close to zero.

Two sites showed a response to N additions in mid-summer; Loch Coire Fionnaraich in the very low N deposition region of north-west Scotland, and Burnmoor Tarn. While Burnmoor Tarn is located in a moderate N deposition region and is very close to the high deposition, high NO_3^- site Scoat Tarn, the lake has very low NO_3^- concentrations. This may be due to differences in land-cover between the two sites. The NO_3^- concentrations and total N (wet + dry oxidised + reduced N) deposition show that while there is a broad correspondence between NO_3^- and N deposition, the relationship between the two does vary (Table 10.10) with catchment specific factors such as land cover (vegetation) type, slope and soil type. Hence high deposition sites do not always have high NO_3^- concentrations, though low deposition sites do have low NO_3^- concentrations.

Table 10.10. Nutrient limitation status of phytoplankton and periphyton yield at AWMN sites in early, mid or late summer bioassays (NO: nutrients not limiting, N = nitrogen; P = phosphorus; CO: co-limitation by both N and P). See text for description of separate studies. Sites ordered by increasing mean NO_3^- concentration (μeq l^{-1}); N deposition (Ndep) in kgN ha^{-1} yr^{-1}.

	2004-06 mean		**Bromley**	**Curtis & Simpson 07**			**Periphyton**	
Site Name	Ndep	NO_3^-	2009	Early	Mid	Late	Early	Late
Loch Coire Fionnaraich	9.8	1.9	Co	Co	N	Co		
Loch Coire nan Arr	8.7	2.3		Co	Co	Co	P	Co
Loch Tinker	23.6	2.5	Co					
Burnmoor Tarn	17.3	5.3	Co	Co	N	Co		
Llyn Llagi	16.2	6.1	Co	P	Co	Co	NO	NO
Round Loch of Glenhead	24.7	9.5	NO	Co	Co	Co	P	NO
Loch Grannoch	16.6	11.7	Co					
Scoat Tarn	23.9	13.9	Co	P	P	P		
Lochnagar	19.1	16	Co	Co	P	P		
Loch Chon	23.6	16.7	Co					
Blue Lough	23.5	20.2	NO	Co	P	P	Co	P

Overall, the predominant response in these studies showed co-limitation of phytoplankton by both N and P on at least two occasions for five out of eight sites. The dominance of co-limitation was even more pronounced in the later study by Bromley (2009) for samples taken in May 2009. Of the 10 sites sampled, eight showed co-limitation of phytoplankton yield while two showed no significant response to N and/or P additions, suggesting some other factor is limiting. The potential role of light as a limiting factor at these sites (cf Karlsson *et al*., 2009) has yet to be examined.

Although the three studies summarised here are separated in time and were carried out at slightly differing periods between spring and early autumn, the overall picture shows that co-limitation of phytoplankton yield by N and P is the most common response, especially in spring and early summer. There is some evidence of N limitation in low NO_3^- sites in mid-summer only, while higher N deposition sites with significant NO_3^- concentrations show P limitation (Table 10.10). The data are broadly consistent with the notion that N deposition and NO_3^- leaching may cause a switch from N to co-limitation which in the most impacted sites may become P limitation (cf. Bergström & Jansson, 2006; Liess *et al*., 2009).

10.4.4.Policy relevance and recommendations

These studies demonstrate the potential role of atmospheric N deposition in changing algal productivity and nutrient regimes in upland lakes, with implications for N emissions policy with respect to several international directives. Eutrophication or exceedance of nutrient N critical loads is of relevance to the Gothenburg Protocol under the Convention on Long-range Transboundary Air Pollution. Increased availability of nutrient N may affect biodiversity in oligotrophic systems adapted to low N availability and the induction of P limitation by N deposition could result in phytoplankton becoming poorer quality food for zooplankton grazers (Elser *et al.* 2009). It has been argued that species diversity is strongly correlated with the number of potentially limiting resources (Sterner, 2008) so the removal of N limitation could have important implications of relevance to the Convention on Biological Diversity. Furthermore, nutrient-poor lakes in the UK uplands designated under the EU Habitats Directive may be undergoing changes that may also be considered a deviation from the good ecological status required under the EU Water Framework Directive. It is therefore important to understand the likely (and in many cases ongoing) changes in the structure and function of oligotrophic lake ecosystems caused by deposition of nutrient nitrogen.

A full picture of the nutrient limitation status of AWMN sites can only be obtained by concurrent sampling at all sites through a whole year, given the evidence of seasonal changes even through the summer period. It is therefore recommended that full nutrient chemistry including total nitrogen (TN) and total phosphorus (TP) as well as chlorophyll-*a* be added to the standard suite of chemical analyses performed routinely at AWMN sites. There is also a need to look beyond the oligotrophic, acid sensitive water bodies traditionally studied in the British uplands to assess wider impacts in more calcareous and mesotrophic lakes that are not acid sensitive but could be adversely impacted by nutrient N inputs. These data would allow for more rigorous assessment of the likely impacts of nutrient N deposition on oligotrophic upland lakes where bottom-up changes to food webs and primary productivity are likely impacts.

10.5. Toxic Substances

Although the emissions of trace metals and persistent organic pollutants (POPs) have decreased as a result of emission control policies and changes to industrial processes, they persist in the environment and continue to pose a threat to the ecology of upland waters. For some waters the threat may increase in future as climate change may lead to the remobilisation of these toxic substances. In the UK, the AWMN site Lochnagar is used as a flagship site to monitor the behaviour of trace metals.

10.5.1.Trends in trace metals and POPs in the UK

Since 1970, emissions of trace metals to the atmosphere in the UK have declined dramatically. The National Atmospheric Emissions Inventory (http://www.naei.org.uk/) shows that emissions of mercury (Hg), lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu) and zinc (Zn) have declined by 89%, 99%, 92%, 91%, 73% and 80%, respectively between 1970 and 2007, principally as a result of declining coal use, reduction in iron and steel production, better controls on incinerators and, for Pb, the introduction of unleaded petrol.

These declines have reduced trace metal emissions to low levels such that the possibilities for continuing declines into the future are limited. RoTAP (in press) describes three factors influencing future metals emissions. First, changes in production processes, second, changes in the levels of emissions abatement (e.g. health-driven policies to reduce particulate matter will lower metals in the atmosphere) and third, changes in the amount and mix of fossil-fuel consumption. This last factor is possibly the most important and depends largely upon strategies employed to mitigate climate change effects. For example, if clean coal technologies (carbon capture and storage) are selected to play a major role in response to future UK electricity demand then this would lead to greater coal combustion and possibly elevated metal emissions. Changes in climate will also inevitably lead to changes in domestic electricity demand. Warmer winters may lead to reduced electricity usage for heating but conversely hotter summers could increase consumption through the increased use of air conditioning. Climate change will undoubtedly be a key driver in future impacts on freshwaters from toxic substances (trace metals and persistent organic pollutants; POPs) not only from the point of view of changing emissions to the atmosphere, but also via transport and deposition and the remobilisation of previously deposited pollutants stored in catchment soils.

The increased use of pesticides resulting from a need to control agricultural pests due to a changing climate need not be confined to the UK in order to impact UK upland waters. Although it is predicted that species from lower latitudes will colonise the UK as temperatures increase, it is unclear whether this will lead to an increasing use of pesticides. However, the same situation will occur across Europe and, in areas where the use of pesticides is less regulated, this may lead to increased usage of currently employed pesticides and/or the development and employment of new ones. Given the potential for increased mobility under a warmer climate (see below) this could result in an increase in inputs to UK upland waters from atmospheric transport and deposition.

The volatilisation of compounds is a temperature dependent process and therefore in a warmer atmosphere those compounds which volatilise readily (e.g. Hg and some POPs) will be able to travel greater distances prior to deposition. However, in upland lakes it is the absorption of compounds in water and their retention, bound to organic matter, that is important and this process is also temperature dependent. In low temperature waters, less volatile POPs (or 'semi-volatile' compounds) are preferentially absorbed in water and selectively trapped in sediments and biota. Thus, higher altitude (colder) lakes are preferentially enriched in less-volatile compounds over more volatile ones. Hence, while mobility within the atmosphere may increase as a result of increasing air temperatures, in upland lakes there will be less absorption of semi-volatile compounds and possibly even some release from them. As a consequence we may expect a shift in the altitudinal (or latitudinal) gradients of POPs accumulation (e.g., Grimalt *et al*., 2001; Fernández *et al*., 1999; 2000; Vives *et al*., 2004a; b) although the predicted temperature increases are unlikely to affect the least-volatile compounds in any significant way.

10.5.2.The remobilisation of legacy pollutants

A major impact of climate change on the input of metals and POPs to upland waters will be via the remobilisation of contaminants stored in catchment soils and their transfer to aquatic ecosystems. Catchment areas are usually significantly (typically an order of magnitude or more) larger than the surface area of a lake and hence deposition to catchments will have been equally larger over the industrial period. There is therefore a massive store of atmospherically deposited contamination within soils and release of even a fraction of this will have a major impact on contaminant inputs to surface waters. As an example, the catchment area of Lochnagar is almost ten times larger than the lake area and the scale of pollutant deposition to the catchment over the industrial period will be around an order of magnitude larger. Therefore, despite the limited soil cover in the catchment, a considerable store of trace metals and POPs are calculated to be stored there. Yang *et al.* (2002) estimated that there is *c*. 400 times the amount of Pb stored in Lochnagar soils as was deposited from the atmosphere onto the loch and its catchment in 2000. A similar figure is also estimated for Hg. Studies of the whole basin flux of Pb and Hg in Lochnagar (Yang *et al.* 2002) have shown that while the patterns of increasing fluxes of Pb and Hg to the lake sediment over the period 1850 - 1950 reflects the increase in deposition, the effects of the subsequent dramatic decline in metal emissions and deposition is not observed in the recent sediment record. As there are no direct sources of contamination the 'additional' metal entering the site and causing this lack of response to depositional changes can only be from metals previously deposited onto the catchment now being transferred to the loch.

There are four hypotheses for the cause of this enhanced catchment transfer (Rose *et al*., 2004). First, a simple time-lag, i.e., metals deposited onto the catchment take a number of years to pass through. Second, increased erosion of atmospherically contaminated catchment soils is bringing metals into the loch (e.g., Lindeberg *et al*., 2006). Third, increasing levels of dissolved organic carbon (DOC), thought to be part of the acidification recovery process (Monteith *et al*., 2007), are being transferred from the catchment, to which metals are adsorbed (Kolka *et al*., 2001; Ravichandran 2004). POPs are also known to have a strong affinity for DOC (Gao *et al*., 1998; Winch *et al*., 2002) and this mechanism could also be applicable for organic contaminants stored in catchments. And fourth, with available nutrients, warmer winters could result in longer growing seasons for algae which could then scavenge metals from the water column eventually becoming incorporated into the sediment record.

As part of the EU-funded Euro-limpacs project a multiple sediment core, multi-pollutant study at nine lakes across Scotland was undertaken to test these hypotheses (Rose *et al*., in revision). Decadal scale, full basin inventories for Pb, Hg and spheroidal carbonaceous particles (SCPs; a component of fly-ash), were constructed at sites with thin soils, sites with eroded soils and sites with non-eroded soils to assess temporal trends. The use of both trace metals and SCPs allowed a comparison between erosive (SCPs and metals) and leaching (metals only) processes. The results showed that the main transfer mechanism was catchment soil erosion thereby explaining the earlier observations from Lochnagar. Although the leaching of metals bound to DOC may also play a role, this appears to be minor in these systems compared to erosive processes. The processes that lead to soil erosion and leaching of DOC from the catchment are exacerbated by increased winter rainfall, decreased summer rainfall and increased frequency of high intensity rain events, all of which are predicted for much of upland UK as a response to climate change. Hence, climatic change may be expected to increase the transfer of these pollutants from catchments to surface waters.

10.5.3.Policy relevance and recommendations

The scale of the catchment storage of previously deposited pollutants is such that this remobilisation could keep contaminant sediment concentrations and fluxes elevated for many decades to come and maintain high levels of toxic substances in all parts of the aquatic food-web in upland lakes and streams. At many sites these processes would offset the effects of emission reductions policies, confound the aims of the EU Water Framework Directive (WFD) and may elevate the exposure of aquatic biota. This is of particular importance as the Water Framework 'Daughter' Directive (2008/105/EC) reaffirms the aim of the WFD to ensure that "existing levels of contamination in biota and sediments will not significantly increase". Of the trace metals, this Directive considers Hg to be of particular concern although Pb and Cd remain priority substances.

While the Euro-limpacs study was concerned only with trace metals, the adsorption of POPs to organic matter is also strong and the same pathways are applicable. Although there are few POPs data for UK upland waters and the depositional period is significantly shorter than that of trace metals, a survey of surface sediments across Scotland revealed widespread organochlorine contamination (Kernan *et al*., 2005) while the sediment record at Lochnagar has shown high concentrations of toxaphene which can only be derived from long-range transport through the atmosphere (Rose *et al.,* 2001). Hence widespread catchment contamination of POPs is likely and exacerbation of the processes leading to increased metals input from catchment storage will also increase the input of POPs to surface waters.

All metals monitoring under the auspices of the AWMN has ceased. In light of the current and future threats it is necessary to re-instate the trace metals monitoring programme at Lochnagar and extend the monitoring protocols to other sites in the Network as a matter of some urgency. The lack of information regarding POPs in UK upland waters should also be addressed.

Finally, much further work is required on the biological impact of metal and POP burdens in surface waters. Previous work has shown clearly how toxic substance concentrations can contaminate the entire food chain and bio-accumulate within the food web such that physiological functioning is impaired. It is still unclear, however, with respect to human health, the extent to which concentrations in fish from UK freshwaters exceed consumption guidelines.

10.6. Climate Change Impacts on Water Acidity

While there is already evidence that climate change may be influencing the chemical and biological trends observed to date from the AWMN sites, climate change is expected to have an increasing influence in future, and may well become the dominant driver of change in upland freshwater ecosystems as pollutant deposition, presently the main control, is progressively reduced.

Climate change will affect all catchment and surface water processes. For example, higher temperatures may increase alkalinity generation, increase primary productivity and directly influence the distribution of stenothermic taxa. However the overall impact on the ecological status of upland waters and their recovery from acidification is uncertain, particularly since interactions between climate and the processes that control surface water acidity, NO_3^- leaching (Monteith *et al*., 2000) and organic matter production are hard to predict. Analyses of AWMN datasets suggest two principal concerns; first, changes in hydrological patterns; and second, changes in the magnitude and frequency of sea-salt deposition. Both would have a bearing on the frequency and intensity of acid episodes.

10.6.1.Acid episodes

Although most surface waters are now recovering from acidification, many remain susceptible to acid episodes, due to the legacy of base cation depletion and pollutant accumulation in soils. Acid episodes are invariably associated with climatic extremes and any increase in their frequency and/or intensity would raise the risk of biologically harmful events, and pose a barrier to biological recovery (Lepori & Ormerod, 2005).

The acidity of runoff entering lakes and streams is strongly dependent on the routing of precipitation within the catchment. Groundwater, because of its exposure to sites of geological weathering, is normally relatively alkaline, and at times of low rainfall this source can dominate inputs, resulting in relatively alkaline surface water chemistry. During and after heavy rainfall, however, the dominant flow paths switch toward overland-flow, pipe-flow and near-surface throughflow, which is likely to be relatively acidic, base cation-dilute and enriched in organic acids. Periods of high rainfall, therefore, are likely to be associated with lower base cation concentrations, pH and ANC, and higher aluminium and DOC concentrations (cf. Evans *et al*., 2008). However, while changing levels of rainfall are likely to impact on the long-term acidity trends of AWMN sites, few regions have experienced clear trends in precipitation over the monitoring period.

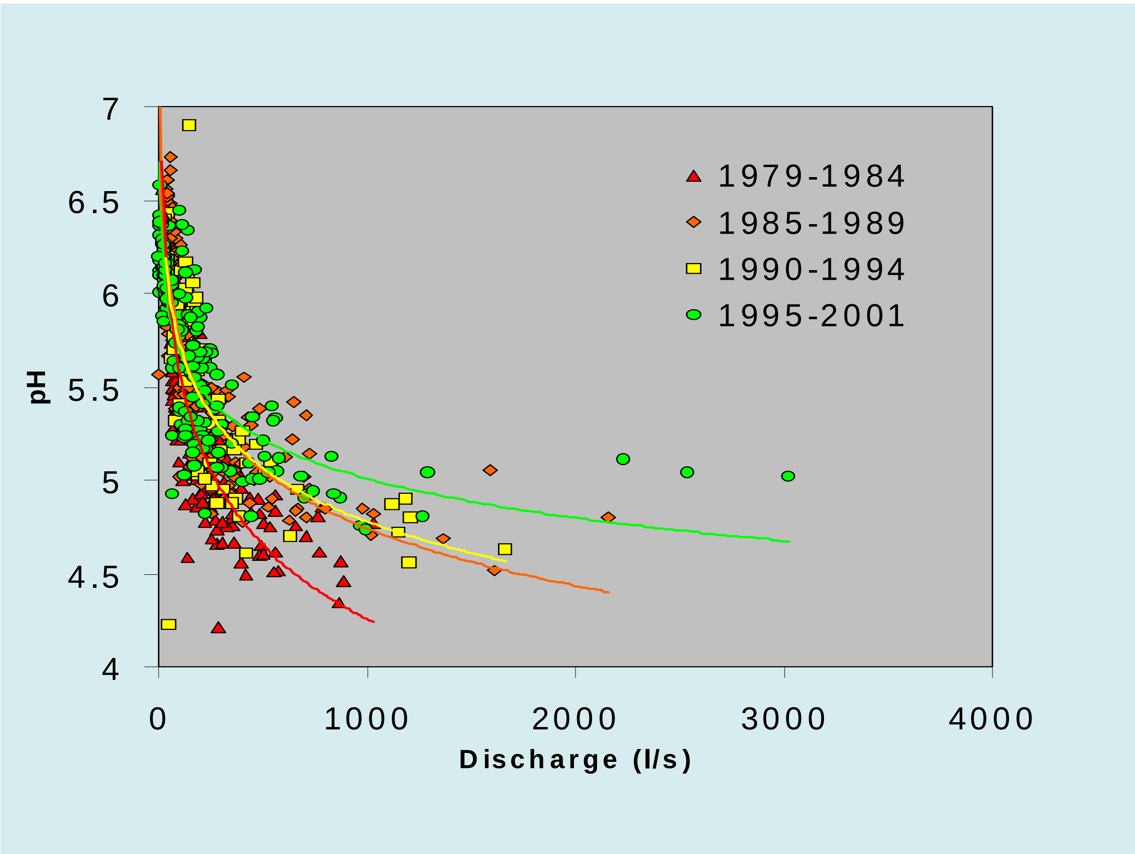


Figure 10.7. pH-discharge data for the Afon Gwy, 1979-2001 (from Evans *et al*., 2008)

In a detailed modelling study of one AWMN stream, the Afon Gwy in mid-Wales, Evans *et al*. (2008) concluded that base cation dilution caused by precipitation, sea-salt inputs and occasional pulses of NO_3^- were the main causes of acid episodes at the site. They noted that changes in the pH-discharge relationship since the late 1980s (Fig. 10.7) indicated that high flow pH, associated with the upper soil, had increased more rapidly than mean flow pH, so that the severity of acid episodes had decreased. However, the dynamic model MAGIC suggested that recovery of ANC of the upper soil would soon stabilise, and after that any climate-related future increase in precipitation would be likely to result in more acidic episodes in future. The extent to which such a change will offset the benefits of reduced acid deposition is not yet clear.

10.6.2.Sea-salt influences

Sites closest to the west coast of Britain are those most vulnerable to the impact of sea-salt inputs. Periods of persistently high wind speeds, normally during winter, over the Atlantic Ocean can result in the entrainment of sea-salt aerosol which can then be deposited for substantial distances inland (Gorham, 1958). Sea-salt deposited in this way represents the overwhelming source of chloride at most AWMN sites, and variation in chloride concentration therefore provides a direct record of sea-salt deposition history (Evans *et al*., 2001). When sea-salt is deposited on acid soils, acid cations are displaced from soil ion exchange sites by marine cations (principally sodium and magnesium) leading to the episodic acidification of runoff (Harriman & Wells, 1985; Langan, 1989; Evans *et al*., 2001). Highly damaging sea-salt events have continued to affect acid-sensitive waters until relatively recently. For example, in January 2003, an event in southwest Norway led to a major fish kill in some rivers for this reason (Larssen & Holme, 2006). Sea-salt driven acid episodes beyond the immediate coastal zone are not a natural phenomenon; under pristine conditions, the soil base cation store would normally be expected to be large enough to counter inputs of marine cations without the release of acidity. When deposited on acidified soils, however, hydrogen and aluminium are displaced instead. Because soil base saturation will be slow to recover, as noted above, the problem of acid sea-salt episodes is expected to persist for several decades into the future (Evans, 2005). If sea-salt episodes become more frequent or intense under a changed climate, their detrimental impact is likely to increase.

The temporal pattern of sea-salt deposition across the AWMN has been linked to the state of the North Atlantic Oscillation (NAO) during winter (Evans *et al*., 2001) and similar observations have been made for south-western Norway (Hindar *et al*., 2004). 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 sea-salt aerosol as waves break near the coast.

Chloride concentration in AWMN surface waters appears 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 & Wallace, 1998). Figure 10.8, for example, demonstrates that the chloride concentration in the Dargall Lane Burn in southwest Scotland reflects variation in the daily AO Index throughout the monitoring record, while Figure 10.9 illustrates the relationship between the annual mean daily AO index and the mean standardised annual mean chloride concentration for the 14 AWMN sites with particular proximity to the west coast.

The link between Cl^- concentrations in AWMN surface waters in western Britain and the AO is important for four key reasons: (i) it suggests that trends in acidity in surface waters in these regions are likely to have benefited from the overall reduction in the AO over the full period of monitoring; (ii) analysis of the longer-term daily AO record that is available back to 1950 (see Fig. 10.10) would suggest that climatic conditions over the first few years of AWMN monitoring (and particularly between 1989-1991) were unprecedented in the last 60 years and it is therefore feasible that sea-salt deposition over this period was also unprecedented, at least for the previous few decades; (iii) there is evidence that the AO Index has been rising since the 1950s, and this has been linked to anthropogenic forcing through both rising CO_2 and declining stratospheric ozone (Yukimoto & Kodera, 2005). It follows, therefore, that the period of intensive sea-salt deposition in the early stages of AWMN monitoring may also be linked to anthropogenic impacts on climate; and (iv) at the time of writing there were indications from the long-term trend (Fig. 10.10) that the AO may be entering another positive phase, and if so this would be likely to result in a resumption of high sea-salt loads to AWMN catchments and a consequent negative impact on recovering levels of ANC.

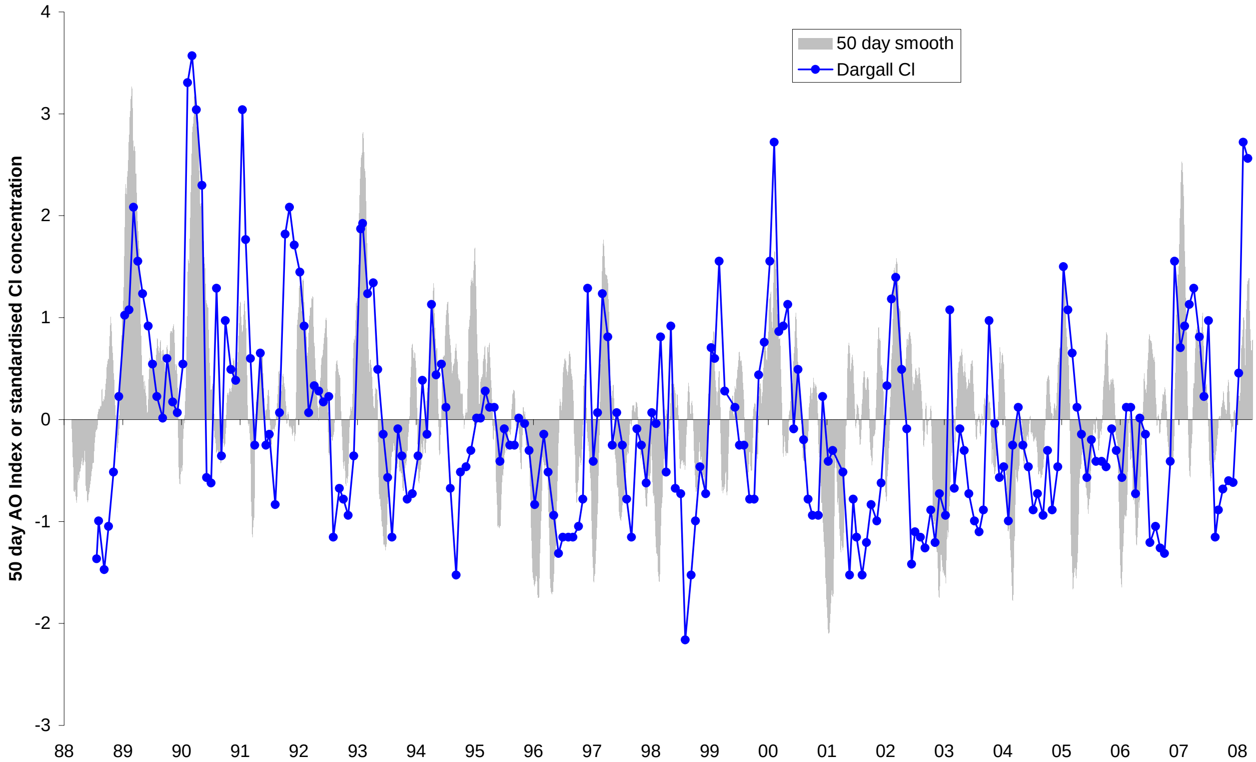


Figure 10.8. Standardised Dargall Lane chloride concentration for monthly samples (blue line), and continuous 50 day running-mean Arctic Oscillation Index (grey hatching). Note that above average Cl^- concentrations are tightly associated with periods of positive AO Index.

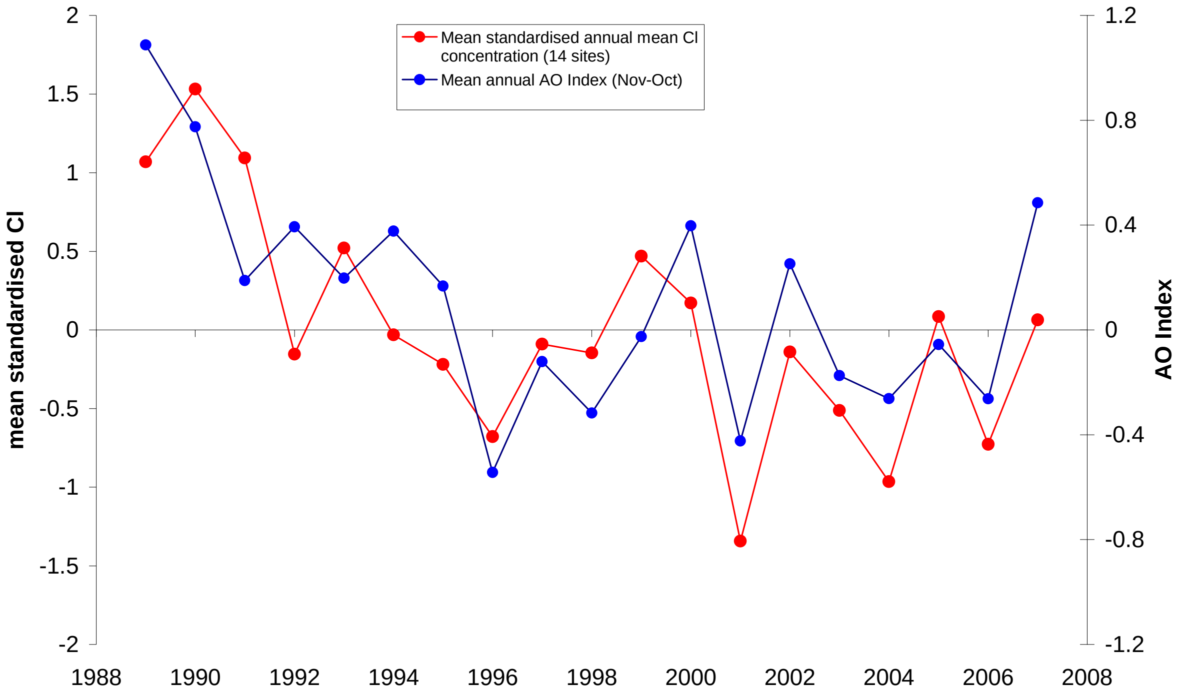


Figure 10.9. Mean of standardised annual mean Cl$^-$ concentration for 14 AWMN sites with west coast locations (red) and mean annual Arctic Oscillation Index (previous Nov-Oct) (blue). Note the overall downward trend in both parameters over the 20 year period.

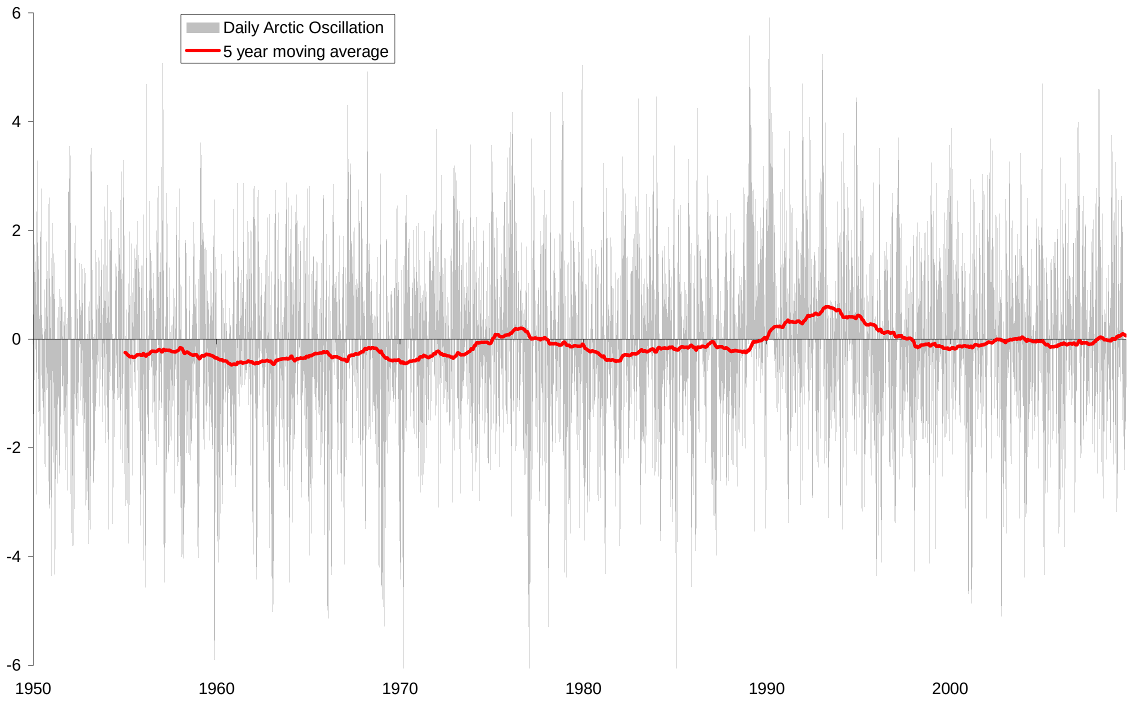


Figure 10.10. Daily Arctic Oscillation Index (grey hatching) and its 5 year moving average (red line). Data source NOAA National Weather Service, Climate Prediction Centre.

We have examined the possible impact of a return to the 1989-1991 level of sea-salt deposition on the ANC of AWMN sites statistically by using linear models to predict the combined effect of anthropogenically derived acids (i.e. sum of xSO_4^{2-} and NO_3^- concentration) and sea-salt (Cl^- concentration) on ANC for 11 AWMN sites that are both geographically vulnerable to sea-salt deposition and particularly acid-sensitive systems.

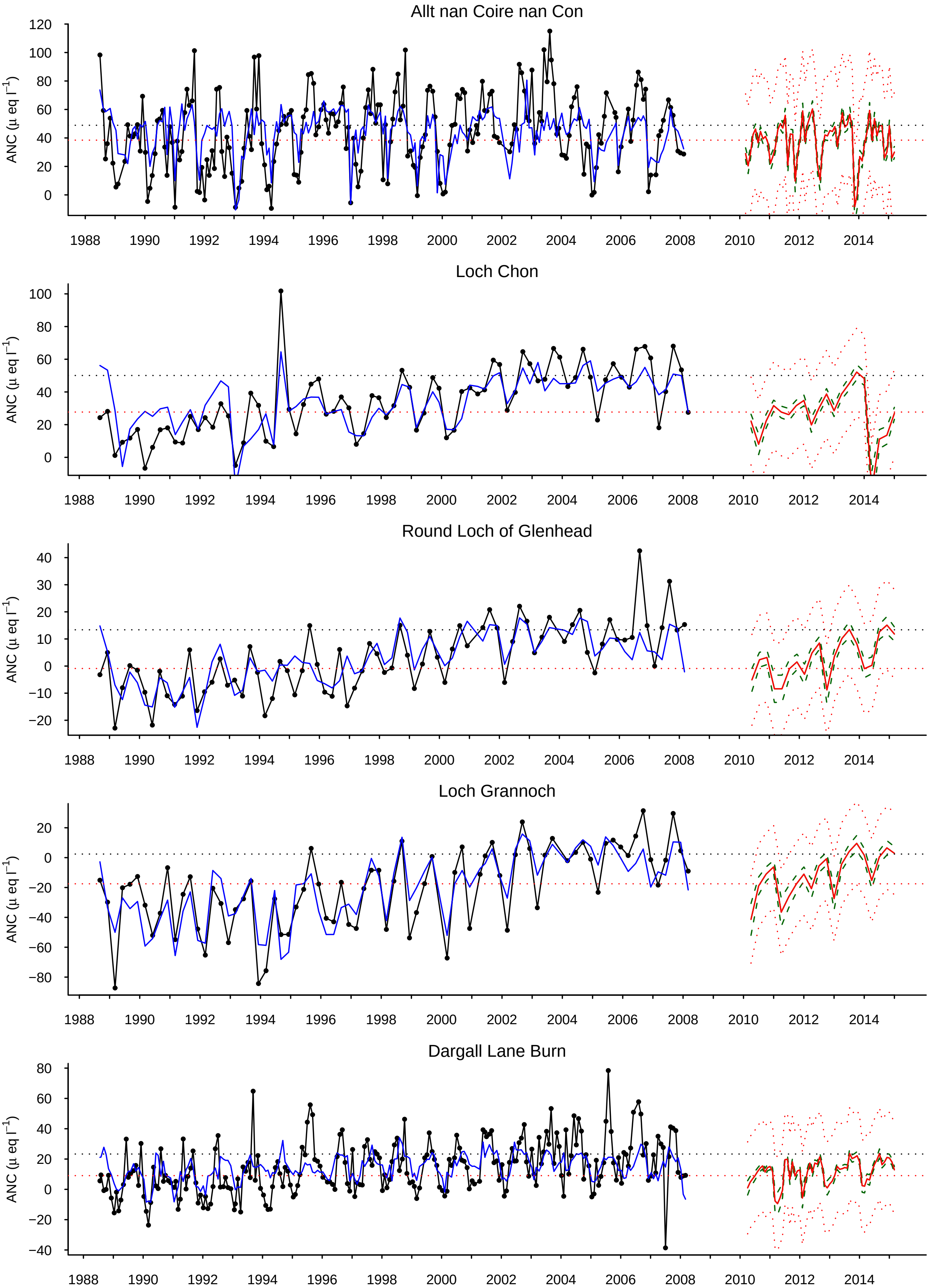
Table 10.11 shows that the two variables explained between 22.6 and 67.9 % of the variance in ANC in individual water samples at the 11 sites. The coefficient for Cl^- concentration was highly consistent (ranging from -0.122 to -0.303: median = -0.186) suggesting that on average a 50 μeq l^{-1} increase in Cl^- concentration would be expected to depress ANC by almost 10 μeq l^{-1}.

Table 10.11. Results from the linear modelling of the ANC concentration of individual samples from 11 AWMN sites deemed most vulnerable to sea-salt events as a function of 'anthropogenically' derived acidity ($[xSO_4^{2-}] + [NO_3^-]$) and sea-salt ($[Cl^-]$). Both variables were highly significant at all sites ($p<0.01$). Recent mean ANC is contrasted against mean ANC for a projected future period during which Cl^- returns to 1989-1991 concentrations while $[xSO_4^{2-}] + [NO_3^-]$ remains at current (2003-2008) levels.

SITES	Coefficients (std error)		Adjusted R^2	Mean ANC (2003-2008)	Projected Mean ANC	ANC reduction
	([xSO4]+[NO3])	[Cl]				
Allt na Coire nan Con	0.269 -0.088	-0.122 -0.014	0.326	48.9	38.5	10.4
Loch Chon	-0.504 -0.117	-0.279 -0.027	0.57	50.1	27.7	22.4
Loch Tinker	-0.024 -0.173	-0.243 -0.021	0.313	72.3	60.9	11.4
Round Loch Glenhead	-0.5 -0.071	-0.146 -0.021	0.554	13.4	-0.9	14.3
Loch Grannoch	-0.667 -0.056	-0.215 -0.027	0.729	2.4	-17.5	19.9
Dargall Lane	-0.223 -0.064	-0.132 -0.019	0.226	23.3	9.06	14.2
Scoat Tarn	-0.415 -0.07	-0.186 -0.016	0.689	-1.5	-16.5	15
Burnmoor Tarn	-0.805 -0.208	-0.192 -0.069	0.284	81.5	61.1	20.4
Llyn Llagi	-0.295 -0.08	-0.135 -0.08	0.45	18.8	9.9	8.9
Afon Hafren	-0.52 -0.078	-0.303 -0.037	0.365	8.2	1.1	7.1
Blue Lough	-0.57 -0.059	-0.132 -0.026	0.679	-7.4	-14.9	7.5

We then used the model coefficients to predict the future effect of a hypothetical return to the sea-salt concentrations experienced at individual sites over the first five years of monitoring on ANC while fixing xSO_4^{2-} and NO_3^- concentrations at recent (2003-2008) levels. The results are illustrated in Figure 10.11, while Table 10.11 contrasts the projected mean ANC for a future three-year period (corresponding with the 1989-1991 period of the most intensive sea-salt inputs) with the mean 2003-2008 ANC.

The results suggest that, were the 1989-1991 levels of sea-salt inputs to recur, a distinct possibility given the long-term ramping of the AO, then mean ANC levels of all these sites would be significantly depressed. At Dargall Lane, ANC would be driven below the critical limit of 20 $\mu eq\ l^{-1}$, while ANC at Round Loch of Glenhead, Loch Grannoch, Scoat Tarn, Llyn Llagi, Afon Hafren and Blue Lough, which is already below this limit, would be depressed on average by a further 12 $\mu eq\ l^{-1}$. In several cases this would be likely to push up concentrations of H^+ and Al^{3+} ions above toxic concentrations for some acid-sensitive biota and would almost certainly result in the loss of some recently re-established taxa.


Allt nan Coire nan Con
ANC (µ eq l−1)
120
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80
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20
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1988
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Loch Chon
ANC (µ eq l−1)
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Round Loch of Glenhead
ANC (µ eq l−1)
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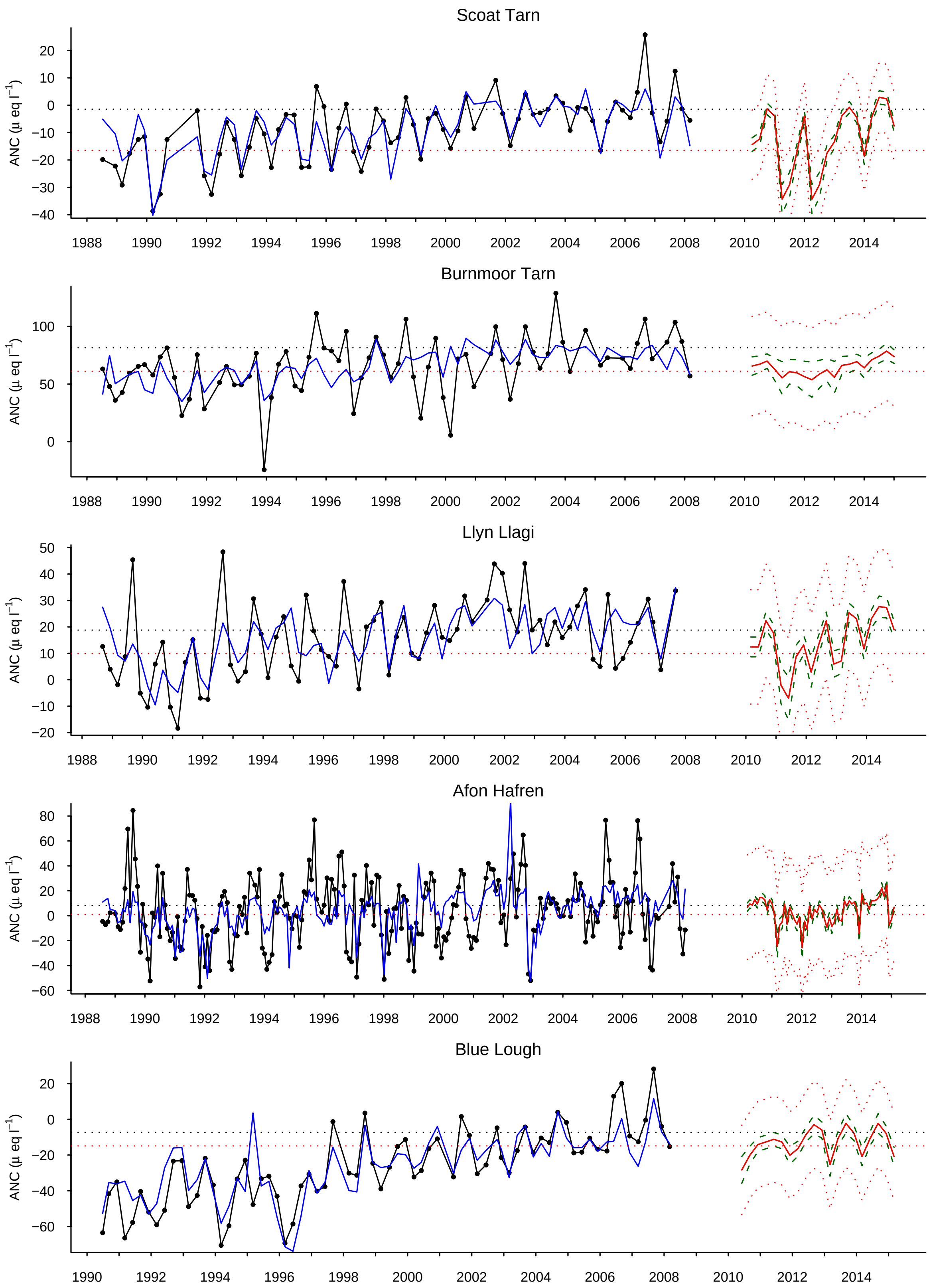

Figure 10.11. ANC concentration (black line and dots), 2-variable linear model fits (blue line), and future predicted ANC (red line) under a scenario of constant modern (2003-2008) [xSO_4^{2-}] and [NO_3^-] concentration and 1988-1993 [Cl^-]. Green-dotted and red-dotted lines represent narrow and wide confidence bands. Horizontal red-dotted line represents future mean ANC for a three-year period with 1989-1991 levels of [Cl-]. Horizontal blue line represents 2003-2008 mean ANC.

Given the possibility that the AO is continuing to ramp over the long-term, the application of 1989-1991 Cl^- concentrations could be seen to be a conservative estimate of levels during future high sea-salt deposition periods. But even if that period remains a unique extreme it is clear that at current levels of xSO_4^{2-} and NO_3^- many of these aquatic ecosystems remain acutely vulnerable to this climatic effect.

10.6.3.Policy relevance and recommendations

The most recent climate change projections for the UK (UKCP09) predict significant increases in temperature and changes in the amounts, intensity, seasonality and geographic distribution of precipitation. Elsewhere it has been argued that the multi-decadal trend in the Arctic Oscillation is also linked with global warming, and if this relationship is sustained, we may expect future increases in frequency and intensity of sea-salt inputs. Net impacts are extremely difficult to predict, but to date, evidence from the AWMN suggests that the negative effects of increasing winter rainfall and high rainfall events, and increased sea-salt deposition (particularly through their influence on the chemistry of episodes) may outweigh benefits of temperature dependent increases in weathering. Another uncertainty is the extent to which episodic extreme chemistry, rather than average chemistry, is limiting, and will continue to limit, biological recovery.

Targets for recovery, fixed by existing legislation, may need to be revised to allow for the effects of future climate change. In particular it may be difficult or impossible to achieve the "good ecological status" objective of the Water Framework Directive for many sites if future changes in precipitation and sea-salt deposition reduce the potential for recovery of acidified lakes and streams to their reference status as is currently intended. This problem may only be resolved if the "good/moderate" boundary is re-defined or if acid deposition controls are strengthened through a policy of decreasing emissions further.

Central to this issue is our poor understanding of the sensitivity of acidified waters to the effects of climate change, an understanding currently limited by the paucity of high frequency measurements of water temperature, water level and water flow at AWMN sites. There is an urgent need to instrument the Network to allow a clearer understanding of the effects of changes in climate for the biological recovery of acidified surface waters, and the effects of climate-mediated changes in land-use, nutrient dynamics and toxic substance exposure on upland aquatic plants and animals more widely, as pointed out in previous sections.

10.7. Key Points

This chapter considers scenarios for the future recovery of acidified waters not only in the context of the future reductions in sulphur and nitrogen deposition projected under the Gothenburg Protocol, but also with respect to the additional pressures faced by upland waters that might be expected to influence the process of recovery from acidification. These include, in particular, land-use change, the future impact of nitrogen deposition where N may promote symptoms of eutrophication, the future role of toxic substances and the influence of climate change.

In the absence of these confounding factors the models predict a continuing chemical recovery from acidification at all sites, and it can be expected that this will be accompanied by a continuing biological recovery. The greatest concern and the greatest uncertainty centres on nitrogen, specifically the extent to which emissions can or will be reduced and the extent to which soils might saturate with N and leach to surface waters. Continued research on this problem is considered a priority, especially with respect to the future influence of climate change on N processes both in catchments and in surface waters themselves.

Future recovery will also be influenced by land-cover change resulting from both land management practices and, more indirectly, from the influence of climate change on catchment hydrology and vegetation. Here we only considered the influence of future forestry. The results from MAGIC show that afforested sites should continue to recover, and that future changes in the proportion of conifer forest are unlikely to significantly alter this process at most sites.

Concern for N in upland waters is not only related to its role as an acidifier but also to its potential role as a nutrient. The extent to which uplands waters are already becoming enriched as a result of N deposition is not clear, mainly because the AWMN does not currently include measurements of water column algal biomass or related variables needed to detect such change. Adapting the AWMN for this purpose is considered a priority, including the addition of new sites needed to represent the full range of upland waters sensitive to such an effect.

Concern over the future role of toxic substances is growing as new research demonstrates that toxic pollutants previously trapped in catchment soils are being remobilised and transported to lakes and streams. Although emissions of most toxic substances have decreased dramatically over recent decades as a result of legislation, the burden of these substances remain high in the aquatic food chain. Any future increase in the intensity of storm events, predicted under most future climate scenarios, is likely to accelerate this process. Toxic trace metal monitoring in the AWMN is presently limited to Lochnagar. Extending the monitoring to all sites is recommended along with further work to assess the extent to which toxic substances impair physiological and ecological functioning.

Perhaps the most serious concern for the future is over the potential impact of climate change. Increase in the frequency and intensity of precipitation is likely to exacerbate the damaging impact of acid episodes in streams. Where precipitation has a high sea-salt content, as is especially the case in the western parts of Britain, the ANC of streams and lakes is likely to be significantly depressed and will limit the extent to which a full recovery can be achieved.

All these concerns highlight the importance of monitoring surface waters in future much more in the context of catchment processes, and with respect to multiple drivers of aquatic ecosystem change, than hitherto. As sulphur deposition ceases to be the single dominant driver, as it once was, surface water quality and biodiversity in the uplands will be controlled by complex interactions between acid deposition, nutrient deposition, remobilised toxic pollutants and climate. Increasing temperatures and changing patterns of precipitation will affect the behaviour of all processes, and will in turn modify how people use the upland regions with respect to land-use, water resources and recreation.

We recommend that, as resources allow, the AWMN should be enlarged to embrace these concerns and become an upland waters network rather than a network concerned only with the problem of acidification in upland waters. This could be achieved by:

- adding sites in more alkaline upland areas vulnerable to the effects of N deposition and climate change;
- expanding the scope of monitoring to include regular surveys of catchment soils, vegetation and land-cover;
- embedding as much research from third parties as possible to improve our understanding of catchment processes relevant to water quality;
- co-locating automatic weather stations and bulk deposition collectors at all sites;
- installing temperature and flow gauges to all sites; and
- modifying protocols for chemical and biological monitoring at all sites to enable the potential impact of N deposition, remobilised toxic substances and climate extremes to be identified.

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11. Summary and Recommendations

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11.1. The Network

The UK Acid Waters Monitoring Network (AWMN) (http://awmn.defra.gov.uk/), established in 1988, is a network of 22, mainly headwater, lakes and streams. It was designed to monitor the chemical and biological response of acidified surface waters in the UK to reductions in the deposition of sulphur (S) and nitrogen (N) compounds following the UK Government undertaking in 1987 to reduce sulphur dioxide emissions from UK fossil-fuel burning power stations.

The Network has been funded by Defra (formerly the DoE) since its beginning, but in recent years, following a reduction in Central Government support in 2007, additional cash funding has been provided by the Welsh Assembly, the Environment Agency (EA), and the Forestry Commission. Significant in-house (in kind) funding has also been provided by the Centre for Ecology and Hydrology (chemical analyses), Marine Scotland Freshwater Laboratory and the Scottish Government (fish survey and chemical analysis), Queen Mary, University of London (macro-invertebrate analysis) and ENSIS-ECRC, University College London (field sampling, diatom and aquatic macrophyte analysis).

The AWMN has been, and continues to be, the key provider of information on surface water acidification to UK Government and Devolved Administrations, and the sole UK provider of data and expertise to the United Nations Economic Commission for Europe (UNECE) International Cooperative Programme on the Assessment and Monitoring of Effects of Air Pollution on Rivers and Lakes, otherwise known as ICP Waters. It underpins our understanding of the ecological status of low alkalinity lakes in the context of the EU Water Framework Directive (WFD), and is integral to the UK Environmental Change Network, providing the bulk of its upland freshwater sites. The Network is the main upland water quality monitoring dataset in the National Ecosystem Assessment. It has also stimulated and supported much of the UK's internationally respected primary research into the ecology of upland waters, especially with respect to major European Union and UK Research Council projects.

The AWMN provides the most definitive data in the UK on trends in water quality, biology and freshwater biodiversity in the UK uplands, the location of the majority of the UK's national parks and the source region for most of the UK's potable water supply. In addition to acidification it has the potential to provide the framework for a comprehensive monitoring system for all upland freshwater ecosystems in the UK faced with multiple pressures from acidification, deposition of nutrients and toxic substances, land-use change and climate change.

The Network was designed to include both non- or only slightly acidified reference sites in the north-west of the UK, and acidified sites across the UK where recovery from acidification was expected. The sites include paired lake and stream sites, paired afforested and moorland sites as well as sites representing a range of sensitivity to acidification and covering most upland regions in the UK. One site (Lochnagar) was instrumented to monitor mercury (Hg) deposition and its concentration in the lake and its catchment (now ended).

With over 20 years of high quality chemical (e.g. major ions, pH, alkalinity, labile aluminium) and biological (diatom, aquatic macrophyte, benthic macroinvertebrate and fish) data the AWMN provides a unique resource for assessing the extent to which water quality in the uplands has changed and is changing and how this affects upland surface water ecology and biodiversity.

In addition, palaeoecological records of diatom assemblages from all 11 lakes allow the twenty year monitoring record to be extended back in time through the period of increasing acidification in the late nineteenth and twentieth centuries to the pre-acidification reference period of the early nineteenth century and before. Sediment traps deployed in each lake and emptied annually allow the sedimenting record to be used for contemporary monitoring and, together with the core record, for long-term reconstruction. The sediment core and sediment trap records have also been used to reconstruct a similar time trajectory for air pollutants, especially trace metals (lead, copper, zinc, nickel) and spheroidal carbonaceous particles (SCPs).

Annual data reports and several detailed interpretative reports (after 5, 10, 15 and 18 years) have been published and are available on line (see http://awmn.defra.gov.uk/resources/interpreports/index.php). Data from the Network have been used in a large number of high-impact peer-reviewed scientific publications (see Appendix 7).

Since its inception, the function of the Network has evolved to address new and emerging issues of upland water quality including:

- the role of N deposition in causing increases in nitrate concentrations in upland surface waters, where nitrate can act both as an acid anion (causing acidification) and a nutrient (causing eutrophication);
- the role of atmospheric deposition in causing toxic trace metal pollution of upland waters;
- the extent to which climate change, directly and indirectly, may modify the hydrology, chemistry and biology of upland waters and confound attempts to reduce acidity.

The extent to which the Network is able, as currently configured, to address fully these emerging concerns needs to be examined. For example, equipping the Network to monitor water temperature and stream flow is seen as a priority if the future effects of climate change are to be fully evaluated.

This report represents the 4th major interpretative analysis of the AWMN that has been undertaken. The length of the record now allows the effectiveness of policies to reduce acidity to be clearly analysed and, as the time-series lengthens, it becomes easier to identify the separate and combined influence of other stressors on upland waters, such as land-use change, climate change and the role of other pollutants.

In addition the length of the record now allows the use of more powerful statistical techniques. For univariate data, for instance on deposition and hydrochemistry, the regression technique of additive modelling has been used, whilst for the multivariate biological data, a variety of ordination-based techniques has been employed. Appendix 2 presents a more detailed explanation of the statistical methods used.

11.2. Trends in Deposition at AWMN Sites

We have used data from the Acid Deposition Monitoring Network (ADMN) (http://www.airquality.co.uk/monitoring_networks.php?n=acid) to analyse trends in the pH, non-marine sulphate (xSO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) concentration and deposition flux for 12 ADMN sites situated closest to the AWMN sites.

Shorter time-series data from bulk deposition monitoring stations co-located with AWMN sites will be used in a future analysis to evaluate the degree to which these extrapolated deposition data from the ADMN sites match the trends in bulk deposition at AWMN sites.

Trends in bulk deposition pH show significant increases at all sites except one, in south-west England, although the timing and pattern vary regionally. These trends are largely matched by trends in xSO_4^{2-} concentration which show a significant decline at all sites, although the latter tend to be significant only in the late 1990s. Trends in NO_3^- concentration in deposition, on the other hand, vary widely. Factors responsible for the early declining trends in pH when xSO_4^{2-} was not declining significantly are so far unexplained.

Trends in deposition loads closely match concentration trends for xSO_4^{2-} but loads for NO_3^- differ from trends in concentration at some sites. The major differences are in significance rather than direction, which is mostly declining for both concentrations and deposition loads for N species.

11.3. Trends in Hydrochemistry

The concentration of xSO_4^{2-} in AWMN lakes and streams, representing the chief acidifying anion in most sensitive UK freshwaters, has fallen substantially across the Network over the 20 year period, in line with reductions observed in bulk deposition concentrations at corresponding Acid Deposition Monitoring Network (ADMN) sites (see above).

Reductions in xSO_4^{2-} are largely monotonic but are far from linear. At most sites the period of significant reductions is largely confined to the latter half of the 1990s.

Trends in the concentration of NO_3^-, the secondary acidifying anion, are not monotonic and show substantial inter-annual variability and marked seasonality. Seven sites show evidence of a long-term decline in NO_3^- concentrations, but two sites, Loch Chon and the Round Loch of Glenhead, show a long-term increase, indicating that NO_3^- is making a significant and rising contribution to the "total acidity" (i.e., xSO_4^{2-} + NO_3^-) of these sites. Concentrations in the control sites in the north-west of Scotland show values close to the limit of detection.

A strong relationship has now been observed between chloride (Cl^-) concentrations at several AWMN sites and the Arctic Oscillation (AO) Index. The AO Index has increased gradually since the 1950s, reflecting a change in climate towards conditions likely to generate more frequent and more intense sea-salt events in western Europe. The data show that the intense sea-salt events observed during the early years of AWMN monitoring were unprecedented in the last 60 years and that surface waters experienced a combined acid stress from sea-salt related acid episodes and from acid (S and N) deposition over those years. If the increase in the AO is caused by anthropogenic impacts on climate (i.e. as a result of increased greenhouse gas emissions), as has been suggested elsewhere, sea-salt events in future may become more frequent and intense and delay or prevent the full recovery of surface waters from the effects of acidification (see below).

Overall there has been significant improvement in the chemistry of the acidified lakes and streams across the Network. However, reductions in acidity represent complex responses to a range of factors involving both changes in acid deposition and changes in climate.

Seventeen AWMN sites show statistically significant trends in water pH and most of these are monotonic demonstrating a progressive improvement in water quality. Sites that do not show a significant change are all control or quasi-control sites situated in the least acidified regions of the UK in Northern Scotland and Northern Ireland (excluding the Mourne Mountains) where little or no change in pH is expected.

A slight reverse trend in pH has occurred since 2005 at some sites (e.g. Round Loch of Glenhead in Galloway and Loch Chon in the Trossachs). These cannot be explained by corresponding declines in bulk acid deposition and are probably related to a recent return to higher levels of sea-salt deposition, and possibly rainfall, during 2007 and 2008.

The overall decrease in acidity across the acidified sites in the Network is clear not only in the smoothed trend but also in the magnitude of short term peaks, i.e. in the strength of acid episodes that occur during high-flow events and during sea-salt deposition events. This observation is of major ecological significance as the intensity of acid episodes is one of the main controls on the re-establishment of biota in streams.

Also of central ecological importance are the significant declines in biologically available, or labile, inorganic aluminium (labile Al) concentrations that have occurred at sixteen sites. The decrease has been most pronounced at the most acidic sites. Labile Al is toxic for aquatic biota, especially fish and benthic invertebrates, even at very low concentrations. However, despite these marked declines, concentrations at many sites remain significantly above those found in non-acidified but geologically sensitive surface waters characteristic of northwest Scotland (e.g. Loch Coire nan Arr). According to our wider data holdings of water chemistry in this region, labile Al concentration rarely rises above 10 $\mu g\ l^{-1}$.

In line with expectations for sites recovering from acidification, concentrations of the base cation calcium (Ca) have decreased at the majority of sites across the Network, driven mainly by the corresponding decreases in the dominant anions SO_4^{2-} and Cl^-.

The increases in dissolved organic carbon (DOC), described in previous reports, have been maintained at almost all sites, and they remain one of the most consistent features of the data from the Network. These increases have now been convincingly attributed to a combination of falling sea-salt deposition in the early years of monitoring followed by more recent reductions in SO_4^{2-} and they indicate a gradual return to higher DOC concentrations that may have occurred naturally in the past. These changes also have significant implications for the recovery of acidified surface waters, associated with the role of DOC as an organic acid, as a substance that complexes toxic aluminium and as a modifier of incident light penetration in lakes.

Despite the clear link with changing deposition chemistry, recent unusually pronounced peaks in DOC in the autumn of 2006 and 2007 cannot be linked solely to declining deposition but appear to be related to extreme climatic conditions in the summer of 2006, when particularly high summer temperatures and a prolonged period of drought may have increased the amount of soluble organic matter available for leaching by autumn rainfall.

Acid Neutralising Capacity (ANC) is a measure used to summarise the overall acid-base status of low alkalinity lakes and streams. Unsurprisingly, given the significant trends in the dominant ions described above, there have been significant increases in ANC across the Network. These trends have major significance for the UK's commitment to minimising critical loads exceedance under UNECE protocols (see above) where the target for the majority of freshwater sites is an ANC of 20 $\mu eq\ l^{-1}$ (see below).

However, the rise in ANC in the more westerly sites on the AWMN is partly attributable to the decline in sea-salt deposition in the early years of monitoring, and this gain could be lost should similar levels of storminess recur.

In general, extremes in acidity (i.e. depressed pH and elevated labile Al during periods of high rainfall and sea-salt deposition) have declined in intensity at a similar rate to declines in annual averages. Although acid episodes continue to occur they are therefore becoming increasingly less harmful to biota and should not be seen as a factor that is likely to prevent biological recovery.

Despite the major improvements that have taken place, most of the lakes and streams in the Network still remain chronically acidified. Sulphate, NO_3^- and labile Al concentrations in many sites remain considerably greater than those observed in the control sites in the north-west of Scotland (see below).

When afforested AWMN sites are compared with nearby moorland "pairs" they have invariably been found to have higher acid anion concentrations and are more acidic, reflecting the enhanced interception of acid deposition provided by the forest canopy. However comparisons of time-series in mean annual chemistry show that if anything acid anion concentrations are falling slightly faster and ANC recovering faster in the afforested systems.

11.4. Biological Trends

11.4.1. Diatoms

These microalgae are highly sensitive indicators of surface water acidity and have been collected and identified annually at all sites in the Network throughout the monitoring period.

Data from the Network show that there have been clear and consistent trends in diatom community composition across most of the acidified sites in the Network throughout the period of observation. For the majority of sites temporal patterns in species assemblages mimic temporal patterns in pH, suggesting that there is little delay between improvements in surface water pH and biological response.

Species changes are significant at almost all the acidified lake sites in the Network with taxa typical of higher pH water gradually replacing those found predominantly at a lower pH. Diatom changes therefore are consistent with the reduction in acidity described above. Exceptions are Blue Lough and Loch Grannoch, where although significant trends are observed diatoms characteristic of strongly acidic water remain dominant. Despite a significant increase in ANC at these strongly acidified sites, labile Al values remain high and pH remains low.

The pattern at the stream sites is less clear but seven of the 11 sites do show a statistically significant change through time. The absence of clear trends in the remaining stream sites is because these sites are situated in low acid deposition regions.

Although we have insufficient data yet to quantify the relationship between diatom response and water chemistry, a comparison between trends in surface water pH over the last 20 years and trends in diatom composition show a close and proportionate correspondence. ANC is a poorer predictor of diatom response at the most acidified sites where ANC increases are the result of decreasing labile Al concentrations rather than an increase in pH.

11.4.2.Aquatic macrophytes

Aquatic macrophytes have been sampled at all lake and stream sites throughout the monitoring period. The results show that new taxa have appeared in seven of the lake sites and four of the stream sites. In most cases these taxa are not found in highly acidic waters and are therefore indicative of water quality improvement as a result of decreased acidity.

At some of the most acidified sites the changes may be related not only to the gradual increase in pH but also to the increased availability of dissolved inorganic carbon. It is also possible that some macrophyte species have responded to changes in the availability of nitrogen as a nutrient, and/or reductions in levels of labile Al.

In the Round Loch of Glenhead *Myriophyllum alterniflorum* (alternate water milfoil), a ubiquitous and abundant plant in non-acidified oligotrophic waters, was first observed in 2003 at around the time positive ANC values began to be recorded and it is now well-established. This is important not only because of the apparent direct response of this species to improving water quality but also because of the changes its appearance have brought about for the structure of the underwater habitat for other biota.

Another notable observation is the appearance of the acid-sensitive isoetid *Subularia aquatica* (water awlwort) in Loch Chon and Loch Tinker since 1995 and in Lochnagar in 2009. Its occurrence in Lochnagar, however, is especially interesting as the discovery equals the altitude record for this species in the UK, and its appearance may be related not only to improving water quality but also to the recent warming at this site, as reflected by the reduction in the duration of ice-cover over the monitoring period.

The primary changes observed in AWMN streams have been the detection in recent years of aquatic mosses, albeit in very small amounts, at sites previously dominated almost solely by acid-tolerant liverworts. This is likely to reflect an improvement in water quality as aquatic mosses tend to dominate the least acidic streams in the Network.

The appearance of new aquatic plant taxa at several sites raises the question of whether these are taxa that previously occurred in those sites and are now re-appearing as acidity decreases, or whether they are new to the sites, either as random colonists or as taxa suited to warmer or more nutrient rich water than occurred during the pre-acidification period at those sites.

Studies of lake macrofossil records and aquatic macrophyte populations at appropriate analogue reference sites are needed to explore these alternatives.

11.4.3.Macroinvertebrates

Invertebrate populations have been monitored by kick sampling in all streams and in the littoral of lakes in the Network on an annual basis over the last 20 years with taxonomy conducted at the species level.

Although faunal change at most sites remains fairly modest, temporal trends are now clearly apparent at 16 of the 22 Network sites. The shifts in community structure are largely consistent with responses to reduced water acidity, as indicated by recently developed tools (Acid Water Indicator Community, AWIC, for streams and the Acid Waters Invertebrate Status Tool, AWIST, for lakes) for determining acidification status on the basis of the macroinvertebrate fauna.

Improvements in macroinvertebrate communities in some streams may be limited by the continuing severity of acid episodes occurring during high-flow and sea-salt episodes. However, the acidity of episodes in most streams has declined sharply over the last 20 years. For example, the macroinvertebrate community of the River Etherow, a highly episodic stream that is particularly acidic at high flow, shows one of the clearest recovery responses of any site on the Network.

Recovery is seen at sites of widely differing acidity status. One of the clearest improvements in the invertebrate assemblage has been in the relatively well-buffered Burnmoor Tarn where ANC has been above the widely applied “critical limit” for acidity from the outset of monitoring but continues to rise in response to declining acid inputs.

The suggestion that the recovery of invertebrate populations is restricted by difficulties of dispersal is not borne out by the evidence. Although episodicity may delay re-colonisation in streams, continued recovery is expected if chemical conditions continue to ameliorate.

11.4.4. Salmonid Fish

Salmonid populations have been monitored in all but one site across the Network over the last twenty years on an annual basis, although fish surveys at some sites have now stopped. In Scotland, the AWMN sites continue to be monitored with funding from the Scottish Government.

Density estimates of salmonids (brown trout, *Salmo trutta*, and salmon, *Salmo salar*) in AWMN streams and lake outflows are based on electrofishing catch data from standard reaches at each site. Populations are divided between species and age classes (0+ (fry) and >0+ (parr)) on the principle that different species and age classes have differing chemical requirements and that 0+ fish are better indicators of local conditions than older fish.

Positive changes in the presence of 0+ brown trout were observed at five sites, but significant positive trends (after accounting for multiple statistical tests using Bonferroni correction) were evident at only two of these; Scoat Tarn and Old Lodge. Analysis was also carried out on the presence of trout of all age classes (0+ and >0+), revealing significant positive trends at two sites; Old Lodge and Blue Lough.

There has been brown trout recruitment for the first time since monitoring began (as indicated by the detection of 0+ group fish) in the later part of the record at three sites, Old Lodge (since 1992), Scoat Tarn (1998) and Blue Lough (2000). These observations are important as they indicate that recruitment is beginning to occur at some of the most acidified sites in the Network.

There were significant relationships between water quality and the presence of trout of both age classes across the Network. Fish presence was significantly associated with a multivariate metric indicative of acidity (pH, ANC etc). However, complex interactions were also observed with multivariate indicators of cation concentrations and DOC. Furthermore, weak, but significant negative correlations were also observed between a multivariate metric indicative of nutrient concentrations and fish presence. This was interpreted as a land-use or N deposition influence and indicates the multi-factorial controls on fish populations.

Despite positive signs of recovery, salmonid fish populations remain heavily impaired at many sites on the Network. Assessing future recovery and the chemical standards required for recovery and protection of fish populations is likely to become increasingly difficult given the reduced range of sites that are now fished across the Network.

11.5. Trends in Toxic Trace Metals

In addition to acid gases, fossil-fuel combustion leads to the emission of toxic trace metals to the atmosphere. The trace metals cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni) and mercury (Hg) in deposition and lake water were monitored at only one site, the mountain lake Lochnagar. Measurements for all elements began in 1996 except for Hg which started in 1997 but all ceased in 2008. The Hg dataset is unique in the UK.

Additionally, the concentration of trace metals and spheroidal carbonaceous particles (SCPs), that are produced by high temperature fossil-fuel combustion, were monitored in samples of seston collected by sediment traps and aquatic and terrestrial mosses in Lochnagar and at the other lake sites in the Network.

At Lochnagar there has been a declining trend in atmospheric depositional fluxes of Hg, Pb and Zn over the period, in good agreement with the concurrent decrease in SCP concentration observed from the sediment trap record, probably reflecting the general decline in emissions since the late 1990s.

However, with the exception of Hg, data for the lake water showed little overall pattern. For Hg there has been a steady decline in lake water concentration over the last 11 years.

At a number of sites across the Network, sediment trap data and full lake basin sediment records indicate that trace metal inputs are not declining in proportion to the decline in emissions, probably as a result of catchment soil erosion transporting polluted top soil to lake basins.

Increased storminess and changes to seasonal precipitation patterns expected as a consequence of future climate change are expected to intensify this process, whereby contaminants stored in catchment soils following decades of atmospheric pollution are remobilised and transported to surface waters, exposing aquatic biota to toxic substances which potentially accumulate in plant and animal tissue.

This is of particular importance for the implementation of the Water Framework 'Daughter' Directive (2008/105/EC) that reaffirms the aim of the WFD to ensure that "existing levels of contamination in biota and sediments will not significantly increase". Of the trace metals, this Directive considers Hg to be especially of concern although Pb and Cd remain priority substances.

The metals data from lake sediments across the Network match the geographical pattern of acid deposition confirming their derivation from largely common fossil fuel combustion sources. The lowest fluxes occur in northern Scotland and the highest across northern England and southern Scotland.

If the aims of the WFD are to be met with respect to priority substances, monitoring protocols for metals need to be restored at Lochnagar and introduced at other sites across the Network.

11.6. Present Status and Recovery Targets

After twenty years there is now consistent and compelling evidence for both chemical and biological improvement for the acidified sites across the Network. The central concern now is whether the improvement can be sustained and whether the targets for recovery can be achieved.

Recovery targets are defined principally by the UNECE Gothenburg Protocol of 1999, the EU National Emissions Ceilings Directive (NECD) and the EU Water Framework Directive (WFD) (2000).

The first two of these are concerned with the reduction of acid emissions from industry and agriculture. For surface waters the legislation requires acid deposition to be reduced to a level where the 'critical load' of acidity to lakes and streams across Europe is not exceeded. The critical load is defined with respect to the ANC of an individual water body, called the 'critical limit'.

In this report we consider first whether current levels of deposition are sufficient in the long-term to allow the recovery of waters above the specified critical limit by calculating critical load "exceedances", and second the extent to which current chemistry and biota deviate from both pre-industrial (reference) conditions and the critical limit.

In the UK we have adopted a value of 20 $\mu eq\ l^{-1}$ ANC as the critical limit, but this has been relaxed for sites known to be very acidic naturally, in which case a value of 0 $\mu eq\ l^{-1}$ is used. Although these targets are defined chemically, they relate to biological conditions as ANC has been shown to be a good predictor of biological, and especially fish, status. In particular, extensive surveys of fish populations in Norway have shown that standing waters with ANC values of at least 20 $\mu eq\ l^{-1}$ have a 90% probability of containing an undamaged brown trout population. However, our observations of apparent biological recovery responses in diatoms, macrophytes and macroinvertebrates in the relatively well-buffered Burnmoor Tarn (where ANC has risen from around 50 to 80 $\mu eq\ l^{-1}$ over the last 20 years) suggests that this level of protection may be completely inadequate for some less acid, but still acid-sensitive, waters.

In calculating critical loads exceedances, we have used both the Steady State Water Chemistry (SSWC) model and the First-order Acidity Balance (FAB) model. The models are similar except that the SSWC uses measured NO_3^- concentrations to estimate the leaching flux from soils, whereas the FAB model calculates a theoretical long-term steady state balance between deposition and leaching. Consequently the two models provide "best case" and "worst case" scenarios respectively.

Critical load exceedances are calculated for three past deposition scenarios (1986-88, 1996-98, 2004-2006) and one future scenario (2020 – see below), for all 23 lake and stream sites (i.e. the original 22 sites plus the replacement for Coire Nan Arr, Loch Coire Fionnaraich) using both the SSWC and FAB models. Whereas the SSWC model indicates that exceedances have already been eliminated at 18 of the 23 sites, the FAB model suggests that the majority (19) are still exceeded. The difference between these figures highlights the importance and uncertainty associated with the future behaviour of NO_3^-, specifically the extent to which leaching may occur in the future as a result of N saturation in soils.

The dynamic soil and water acidification model MAGIC was successfully calibrated to the 20 year AWMN chemistry data, using corresponding ADMN deposition data, for all sites except Llyn Cwm Mynach and Old Lodge. MAGIC simulations provided chemical reference conditions in terms of ANC, pH and soil base saturation (see below). Loch Coire Fionnaraich was not included in this calibration due to the much shorter time-series of data.

The third of the main legislative programmes, the WFD, adopts a different conceptual approach from the critical loads approach. Whereas the critical loads approach is concerned with achieving a minimum standard for the restoration of acidified waters the WFD requires restoration to "good ecological status" in comparison with a reference condition.

The reference condition is defined as the ecological status of lakes and streams of the same lake or stream type in pristine or almost pristine condition.

Defining “reference conditions” for a lake or stream type or an individual water body can be problematic, although several complementary methods (e.g. using palaeo/historic data, non-polluted analogues, modelling) have been and are being developed and trialled at AWMN sites.

The AWMN provides the UK with the most representative and reliable data needed to assess progress towards meeting the “good ecological status” objectives of the WFD. It has a special role to play in this respect as current Environment Agency WFD protocols consider lakes with a surface area greater than 50 ha only, a threshold that consequently ignores the majority of the water bodies in the UK suffering from acidification (i.e. headwater lakes).

Using these methods we have evaluated the extent to which the AWMN sites diverge from reference conditions. We have not yet, however, attempted to identify the criteria needed to differentiate between “good” and “moderate” status that is central to the implementation of the Directive.

So far we have explored divergence from the reference state with respect to chemical change (ANC, pH, soil base saturation) and biological change (diatoms).

Reference ANC values for AWMN sites have been estimated with the MAGIC model scaled back from the calibration data of the ADMN using historic emissions inventories. The MAGIC results indicate that all sites except Blue Lough had a reference ANC value above the critical limit of 20 μeq l^{-1}, and all but four sites had pre-industrial ANC values of less than 100 μeq l^{-1} indicating high acid sensitivity. Ten sites have current ANC values below both the critical limit of 20 μeq l^{-1} and below their respective reference values, five sites have improved to the critical limit but are still below their reference and five sites have never had ANC values below the critical limit but are nevertheless below their reference values. There are also two sites in Northern Ireland (Coneyglen Burn and Beagh's Burn) which appear to have changed little from their reference values, varying only within the probable errors of prediction of the models.

These results indicate the importance of setting recovery targets that are appropriate for individual sites to allow for sites with reference ANC values that fall both below (Blue Lough) and above (all other sites) the ANC value of 20 μeq l^{-1}.

Reference pH values for AWMN sites can be obtained using both palaeolimnological reconstruction (lakes only) and MAGIC-modelling hindcasts.

Although the MAGIC hindcasts tend to provide somewhat higher estimates of reference pH values than the palaeolimnological method, both show that for all strongly acidified lake sites there are very significant differences between reference pH and present day values, indicating that the recovery in pH has so far been significantly less than expected on the basis of the reduction in acid deposition that has taken place.

A measure of biological recovery can be estimated from the differences between the diatom floras preserved in pre-acidification lake sediments of the early nineteenth century and the present day. Combined data from sediment cores and sediment traps indicate that, with the exception of Llyn Llagi in north Wales, only a muted recovery has taken place over the last 20 years when compared with the reference.

Of interest from the diatom analysis is that for some sites the species composition of the diatom assemblages during the recovery phase is different from the equivalent stage during acidification. The possible reasons for this may be related to chance, to internal community dynamics or micro-habitat shifts, or to a change in external pressures linked e.g. to land-use change, to nutrient enrichment from N deposition or to climate change.

11.7. Processes Limiting Recovery

Despite the clear and consistent evidence now available to show that the chemical and biological status of acidified waters in the UK are improving, the analysis presented here suggests that the improvement is limited when the current status of lakes and streams in the Network is compared to their reference state and when compared with the extent of reduction in acid gas emissions. Reasons for the limited response include:

(i) *Inadequate reduction in acid deposition.* Although S deposition has declined to very low levels in comparison with the ca. 1980 maximum, N deposition is still relatively high and contributes a small but significant fraction of the total acid anion concentration at some sites. However, this cannot account for the limited recovery overall as the reduction in S deposition since 1987, accounting for the major proportion of acidifying anions, has been greater than 80%, while NO_3^- leaching is still a very small proportion of deposited N in most catchments.

(ii) *Limited or no recovery of soil base saturation.* According to MAGIC model simulations, limited recovery in the soil base cation status (base saturation) is predicted to partially offset the rate of chemical recovery of surface waters at the AWMN sites. Some sites show small increases in response to declining acid deposition while others show a continuing decline to the present day, restricting the ability of ion-exchange in catchment soils to buffer deposition inputs of acidity.

(iii) *Continued release of S from catchment soils.* Although many studies have shown that S acts conservatively in catchment soils and that reductions in deposition are rapidly followed by concomitant reductions in SO_4^{2-} flux to surface waters there is also evidence that stored 'legacy' S may continue to be released through time even after deposition is reduced to negligible levels, especially at sites with organic soils, through both oxidation and erosion processes. Sulphate levels at many of the AWMN sites remain high compared to expected background values typical of those at the AWMN control sites in the North-west of Scotland.

(iv) *An offsetting increase in the release of NO_3^- from catchment soils.* Not only has the reduction in N deposition been small in comparison to S deposition, but at a small number of sites in the Network (e.g. Round Loch of Glenhead, Loch Chon) NO_3^- concentrations have risen, offsetting some of the effects of reduced SO_4^{2-} concentrations. At many other sites (e.g. River Etherow, Scoat Tarn) NO_3^- levels remain at much higher levels than the expected background values of <5 μeq l^{-1} found in the control sites, as a result of sustained historic N deposition and soil saturation by N, leading to seasonal or all year round N leaching.

(v) *pH has not responded as rapidly to declining acid deposition as initially expected.* The reduction in acid anion concentrations across the Network has been balanced by a reduction in Ca^{2+} concentration, an increase in DOC, and at a number of the most acidified sites, a reduction in labile Al^{3+}, and relatively little of the change in ANC to date has been expressed by an increase in pH. It is also now clear that the increase in DOC, once thought to be caused by climate change, is also the result of a reduction in acid deposition. It is possible therefore, that the overall chemical response, as indicated by the change in ANC, is indeed proportionate to the deposition reduction, but that at many sites this has not yet led to a significant increase in pH.

(vi) *Recovery is being confounded by other stresses.* Whereas acid deposition, especially S deposition, has been the dominant factor controlling the composition of biological communities in acidified upland surface waters, these water bodies have also have been subject to other external influences including land-use change and climate change over the last 200 years. Base cation depletion of catchment soils through acid deposition has reduced soil alkalinity, and forest growth may have contributed to this process at some sites, although the results for this effect across the network are equivocal. Small but significant changes in climate have also occurred over the last 200 years and there appear to be small declining trends in precipitation over the monitoring period.

11.8. Future Prospects and Threats

The steady-state models SSWC and FAB and the dynamic model MAGIC have been used to project the hydrochemical response of AWMN sites to assumed changes in acid deposition by 2020 under the Gothenburg Protocol. In addition MAGIC has also been used to simulate hydrochemical change up to 2100, maintaining deposition at 2020 levels.

For 2020, the results from the models differ. The FAB model represents the worst case scenario predicting 15 sites to have long-term ANC <20 $\mu eq\ l^{-1}$ compared with five sites using SSWC and MAGIC. These five most acidified sites are predicted by MAGIC to remain below the critical limit even by 2100.

The main reason for the differences between models lies in the uncertainty about the behaviour of nitrogen in catchment soils and its release to surface waters in future. Whereas MAGIC accounts explicitly for the timing of different chemical processes, FAB, as a steady-state model, does not include a time-scale for N saturation and this is likely to be a very slow, long-term process according to MAGIC.

It is not yet clear whether, or how quickly, N saturation will occur at different sites. The strong non-linearities in both bulk deposition of N species and surface water NO_3^- concentrations over the last 20 years highlighted in Chapters 2 and 3 demonstrate that predicting future trends is very difficult. Until these uncertainties are resolved these models will continue to be used to provide lower and upper bounds on surface water acidification and ANC recovery (or decline).

MAGIC predicts a recovery at the acidified afforested sites in line with the recovery of moorland sites, with all except Loch Grannoch predicted to have an ANC >20 $\mu eq\ l^{-1}$ by 2020. However, the prediction for Llyn Cwm Mynach is unsafe as MAGIC is not able to simulate current chemistry at this site.

Planned reductions in forest cover will have a small effect on the risk of critical loads exceedance and are unlikely to significantly alter the path to recovery. However, the conversion of closed canopy conifer forest to native broadleaved woodland within riparian zones can improve the quality of freshwater and riparian habitats. The establishment of native woodland riparian buffer zones may also play a role in controlling nitrate leaching

Current research has demonstrated the potential role of atmospheric N deposition in causing eutrophication in upland waters, a finding that has implications for N emissions policy with respect to international directives. Increased availability of nutrient N may affect biodiversity in oligotrophic systems adapted to low N availability. This effect is likely to extend to all surface water systems in the British uplands, not only those that are sensitive to acidification.

Although the deposition of trace metals has declined significantly over recent decades their concentration in aquatic biota and in surface sediments of AWMN sites remains high. There is now strong evidence that this is related to the re-mobilisation of pollutants that have accumulated in soils over the industrial period and their transport to surface waters by soil erosion. Climate change is expected to intensify this process potentially leading to an increase in the exposure of aquatic biota to both trace metals and persistent organic pollutants.

In the UK threats to the recovery of acidified upland waters from climate change are likely to be more related to changes in the seasonality, intensity and frequency of precipitation and sea-salt deposition events, than to temperature. Any increase in rainfall is expected to generate runoff with lower base cation concentration, lower pH and ANC, and higher aluminium and DOC concentrations, while increased storminess may lead to an increase in episodic sea-salt deposition, increasing the frequency and intensity of a process by which marine cations temporarily displace acid cations from the exchange sites of acid soils, causing pulses of highly acidic runoff.

Analysis of AWMN data shows that the temporal pattern of sea-salt deposition across the Network can be linked to the state of the North Atlantic Oscillation (NAO) and, even more strongly, to the Arctic Oscillation (AO). This observation explains the higher than expected acidity that occurred at sites across the Network in the early period of monitoring when, as noted above, the AO index was at its highest for 60 years. It also indicates the possible future threat of sea-salt deposition if the AO continues to become more intense as recent trends indicate.

Our analysis suggests that, were the 1989-1991 levels of sea-salt inputs to recur, the mean ANC levels of all 11 AWMN sites that are both geographically vulnerable to sea-salt deposition and particularly acid-sensitive systems, would be significantly depressed, and ecologically damaging increases in acidity could result at some sites.

11.9. Recommendations

As acidified waters begin to recover it is essential to maintain and, where necessary, restore, all chemical and biological observations across the Network to assess the extent of recovery, with respect to: (i) the legislative demands of UNECE protocols and the EU WFD placed on Defra; (ii) understanding the future influence of climate change and other potential stresses on upland waters; and (iii) the needs of users including Environment Agencies (EA, SEPA, EANI), Conservation Authorities (Natural England, CCW, SNH), the Forestry Commission and Water Utilities. Reductions in the Network reduce the environmental range and statistical power of the Network and consequently its value to UK government and science.

The importance of upland water monitoring extends beyond the aquatic system as changes in water chemistry and biota integrate and reflect the impact of stressors on the wider catchment. Considerable advances, for example, have been made in the field of upland soil biogeochemistry in recent years as a direct result of the data gathered by the AWMN and comparable networks in North America and continental Europe. Data from the AWMN have been central to four biogeochemically-related scientific papers published in Nature since 1999, and the subject of many other important peer-reviewed publications in this area. As concern develops over the future of upland habitats and how they should be managed (e.g. with respect to threats to upland peat stocks and upland biodiversity from changes in climate, pollution and land use) it is vital that this crucial component of National Capability continues to function. It is equally important that the role of the AWMN as an indicator of upland ecosystem health is reviewed and if necessary developed to provide an even stronger evidence base for a wider group of national and regional stake holders. In this context an extension of the Network to include a stream site in the North York Moors is recommended.

To evaluate the future role of climate change, the installation of temperature and water level/water flow recorders at AWMN sites is urgently required.

As evidence grows for the enriching effect of N deposition, the Network needs to be enhanced to include measurements of chlorophyll *a* and algal standing crop, and a range of new non-acidified sites sensitive to N enrichment need to be added to the Network.

To meet the aims of the WFD with respect to priority substances, monitoring protocols for metals need to be restored at Lochnagar and introduced at other sites across the Network.

Recent funding reductions threaten the continuity and integrity of the AWMN. As one of the UK's highest quality unbroken long-term monitoring programmes, and the only one dedicated to the monitoring of water quality and freshwater biodiversity in the uplands, the Network needs long-term protection from funding constraints.

We need a strategic vision for the Network so that it can fulfil its potential as a system capable of tracking the hydrochemical and ecological response of all types of upland waters and their catchments to future changes in pressures from human activity. This is likely to require a more integrated monitoring approach than hitherto, linking biogeochemical processes with fluvial and limnological indicators of stress and recovery. A workshop to develop a long-term strategy for the AWMN is recommended.

APPENDIX 1 AWMN – Policy support and wider relevance (2005-2010)

The AWMN not only provides definitive data on trends in the chemistry and biology of acid waters in the UK, it also supports UK policies on acid deposition and water quality, provides the evidence base for upland water management in the UK and underpins both national and international research programmes on freshwater ecosystems. Here we summarise the role of the AWMN in these fields over the last five years

Policy support

The AWMN provides the evidence base to show the effectiveness of policy with respect to principal EU and UNECE legislation on acid deposition and surface waters in the UK as outlined in Chapter 1. It contributes data from six sites to the UNECE International Cooperative Programme on the Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) at the Focal Centre, NIVA, Oslo, as well as the ICP on Integrated Monitoring (two sites). Within the UK, data from four AWMN sites are contributed to the UK Environmental Change Network. Data from the AWMN has also been used to provide information on acidification status of Scottish rivers to NASCO (North Atlantic Salmon Conservation Organisation) to demonstrate improving status and was explicitly mentioned as an important source of data in the recent NASCO implementation plan for Scotland.

Management of upland waters

The AWMN is a major resource for organisations responsible for the management of upland water catchments in the UK, with many sites being located in SSSIs/SACs, and/or National Parks and National Trust land. These include:

The Environment Agency (Water Framework Directive and Daughter Directive on priority substances)
The Scottish Environment Protection Agency (Water Framework Directive and Daughter Directive on priority substances)
Environment and Heritage Service (NI) (Water Framework, Daughter Directive on priority substances and Habitat Directives)
Natural England (Habitats Directive)
Countryside Council for Wales (Habitats Directive)
Scottish Natural Heritage (Habitats Directive)
Forestry Commission (Forest and Water Guidelines)

Data from the Network has been used in WFD (Water Framework Directive) acidification tools for diatoms and invertebrates and will shortly be included in fish tool development for Scotland. Data from the Network continues to be useful in informing environmental standards and has been used indirectly to support the UK Rivers Task Team (RTT).

Several AWMN catchments are located in important drinking water catchment areas managed in association with water companies (e.g. River Etherow – North-west Water, Loch Tinker – Scottish Water).

Research support

The AWMN has been central to acid waters research in the UK with respect to both international and national research programmes, underpinning the UK's leading international position in this field. Key projects include:

Euro-limpacs, an integrated project under the EU's 6th Framework programme on "The impacts of global change on European freshwater ecosystems" GOCE-CT-2003-505540, (2004-2009)
WISER, an integrated project under the EU's 7th Framework programme on "Water bodies in Europe: Integrative systems to assess ecological status and recovery" Project Code 226273, (2009-2012)
REFRESH an integrated project under the EU's 7th Framework programme on "Adaptive strategies to Mitigate the Impacts of Climate Change on European Freshwater Ecosystems" Project Code 244121, (2010-2014)
BIOFRESH an integrated project under the EU's 7th Framework programme on "Biodiversity of Freshwater Ecosystems: Status, Trends, Pressures, and Conservation Priorities" Project Code 226874, (2010-2014).

Within the UK the AWMN has been central to UK Government research through Defra. Under the Freshwater Umbrella programme current research uses the AWMN to support:

Biogeochemical studies into the fate of deposited N at AWMN catchments to quantify mass balances for N and develop critical load and dynamic models
Palaeolimnological studies of lake sediment isotopes as indicators of nutrient N impacts
Isotopic tracer and natural abundance studies of the fate of deposited N
Nutrient bioassay studies into changing lake and stream productivity induced by N deposition

These research programmes are heavily dependent on the long-term, high quality chemical and biological datasets available only from AWMN sites. They also benefit greatly from the co-location of Acid Deposition Monitoring Network sites with eight of the AWMN sites, with the direct aim of providing site specific deposition input data for computing mass balances and informing biogeochemical studies in areas of high scientific and conservation interest.

Beyond Government-funded research the AWMN is an invaluable resource for University and CEH-based research and teaching. These have included:

NERC standard grant (University of Leeds) to determine the influence of precipitation chemistry on DOC concentration
NERC Ecology and Hydrology Funding Initiative grant (CEH Bangor) concerned with examining possible inter-relationships between sulphur, nitrogen and carbon dynamics in upland soils.
Numerous PhD projects.
Teaching resource for the NERC recognised Freshwater and Coastal Sciences MSc. Programme, including MSc dissertations based around AWMN data (two in 2009) (UCL and QMUL)
Leverhulme funded project on "Runoff processes and catchment hydrology" (Aberdeen University)

APPENDIX 2 Statistical methods

Several statistical techniques have been used to investigate trends in the AWMN datasets. For univariate data, such as the deposition and hydrochemistry data, a regression technique known as an additive model was used, whilst for the multivariate biological data, a variety of ordination-based techniques has been employed.

Additive Models

Additive models are similar, in many respects to the more familiar linear or least squares regression technique. In a linear regression we estimate coefficients for one or more predictor variables that represent the effect on the response of a unit change in a predictor. In the time-series setting, a linear regression with time as a predictor variable will result in a coefficient estimate that is the rate of change in the response over the period of interest. This effect is global, being the same throughout the time period of the data.

In an additive model we can relax this global effect and fit more flexible regression models that allow the rate of change in the response to vary through time; in effect we can model non-linear trends or patterns in the observed data. This is achieved by replacing the estimated regression coefficients in linear regression with smooth functions of the predictors, fitted using splines or smoothers. A key feature of these additive models is that they allow the data to inform the shape of the fitted trend. In linear regression we impose a fixed, parametric form for the relationship between response and predictors, whereas the smooth functions of the additive model adapt to features of the data.

For trend analysis of the deposition and hydrochemistry time-series we fitted additive models consisting of two smooth functions; (i) a cyclic cubic regression spline for the seasonal component, and (ii) a cubic regression spline (CRS) for the longer term trend. A cyclic CRS is a special type of spline in which the end points of the spline are constrained to be the same, which allows for smooth transitions between December and January. The degree of smoothing allowed in each of the splines was determined by estimating a smoothing parameter as part of the model fitting procedure. Restricted Maximum Likelihood (REML) was used to fit the additive time-series models.

Regression models assume independence of residuals. With time-series data, there is the possibility that the model residuals are not independent because of temporal autocorrelation. To handle this complication, a dependence structure can be assumed for the model residuals that allows the residuals to be autocorrelated. The data here are irregularly sampled in time and as such we assume a continuous time first order autoregressive (CAR(1)) process for the residuals. Likelihood ratio tests can be used to identify if the CAR(1) process is required or not. For the models presented here, the CAR(1) did not significantly improve the fit of the additive models and was therefore dropped for further analysis. The implication of this result is that the seasonal and trend components of the fitted models adequately modelled the temporal dependence structure in the data.

Additive models are so-called because they have a very simple additive nature; the model components are added together to give a fitted value. In the case of the time-series models fitted here, the fitted value is the sum of the overall mean value of the response (the model intercept), the contribution from the seasonal smoother, and the contribution of the trend smoother. This decomposition of the fitted model into its constituent components allows us to consider the trend component only and investigate how this component changes through time. Plots of the fitted trend are augmented by adding on the model intercept term so values on the y-axis are more easily interpreted.

Additive models take their form from the data and as such we might like to investigate whether features of the fitted smoothers are significant or not. In the case of the time-series models fitted here, we wish to know whether features in the fitted trends are significantly increasing or decreasing. We estimate this significance using the first derivatives of the fitted spline for the trend, computed using finite differences. A confidence interval, here 0.95 (95%), for the derivative is computed, which allows the identification of intervals of the spine where the derivative is significantly different from zero, i.e. significantly increasing or decreasing. The portions of the fitted trends that are significantly changing are identified in the plots using a thicker, coloured, line for the trend. In these plots, red indicates significantly decreasing and blue significantly increasing.

For the deposition data, a preliminary analysis was performed where all the data from the co-located acid deposition monitoring network sites were analysed in a single model to investigate general patterns of change for this set of sites. The model fitted was an additive model of the form discussed above for the individual sites, with a cyclic CRS for the seasonal component and a CRS for the trend component of the observed time-series respectively. To accommodate the differences between sites in their respective means, we introduced to the model a random effect for site. In the same way that temporal autocorrelation introduces dependence structure in the residuals, the clustering or grouping of the observed data due to them being recorded at a number of distinct sites also introduces dependencies in the residuals.

There are several ways in which these dependencies can be modelled but here we chose to model this dependence using a random effect as part of an additive mixed effects model fitted to the deposition time-series for all sites. The random effect is treated as a Gaussian random variable with mean zero and unknown variance, which is to be estimated as part of the model fitting process. The random effect for site is introduced as a random intercept for each site, whilst the seasonal and trend smooth components are general patterns pertaining to and being modelled from all the available data. The random intercept models the differences in the mean values of the respective sites and can be thought of as shifting the seasonal and trend smoothers up or down depending on the mean deposition value for each site. This dependence structure also induces a correlation between residuals from a single site.

This model was used as a starting point from which to investigate common patterns of change in deposition at AWMN sites. At this stage we have not investigated whether the model needs to be increased in complexity to allow for different trends for some or all sites, or different seasonal patterns for some or all sites. Furthermore, we have not ascribed statistical significance to the extracted trend and seasonal components as analysis of the model residuals for heterogeneity has not yet been conducted.

Multivariate Methods

The key techniques used to evaluate trends in the biological data are ordination based, which extract the main patterns in multivariate response data and express these on a few dimensions or axes which are displayed in ordination diagrams. Unconstrained ordination techniques are used to simply look at patterns within biological data, whilst constrained ordination techniques are used to extract patterns that are related to one or more predictor variables.

The biological data analysed here represent two distinct groups; aquatic macroinvertebrates and epilithic diatoms. The macroinvertebrate and diatom data are collected as a series of replicate samples recorded as counts of individuals of different taxa and were analysed in a similar manner. The data for each site were analysed separately. Prior to analysis, the replicated macroinvertebrate and diatom data counts were aggregated to give a total count for each year at each site and then converted to percentages. The data were $\log_{10}$ transformed (a count of 1 was added to zero macroinvertebrate counts to allow the log transformation), and subsequently double centred (by samples and by species) before being analysed using principal components analysis (PCA) to investigate the main patterns of change in the species assemblages.

Redundancy Analysis (RDA), the constrained form of PCA, was used to investigate the degree to which linear trends were present in the macroinvertebrate and diatom data. Time, expressed as the sample year, was used as the sole explanatory variable in the constrained analyses.

The presence of a trend in the species data was determined using a restricted permutation test to assess the significance of the variance explained by sample year. A restricted permutation was used to preserve the dependence structure between samples; samples one year apart are likely to be more similar to one another than samples separated by several years. The restricted permutation test used preserves the ordering of samples within the series, whilst generating permuted data via a series of random, cyclic shifts, by joining the two ends of the time-series together and rotating this joined series to a set of random starting years. The number of permutations possible for such data is n, the number of samples, as time flows in only a single direction; the species composition in year 2 does not influence that of year 1. For AWMN sites other than Loch Coire Fionnaraich the numbers of samples per site are at the limit for detection of trends at the 95% level. With the 20 years of observations the minimum p-value obtainable is 0.05. For the macrophyte data, which are not sampled every year, the minimum p-value is larger than the 0.05 level normally taken as the boundary of a significant result.

Principal response curves (PRC) is a constrained ordination technique, based on RDA, which can be used to analyse repeated measures data, such as the short biological time-series data collected on the AWMN. PRC is more sophisticated than RDA as it optimally displays the effects of a “treatment”, here time, relative to a “control”, over time, such that the treatment effects are expressed on a single axis. PRC can be used for monitoring data if a suitable control can be identified. Here we generate a synthetic control time-series for each site, by averaging the raw data of the first three years of sampling and then repeating this averaged sample to equal the length of the observed time-series for each site. In this manner, the PRCs reflect the time dependent changes in species composition relative to the start of monitoring. We chose the first three years of monitoring for the controls to reduce the potential for bias in selecting a single sample year that may potentially be unusual. Whilst there is no theoretical reason why a PRC analysis can not be formulated from CAP, rather than RDA, this analysis has not been attempted before, to our knowledge, and no existing software is capable of producing such an analysis. As such we restrict the PRC analysis, at this stage, to the macroinvertebrate and diatom data. We will investigate the potential for including the lake macrophyte data in a CAP-based PRC analysis at a later stage.

APPENDIX 3 Hydrochemical Analyses – Figures and Tables

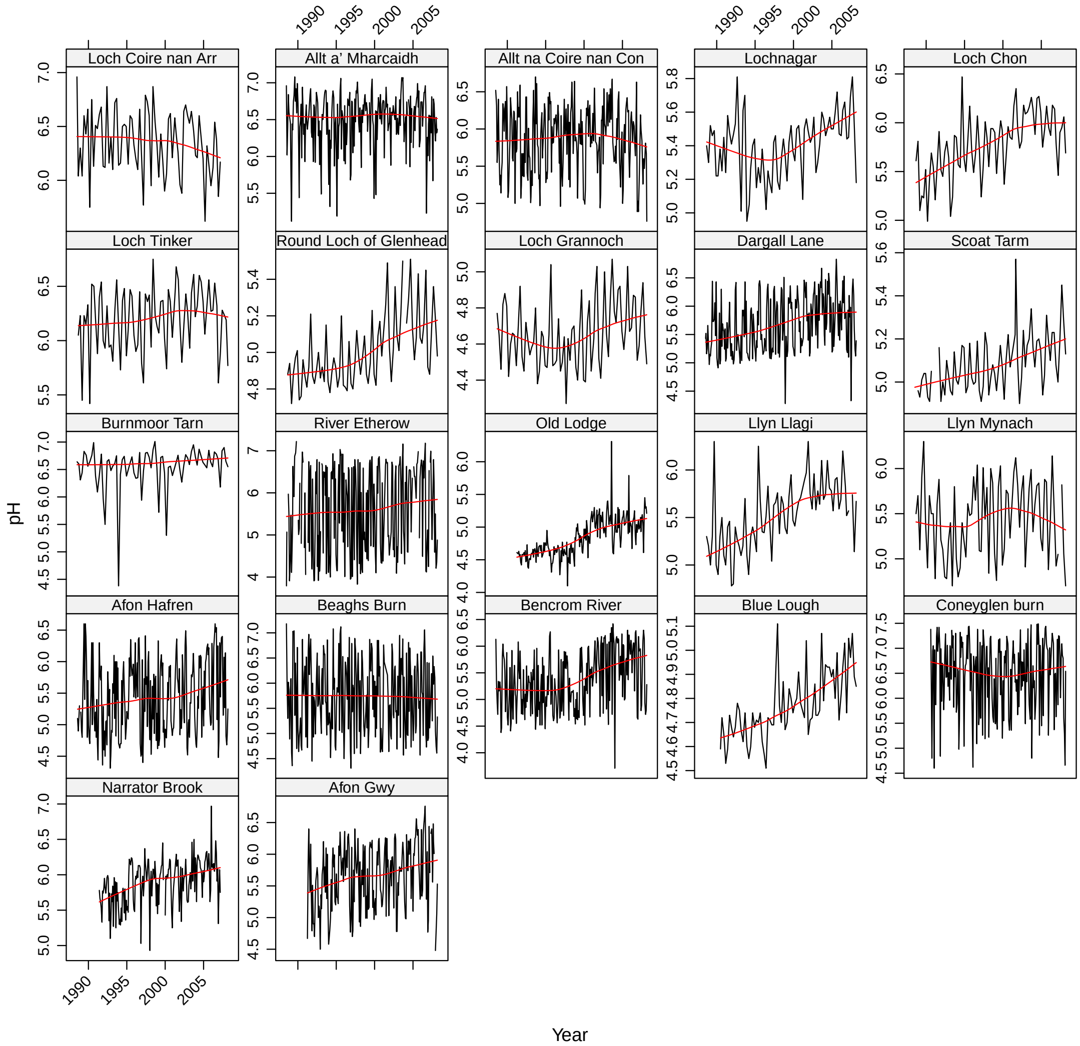

Figure 1: Time-series of observed pH at AWMN sites

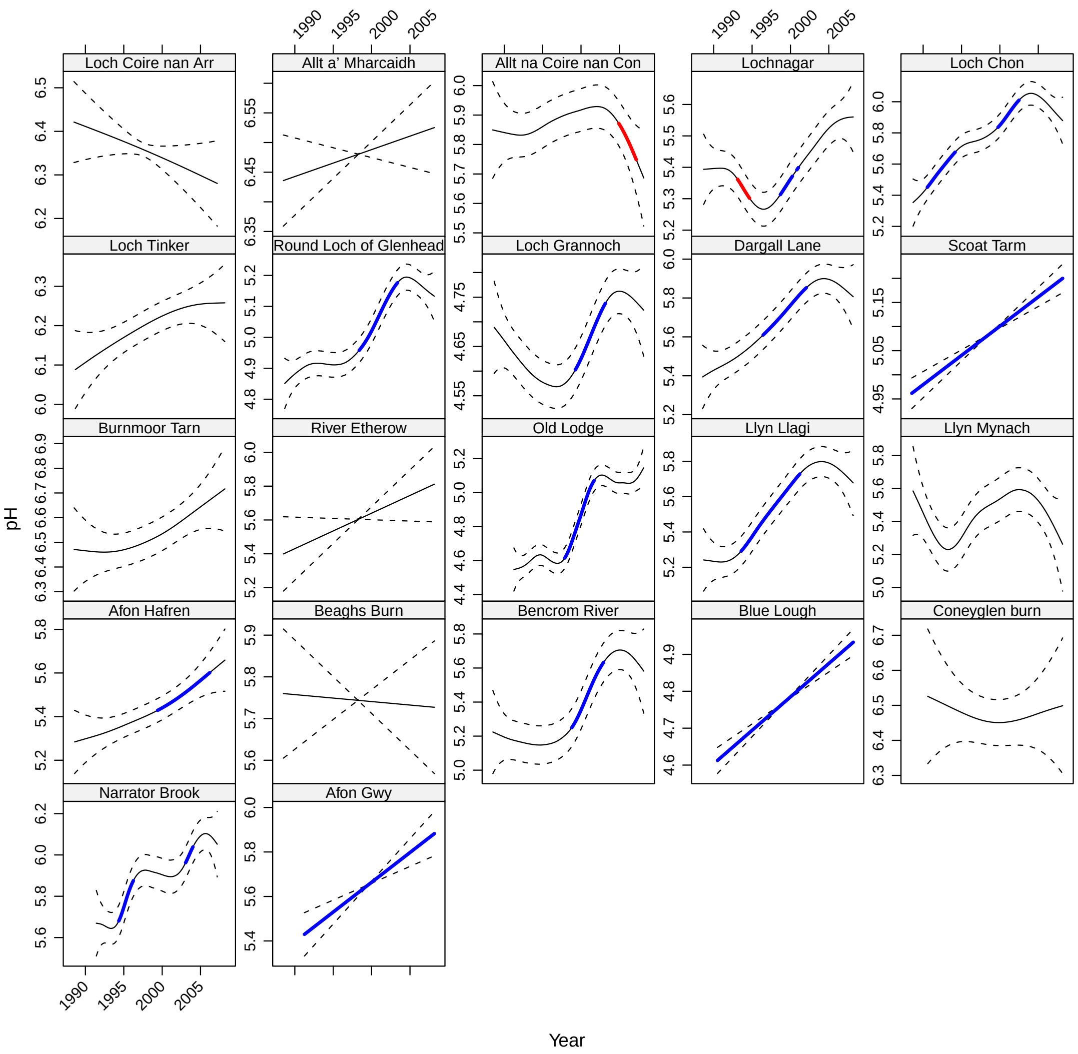

Figure 2: Fitted trends in pH for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

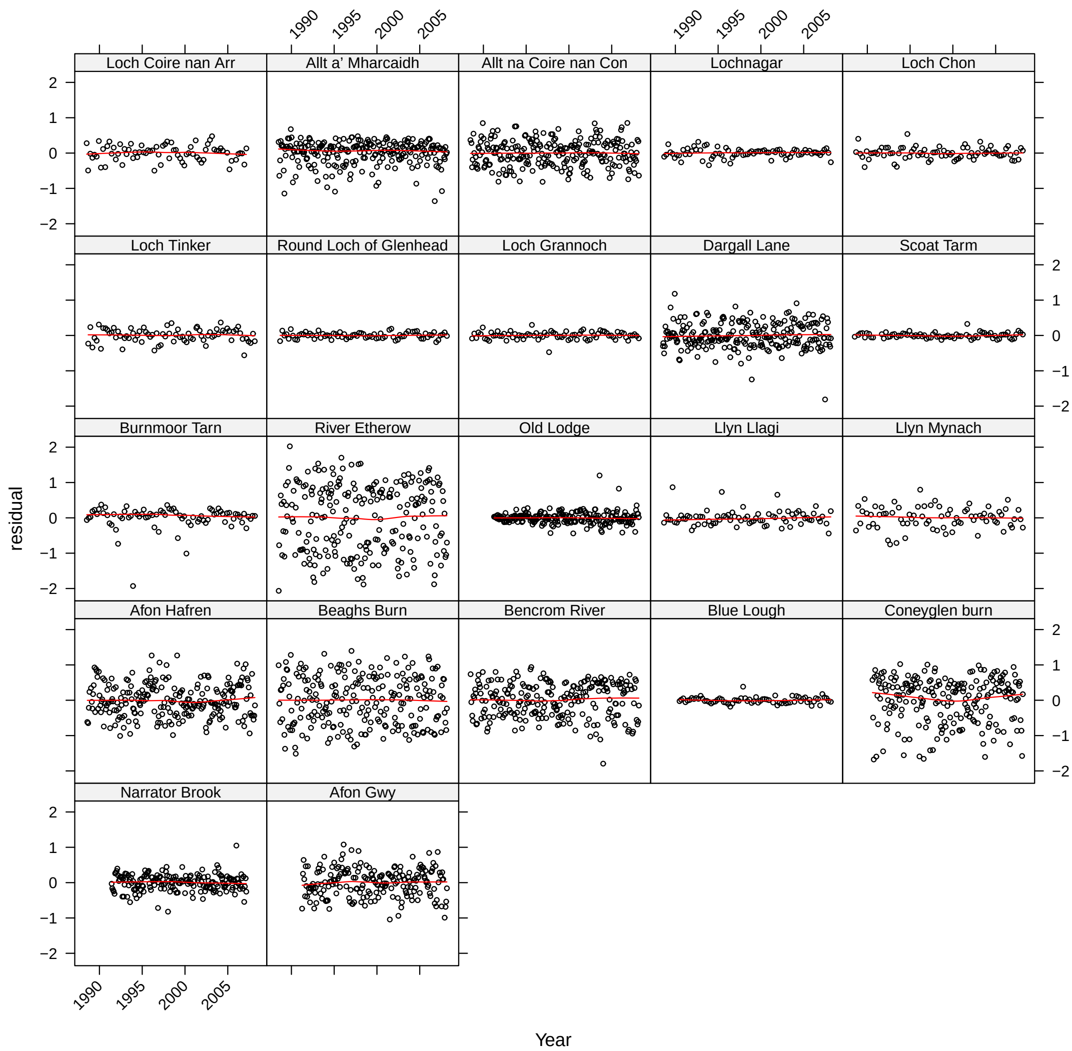

Figure 3: Residuals for the models fitted to pH for AWMN sites

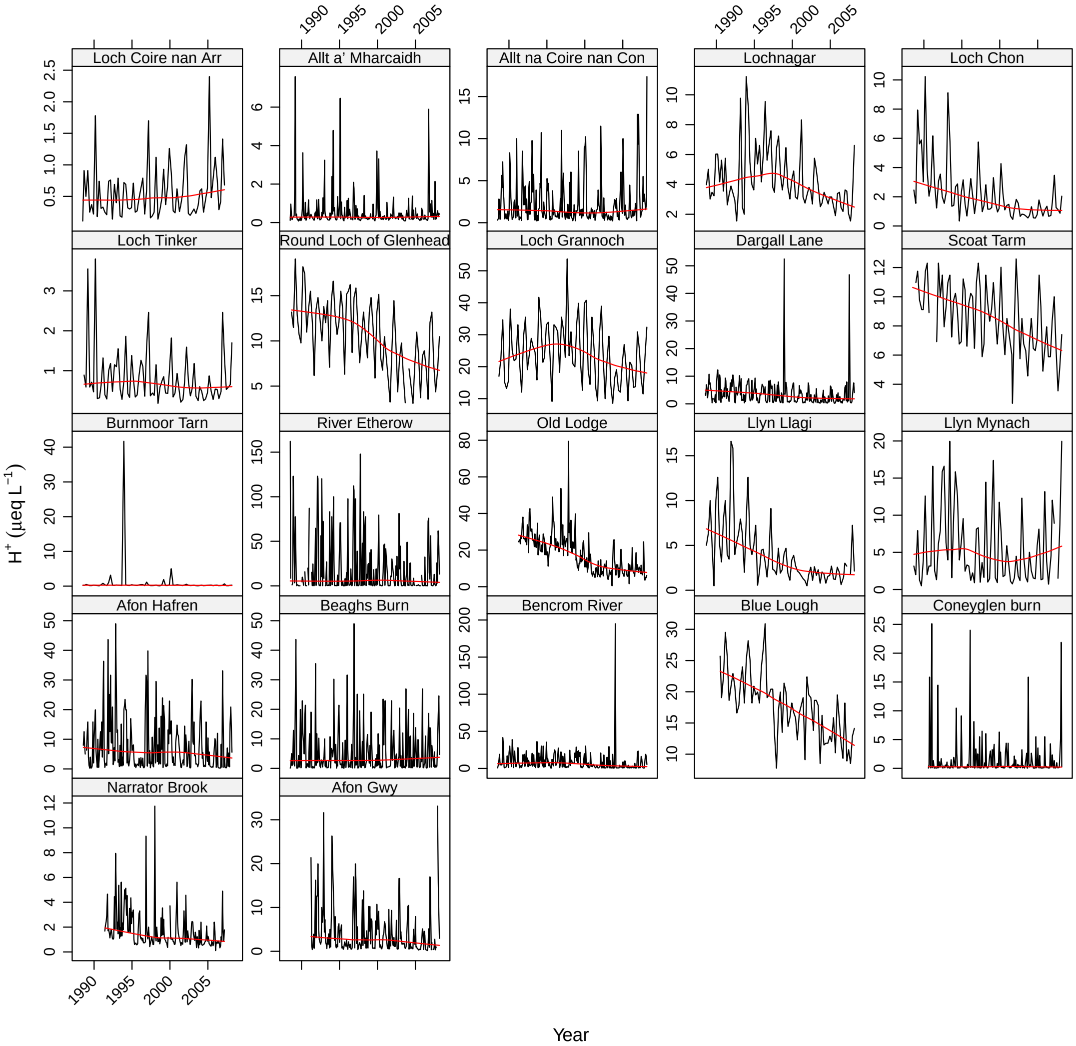

Figure 4: Time-series of observed H^+ at AWMN sites

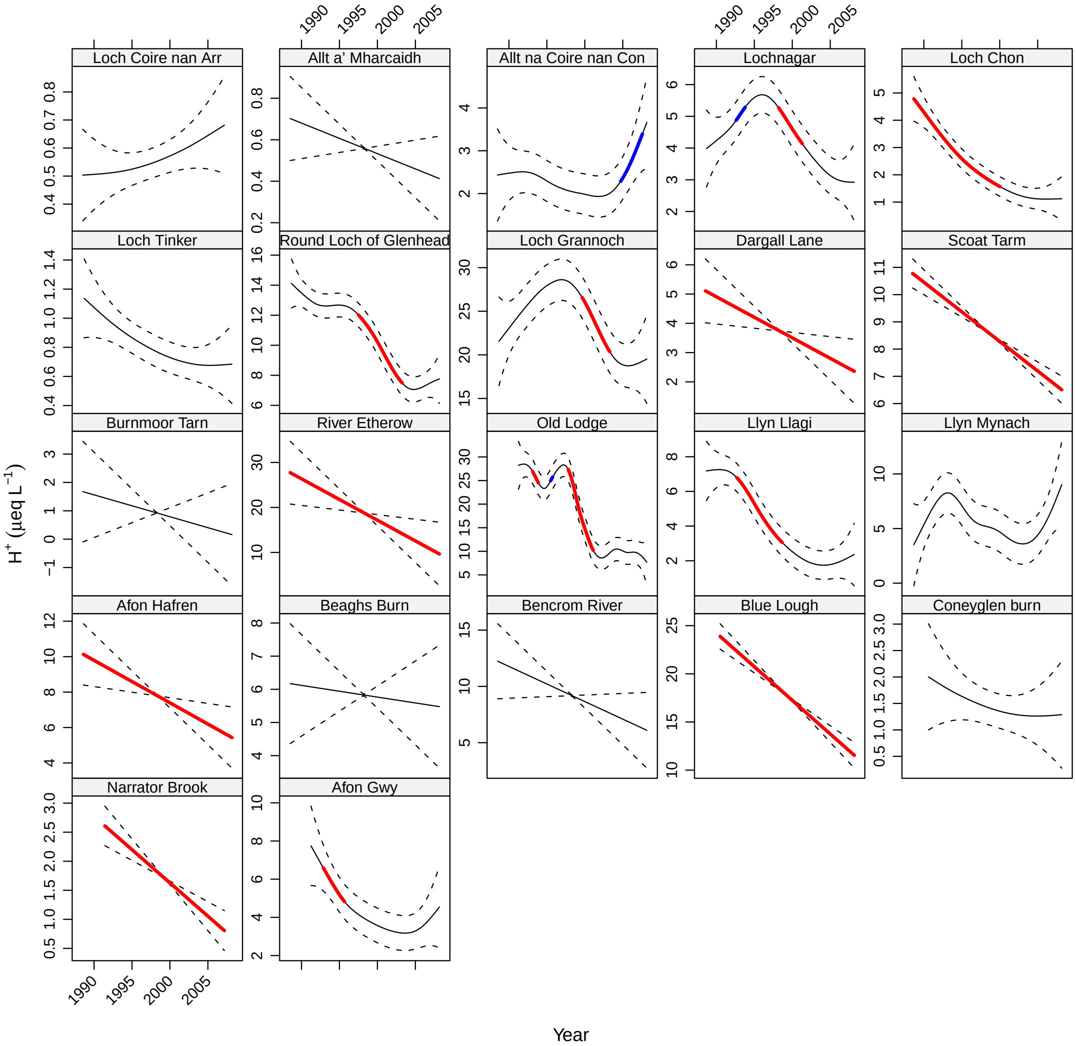

Figure 5: Fitted trends in H+ for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

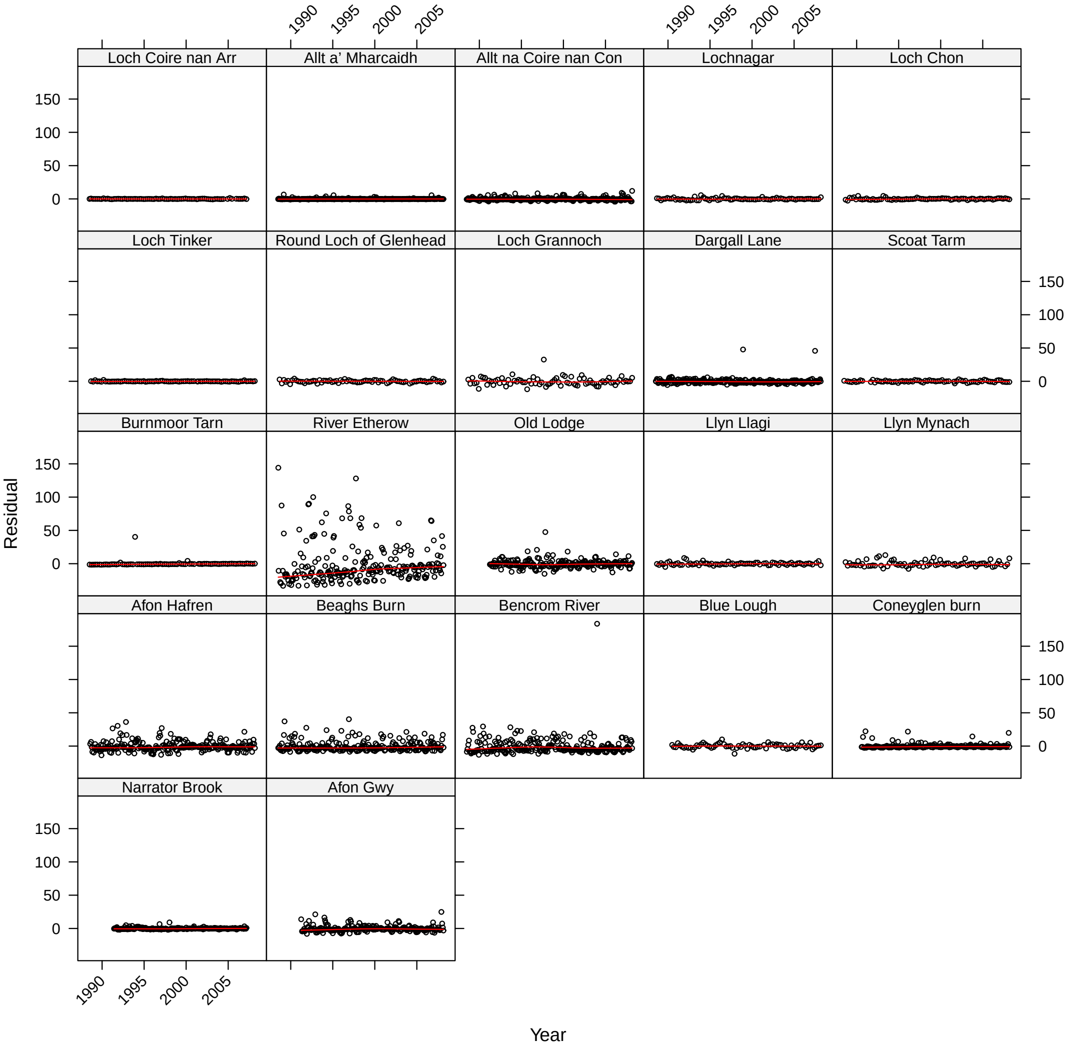

Figure 6: Residuals for the models fitted to H^+ for AWMN sites

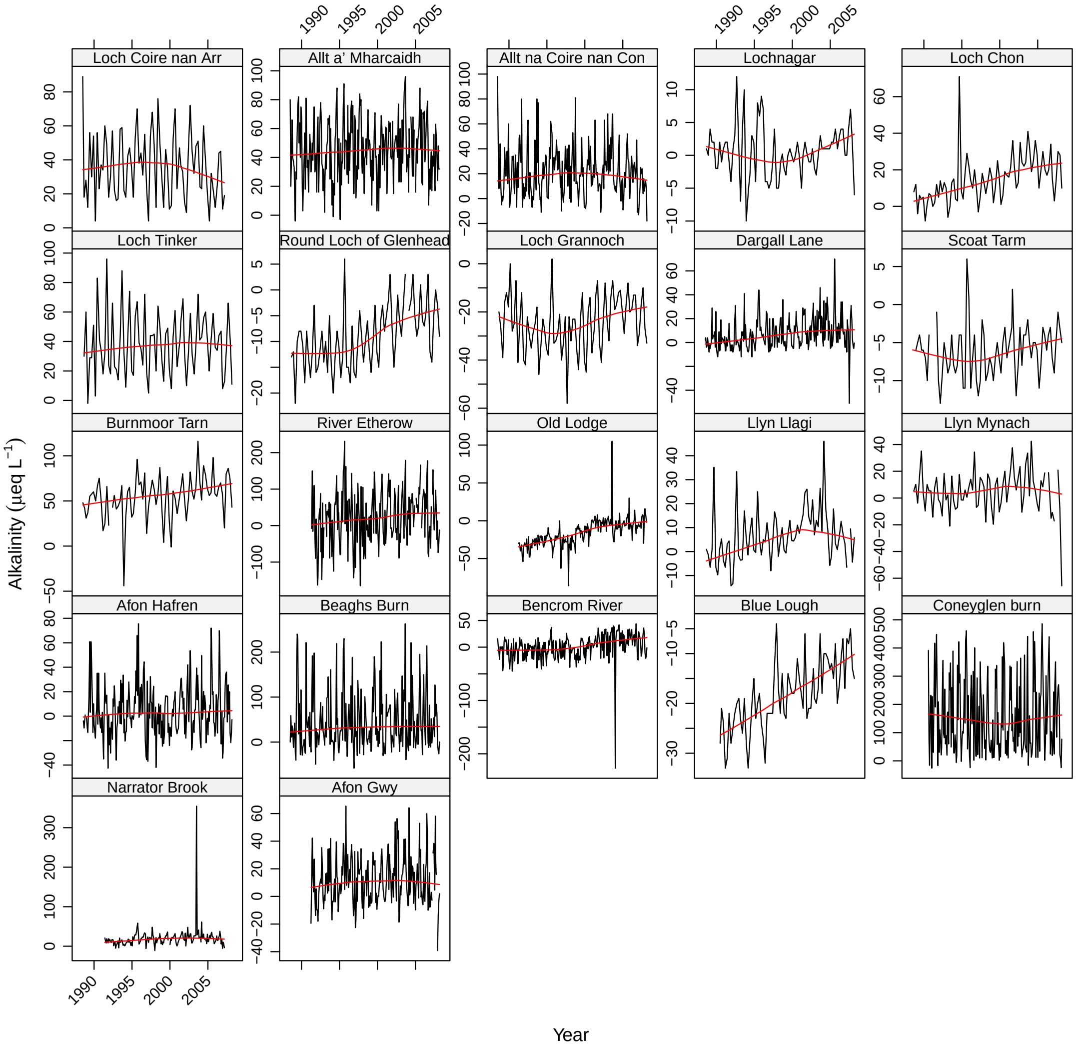

Figure 7: Time-series of observed alkalinity at AWMN sites

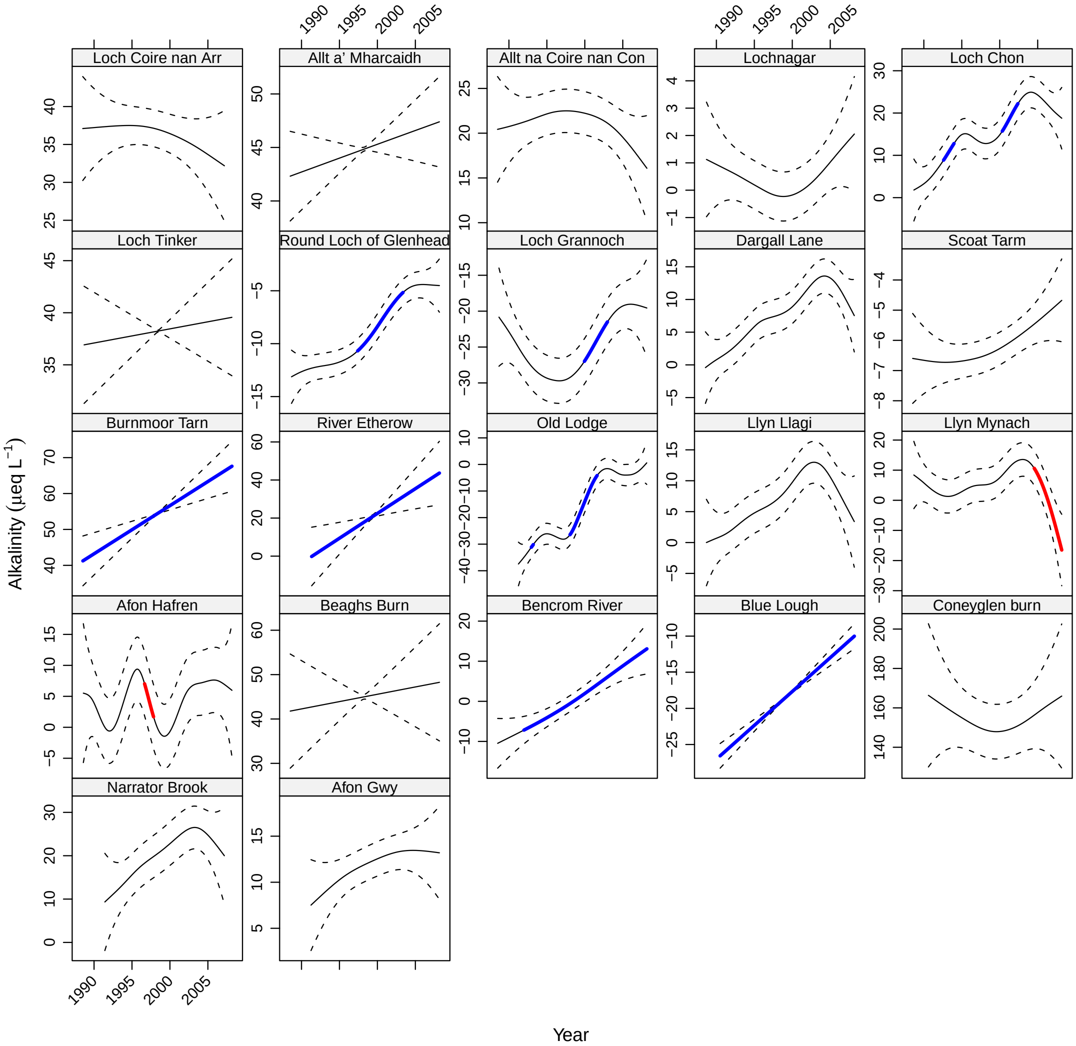

Figure 8: Fitted trends in alkalinity for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

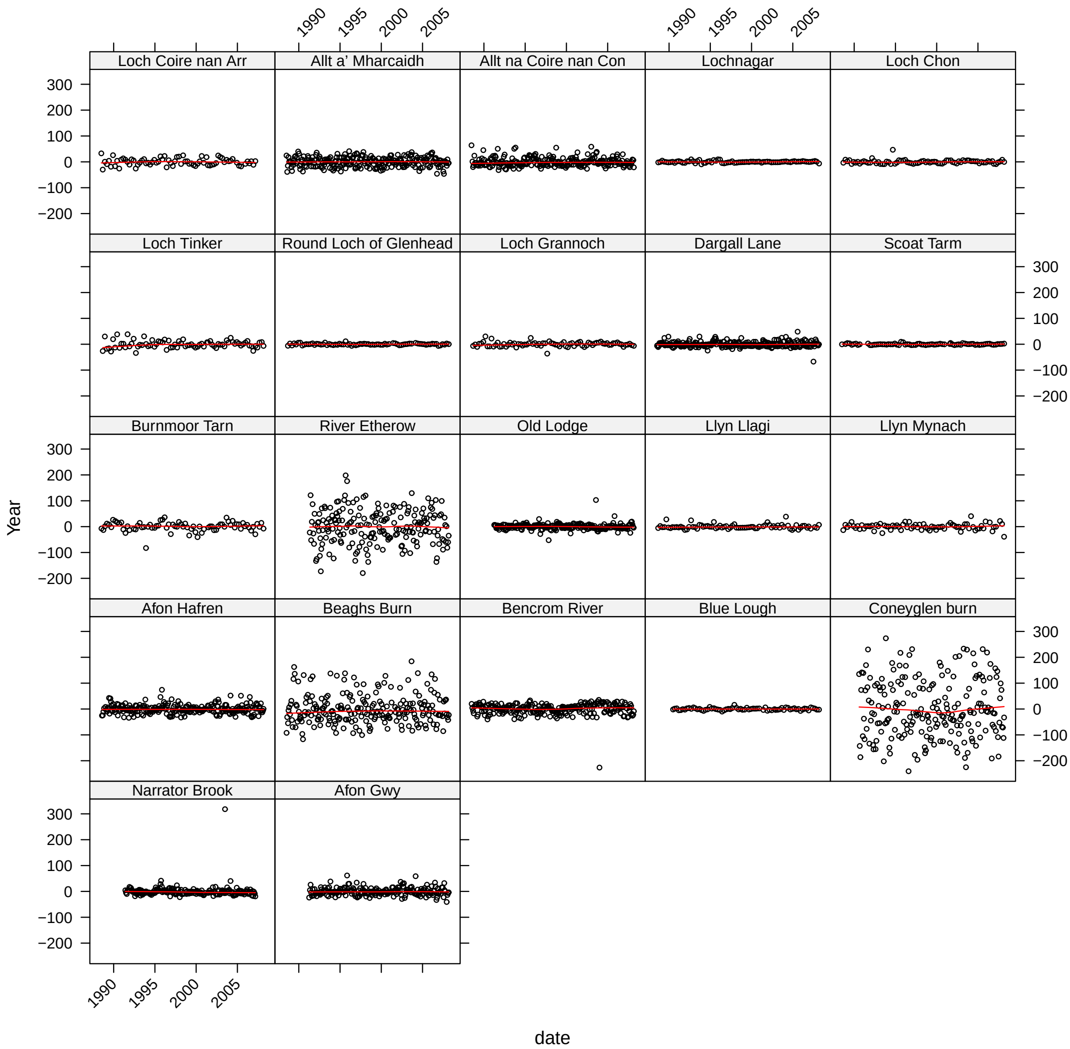

Figure 9: Residuals for the models fitted to alkalinity for AWMN site

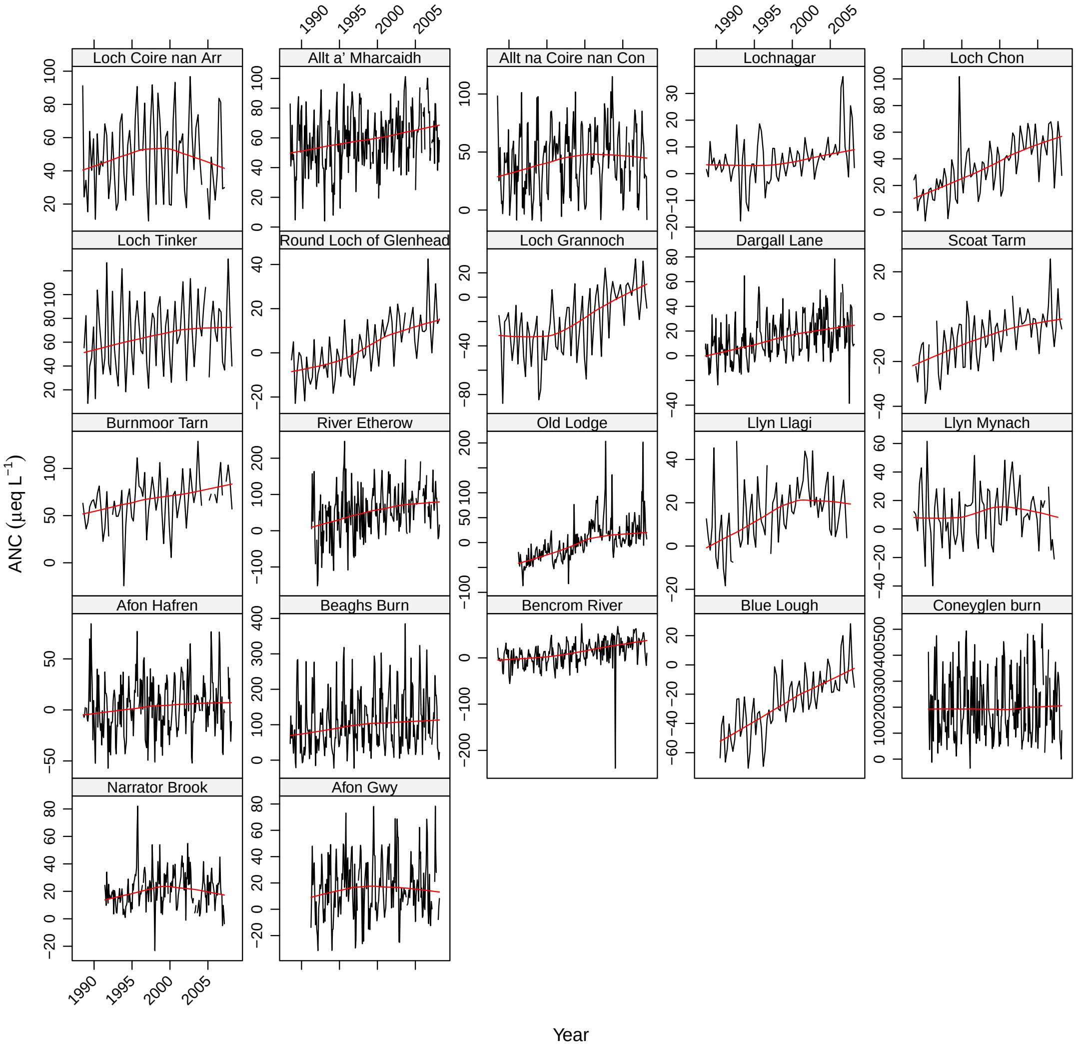

Figure 10: Time-series of observed ANC at AWMN sites

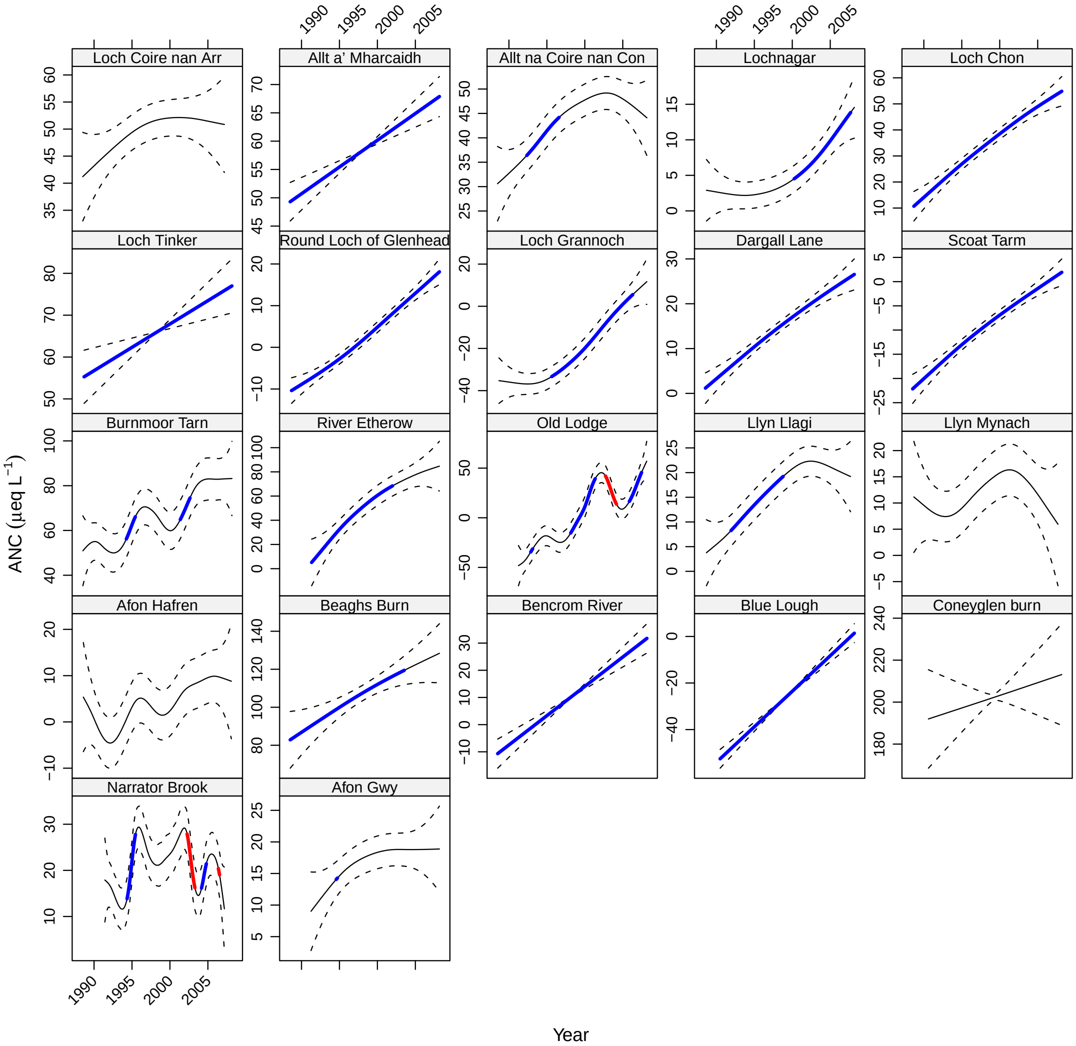

Figure 11: Fitted trends in ANC for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

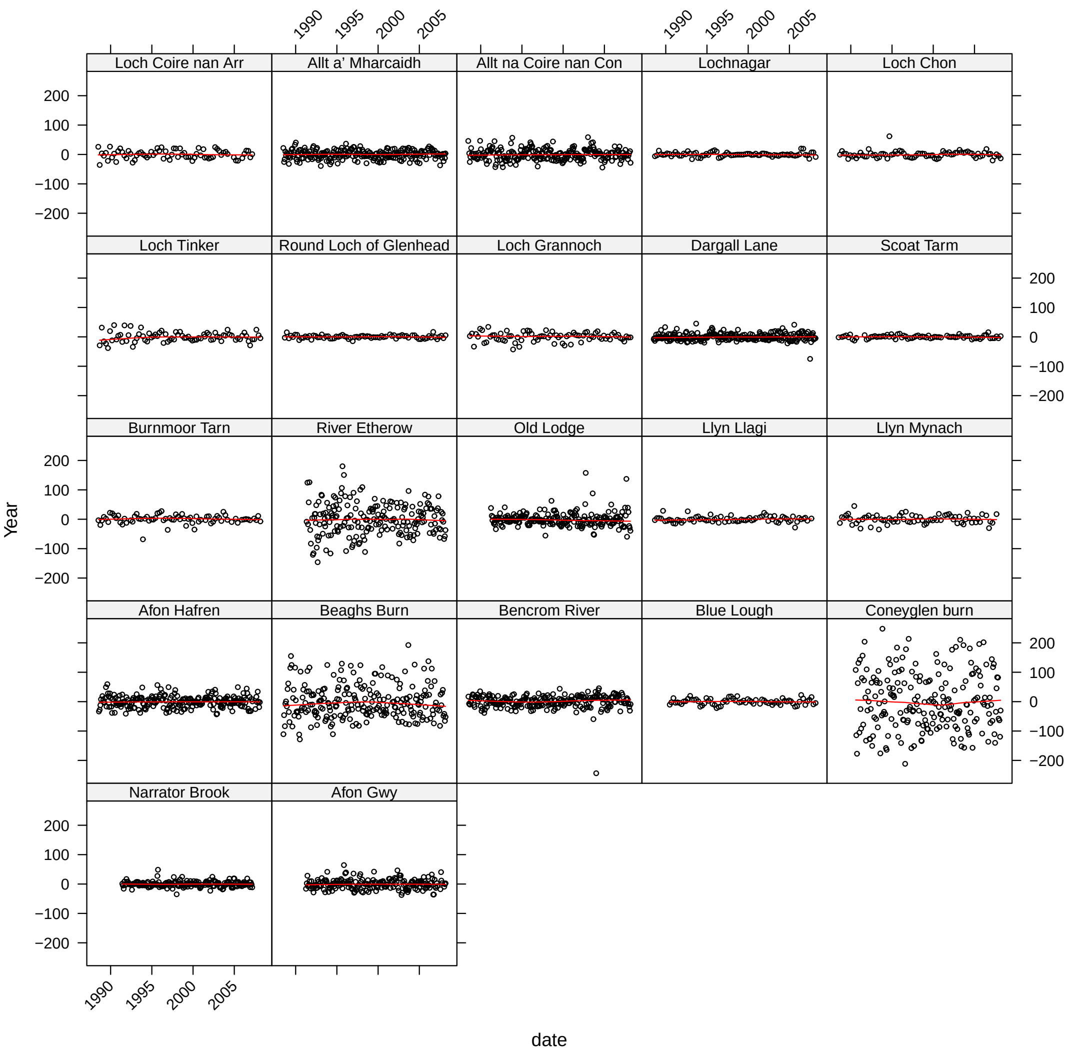

Figure 12: Residuals for the models fitted to ANC for AWMN site

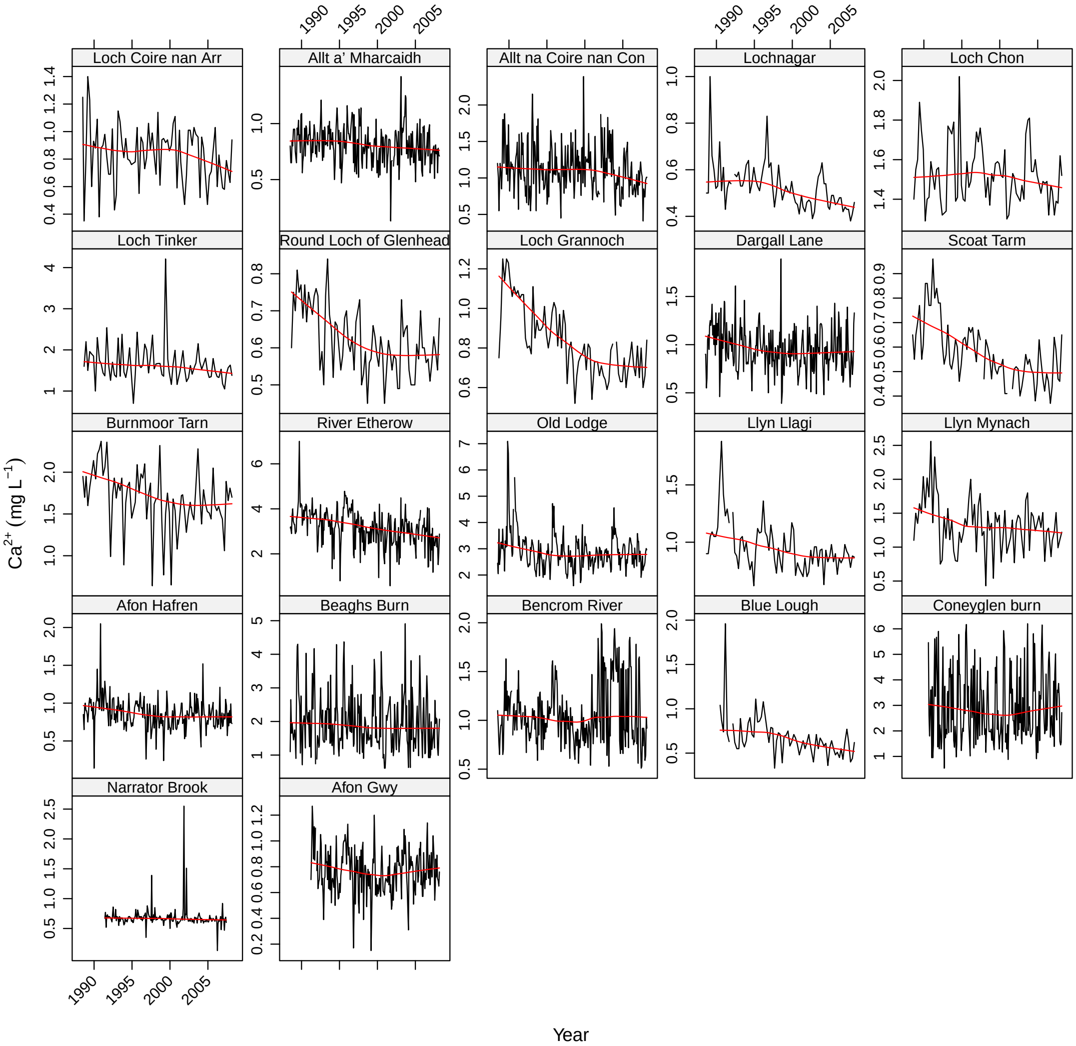

Figure 13: Time-series of observed Ca^{2+} at AWMN sites

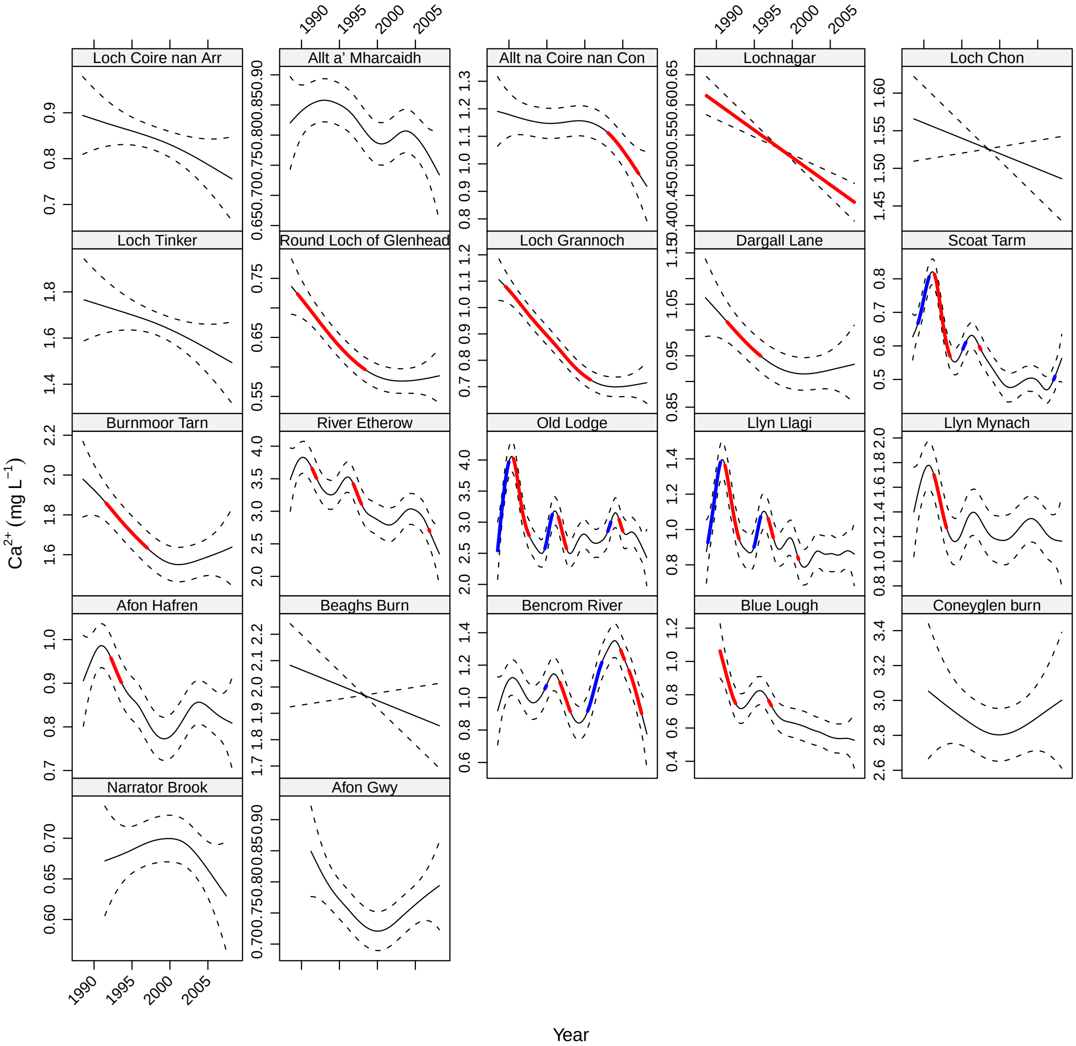

Figure 14: Fitted trends in Ca^{2+} for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

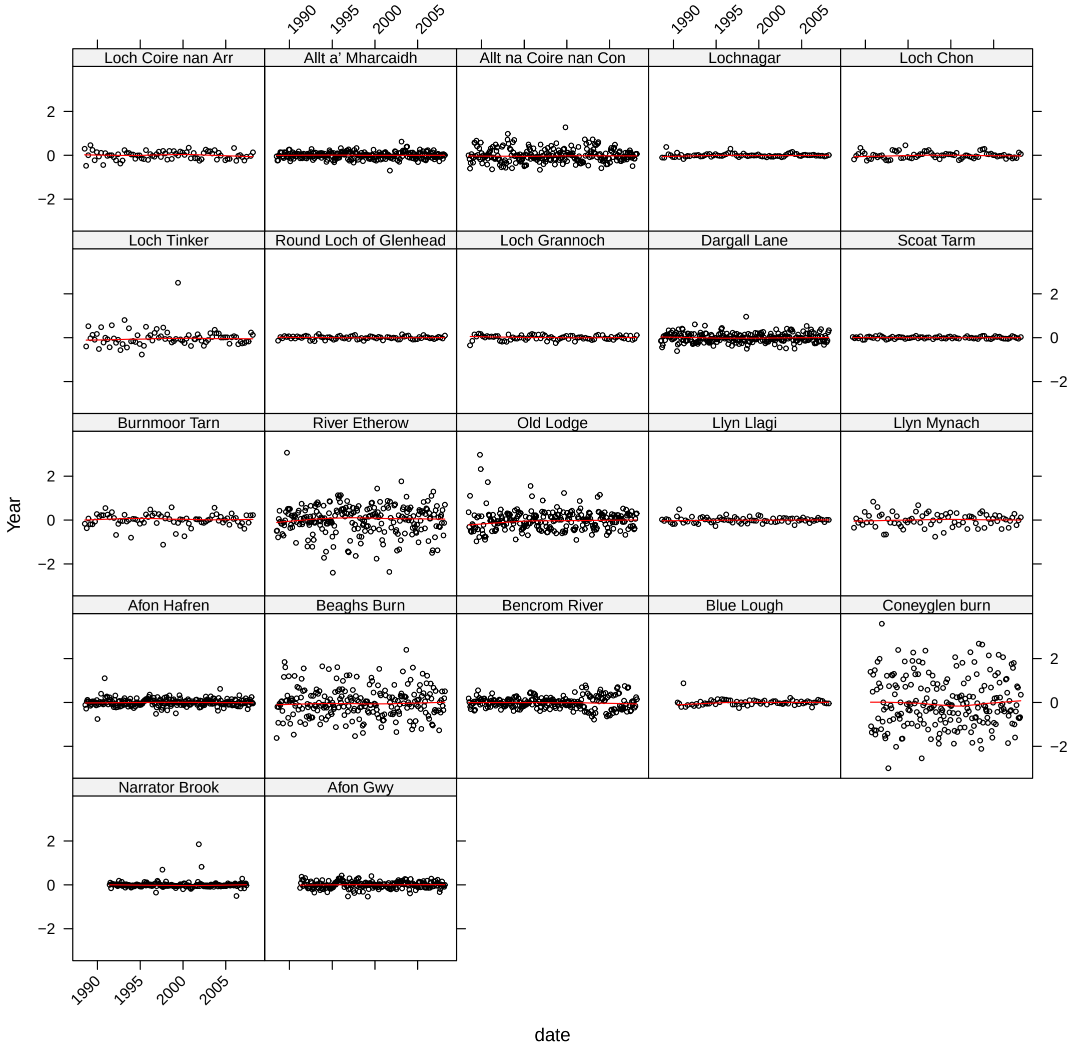

Figure 15: Residuals for the models fitted to Ca^{2+} for AWMN site

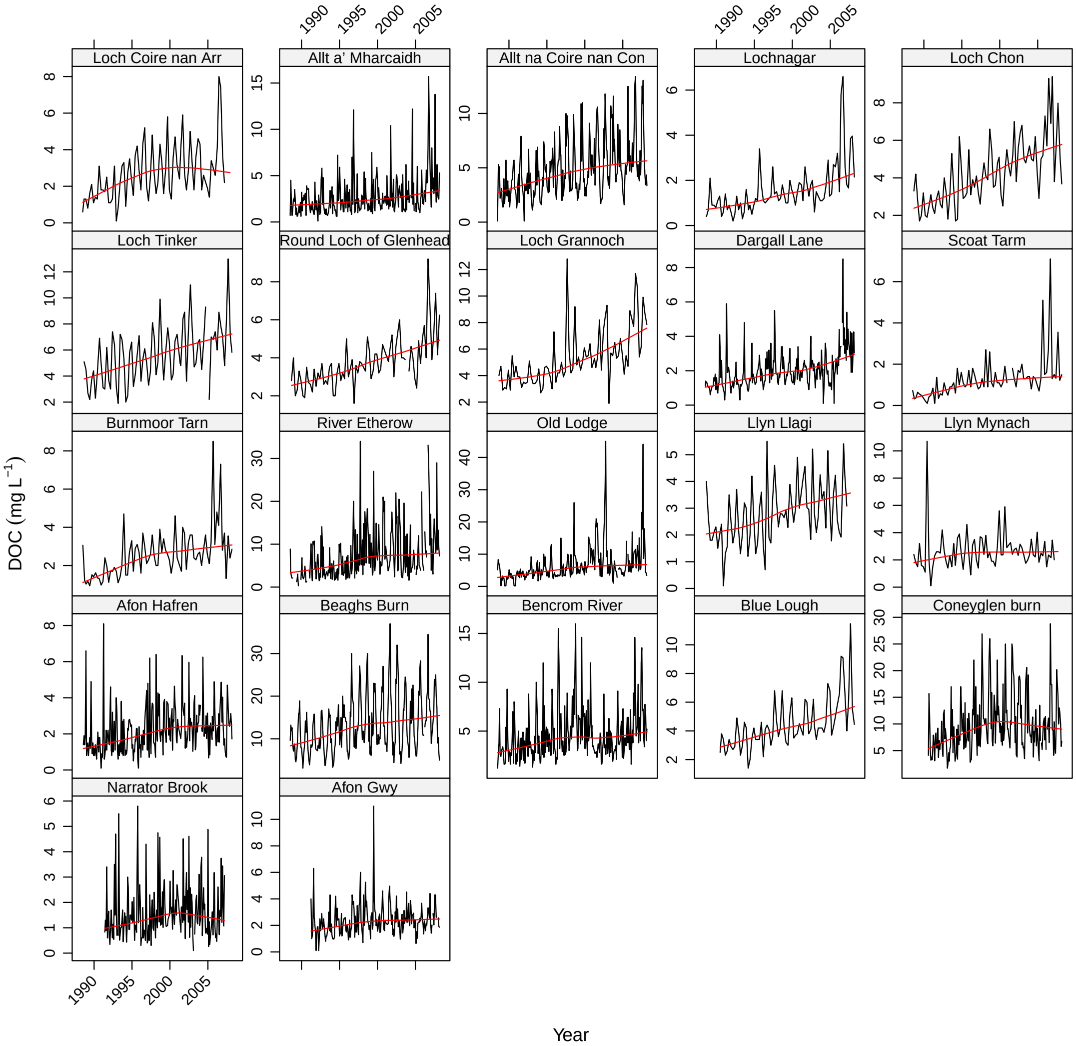

Figure 16: Time-series of observed DOC at AWMN sites

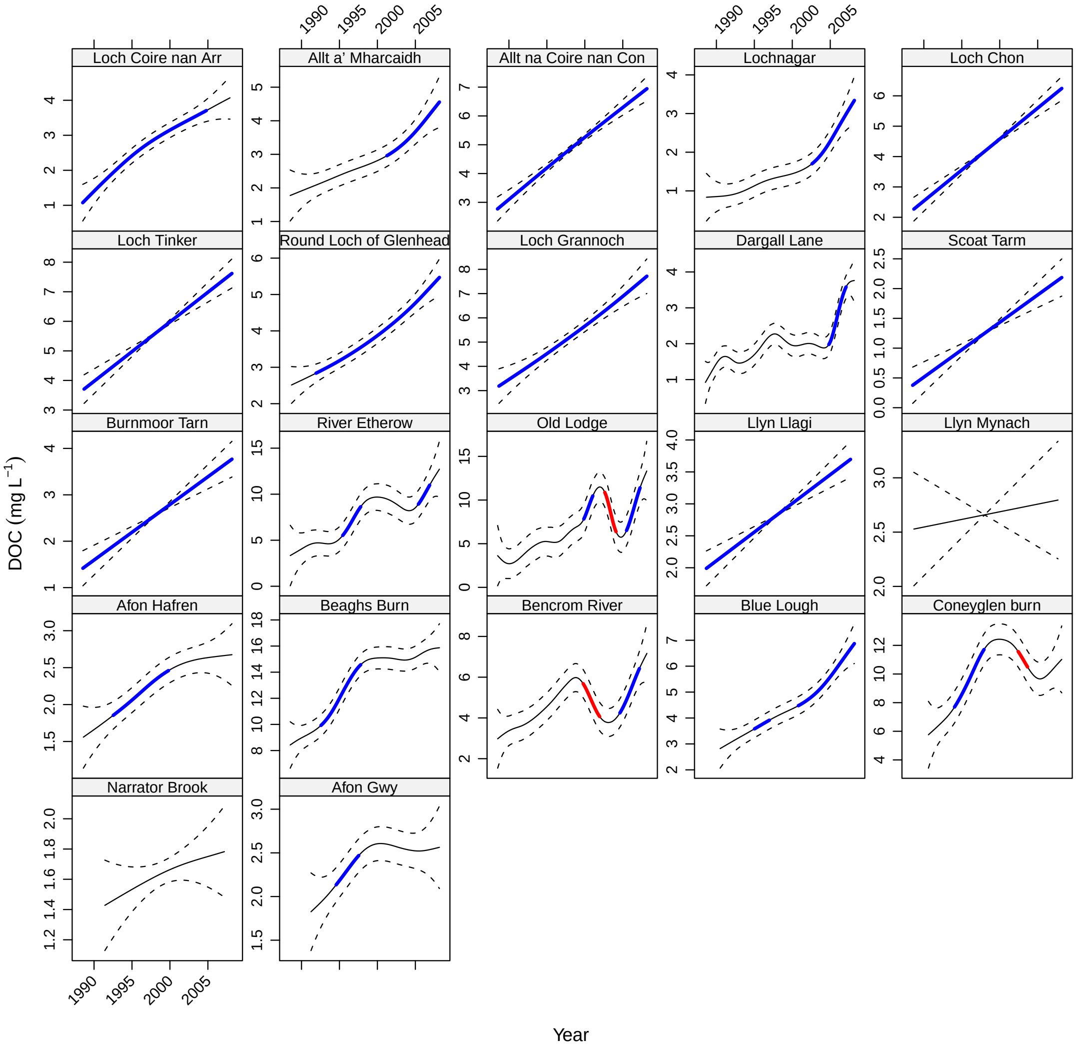

Figure 17: Fitted trends in DOC for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

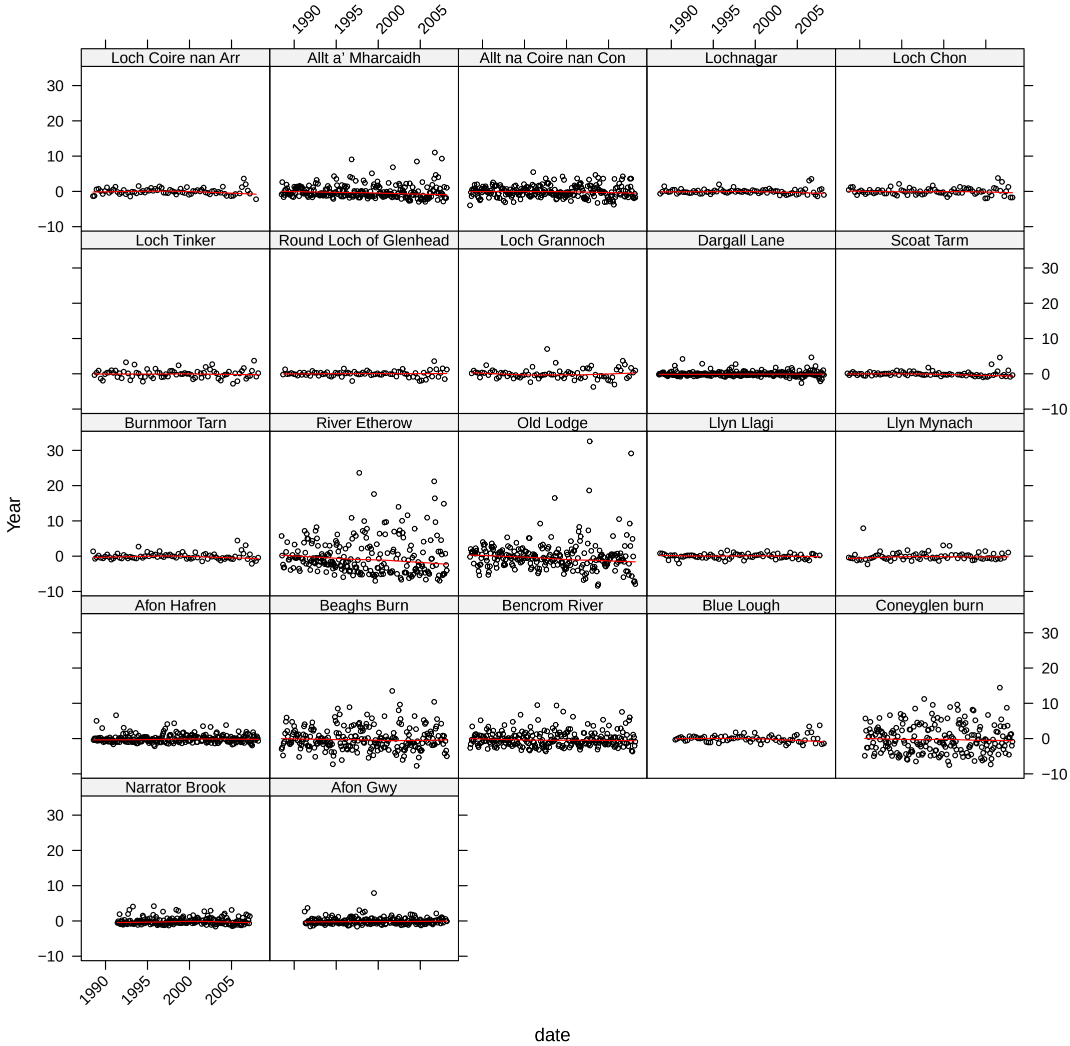

Figure 18: Residuals for the models fitted to DOC for AWMN site

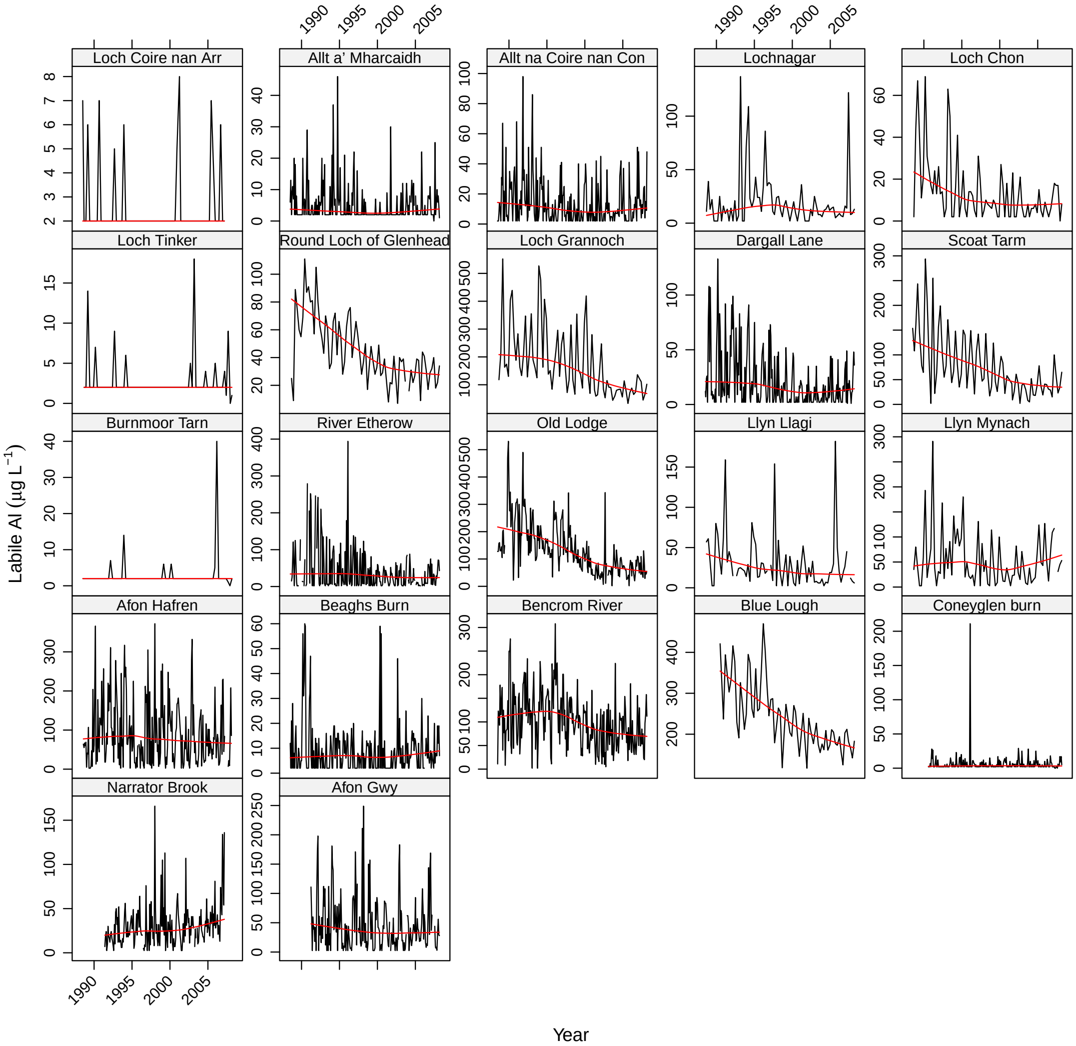

Figure 19: Time-series of observed Labile Aluminium at AWMN sites

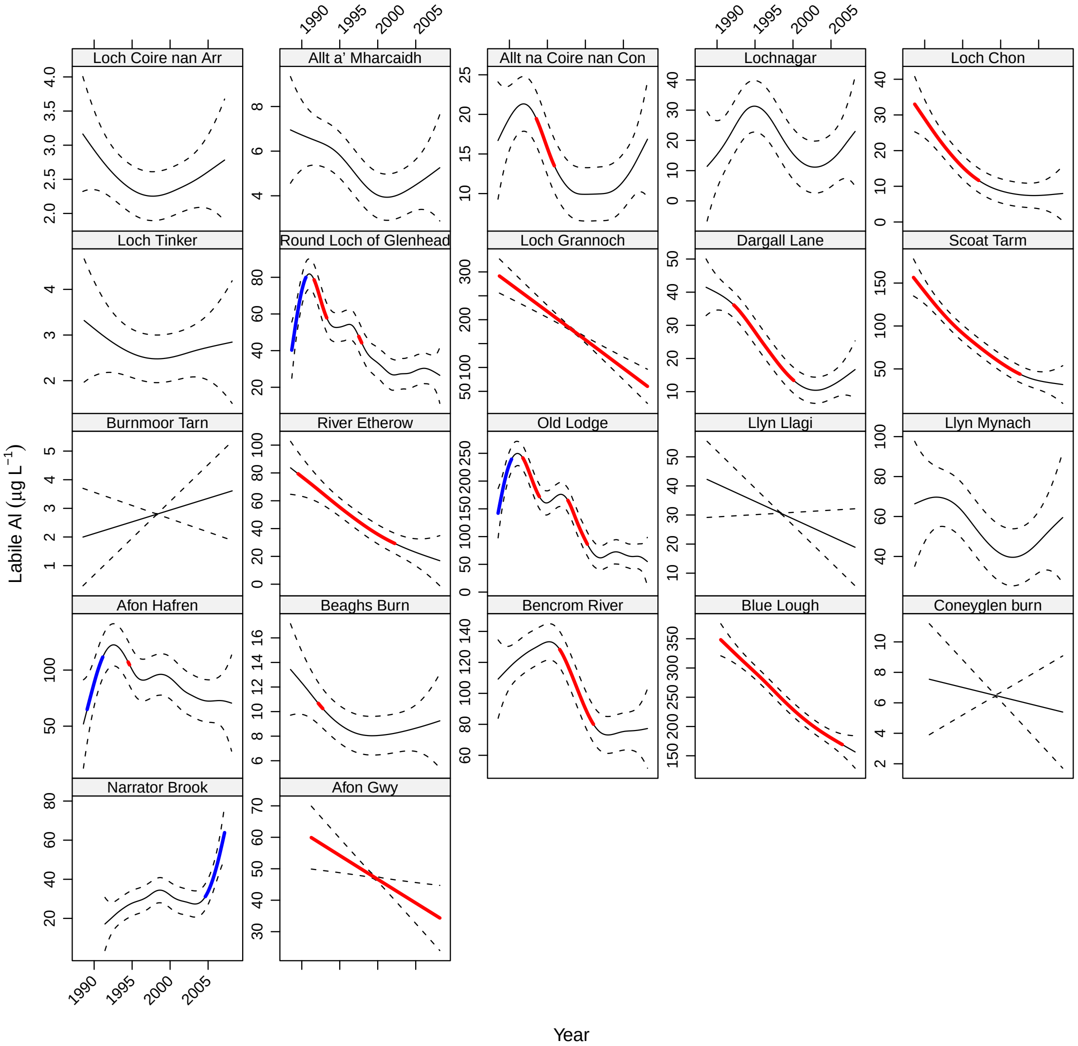

Figure 20: Fitted trends in Labile Aluminium for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

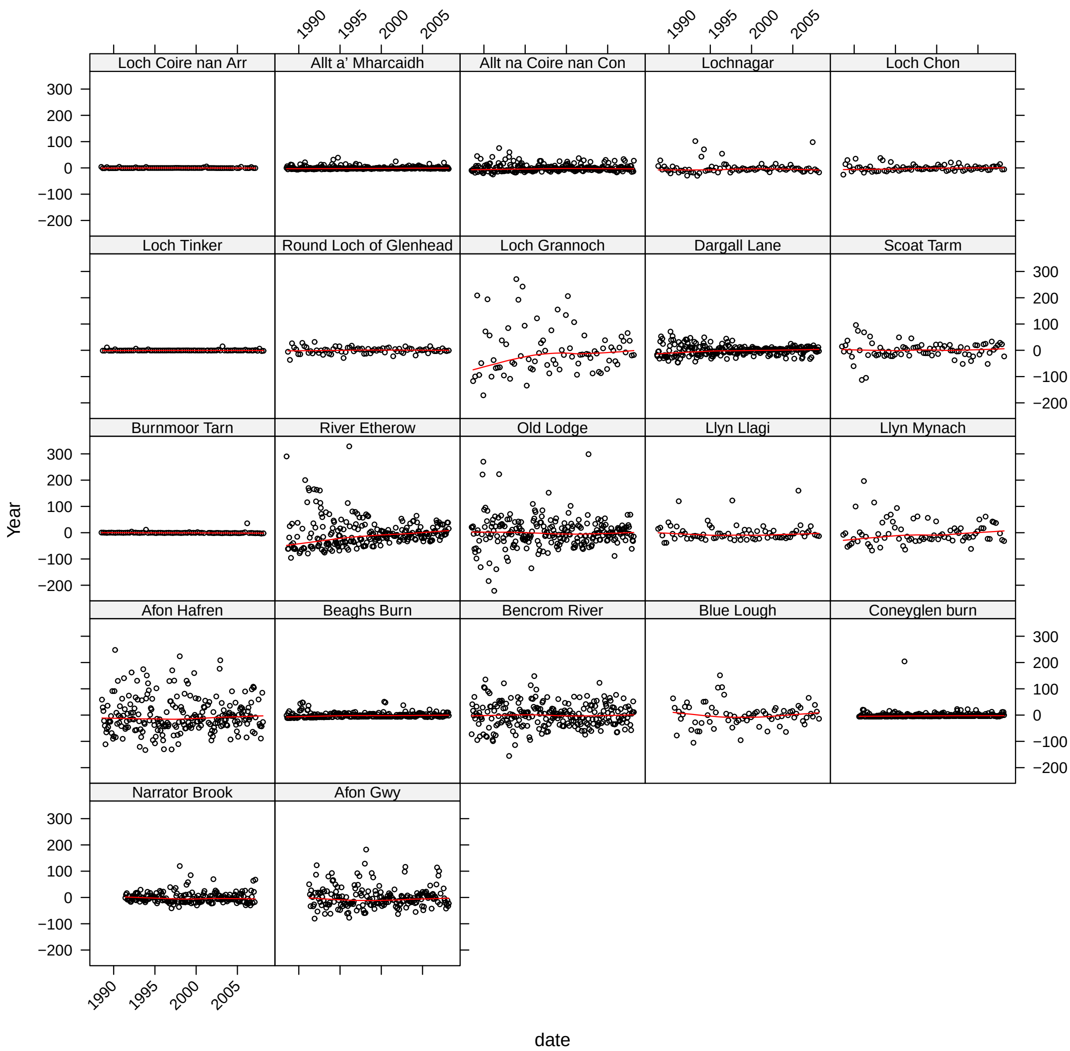

Figure 21: Residuals for the models fitted to Labile Aluminium for AWMN site

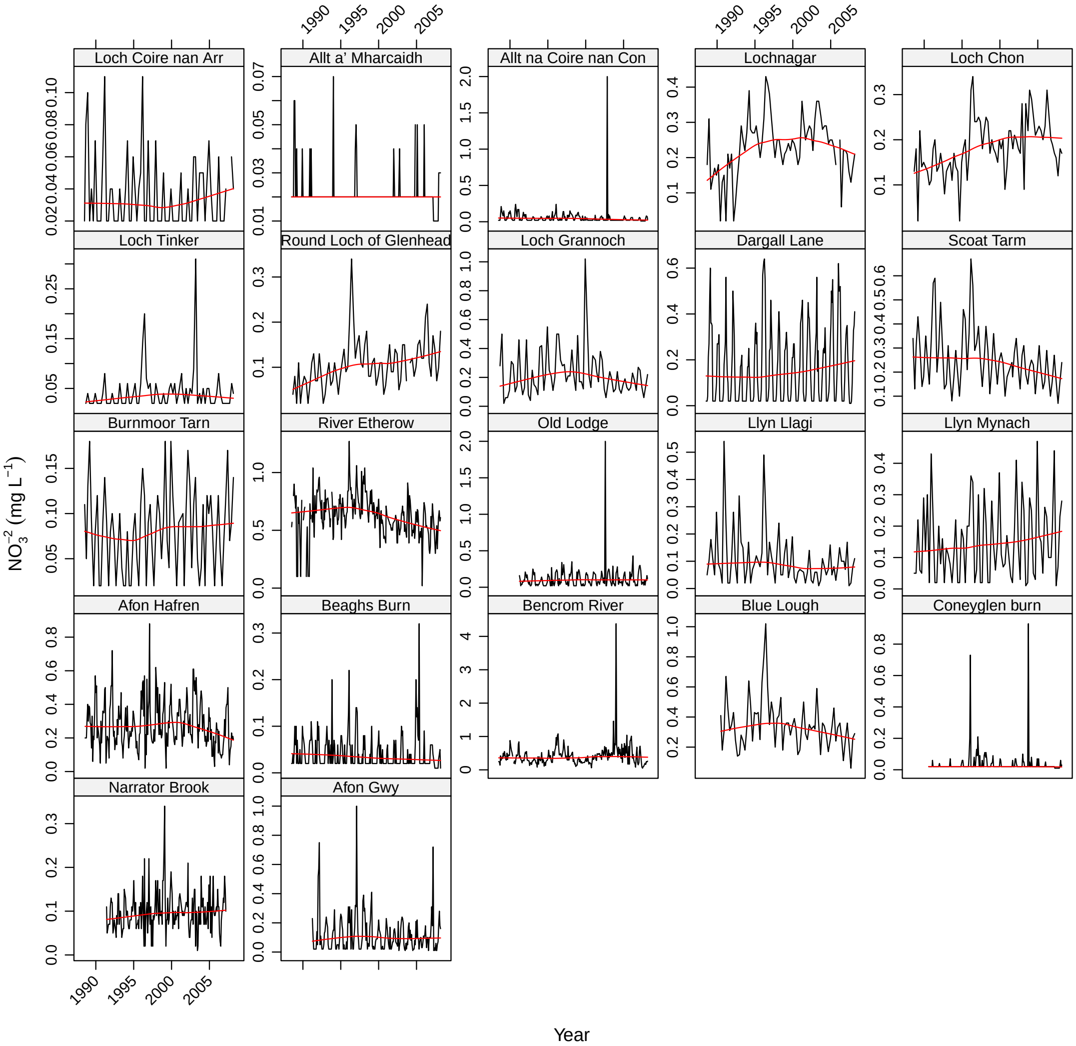

Figure 22: Time-series of observed NO_3^- at AWMN sites

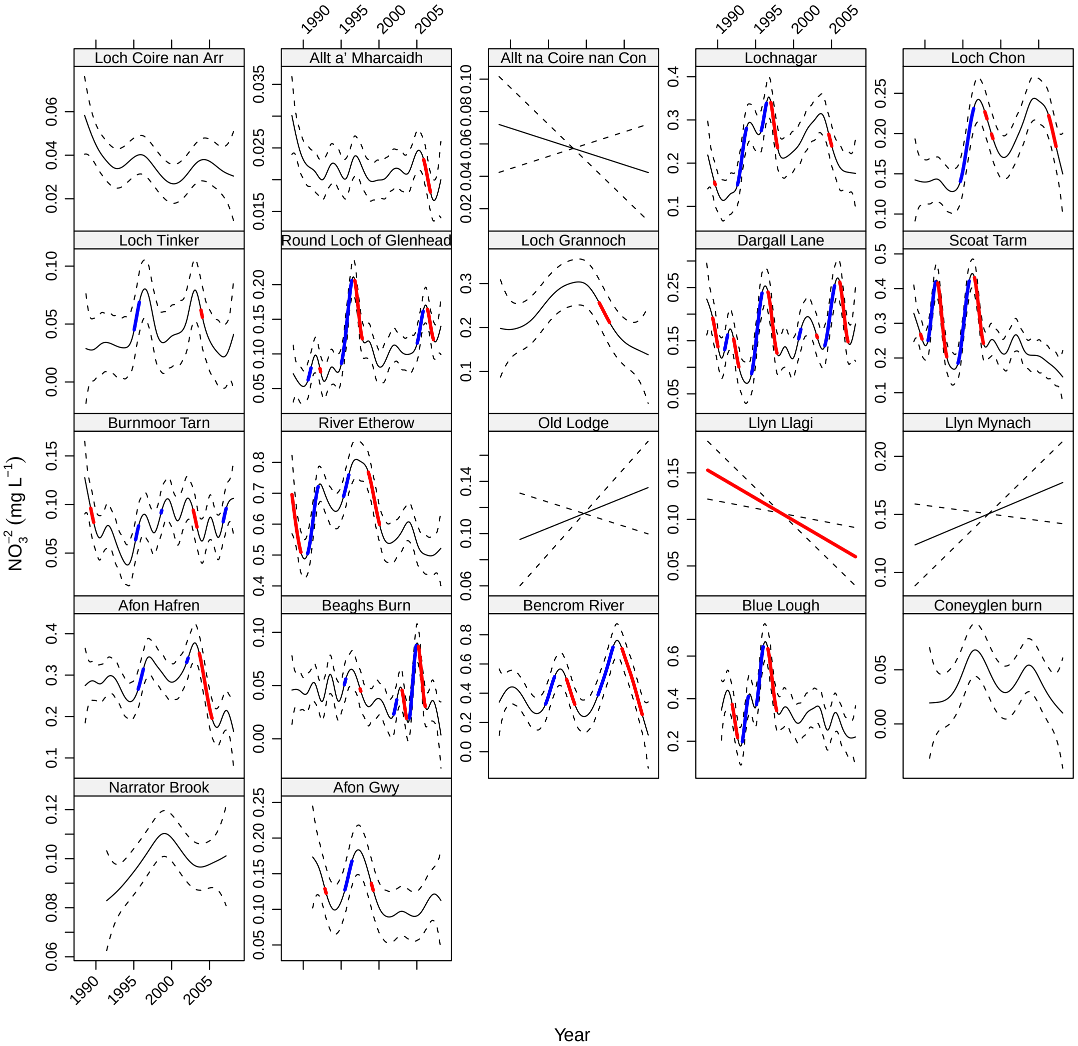

Figure 23: Fitted trends in NO_3^- for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

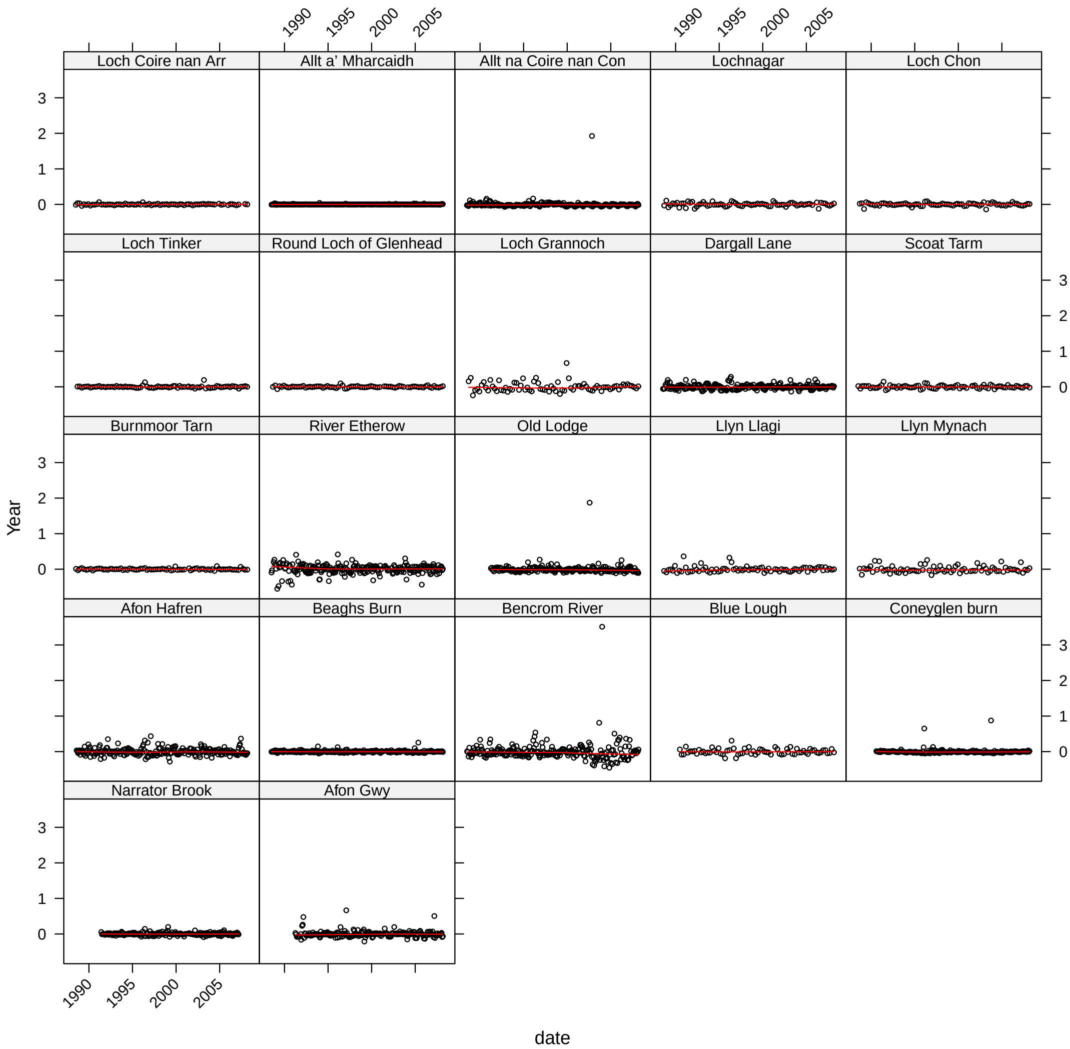

Figure 24: Residuals for the models fitted to NO_3^- for AWMN site

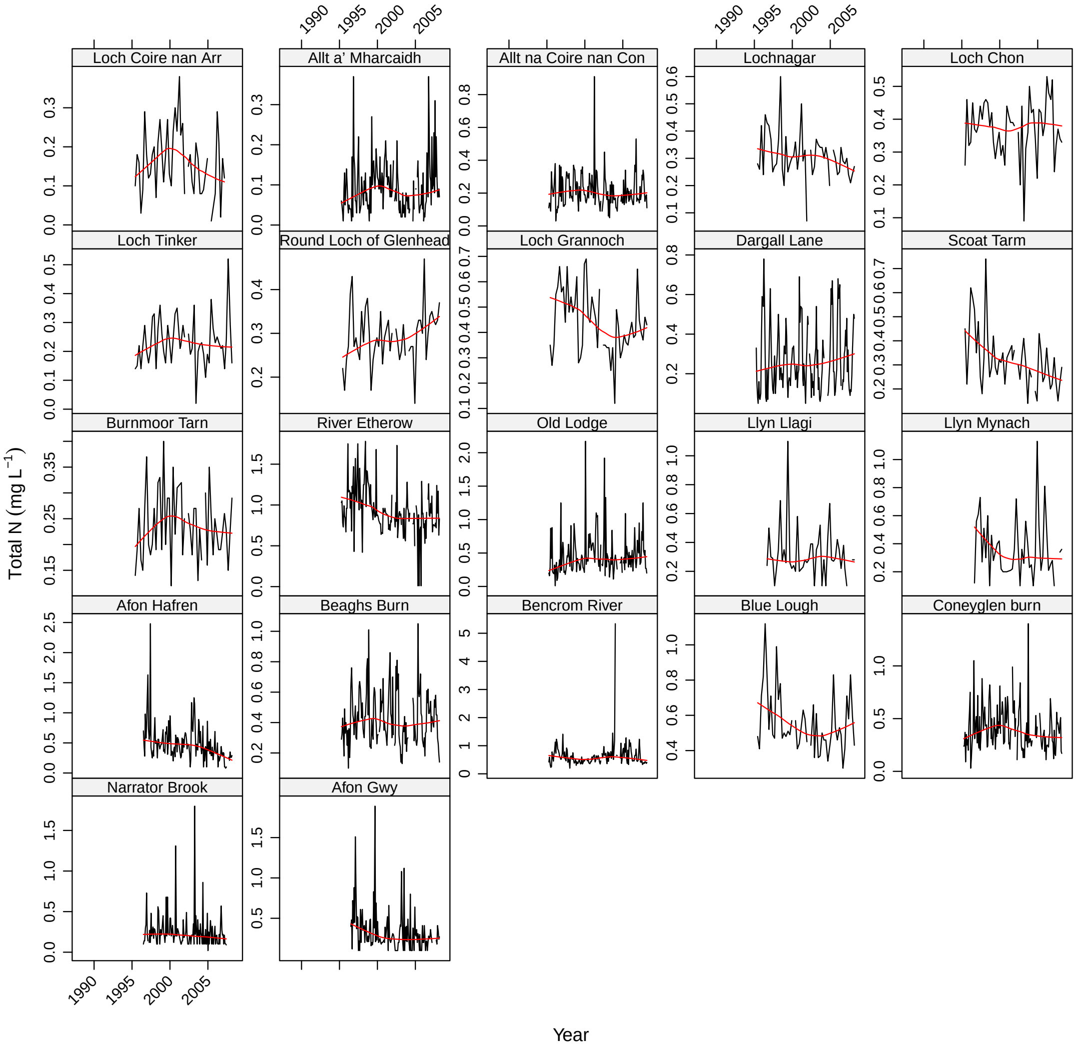

Figure 25: Time-series of observed Total N at AWMN sites

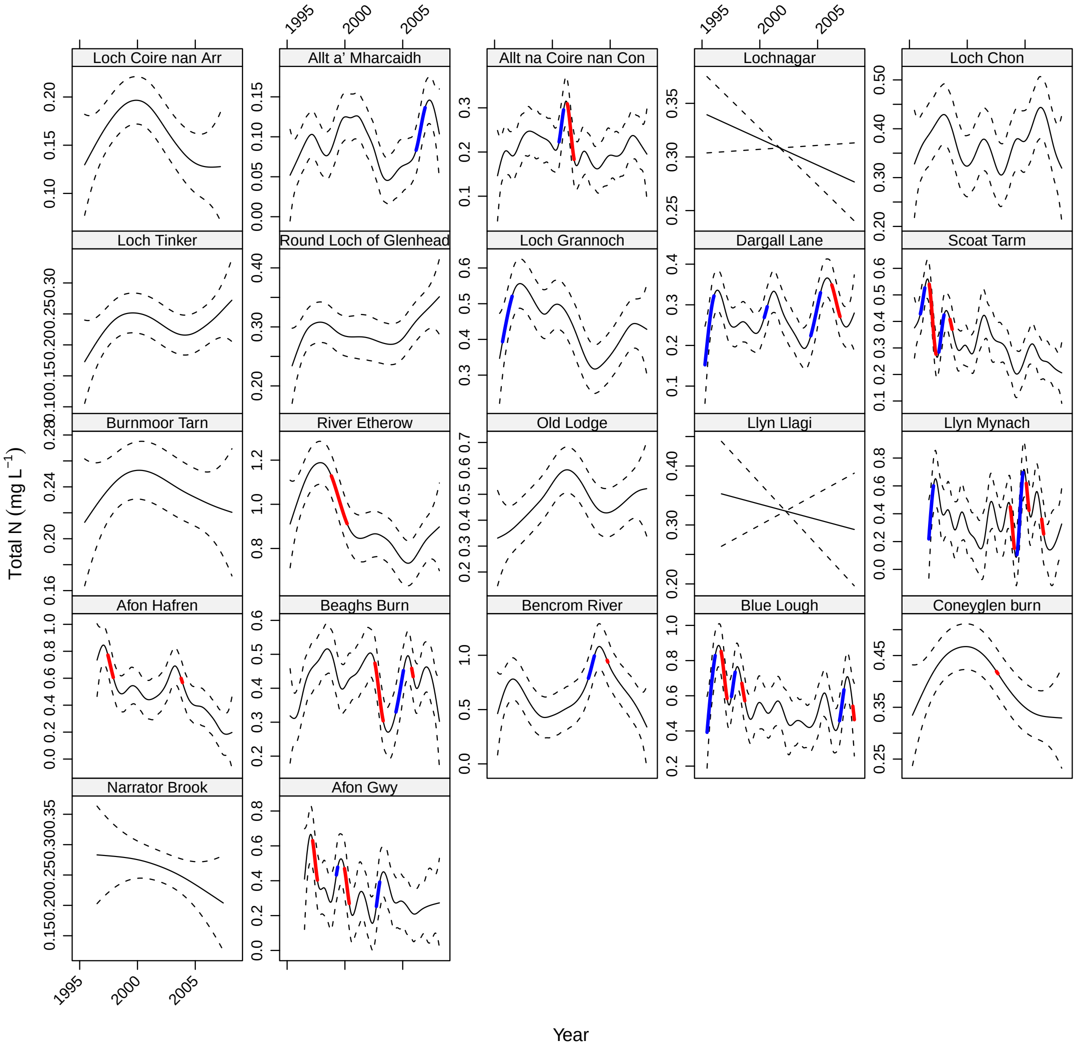

Figure 26: Fitted trends in Total N for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

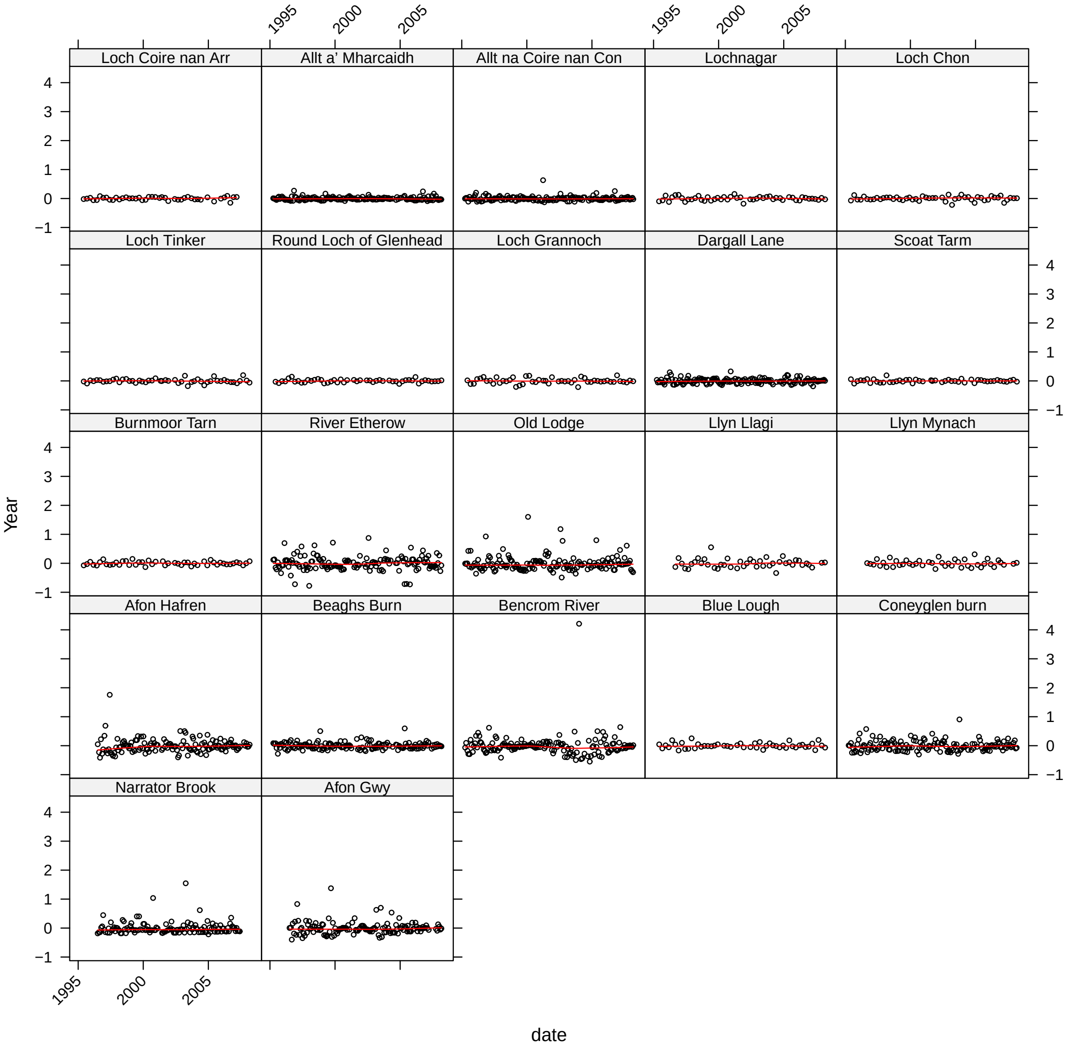

Figure 27: Residuals for the models fitted to Total N for AWMN site

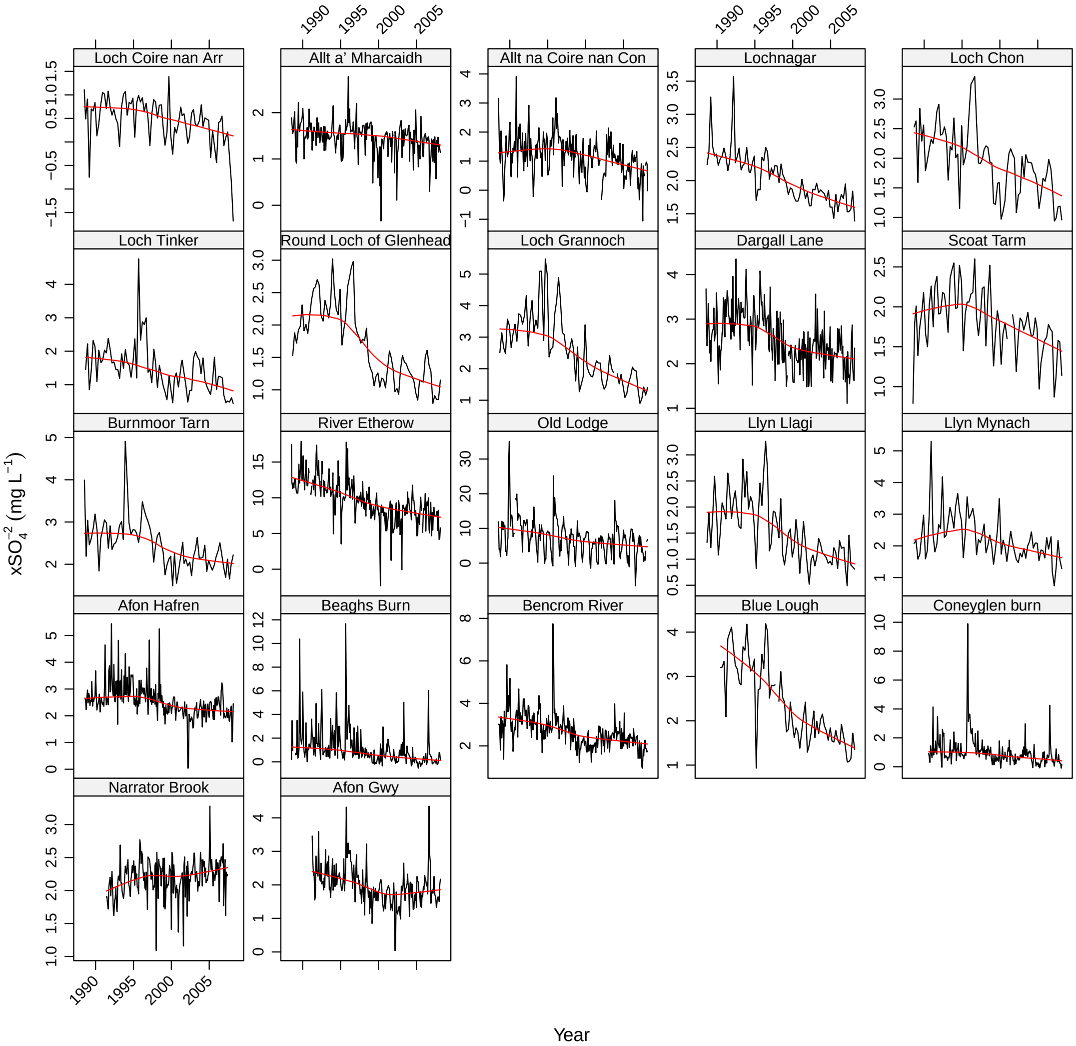

Figure 28: Time-series of observed xSO_4^{2-} at AWMN sites

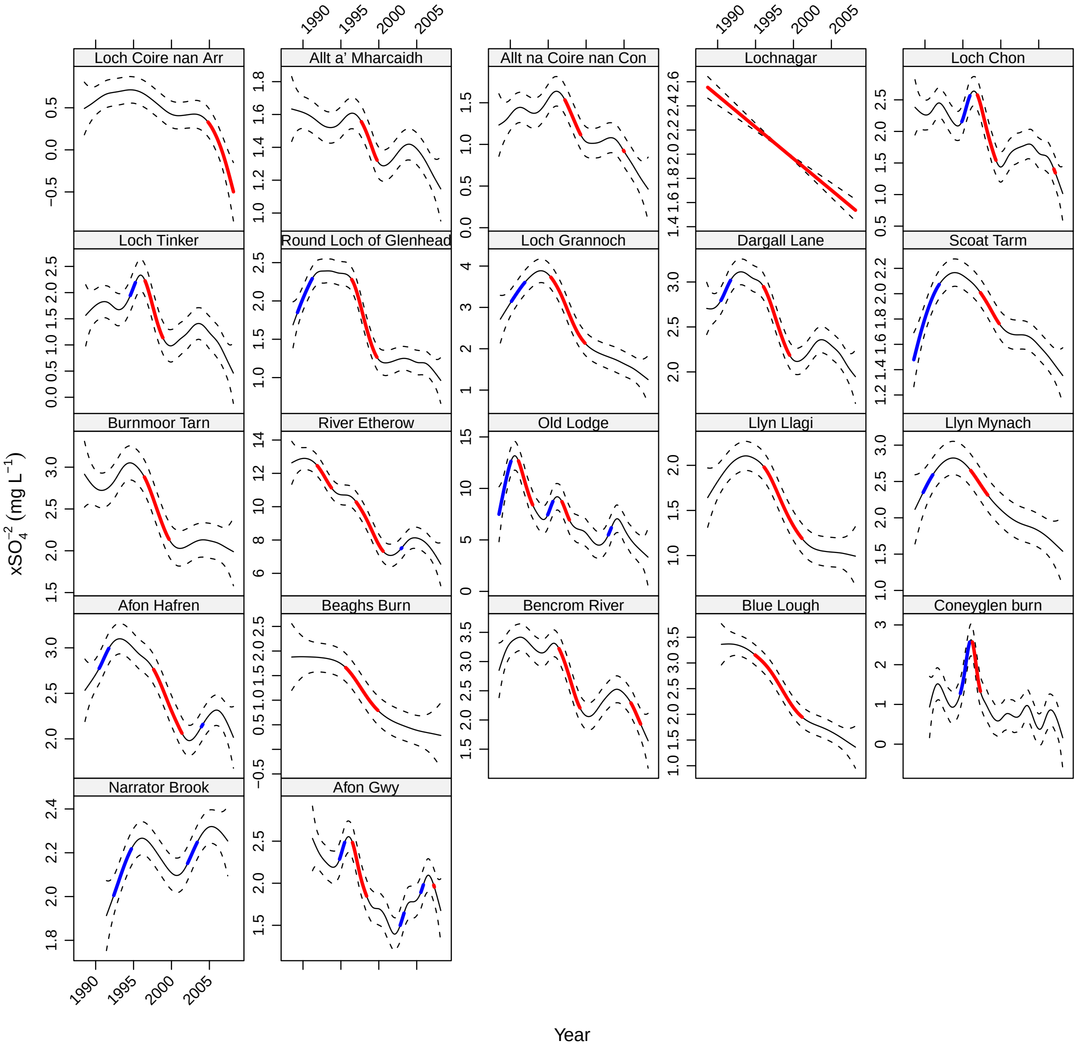

Figure 29: Fitted trends in xSO_4^{2-} for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

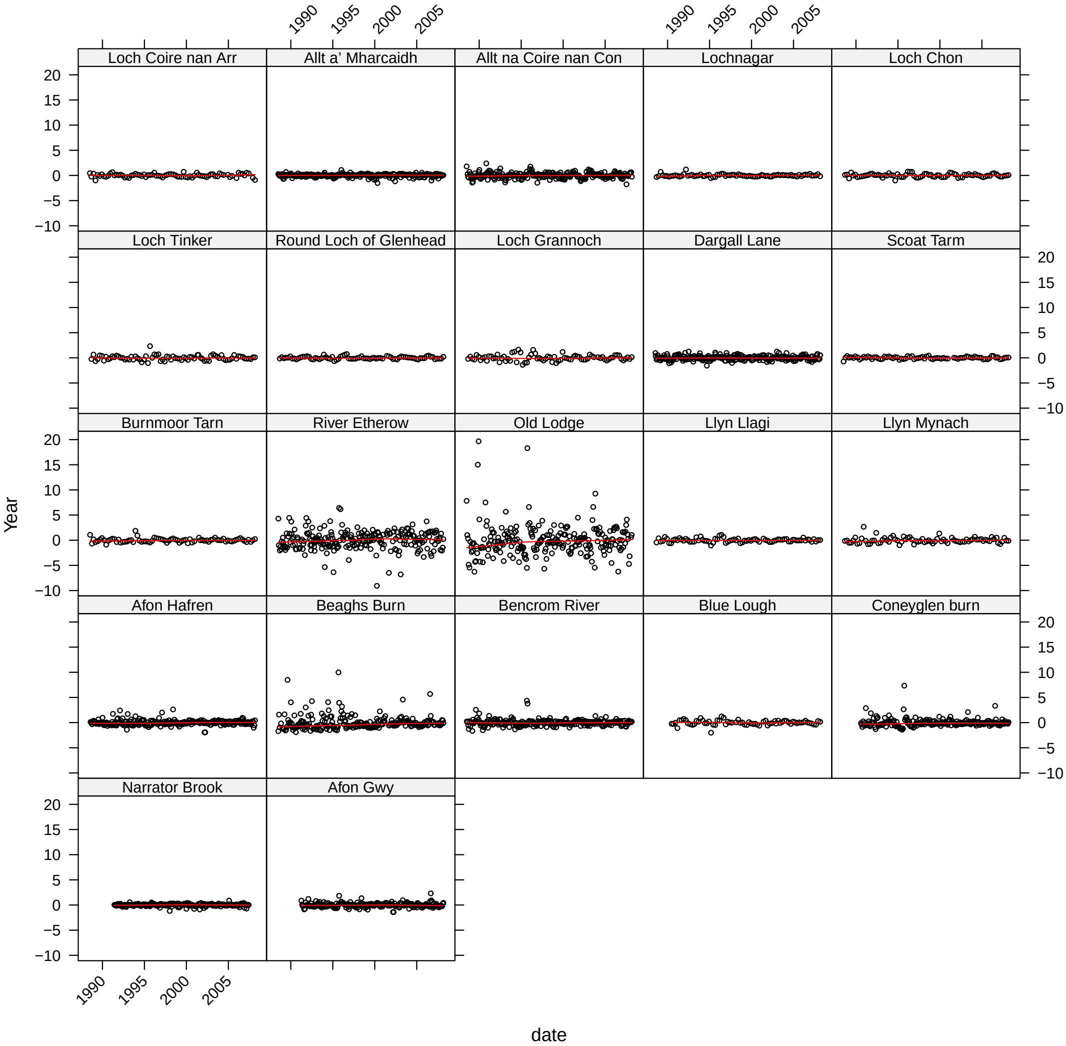

Figure 30: Residuals for the models fitted to xSO_4^{2-} for AWMN site

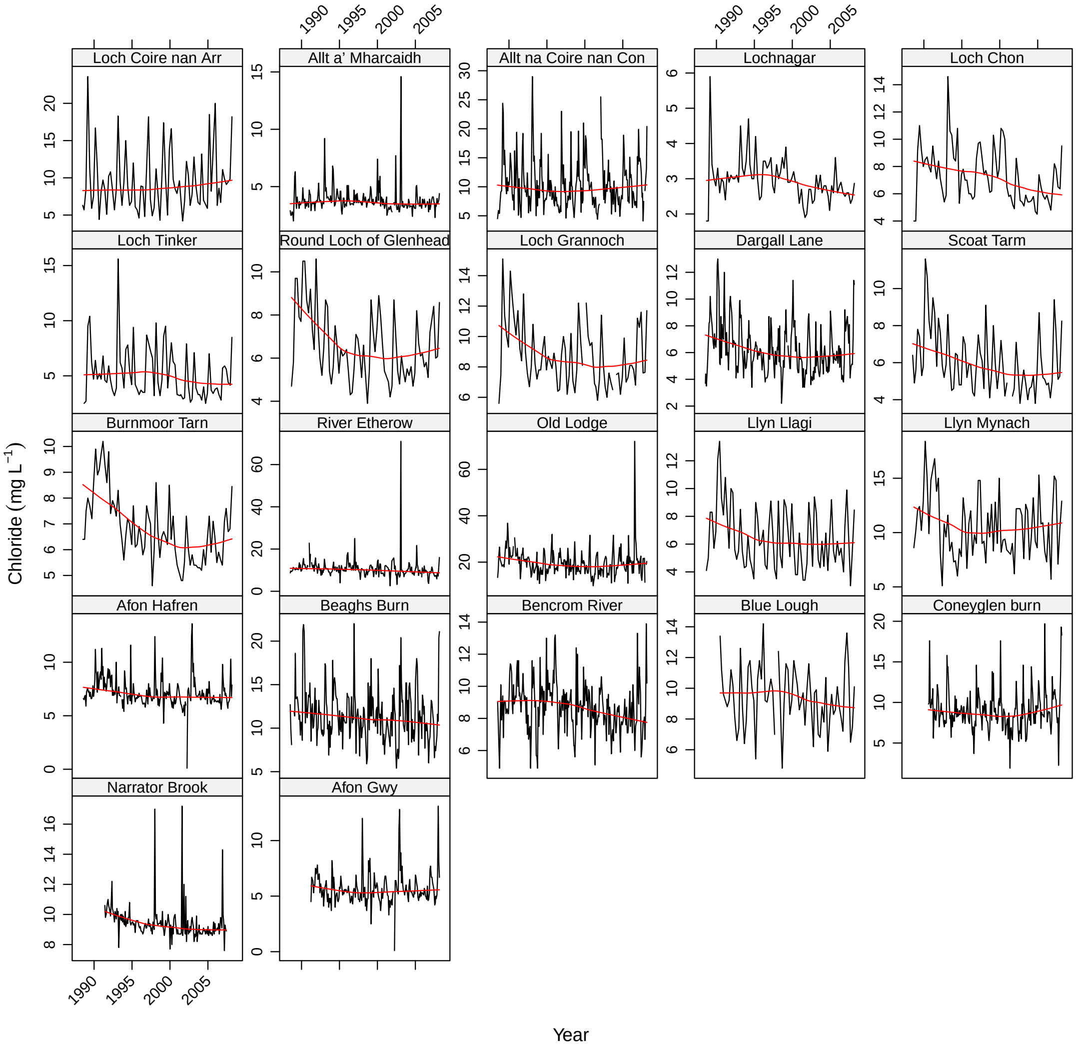

Figure 31: Time-series of observed Cl^- at AWMN sites

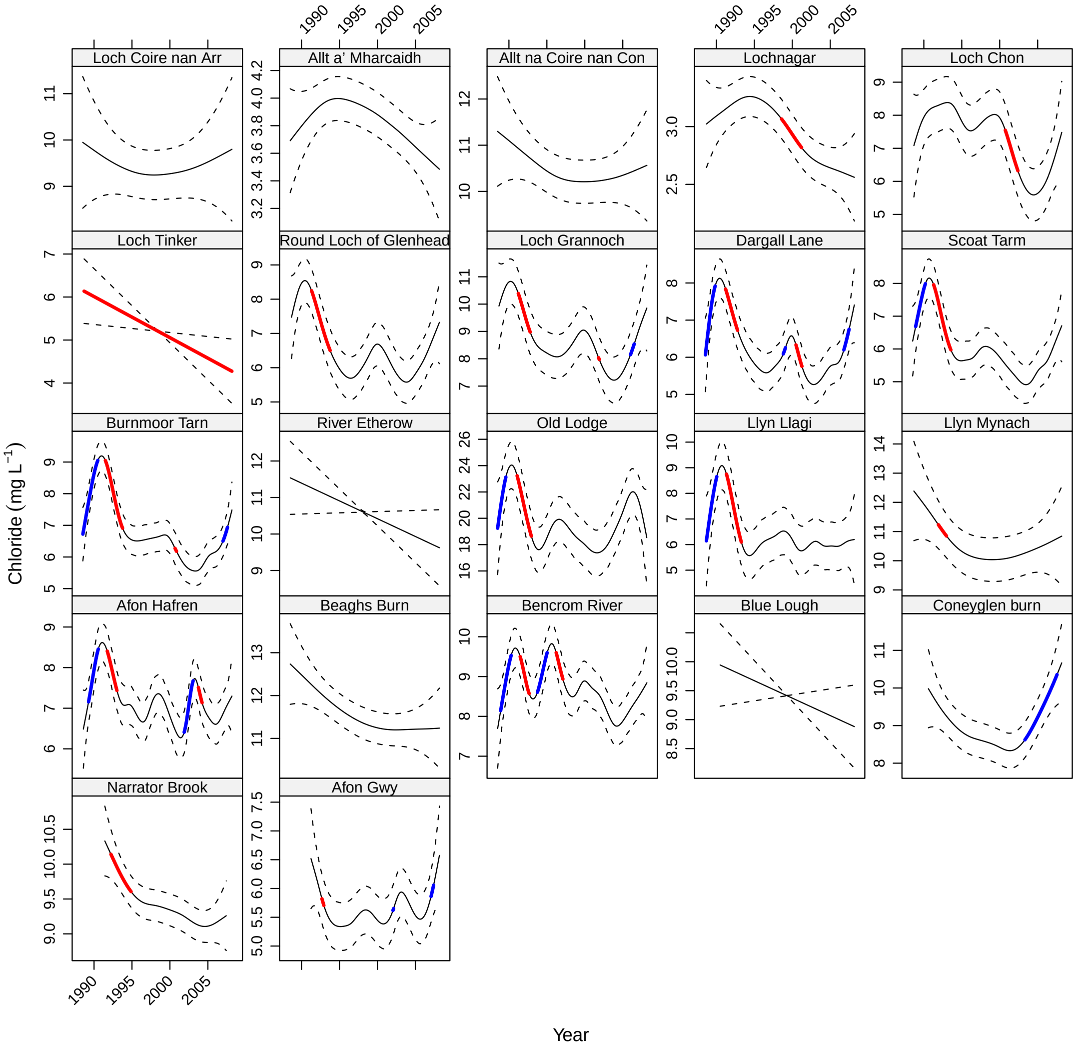

Figure 32: Fitted trends in Cl^- for AWMN sites. Periods of significant change in the fitted trend are shown by thick, coloured sections of the trend line (Blue = increase; Red = decrease)

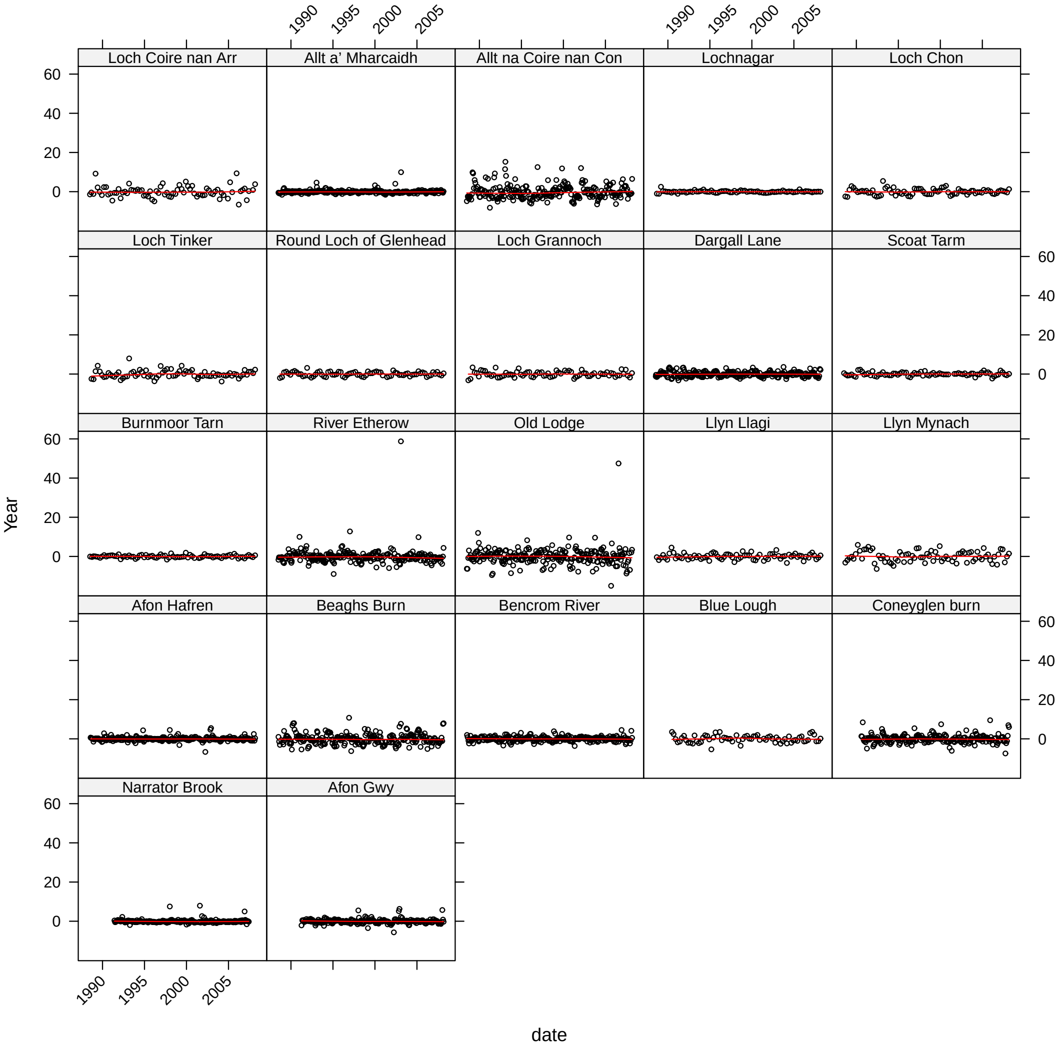

Figure 33: Residuals for the models fitted to Cl^- for AWMN site

Table 1: Sen slope estimates, expressed per year, for key determinands observed at AWMN Sites

	pH	Hplus	alk	anc	Ca	doc	no3	totalN	xso4	Cl
Loch Coire nan Arr	-0.009	0.007	-0.444	0.247	-0.007	0.120	0.000	-0.002	-0.036	0.050
Allt a' Mharcaidh	0.002	-0.001	0.216	0.921	-0.005	0.081	0.000	0.000	-0.017	-0.015
Allt na Coire nan Con	-0.002	0.004	0.000	0.898	-0.010	0.173	0.000	-0.001	-0.043	-0.010
Lochnagar	0.011	-0.094	0.059	0.410	-0.008	0.081	0.003	-0.006	-0.048	-0.031
Loch Chon	0.034	-0.119	1.121	2.386	-0.004	0.198	0.004	0.000	-0.058	-0.133
Loch Tinker	0.008	-0.009	0.235	1.225	-0.013	0.181	0.000	0.001	-0.059	-0.075
Round Loch of Glenhead	0.016	-0.398	0.545	1.423	-0.008	0.131	0.004	0.005	-0.076	-0.074
Loch Grannoch	0.006	-0.313	0.426	2.494	-0.022	0.193	-0.001	-0.009	-0.123	-0.088
Dargall Lane	0.029	-0.131	0.626	1.264	-0.007	0.080	0.000	0.003	-0.055	-0.068
Scoat Tarm	0.011	-0.229	0.107	1.082	-0.013	0.061	-0.006	-0.014	-0.030	-0.084
Burnmoor Tarn	0.009	-0.004	1.184	1.533	-0.021	0.104	0.000	0.000	-0.052	-0.115
River Etherow	0.015	-0.014	2.223	4.399	-0.054	0.296	-0.009	-0.025	-0.323	-0.113
Old Lodge	0.040	-1.387	2.271	4.630	-0.019	0.262	0.000	0.010	-0.333	-0.135
Llyn Llagi	0.038	-0.262	0.574	1.105	-0.014	0.089	-0.002	0.000	-0.065	-0.074
Llyn Mynach	0.008	-0.038	0.193	0.378	-0.016	0.031	0.002	-0.005	-0.052	-0.053
Afon Hafren	0.019	-0.106	0.169	0.590	-0.008	0.070	-0.002	-0.028	-0.042	-0.044
Beaghs Burn	-0.003	0.004	0.120	2.108	-0.014	0.350	0.000	-0.001	-0.077	-0.079
Bencrom River	0.037	-0.247	1.388	2.285	-0.003	0.094	0.002	0.000	-0.074	-0.065
Blue Lough	0.017	-0.687	0.903	2.903	-0.019	0.160	-0.007	-0.009	-0.137	-0.064
Coneyglen burn	-0.004	0.001	-0.330	0.466	-0.001	0.227	0.000	-0.006	-0.048	0.000
Narrator Brook	0.027	-0.069	0.619	0.276	-0.003	0.027	0.001	-0.004	0.015	-0.069
Afon Gwy	0.028	-0.082	0.200	0.315	-0.002	0.046	0.000	-0.012	-0.041	0.000

Table 2: Change estimates for key determinands observed at AWMN sites based on Sen slopes

	pH	Hplus	alk	anc	Ca	doc	no3	totalN	xso4	Cl
Loch Coire nan Arr	-0.17	0.13	-8.30	4.61	-0.13	2.33	0.00	-0.02	-0.70	0.98
Allt a' Mharcaidh	0.04	-0.02	4.25	18.13	-0.10	1.59	0.00	0.00	-0.34	-0.29
Allt na Coire nan Con	-0.04	0.09	0.00	17.69	-0.19	3.41	0.00	-0.01	-0.85	-0.19
Lochnagar	0.22	-1.83	1.15	8.00	-0.16	1.59	0.06	-0.07	-0.94	-0.60
Loch Chon	0.66	-2.32	21.85	46.53	-0.07	3.86	0.09	0.00	-1.14	-2.59
Loch Tinker	0.15	-0.17	4.58	23.87	-0.25	3.52	0.00	0.02	-1.14	-1.47
Round Loch of Glenhead	0.32	-7.76	10.63	27.76	-0.16	2.56	0.07	0.06	-1.49	-1.44
Loch Grannoch	0.12	-6.10	8.30	48.64	-0.44	3.77	-0.02	-0.12	-2.40	-1.72
Dargall Lane	0.57	-2.57	12.28	24.82	-0.14	1.57	0.00	0.04	-1.07	-1.33
Scoat Tarm	0.22	-4.50	2.10	21.28	-0.25	1.21	-0.12	-0.18	-0.58	-1.65
Burnmoor Tarn	0.18	-0.08	23.27	30.15	-0.42	2.04	0.00	0.00	-1.03	-2.25
River Etherow	0.29	-0.28	37.46	74.11	-1.06	5.81	-0.17	-0.32	-6.35	-2.23
Old Lodge	0.69	-23.47	38.43	78.34	-0.38	5.14	0.00	0.13	-6.55	-2.66
Llyn Llagi	0.74	-5.11	11.20	21.00	-0.27	1.69	-0.04	0.00	-1.27	-1.44
Llyn Mynach	0.15	-0.74	3.75	7.19	-0.32	0.60	0.03	-0.05	-1.01	-1.03
Afon Hafren	0.38	-2.08	3.31	11.53	-0.15	1.36	-0.04	-0.33	-0.82	-0.86
Beaghs Burn	-0.06	0.08	2.36	41.49	-0.28	6.89	0.00	-0.02	-1.52	-1.56
Bencrom River	0.73	-4.86	27.31	44.96	-0.06	1.85	0.05	0.00	-1.46	-1.29
Blue Lough	0.30	-12.17	15.97	51.38	-0.33	2.83	-0.13	-0.11	-2.42	-1.13
Coneyglen burn	-0.07	0.01	-5.80	8.19	-0.01	3.99	0.00	-0.07	-0.84	0.00
Narrator Brook	0.43	-1.09	9.75	4.35	-0.04	0.43	0.02	-0.04	0.24	-1.11
Afon Gwy	0.47	-1.39	3.38	5.33	-0.04	0.78	0.00	-0.14	-0.70	0.00

Table 3: Summary of trends in pH for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.07	2.08	0.1533
Allt a' Mharcaidh	1.00	1.34	0.2488
Allt na Coire nan Con	3.16	1.75	0.1556
Lochnagar	4.44	9.71	1.1e-06
Loch Chon	4.73	25.66	2.9e-14
Loch Tinker	1.58	3.02	0.0669
Round Loch of Glenhead	5.00	28.36	2.0e-15
Loch Grannoch	4.08	7.75	2.7e-05
Dargall Lane	3.27	15.75	6.7e-10
Scoat Tarn	1.00	60.05	5.3e-11
Burnmoor Tarn	1.70	3.91	0.0306
River Etherow	1.00	3.47	0.0638
Old Lodge	6.95	46.63	$< 2e-16$
Llyn Llagi	3.73	20.61	7.6e-11
Llyn Mynach	4.26	3.08	0.0193
Afon Hafren	1.61	6.43	0.0039
Beaghs Burn	1.00	0.04	0.8346
Bencrom River	4.08	12.37	3.1e-09
Blue Lough	1.00	80.73	4.5e-13
Coneyglen burn	1.43	0.25	0.7023
Narrator Brook	5.71	12.43	2.9e-11
Afon Gwy	1.00	21.12	7.7e-06

Table 4: Summary of trends in H+ for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.35	0.87	0.3856
Allt a' Mharcaidh	1.00	2.03	0.1559
Allt na Coire nan Con	3.22	1.95	0.1186
Lochnagar	3.80	8.35	1.9e-05
Loch Chon	2.54	25.97	1.6e-10
Loch Tinker	1.72	2.75	0.0785
Round Loch of Glenhead	4.65	29.92	1.9e-15
Loch Grannoch	3.76	7.38	7.0e-05
Dargall Lane	1.00	6.33	0.0125
Scoat Tarm	1.00	68.18	6.2e-12
Burnmoor Tarn	1.00	0.72	0.3997
River Etherow	1.00	6.63	0.0106
Old Lodge	8.24	37.39	$< 2e{-}16$
Llyn Llagi	3.64	20.72	9.6e-11
Llyn Mynach	4.46	2.65	0.0348
Afon Hafren	1.00	7.38	0.0071
Beaghs Burn	1.00	0.14	0.7052
Bencrom River	1.00	3.36	0.0682
Blue Lough	1.00	86.60	1.2e-13
Coneyglen burn	1.35	0.39	0.5967
Narrator Brook	1.00	27.79	3.8e-07
Afon Gwy	2.68	5.42	0.0020

Table 5: Summary of trends in alkalinity for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.46	0.34	0.64430
Allt a' Mharcaidh	1.00	1.46	0.22766
Allt na Coire nan Con	2.05	1.18	0.31040
Lochnagar	2.16	1.69	0.18971
Loch Chon	5.33	12.06	1.0e-08
Loch Tinker	1.00	0.22	0.63925
Round Loch of Glenhead	3.53	21.77	6.1e-11
Loch Grannoch	3.37	4.48	0.00453
Dargall Lane	4.10	8.19	2.8e-06
Scoat Tarm	1.74	3.69	0.03568
Burnmoor Tarn	1.00	14.44	0.00029
River Etherow	1.01	7.51	0.00659
Old Lodge	6.13	34.50	$< 2e-16$
Llyn Llagi	3.66	5.18	0.00142
Llyn Mynach	4.78	4.30	0.00216
Afon Hafren	6.16	1.82	0.09428
Beaghs Burn	1.00	0.25	0.61978
Bencrom River	1.35	14.66	2.6e-05
Blue Lough	1.00	93.15	2.9e-14
Coneyglen burn	1.66	0.44	0.60867
Narrator Brook	2.54	3.27	0.02942
Afon Gwy	1.61	2.38	0.10690

Table 6: Summary of trends in ANC for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.81	1.59	0.2127
Allt a' Mharcaidh	1.00	28.67	2.1e-07
Allt na Coire nan Con	2.73	8.93	2.6e-05
Lochnagar	2.38	10.53	3.6e-05
Loch Chon	1.57	63.57	8.7e-15
Loch Tinker	1.00	11.50	0.0011
Round Loch of Glenhead	1.82	103.28	< 2e-16
Loch Grannoch	2.82	30.58	1.8e-12
Dargall Lane	1.40	63.31	< 2e-16
Scoat Tarm	1.60	70.83	1.4e-15
Burnmoor Tarn	6.29	6.21	2.8e-05
River Etherow	1.91	17.53	1.7e-07
Old Lodge	8.63	30.96	< 2e-16
Llyn Llagi	2.66	10.34	2.4e-05
Llyn Mynach	2.91	1.32	0.2742
Afon Hafren	5.06	2.29	0.0461
Beaghs Burn	1.22	8.82	0.0018
Bencrom River	1.00	62.25	1.1e-13
Blue Lough	1.00	177.51	< 2e-16
Coneyglen burn	1.01	0.78	0.3789
Narrator Brook	10.77	5.25	5.3e-07
Afon Gwy	1.95	2.69	0.0719

Table 7: Summary of trends in Ca2+ for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.29	2.01	0.1566
Allt a' Mharcaidh	3.96	2.68	0.0330
Allt na Coire nan Con	2.71	4.94	0.0034
Lochnagar	1.00	31.45	3.2e-07
Loch Chon	1.00	2.00	0.1613
Loch Tinker	1.23	2.05	0.1524
Round Loch of Glenhead	2.48	16.20	2.3e-07
Loch Grannoch	3.06	39.33	2.1e-15
Dargall Lane	2.11	5.19	0.0054
Scoat Tarm	11.65	23.47	$< 2e-16$
Burnmoor Tarn	2.44	6.36	0.0015
River Etherow	7.80	8.05	2.2e-09
Old Lodge	13.40	10.36	$< 2e-16$
Llyn Llagi	11.99	8.40	3.0e-09
Llyn Mynach	7.63	3.85	0.0010
Afon Hafren	5.56	5.56	3.7e-05
Beaghs Burn	1.00	2.07	0.1512
Bencrom River	8.78	7.05	8.0e-09
Blue Lough	6.52	8.35	7.5e-07
Coneyglen burn	1.74	0.54	0.5609
Narrator Brook	2.04	1.17	0.3119
Afon Gwy	2.70	3.04	0.0350

Table 8: Summary of trends in DOC for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.89	29.70	9.9e-10
Allt a' Mharcaidh	2.33	13.64	5.9e-07
Allt na Coire nan Con	1.15	104.26	$< 2e-16$
Lochnagar	3.32	16.51	9.4e-09
Loch Chon	1.00	102.72	1.2e-15
Loch Tinker	1.00	64.26	1.3e-11
Round Loch of Glenhead	1.95	39.33	4.2e-12
Loch Grannoch	1.32	40.69	4.9e-10
Dargall Lane	8.92	15.27	$< 2e-16$
Scoat Tarm	1.00	34.41	1.2e-07
Burnmoor Tarn	1.00	37.98	3.3e-08
River Etherow	5.28	10.47	2.2e-09
Old Lodge	8.76	10.27	5.7e-13
Llyn Llagi	1.00	37.79	4.3e-08
Llyn Mynach	1.00	0.25	0.617
Afon Hafren	1.99	9.95	7.5e-05
Beaghs Burn	4.52	29.51	$< 2e-16$
Bencrom River	6.07	7.83	1.0e-07
Blue Lough	2.63	28.25	5.1e-11
Coneyglen burn	4.66	11.04	5.7e-09
Narrator Brook	1.18	1.78	0.184
Afon Gwy	2.57	4.05	0.012

Table 9: Summary of trends in labile aluminium for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	2.03	1.53	0.2225
Allt a' Mharcaidh	2.58	3.13	0.0331
Allt na Coire nan Con	4.17	4.51	0.0013
Lochnagar	3.58	2.32	0.0715
Loch Chon	2.46	13.52	2.2e-06
Loch Tinker	1.65	0.28	0.7100
Round Loch of Glenhead	8.67	16.71	1.3e-13
Loch Grannoch	1.02	41.88	6.9e-09
Dargall Lane	3.32	23.20	4.2e-14
Scoat Tarm	2.52	40.59	3.6e-14
Burnmoor Tarn	1.00	0.88	0.3501
River Etherow	1.66	17.89	4.9e-07
Old Lodge	8.65	32.00	$< 2e-16$
Llyn Llagi	1.00	3.14	0.0804
Llyn Mynach	2.64	2.21	0.1020
Afon Hafren	5.16	2.83	0.0157
Beaghs Burn	2.12	2.76	0.0621
Bencrom River	4.47	12.78	3.8e-10
Blue Lough	1.99	56.98	5.3e-15
Coneyglen burn	1.00	0.35	0.5577
Narrator Brook	5.07	5.95	3.8e-05
Afon Gwy	1.01	6.34	0.0124

Table 10: Summary of trends in NO3- for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	5.68	1.87	0.10368
Allt a' Mharcaidh	12.98	1.78	0.04831
Allt na Coire nan Con	1.00	1.00	0.31920
Lochnagar	14.71	7.58	4.5e-09
Loch Chon	9.47	7.72	8.0e-08
Loch Tinker	10.80	1.62	0.11732
Round Loch of Glenhead	16.87	9.19	9.8e-11
Loch Grannoch	3.98	3.31	0.01513
Dargall Lane	16.10	6.92	1.0e-12
Scoat Tarm	16.80	10.72	5.1e-12
Burnmoor Tarn	14.77	2.93	0.00165
River Etherow	12.90	10.16	$< 2e-16$
Old Lodge	1.00	1.25	0.26427
Llyn Llagi	1.00	8.90	0.00386
Llyn Mynach	1.00	2.31	0.13294
Afon Hafren	12.16	4.99	2.4e-07
Beaghs Burn	17.83	2.96	0.00011
Bencrom River	9.84	6.67	6.1e-09
Blue Lough	16.38	5.69	7.8e-07
Coneyglen burn	5.83	1.45	0.20066
Narrator Brook	3.75	2.18	0.07714
Afon Gwy	7.57	2.81	0.00676

Table 11: Summary of trends in total N for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	2.96	3.31	0.03206
Allt a' Mharcaidh	10.40	3.22	0.00079
Allt na Coire nan Con	15.18	1.37	0.16870
Lochnagar	1.00	3.03	0.08921
Loch Chon	9.36	1.36	0.23703
Loch Tinker	3.19	1.81	0.15602
Round Loch of Glenhead	5.04	1.59	0.18690
Loch Grannoch	7.17	4.12	0.00150
Dargall Lane	11.84	3.89	4.6e-05
Scoat Tarm	16.76	4.97	8.8e-05
Burnmoor Tarn	2.23	1.14	0.33185
River Etherow	6.20	7.41	5.2e-07
Old Lodge	4.67	2.44	0.04109
Llyn Llagi	1.00	0.43	0.51625
Llyn Mynach	17.41	1.99	0.06119
Afon Hafren	10.51	4.98	3.3e-06
Beaghs Burn	13.48	3.30	0.00021
Bencrom River	8.73	3.09	0.00230
Blue Lough	15.74	3.61	0.00151
Coneyglen burn	3.15	4.22	0.00605
Narrator Brook	1.32	0.80	0.40544
Afon Gwy	14.82	2.18	0.01084

Table12: Summary of trends in xSO42- for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	5.05	8.62	2.1e-06
Allt a' Mharcaidh	6.54	7.35	1.3e-07
Allt na Coire nan Con	6.68	9.60	4.2e-10
Lochnagar	1.00	128.90	< 2e-16
Loch Chon	9.97	11.50	4.3e-11
Loch Tinker	8.02	7.98	1.5e-07
Round Loch of Glenhead	7.59	38.65	< 2e-16
Loch Grannoch	5.33	31.28	< 2e-16
Dargall Lane	7.35	23.02	< 2e-16
Scoat Tarm	5.41	16.89	2.8e-11
Burnmoor Tarn	5.78	12.92	1.2e-09
River Etherow	7.02	38.63	< 2e-16
Old Lodge	10.45	13.43	< 2e-16
Llyn Llagi	4.50	22.87	7.5e-13
Llyn Mynach	3.93	9.60	3.2e-06
Afon Hafren	6.64	18.30	< 2e-16
Beaghs Burn	3.25	13.82	9.0e-09
Bencrom River	8.11	18.87	< 2e-16
Blue Lough	3.78	40.30	2.3e-16
Coneyglen burn	12.37	6.98	1.1e-10
Narrator Brook	5.15	6.17	2.1e-05
Afon Gwy	9.64	11.06	2.0e-14

Table 13: Summary of trends in Cl- for AWMN sites. EDF is the effective degrees of freedom of the smooth term for the trend

	edf	F	p-value
Loch Coire nan Arr	1.57	0.27	0.70991
Allt a' Mharcaidh	2.38	2.04	0.12269
Allt na Coire nan Con	1.78	0.75	0.46042
Lochnagar	2.97	6.42	0.00067
Loch Chon	5.83	5.05	0.00027
Loch Tinker	1.00	6.17	0.01521
Round Loch of Glenhead	7.04	7.30	1.6e-06
Loch Grannoch	6.81	5.32	8.4e-05
Dargall Lane	9.72	9.31	1.4e-12
Scoat Tarn	8.19	8.43	6.8e-08
Burnmoor Tarn	9.38	16.72	3.3e-14
River Etherow	1.00	3.52	0.06188
Old Lodge	8.58	4.71	1.4e-05
Llyn Llagi	8.06	4.01	0.00061
Llyn Mynach	2.27	1.93	0.14626
Afon Hafren	11.44	5.58	4.7e-08
Beaghs Burn	1.86	2.89	0.06141
Bencrom River	10.19	5.36	3.6e-07
Blue Lough	1.00	2.21	0.14155
Coneyglen burn	3.37	4.95	0.00161
Narrator Brook	3.14	5.65	0.00084
Afon Gwy	6.40	2.29	0.03343

APPENDIX 4 Diatom Analyses – Figures and Tables

Appendix 4.1: Triplots of the results of applying RDA to each of the diatom epilithon time-series from the AWMN sites (Figures 1-23). The triplots are drawn using symmetric scaling, with the samples indicated by points joined by lines and labelled with the sampling year, species represented by species codes in italics or, if insufficient room to fit in the label, a cross. The horizontal axis is the time axis and the biplot arrow for time points in the direction of time flow from left to right.

Appendix 4.2: Principal Response Curves (PRC) diagrams are shown in Figures 24–46. Time is oriented along the horizontal (x) axis, whilst the vertical axis represents the sample scores. The "control" is represented by the horizontal grey line positioned at 0 on the y-axis. The plotted points are therefore the sample scores on the first RDA axis against time. The distance between these plotted points and the "control" line represents the magnitude of compositional change at each time point. As we conditioned the analysis on the first few observations in each series, this distance represents the compositional change since the initial monitoring period. The PRC plots are supplemented by the labelled rug plot on the right-hand axis, which represents the species scores on the first PRC axis (the y-axis). If the sample scores are positive then those taxa with positive species scores become more abundant and those with negative species scores become less abundant. The opposite is true when sample scores are negative. Currently, we display all taxa present in the samples for a particular site. The larger the species score, the greater the change in that species.

Lakes

Round Loch of Glenhead (Figs. 20, 43)

Numerical analysis of the species data demonstrates a consistent and increasing trend in diatom species changes throughout the monitoring period according to RDA axis 1 scores constrained by year of sampling (Chapter 4, Fig. 4.1). The RDA trend analysis indicates that the floristic change trend is significant since the permutation probability p is < 0.05 (Chapter 4, Table 4.1). Principal Response Curve (PRC) analysis shows that the RDA scores are generally increasing through the monitoring period. *Navicula leptostriata* and *Eunotia denticulata* show the most positive relative changes while *Tabellaria quadriseptata* and acid indicating *Navicula* taxa show the most negative changes.

Scoat Tarn (Figs. 21, 44)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes during the monitoring period (see Chapter 4, Fig. 4.1). The RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability p is < 0.05 (see Chapter 4, Table 4.1). PRC analysis shows that the RDA scores increase from 1988 to 1989 and thereafter scores decline irregularly until about 2000. Scores show no clear trend change after this period. Species of *Eunotia* showed relatively the greatest positive changes whilst *Navicula subtilissima, Eunotia denticulata* and *Achnanthes marginulata* had the greatest negative changes.

Lochnagar (Figs. 18, 41)

Numerical analysis of the species data demonstrates clear species changes and a generally increasing trend (see Chapter 4, Fig. 4.1) throughout the monitoring period. The RDA trend analysis indicates that floristic change is significant since the permutation probability *p* is < 0.05 (see Chapter 4, Table 4.1). PRC analysis shows a declining trend from 1989 to 2006. Abundances of *Achnanthes minutissima* and *Eunotia pectinalis* var. *minor* showed the most positive relative changes while *Aulacoseira* taxa and *Diatoma hiemale* showed the greatest negative change. The latter are consistent with a small recovery in water quality.

Blue Lough (Figs. 5, 28)

Numerical analysis of the species data demonstrates an increasing trend in diatom species changes during the monitoring period (Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period indicates that the floristic change trend is just significant since the permutation probability *p* is 0.05 (Chapter 4, Table 4.1). PRC analysis shows irregularly increasing scores from 1988 until 2006 after which time scores show a modest decline. Species identified as those showing relatively the most positive changes are *Brachysira brebissonii* and *Navicula subtilissima* while *Achnanthes minutissima* showed the greatest negative change.

Loch Coire nan Arr (Figs. 2, 25)

Numerical analysis confirms the significance of the species changes at this site and the RDA axis scores (constrained by year of sampling) show an increasing change trend in 1995-2000 (see Chapter 4, Fig. 4.1). The permutation probability *p* of trend change was significant at the <0.05 level (Chapter 4, Table 4.1). PRC analysis of the RDA scores shows increasingly positive scores at the start of monitoring and persisting until 1990. The analysis indicates that *Tabellaria flocculosa* and *Cymbella microcephala* showed the most positive changes. After 1990 the trend declines until c. 2005 and the species showing the most negative changes are *Achnanthes minutissima* and *Eunotia exigua*.

Loch Grannoch (Figs. 14, 37)

Numerical analysis of the species data demonstrates that the consistent and increasing trend in diatom species changes occurred only in the 1988-2000 period (see Chapter 4, Fig. 4.1). Since 2000 the scores are stable indicating little floristic change of significance. However, the RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability *p* is < 0.05 (Chapter 4, Table 4.1). PRC analysis shows that the RDA scores decrease from 1989 to around 1998 and thereafter remain stable. *Asterionella ralfsii* and *Eunotia exigua* are indicated as showing the most positive changes in the late 1980s while *Tabellaria quadriseptata, Brachysira brebissonii* and *E. incisa* show the most negative changes.

Llyn Llagi (Figs. 13, 36)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes throughout the monitoring period (Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period indicates that the floristic change trend is significant as the permutation probability *p* is 0.5 (see Chapter 4, Table 4.1). PRC analysis shows a clear trend with positive scores gradually increasing after 1988 until 2004 when scores become fairly uniform. Predictably, *T. quadriseptata* is identified as the species showing the most negative change whilst *B. vitrea* and *N. perminuta* show the greatest positive changes.

Llyn Cwm Mynach (Figs. 17, 40)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes throughout the monitoring period (see Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability p is < 0.05 (Chapter 4, Table 4.1). The PRC analysis is similar to that for Llyn Llagi and shows a clear trend with positive scores gradually increasing after 1988 until 2004 when scores become fairly uniform. Several species of *Eunotia* show the most negative changes whilst *B. vitrea* and several *Navicula* species have the greatest positive changes.

Loch Chon (Figs. 7, 30)

Numerical analysis of the species data demonstrates a consistent and increasing trend in diatom species changes throughout the monitoring period according to RDA axis 1 scores (constrained by year of sampling; Chapter 4, Fig. 4.1). The RDA trend analysis indicates that the floristic change trend is significant since the permutation probability p is < 0.05 (Chapter 4, Table 4.1). PRC analysis shows a modest and declining trend in RDA scores after 1990 which stabilises after 2001. Abundances of *Achnanthes marginulata* and *Navicula leptostriata* contributed most to the positive scores and *Brachysira* taxa and *Tabellaria flocculosa* to the negative scores. The latter are consistent with a slight recovery in water quality.

Loch Tinker (Figs. 22, 45)

Numerical analysis of the species data demonstrates a consistent and increasing trend in diatom species changes throughout the monitoring period (see Chapter 4, Fig. 4.1). The RDA trend analysis indicates that the floristic change trend is significant since the permutation probability p is < 0.05 (see Chapter 4, Table 4.1). PRC analysis shows an increasing trend in RDA scores from 1988 to 1993 which then remains fairly stable until 2008. *Cymbella microcephala* and *Nitzschia* taxa are indicated as contributing most to the positive RDA scores while *Tabellaria flocculosa* and *Fragilaria virescens* are most associated with negative scores.

Burnmoor Tarn (Figs. 6, 29)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes from 1988 to 2000 (see Chapter 4, Fig. 4.1). The RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability p is < 0.05 (Chapter 4, Table 4.1). PRC analysis shows that the RDA scores increase from 1988 to 1989 and thereafter scores decline irregularly until about 2003 showing a similar pattern to Scoat Tarn. Scores show an initial small increase after 2003 but no clear trend change after this period. Species of *Tabellaria flocculosa* and *Nitzschia perminuta* show the relatively greatest positive changes whilst *Cymbella cesatii* and *Denticula tenue* had the greatest negative changes.

Loch Coire Fionnaraich (Figs. 23, 46)

Numerical analysis confirms the significance of these species changes with first axis scores RDA showing a marked change trend since 2004 (see Chapter 4, Fig. 4.1). Although the permutation probability *p* of trend change significance was not better than 0.125 (Chapter 4, Table 4.1), the sampling time span (eight years) is relatively short. PRC analysis nevertheless shows unequivocally an increasing shift in species composition scores that began in 2004 and persists until 2008. As above, this plot also shows that the species showing the most positive relative change is *Tabellaria flocculosa* while *Peronia fibula* and *Brachysira vitrea* show the most negative relative changes.

Streams

Allt a' Mharcaidh (Figs. 16, 39)

Numerical analysis of the species data demonstrates these species changes and the RDA axis scores show a generally increasing trend (see Chapter 4, Fig. 4.1). The significance of this trend according to the permutation probability *p* value is better than 0.05 (see Chapter 4, Table 4.1). PRC analysis also shows a significant but modest trend towards increasingly declining scores after c. 1989. The species with the highest RDA scores are not necessarily the most common but those that have the greatest changes in abundance. Hence, changes in *Achnanthes modestiformis, A. minutissima* and *Eunotia incisa* contributed most to the negative PRC score trend; *Hannaea arcus* and *Fragilaria vaucheriae* contributed most to the earlier (pre 1990) positive score trend.

Allt na Coire nan Con (Figs. 1, 24)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes throughout the monitoring period (see Chapter 4, Fig. 4.1). The significance of the RDA trend analysis is weak and the permutation probability *p* is the lowest in the whole AWMN data set at 0.191 (Chapter 4, Table 4.1). PRC analysis shows a trend, of relatively low magnitude, towards higher scores that persisted until 2005. After 2005 scores show a declining trend. The most negative relative changes are shown by *Achnanthes saxonica* and *Eunotia exigua* and the species showing the most positive changes after 2005 are *Tabellaria flocculosa* and *Eunotia incisa*.

Dargall Lane (Figs. 9, 32)

Numerical analysis of the species data demonstrates a consistent and increasing trend in diatom species changes during the monitoring period (see Chapter 4, Fig. 4.1). The RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability *p* is < 0.05 (see Chapter 4, Table 4.1). PRC analysis shows that the RDA scores increase from 1988 to 1991 and thereafter scores decline irregularly until 2006. After this time scores show no clear trend. Species of *Eunotia* show the greatest positive change whilst *Peronia fibula* and *Tabellaria flocculosa* have the greatest negative changes.

River Etherow (Figs. 10, 33)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes occurring after about 1996 (Chapter 4, Fig. 4.1). The RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability p is < 0.05 (Chapter 4, Table 4.1). Somewhat surprisingly the PRC analysis shows little change in RDA scores until 1993 when scores begin to decline irregularly before stabilizing after 2003. *Eunotia exigua* and *Achnanthes minutissima* showed relatively the greatest positive changes whilst *A. saxonica* and *Gomphomema angustatum* showed the most negative changes.

Old Lodge (Figs. 15, 38)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes occurring after about 1995 (see Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period indicates that the floristic change trend is not significant since the permutation probability p is only marginally < 0.1 (see Chapter 4, Table 4.1). PRC analysis initially shows a positive score in 1989 followed by an irregularly declining trend until 2002 with fluctuating scores thereafter. The species *Achnanthes minutissima* and *Synedra minuscula* showed the greatest positive changes whilst *Eunotia rhomboidea* and *Frustulia rhomboides* varieties showed the greatest negative changes.

Narrator Brook (Figs. 19, 42)

Numerical analysis of the species data indicates an increasing trend in diatom species changes only during the late 1990s (see Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period indicates that the floristic change trend is not significant since the permutation probability p is only 0.35 (see Chapter 4, Table 4.1). PRC analysis initially shows positive scores in the early period of monitoring (1989 - 1990), followed by a decline in score values that fluctuate strongly after 1991. The species *Gomphonema gracile* and *Fragilaria vaucheriae* showed the relatively greatest positive changes whilst *Eunotia vanheurkii* var. *intermedia* and *A. austriaca* had the greatest negative changes.

Afon Hafren (Figs. 12, 35)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes throughout the monitoring period (see Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period does indicate that the floristic change trend is significant since the permutation probability p is < 0.05 (see Chapter 4, Table 4.1). PRC analysis shows a clear trend with the 1988 positive score initially declining to negative vales in 1989-1990. After 1990 scores gradually increase until 2006 when scores become fairly uniform. Species identified as those showing relatively the most positive changes are *T. flocculosa* and *Eunotia incisa* whilst *E. vanheurckii* var. *intermedia* and *Achnanthes austriaca* var. *minor* have the greatest negative changes.

Afon Gwy (Figs. 11, 34)

Numerical analysis of the species data demonstrates a fairly consistent and increasing trend in diatom species changes throughout the monitoring period (see Chapter 4, Fig. 4.1). However, RDA trend analysis for the whole monitoring period indicates that the floristic change trend is not significant since the permutation probability p is >0.05 (see Chapter 4, Table 4.1). PRC analysis shows a clear trend with the 1988 positive score declining to increasingly negative vales until 1996. After 1996, scores remain essentially uniform until increasing in 2007/8. Species identified as those showing relatively the most positive changes are *Eunotia vanheurckii* var. 1 and *Peronia fibula* while *Tabellaria flocculosa* has the greatest negative change.

Beagh's Burn (Figs. 3, 26)

Numerical analysis of the species data demonstrates a fairly regular and increasing trend in diatom species changes throughout the monitoring period (see Chapter 4, Fig. 4.1). However, RDA trend analysis for the whole monitoring period indicates that the floristic change trend is not significant since the permutation probability p is >0.05 (see Chapter 4, Table 4.1). PRC analysis shows irregularly declining scores from 1988 until 1995 after which time scores fluctuate. Species identified as those showing relatively the most positive changes are *Eunotia rhomboidea* and *E. pectinalis* var. *minor* while *Synedra minuscula* and *Gomphonema angustatum* has the greatest negative change.

Bencrom River (Figs. 4, 27)

Numerical analysis of the species data demonstrates an increasing trend in diatom species changes during the post 1995 period (see Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period indicates that the floristic change trend is just significant since the permutation probability p is <0.05 (Chapter 4, Table 4.1). PRC analysis shows declining scores from 1988 to 1990 after which time scores irregularly increase until 2003. After 2003 scores declined until the end of monitoring in 2008. Species identified as those showing relatively the most positive changes are *Eunotia naegelii* and *Tabellaria flocculosa* while *T. quadriseptata* has the greatest negative change.

Coneyglen Burn (Figs. 8, 31)

Numerical analysis of the species data demonstrates an increasing trend in diatom species changes during the monitoring period (see Chapter 4, Fig. 4.1). RDA trend analysis for the whole monitoring period indicates that the floristic change trend is not significant since the permutation probability p is 0.25 (see Chapter 4, Table 4.1). PRC analysis shows little change until 1991 when scores decline irregularly until 1999. Scores then fluctuate with lowest values occurring in the last two years of monitoring. Species identified as those showing relatively the most positive changes are *Achnanthes minutissima* and *Nitzschia* sp. while *Achnanthes modestiformis* and *Pinnularia subcapitata* have the greatest negative change.

APPENDIX 4.1: Redundancy Analyses

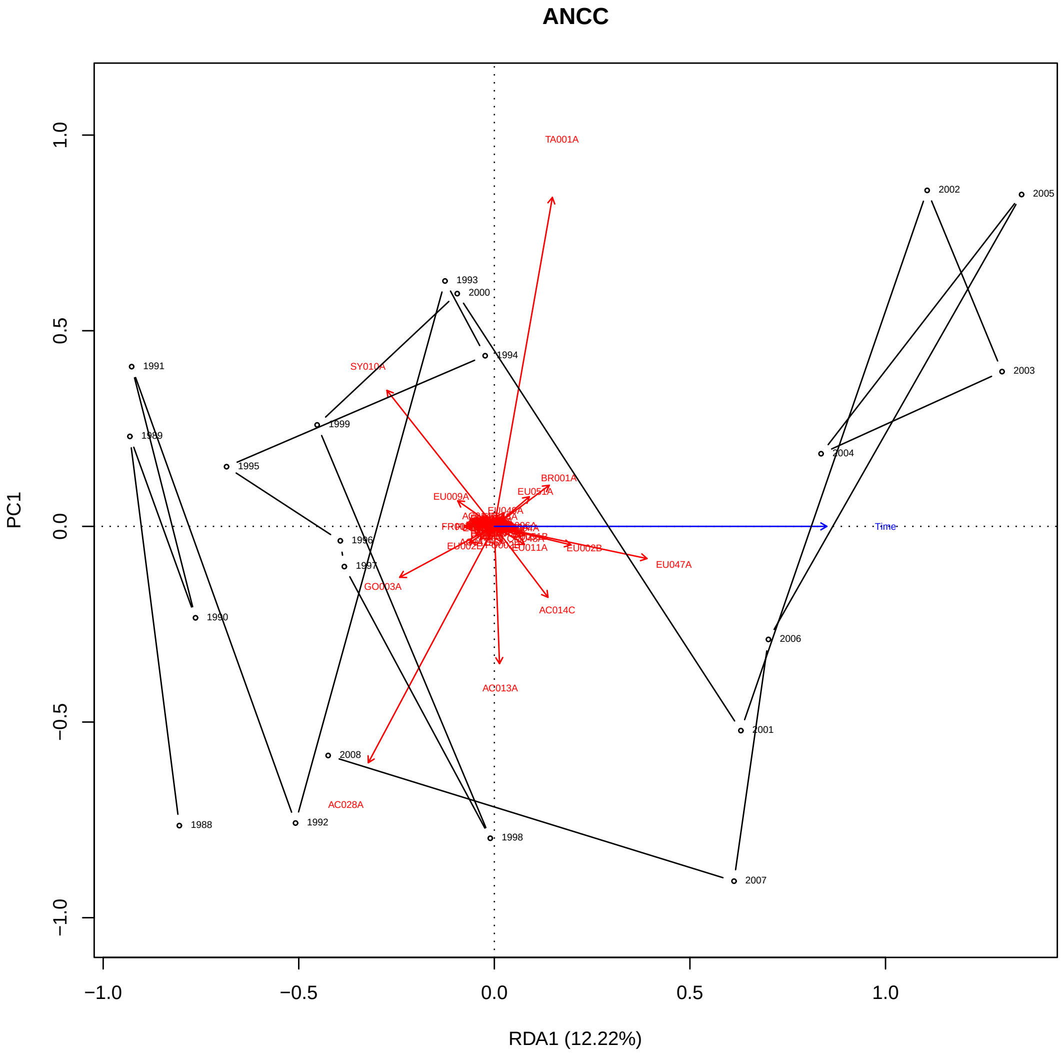

Figure 1: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Allt na Coire nan Con

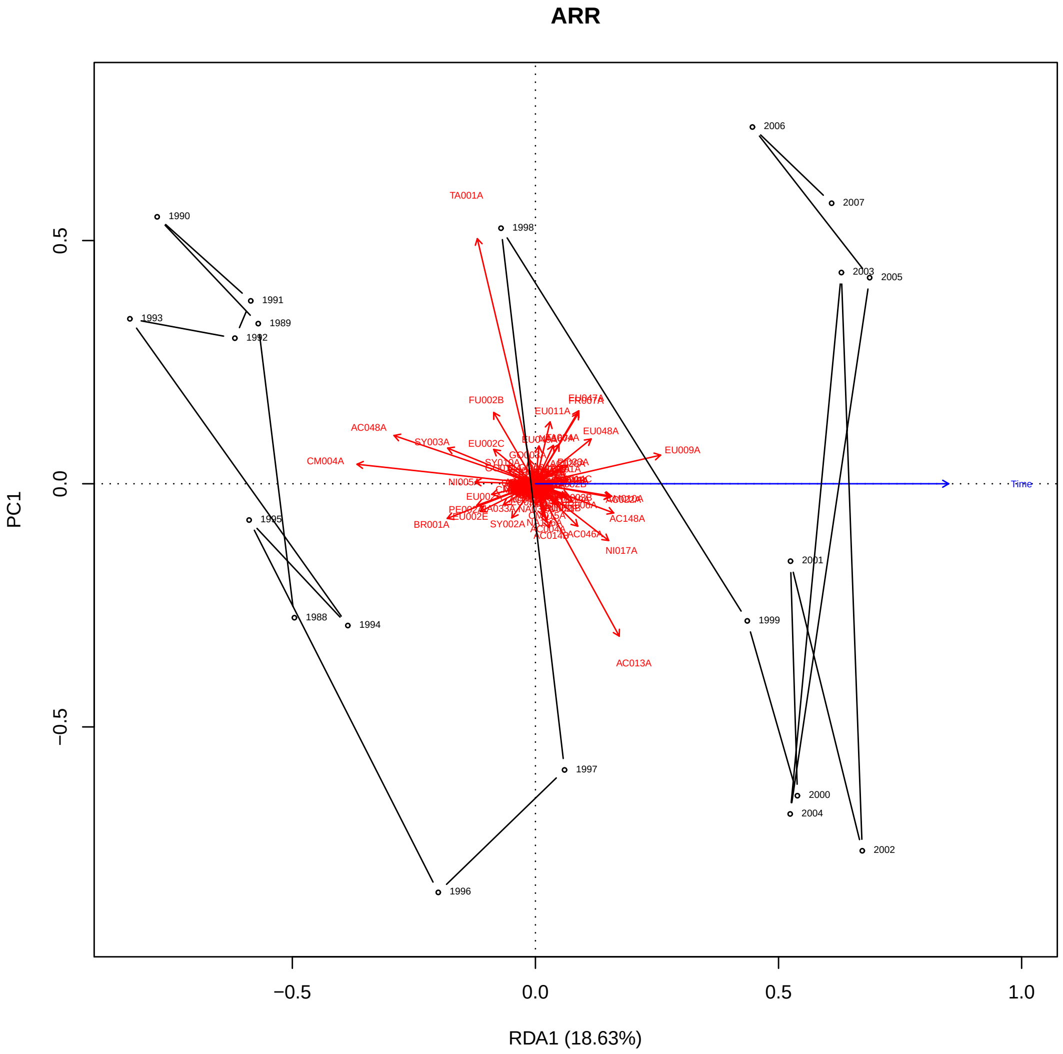

Figure 2: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Loch Coire nan Arr

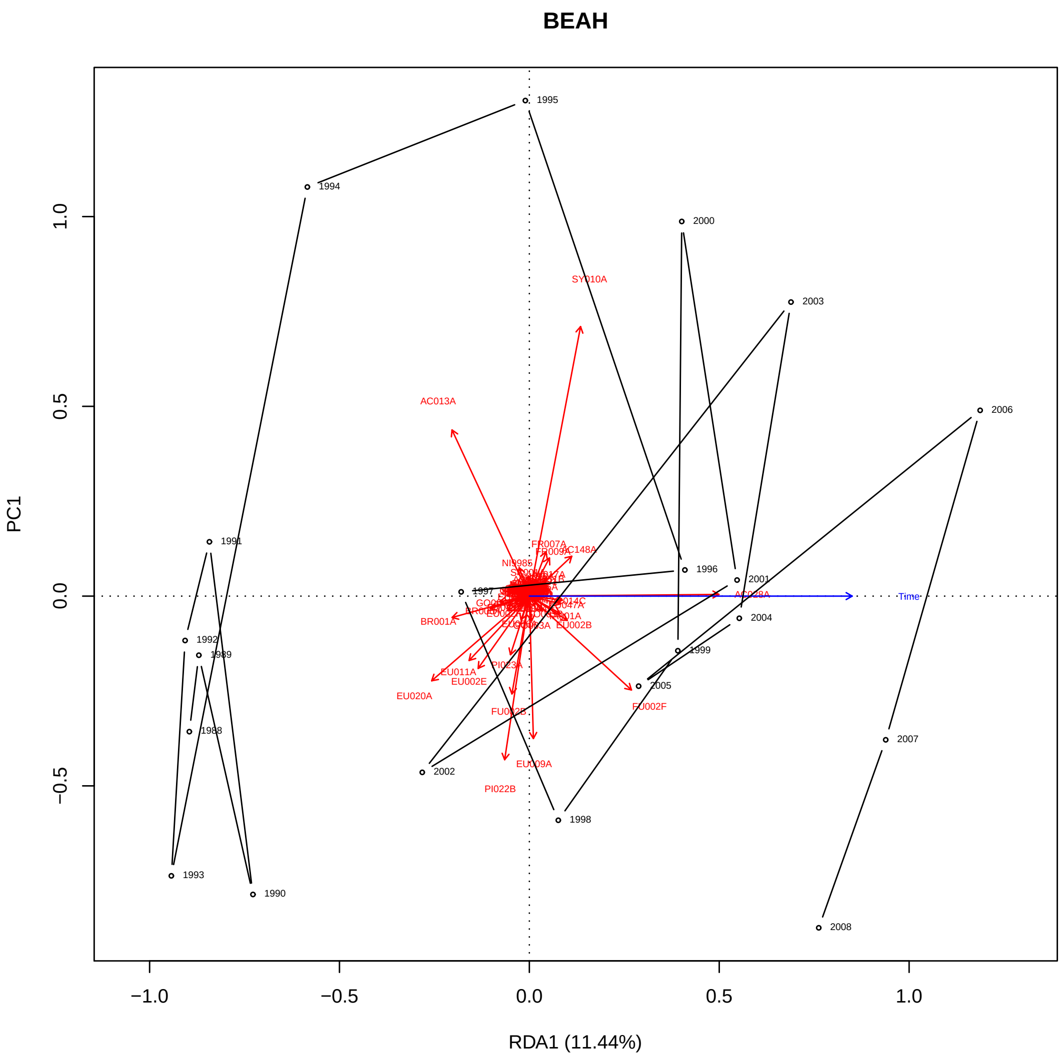

Figure 3: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Beagh's Burn.

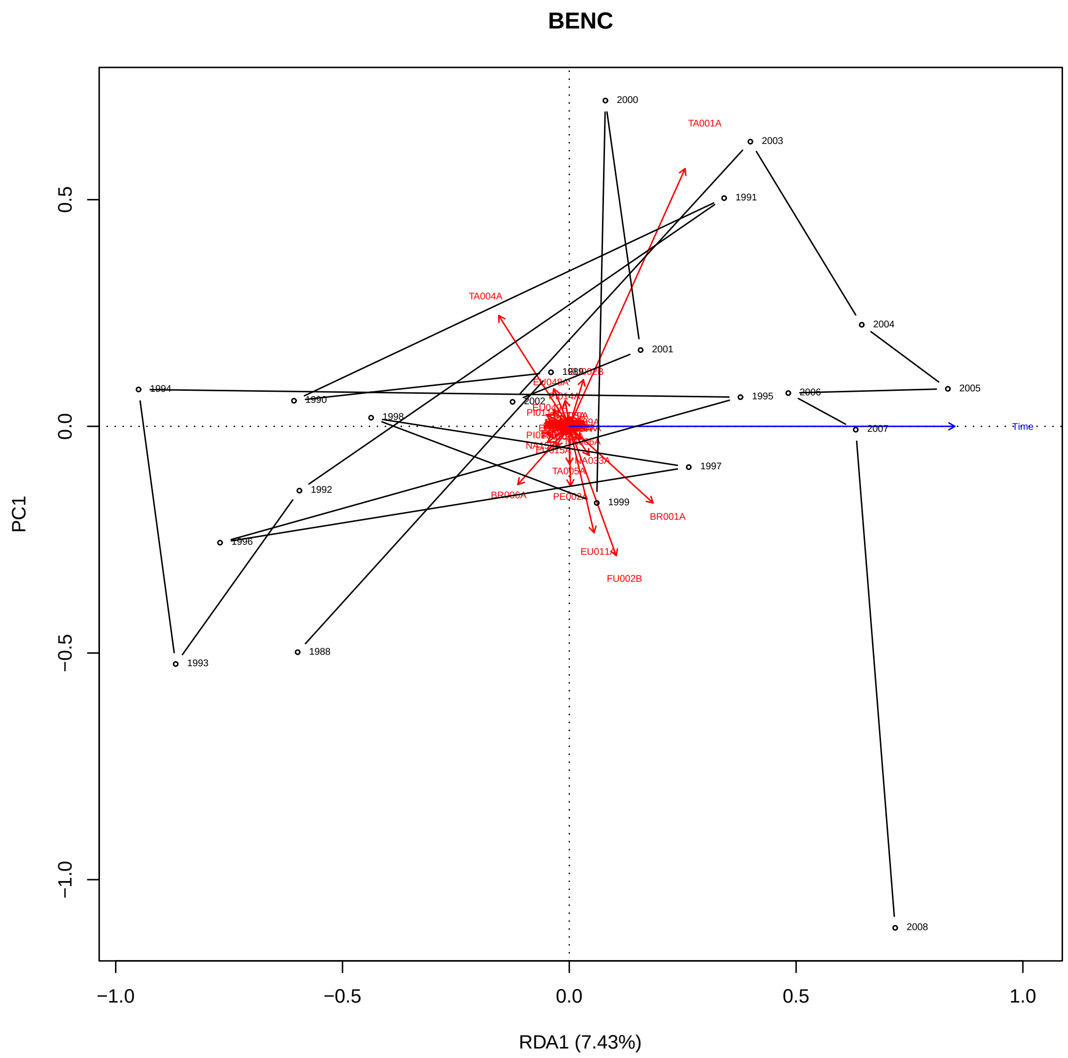

Figure 4: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Bencrom River.

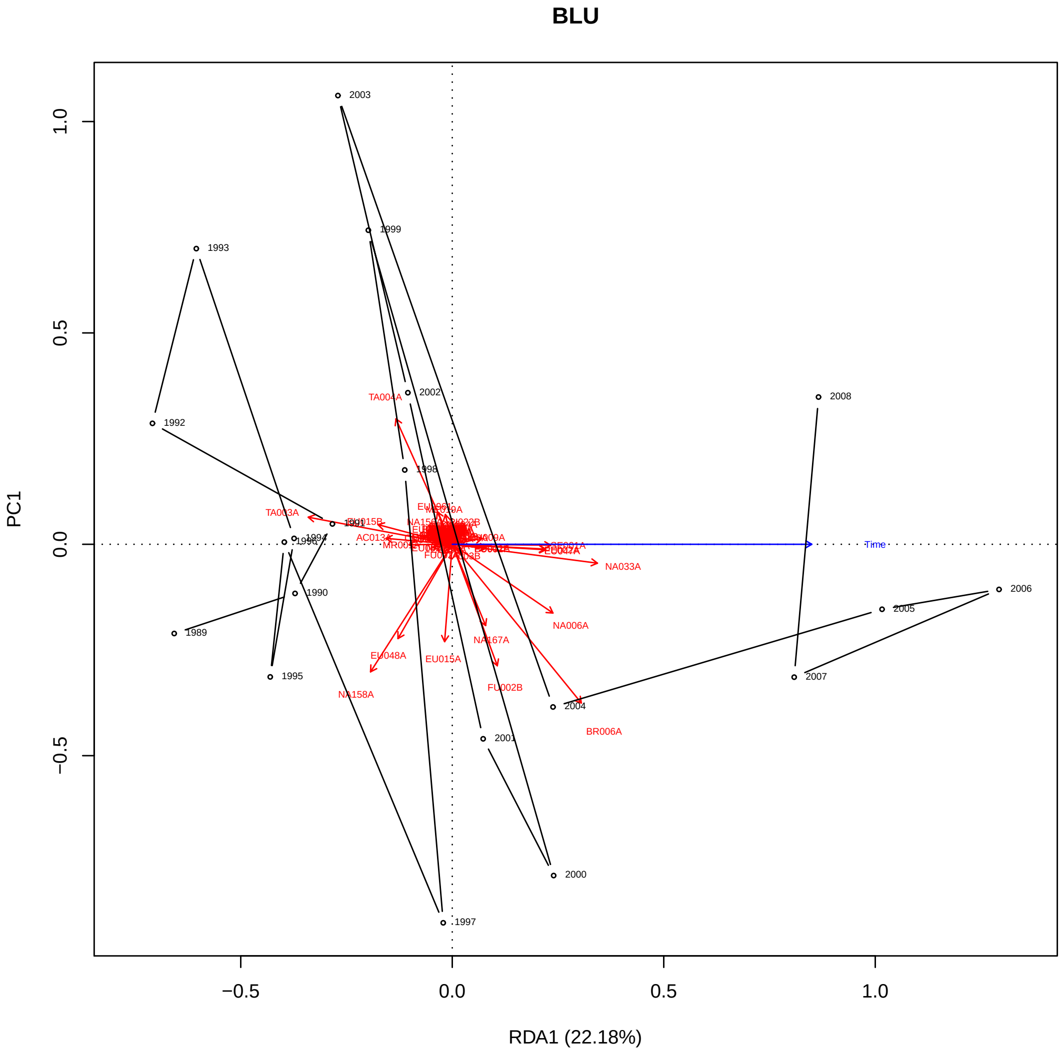

Figure 5: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Blue Lough.

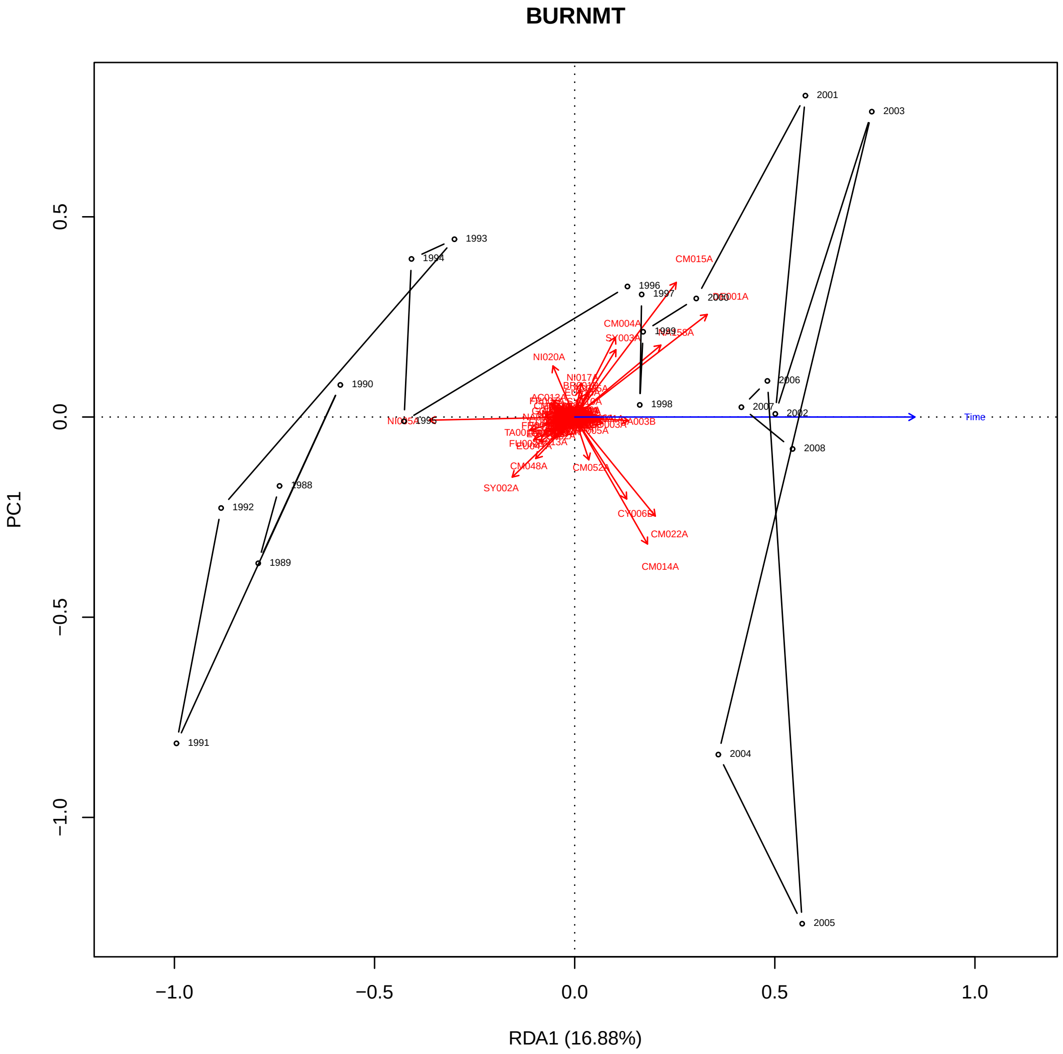

Figure 6: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Burnmoor Tarn.

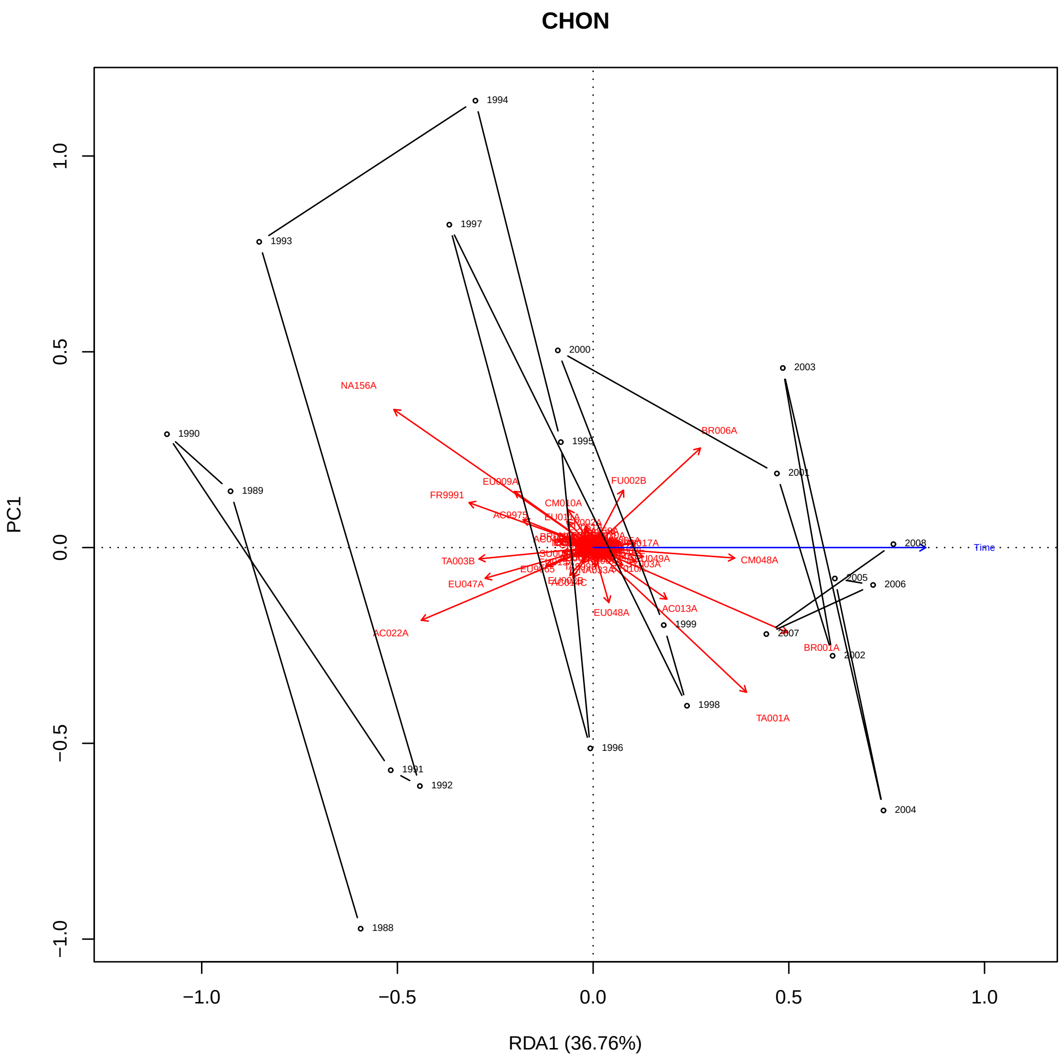

Figure 7: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Loch Chon.

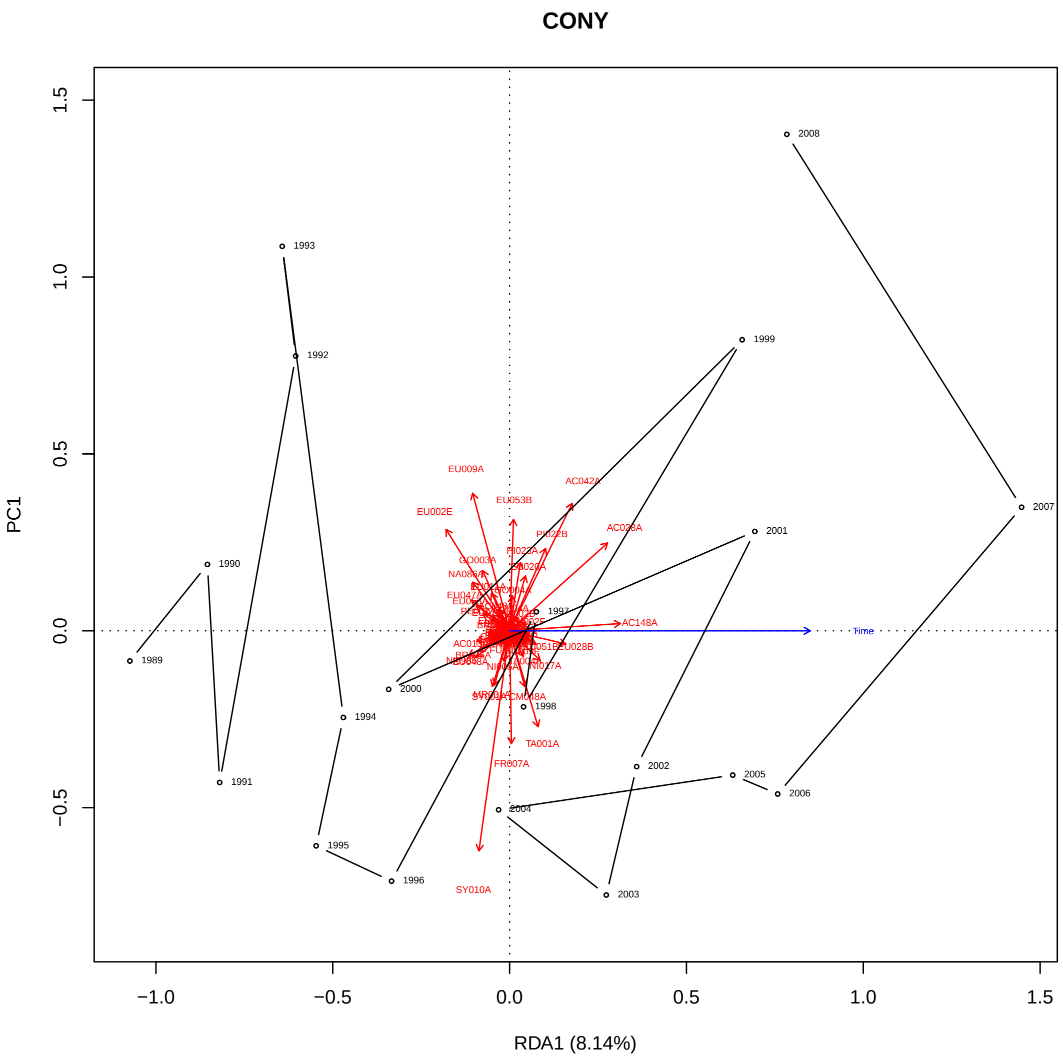

Figure 8: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Coneyglen Burn.

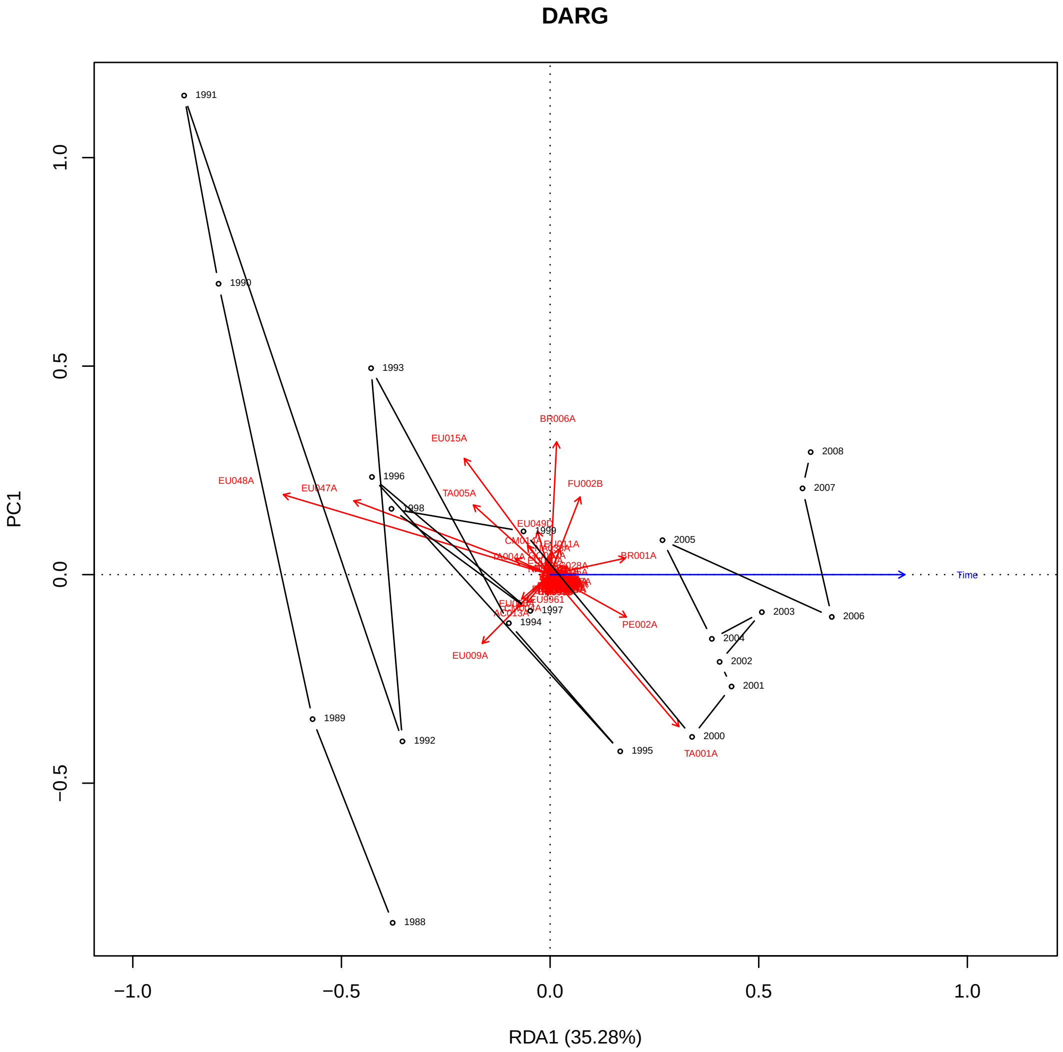

Figure 9: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Dargall Lane.

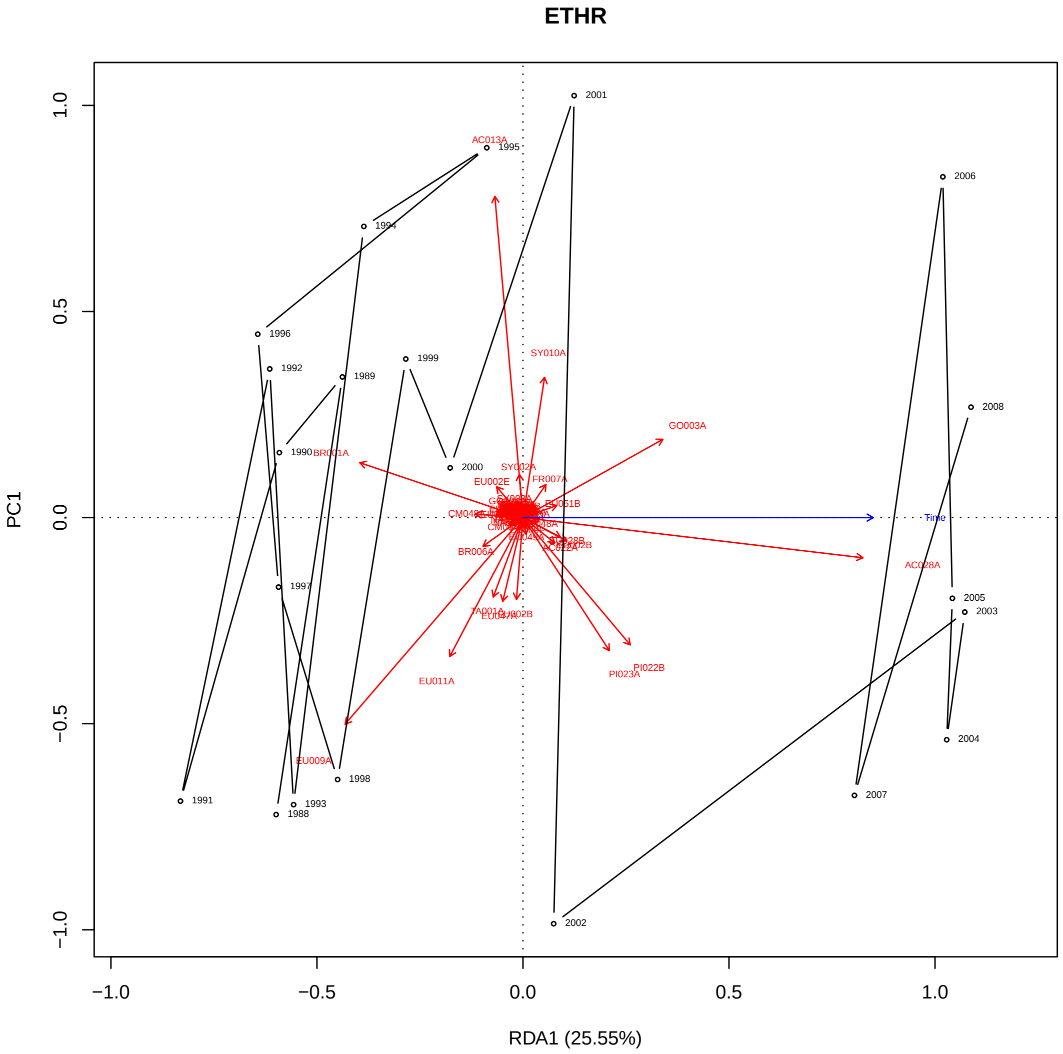

Figure 10: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at River Etherow.

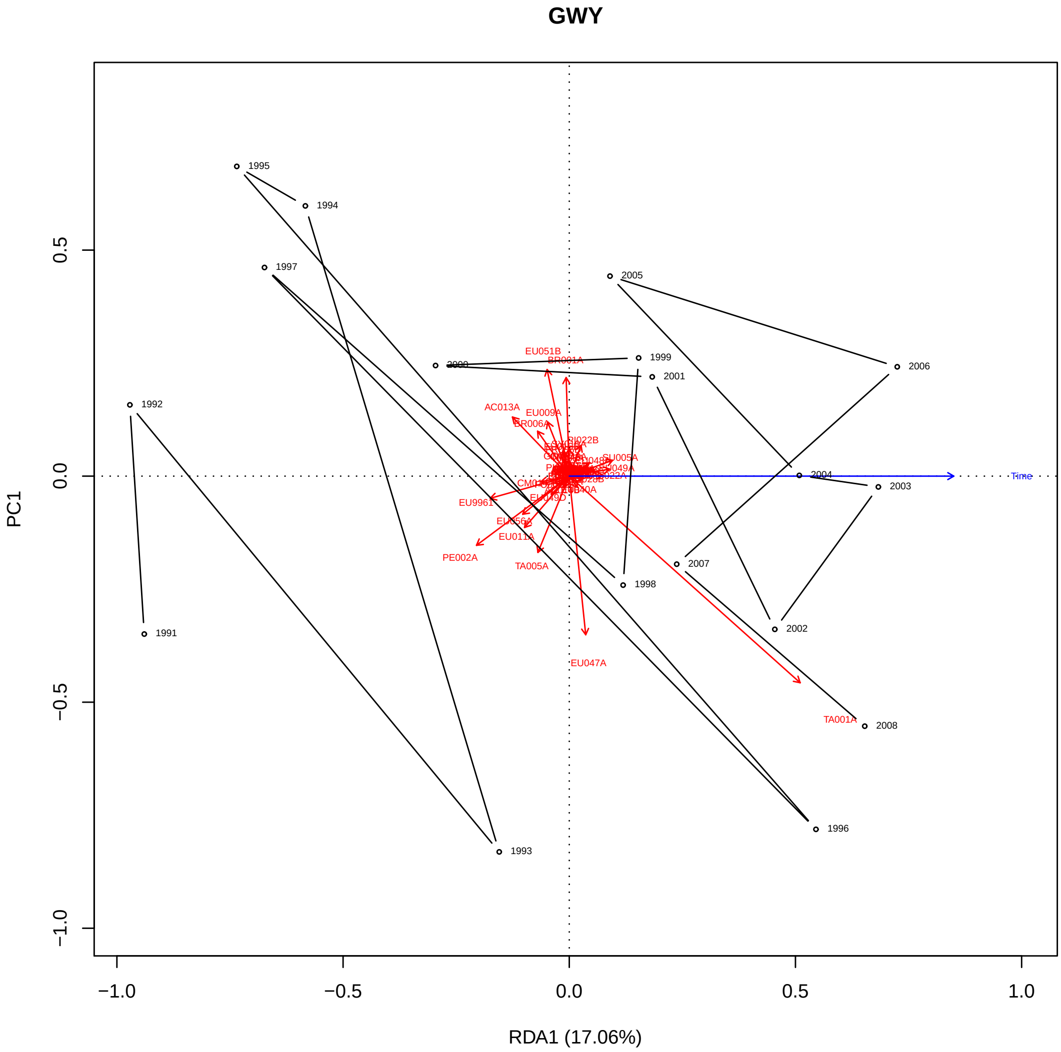

Figure 11: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Afon Gwy

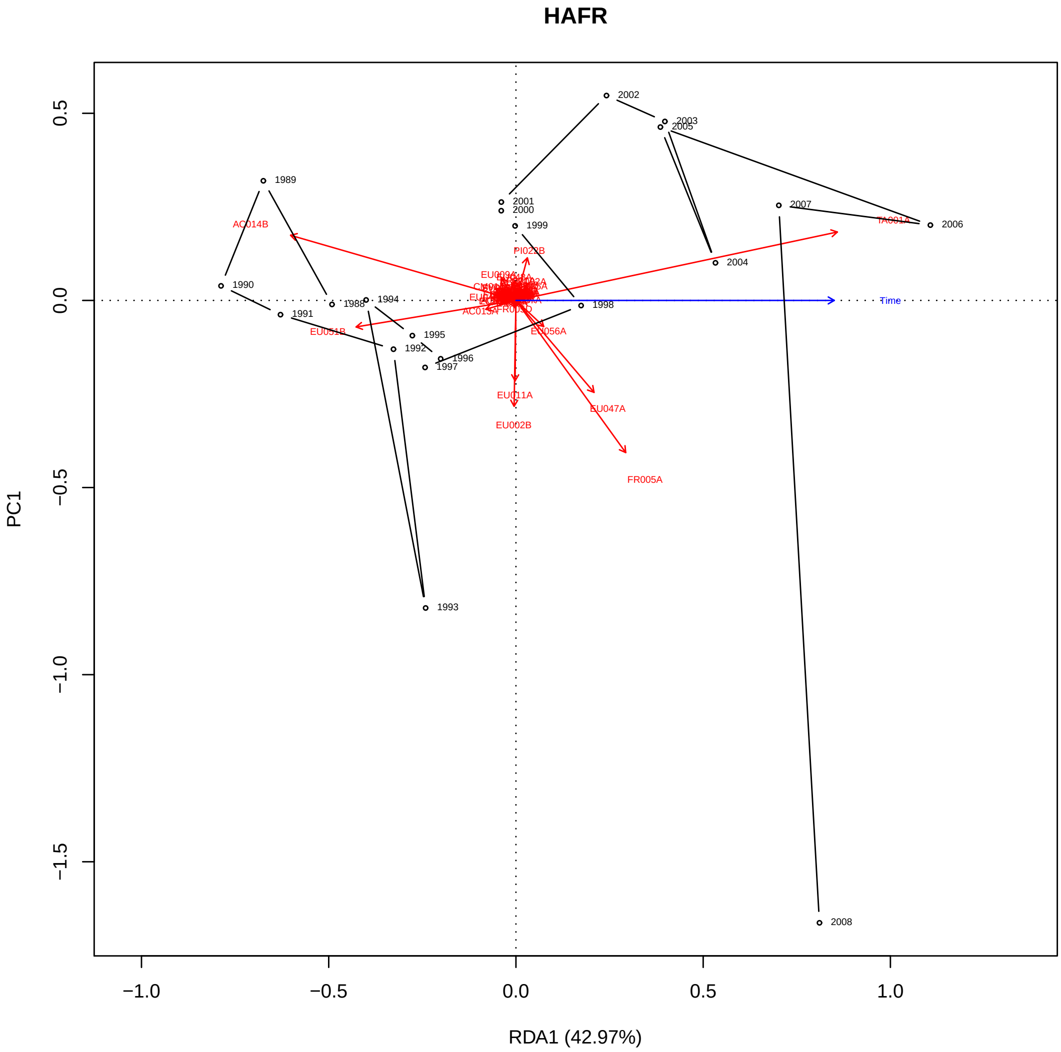

Figure 12: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Afon Hafren.

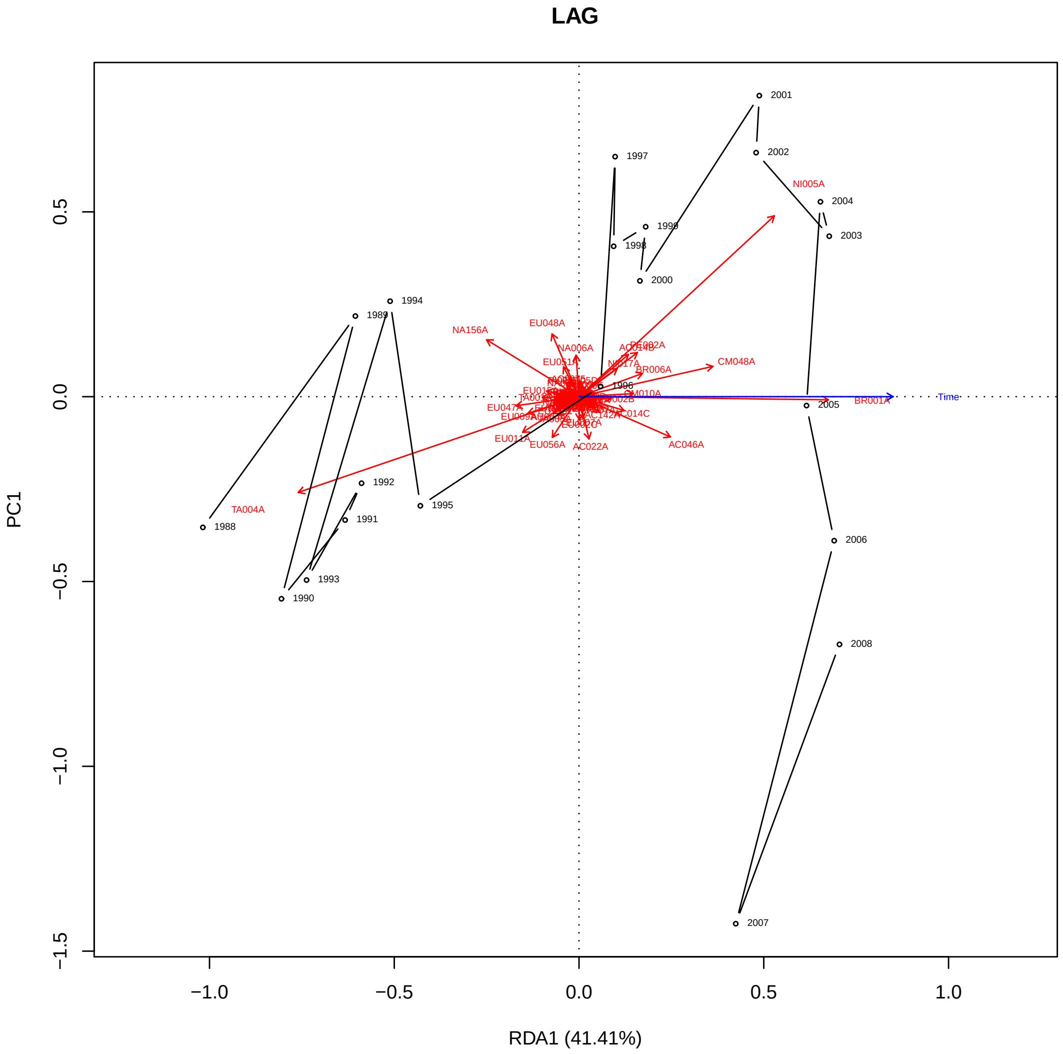

Figure 13: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Llyn Llagi.

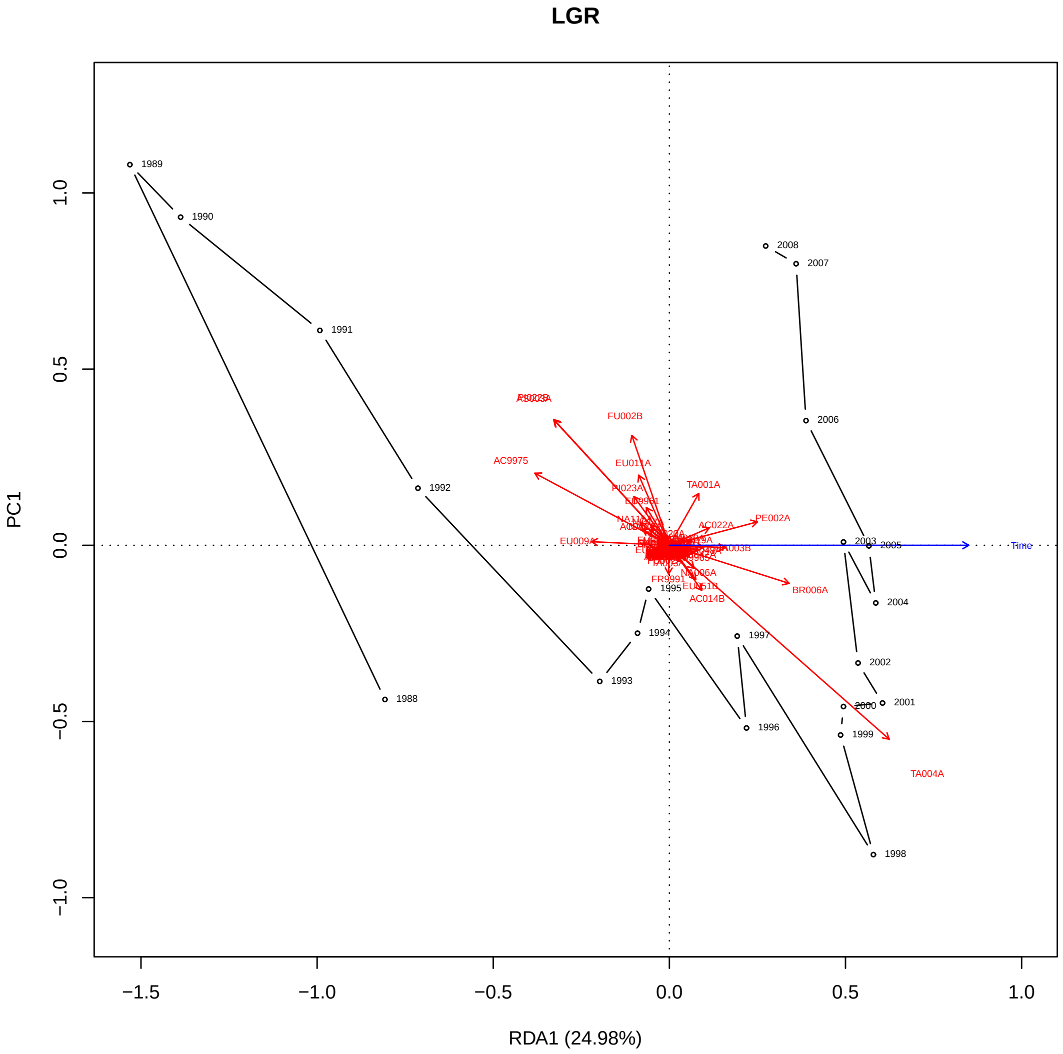

Figure 14: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Loch Grannoch.

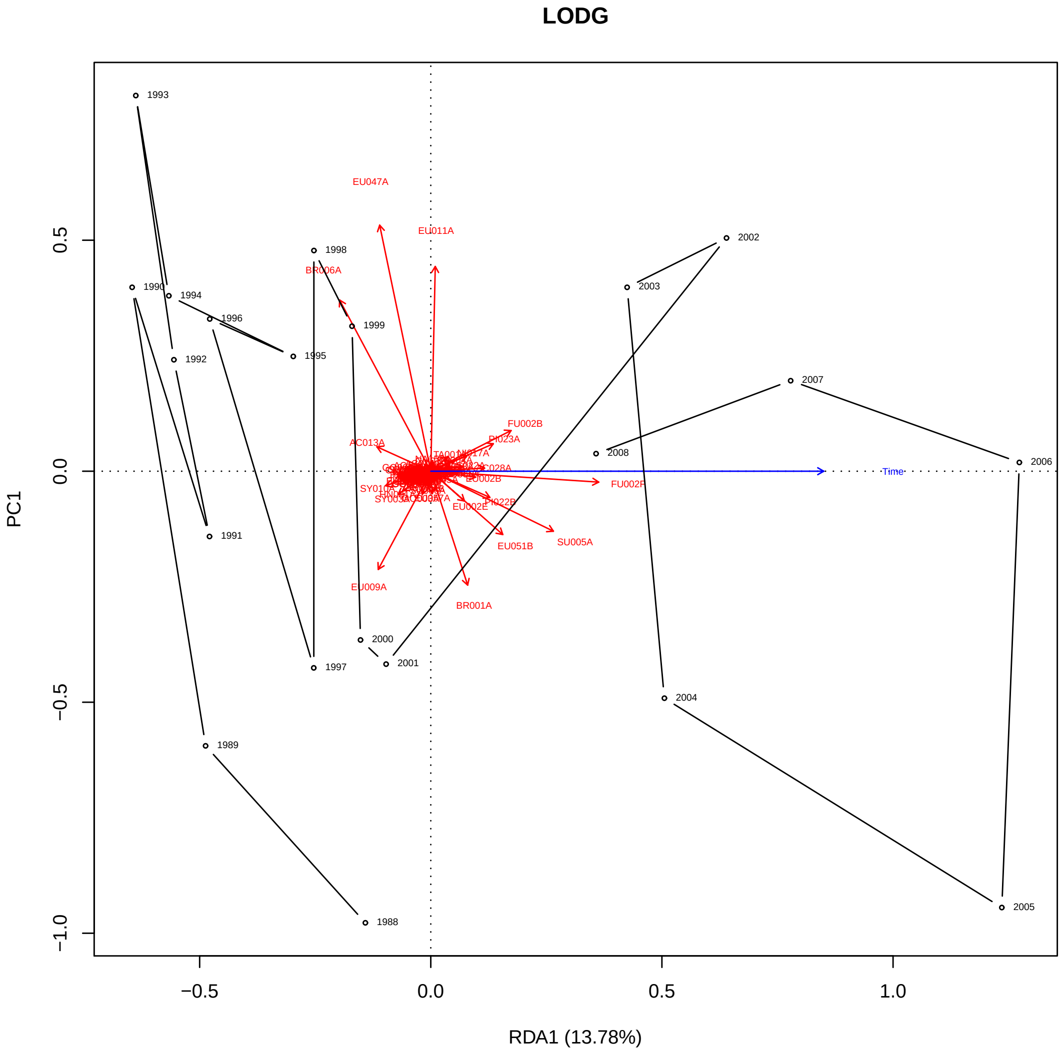

Figure 15: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Old Lodge.

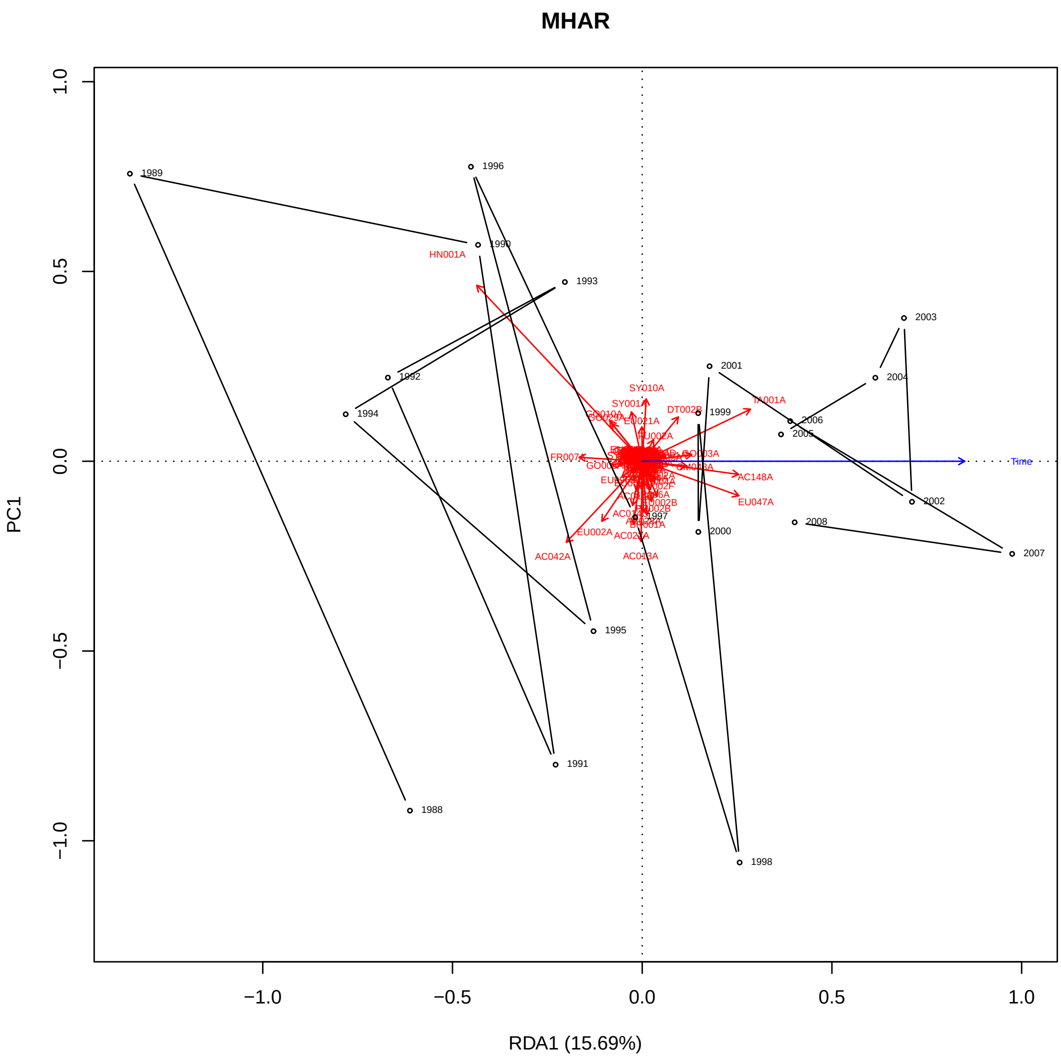

Figure 16: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Allt a' Mharcaidh.

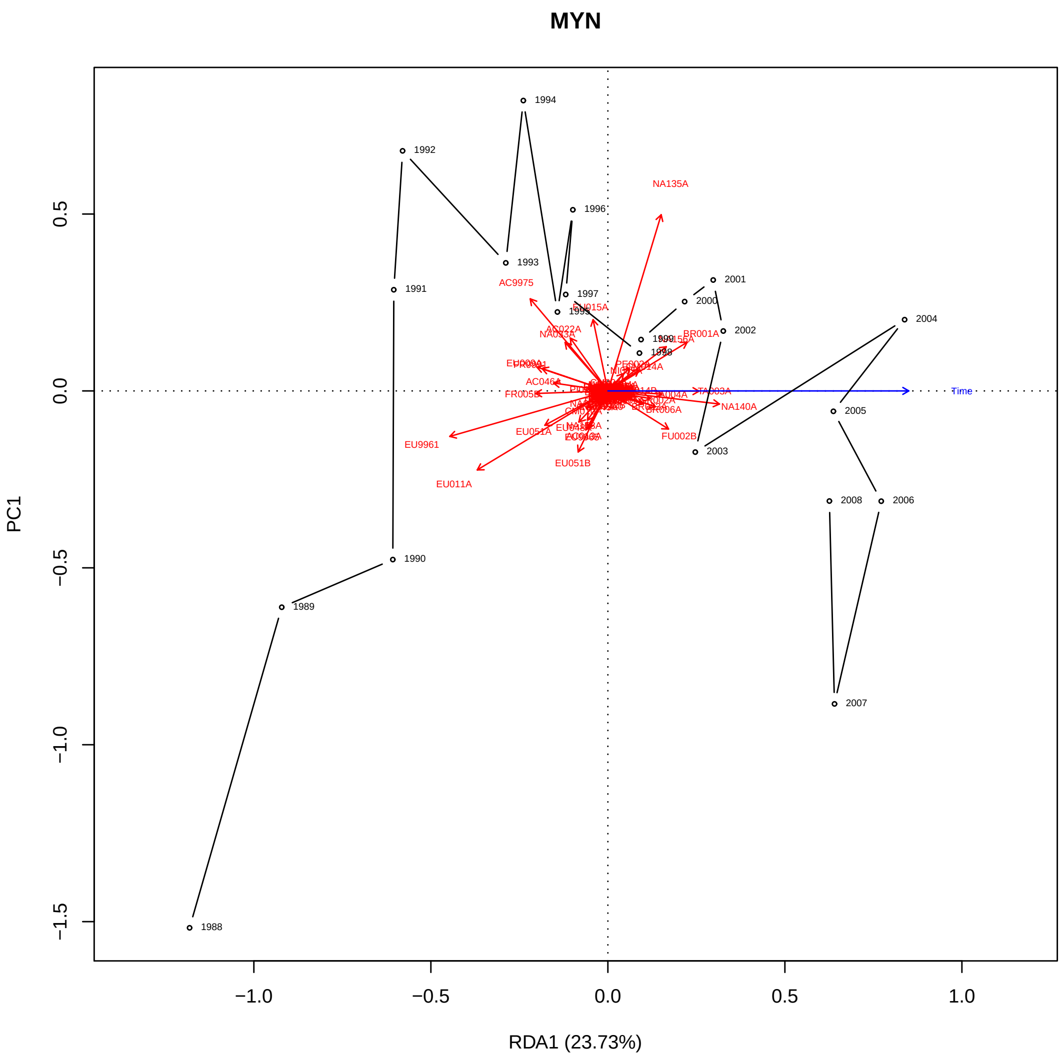

Figure 17: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Llyn Cwm Mynach.

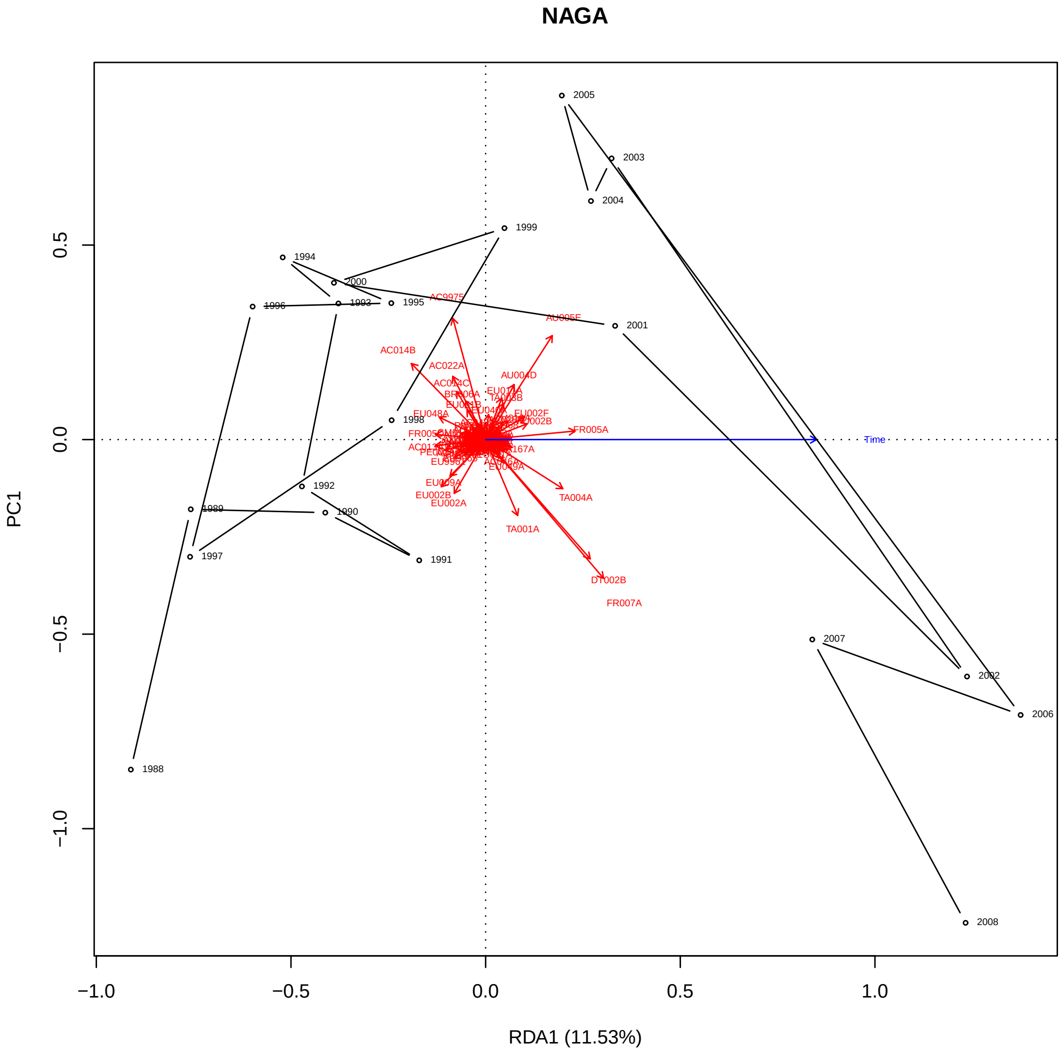

Figure 18: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Lochnagar.

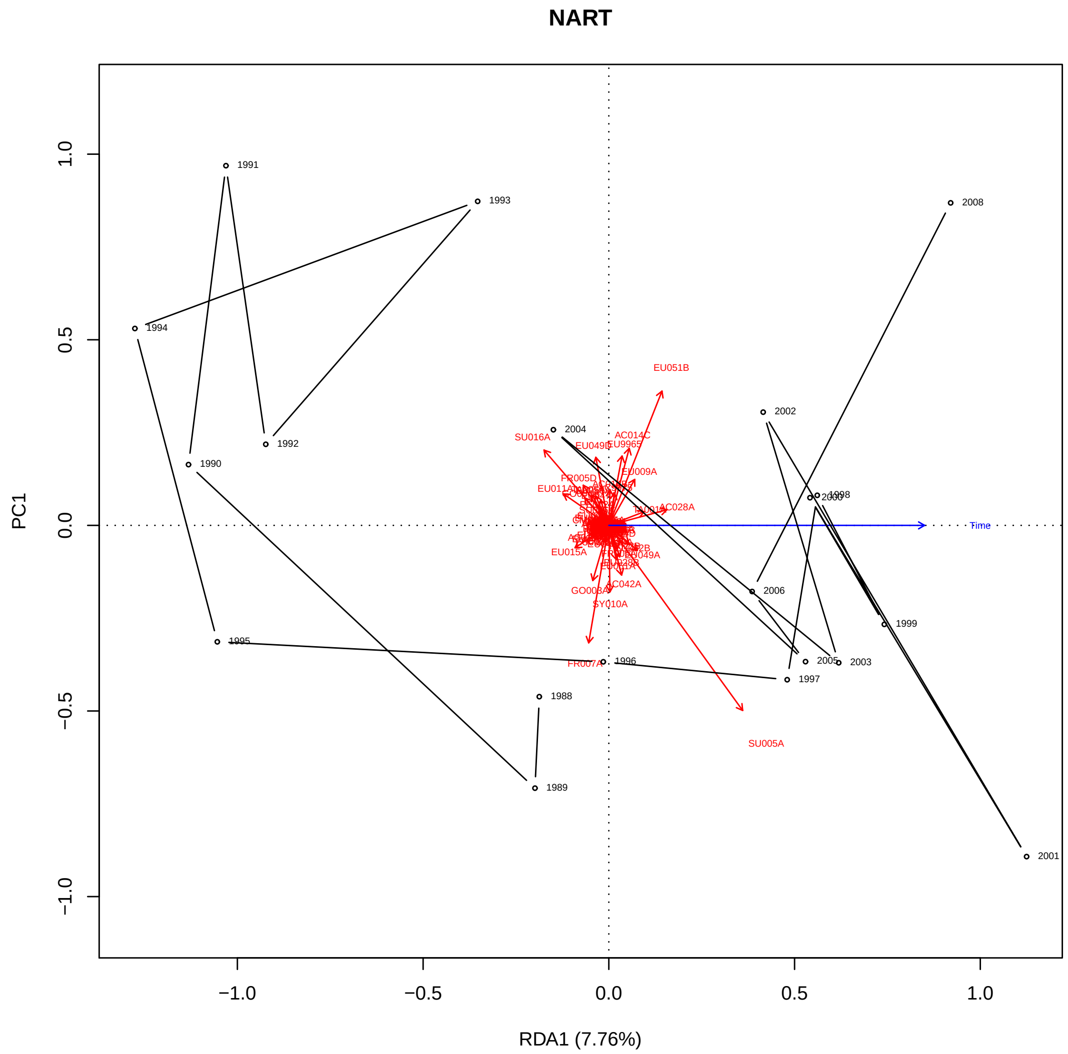

Figure 19: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Narrator Brook.

RLGH

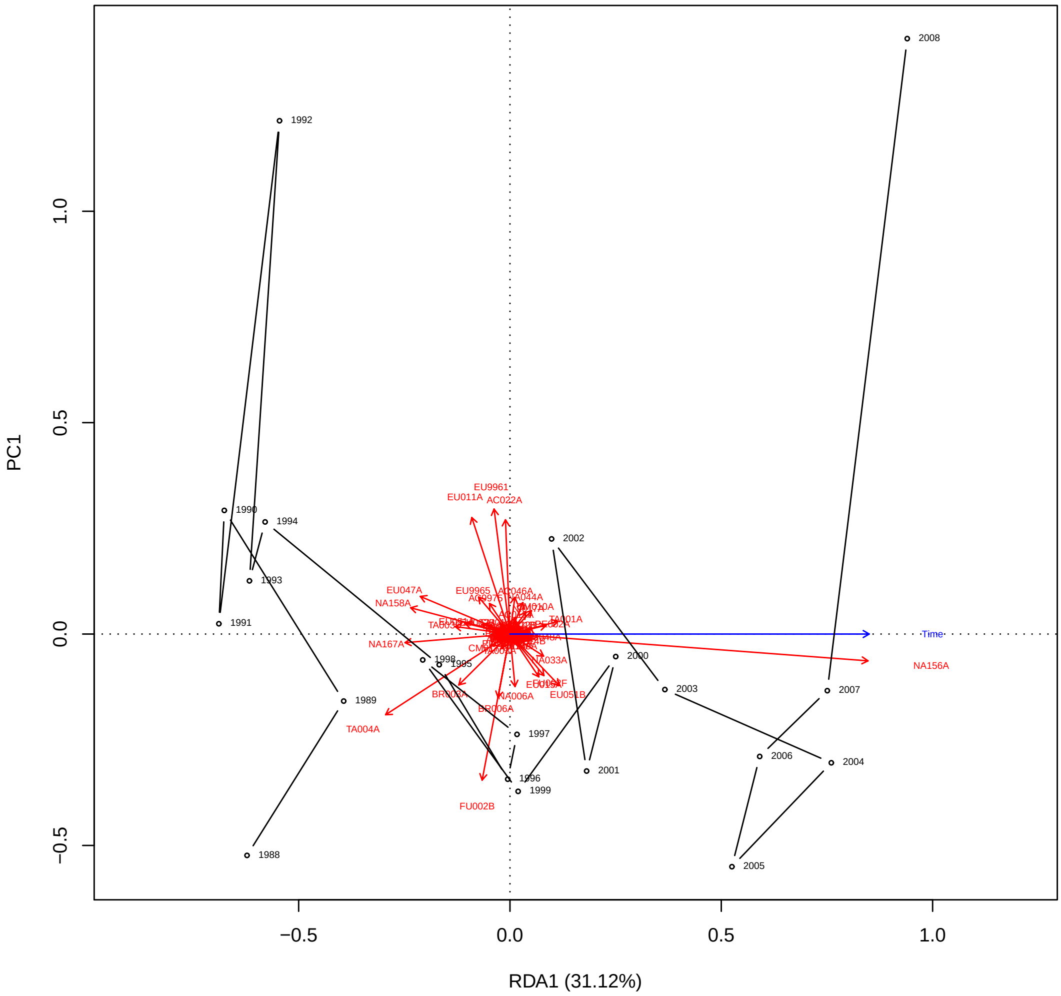

Figure 20: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Round Loch of Glenhead.

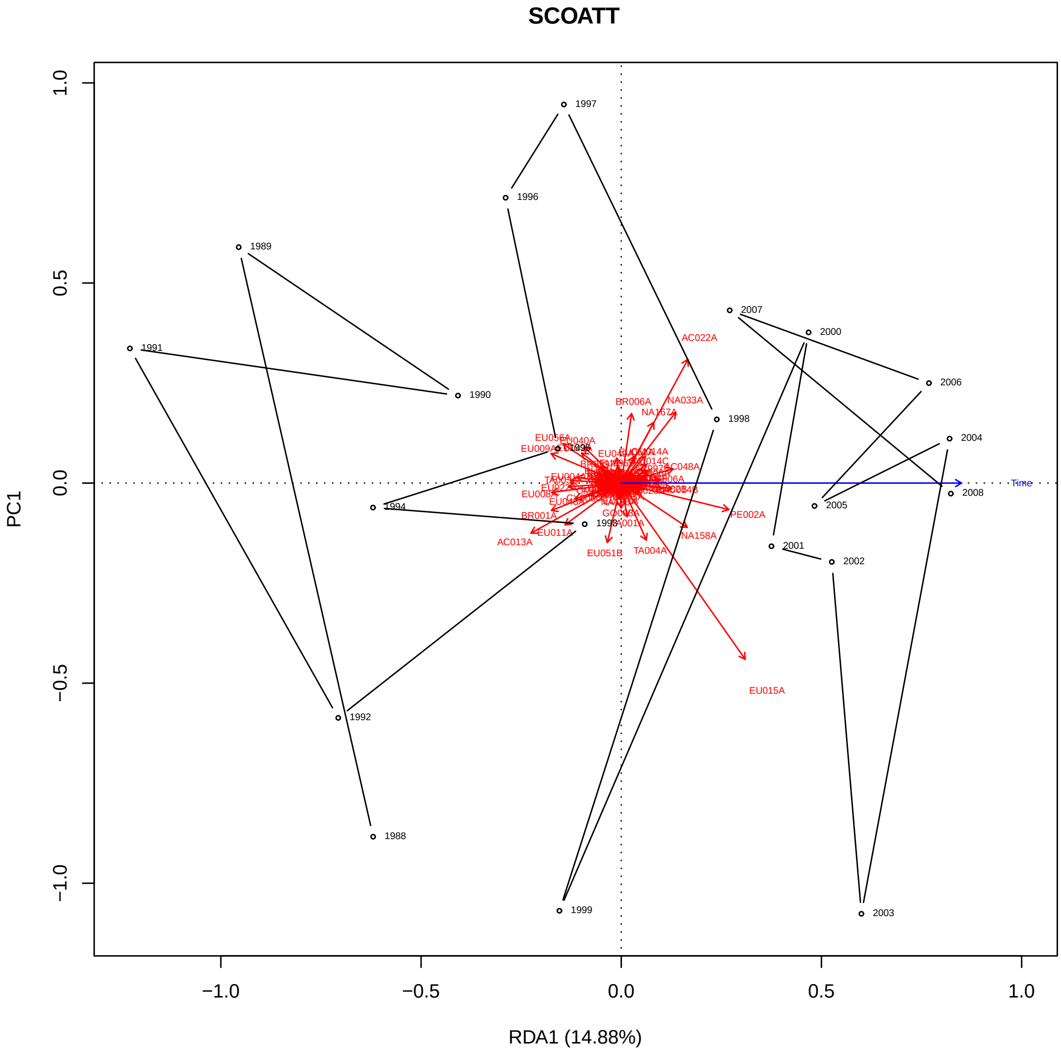

Figure 21: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Scoat Tarn.

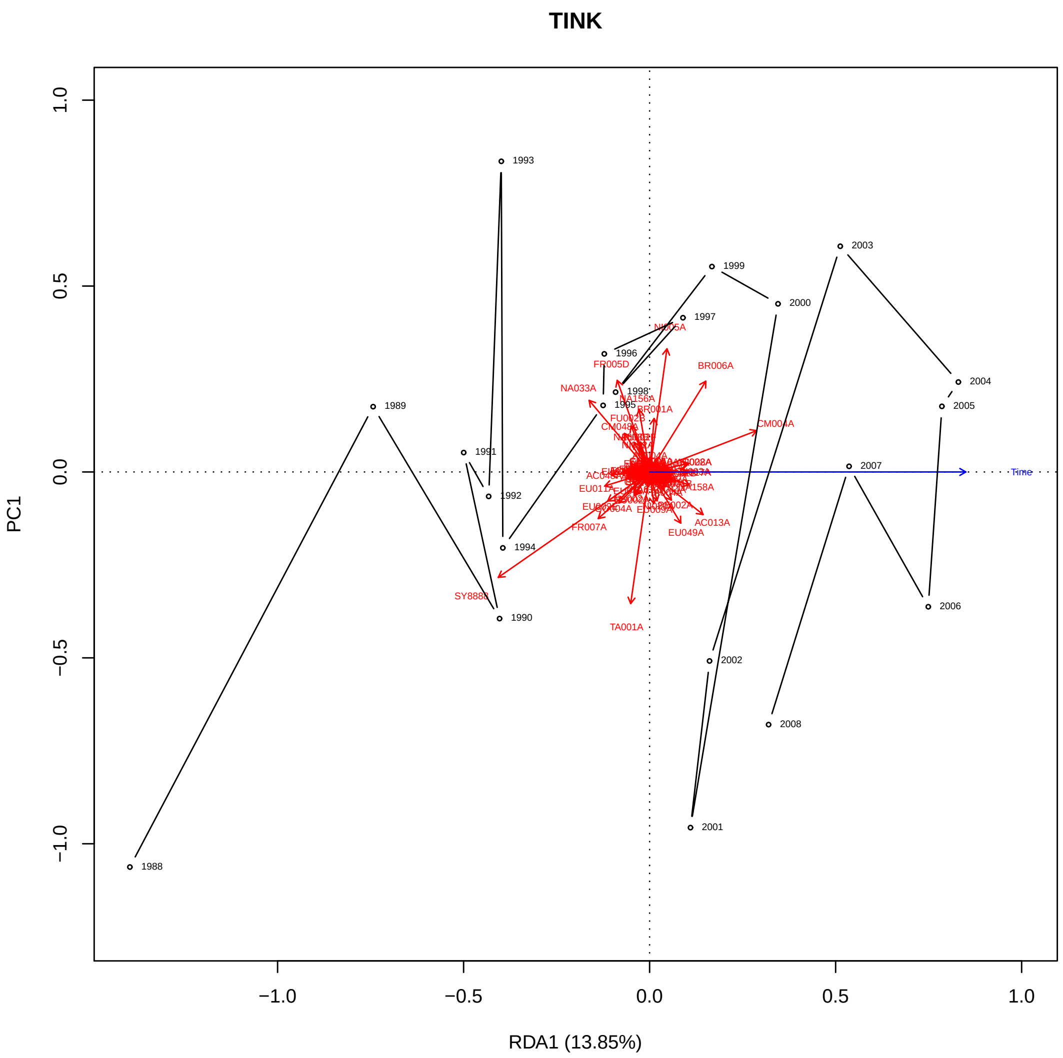

Figure 22: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Loch Tinker.

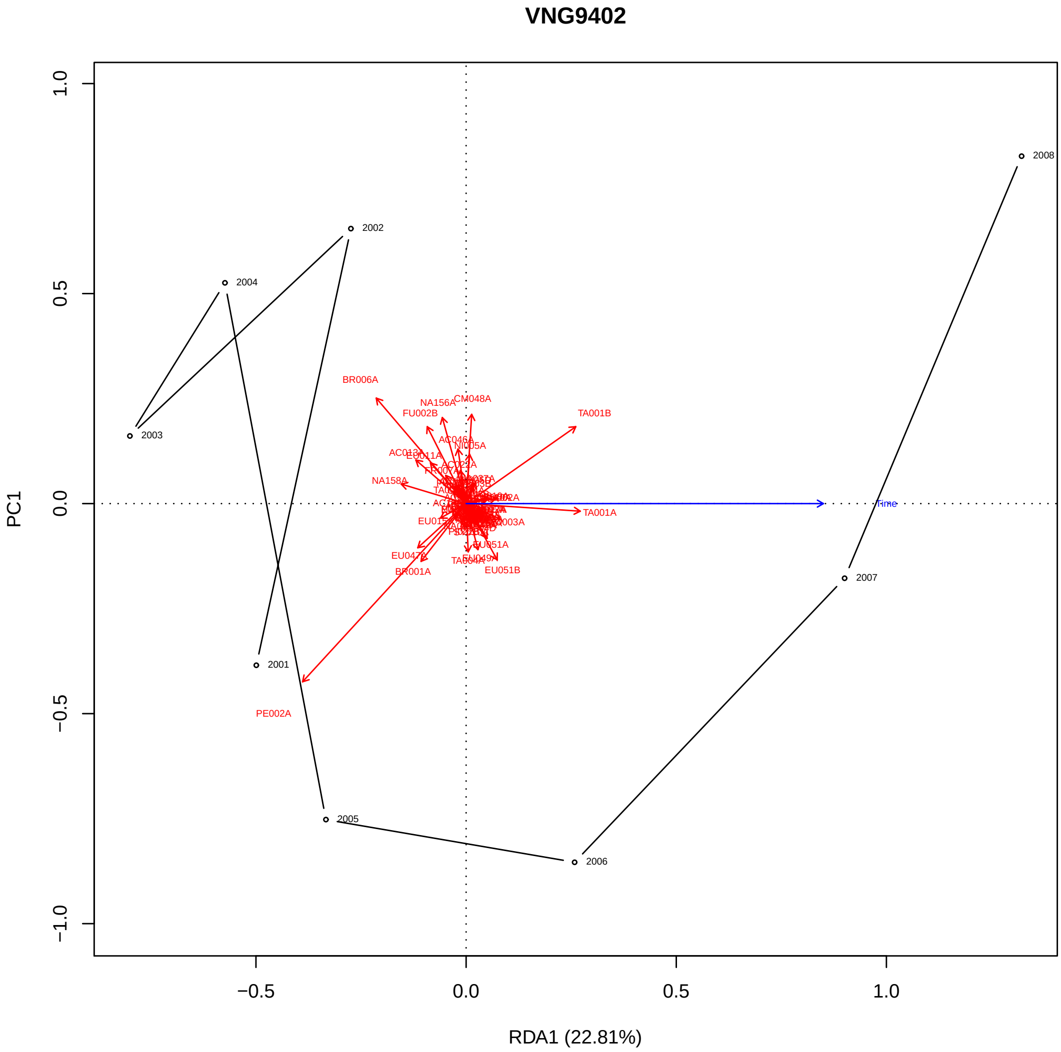

Figure 23: RDA time tracks showing axis 1 and 2 scores for the diatom epilithon data at Loch Coire Fionnaraich

APPENDIX 4.2: Principal response curves

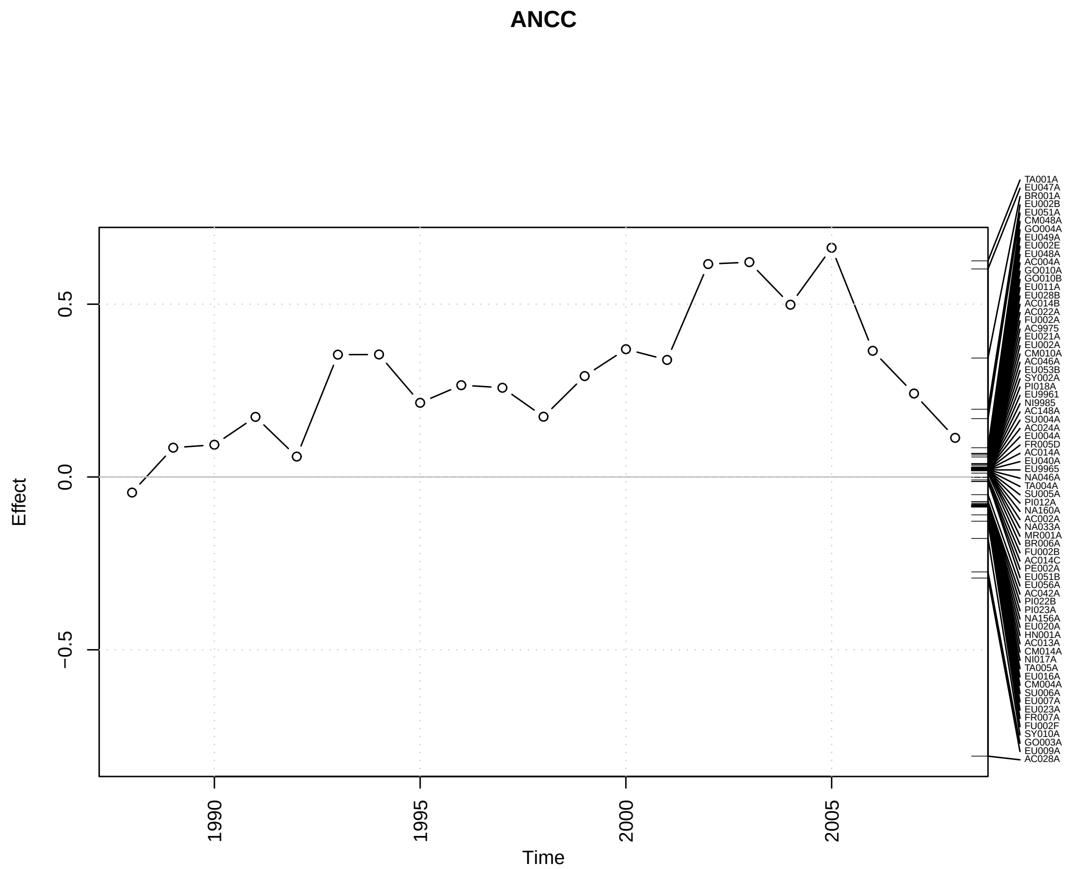

Figure 24: PRC plot of the diatom epilithon data for Allt na Coire nan Con

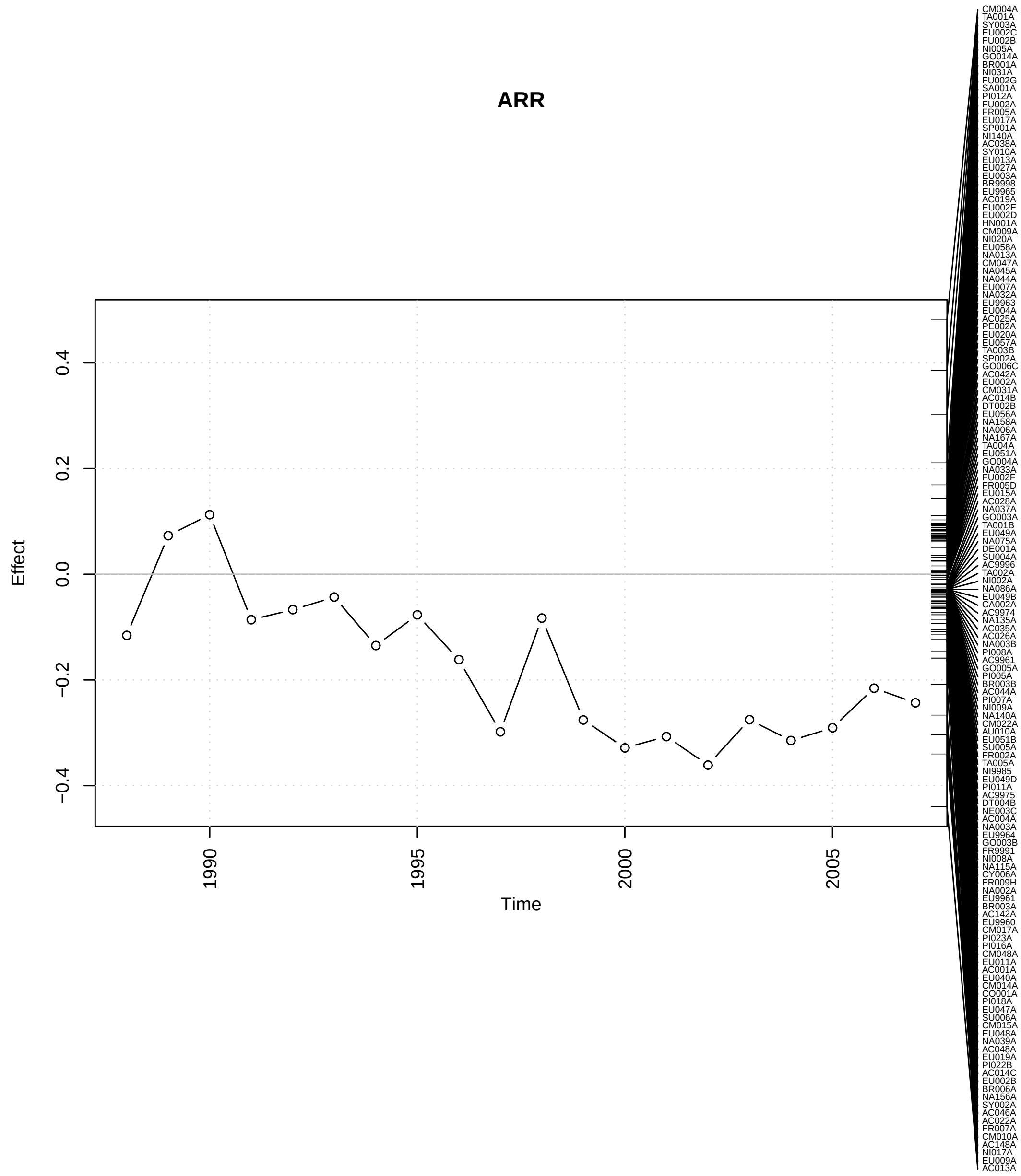

Figure 25: PRC plot of the diatom epilithon data for Loch Coire nan Arr

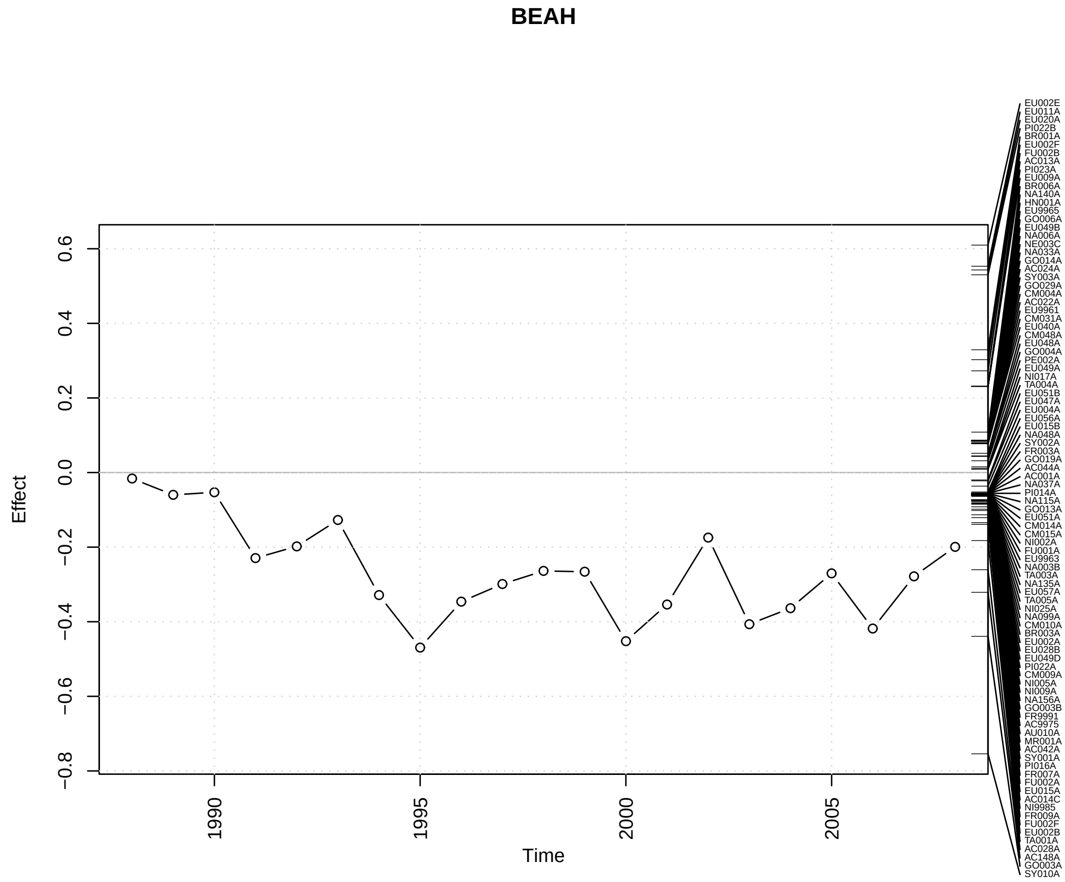

Figure 26: PRC plot of the diatom epilithon data for Beagh's Burn

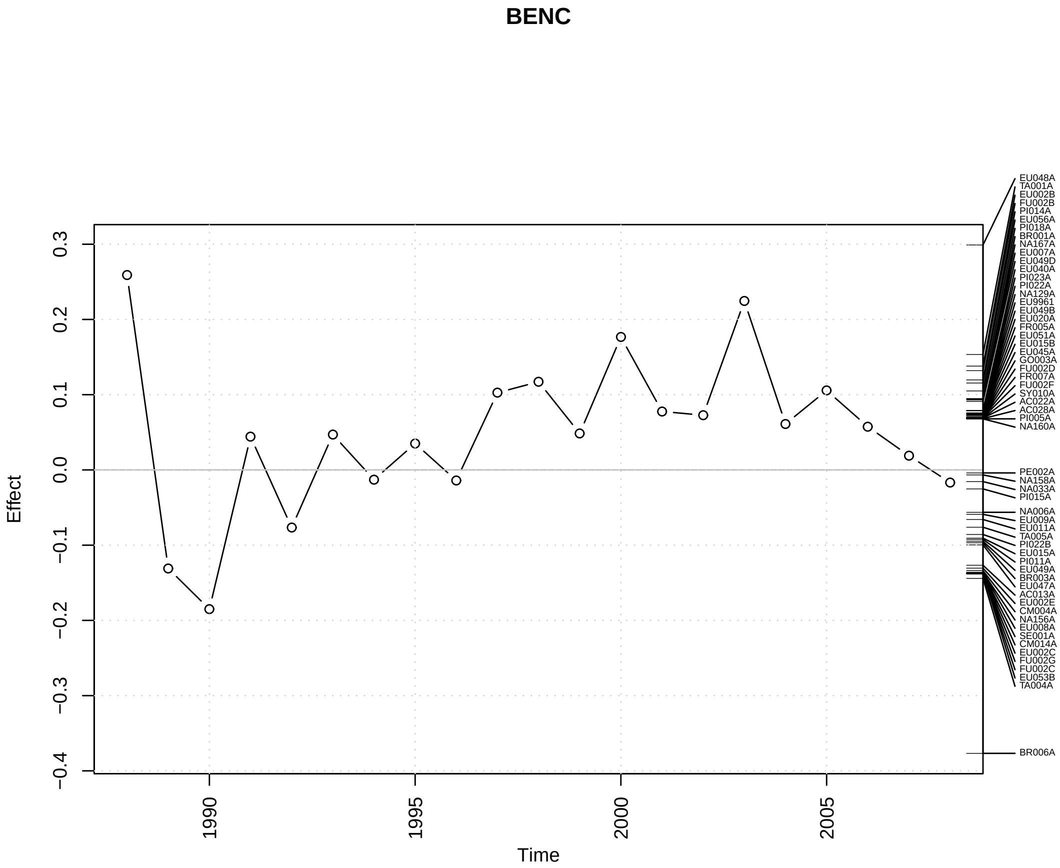

Figure 27: PRC plot of the diatom epilithon data for Bencrom River

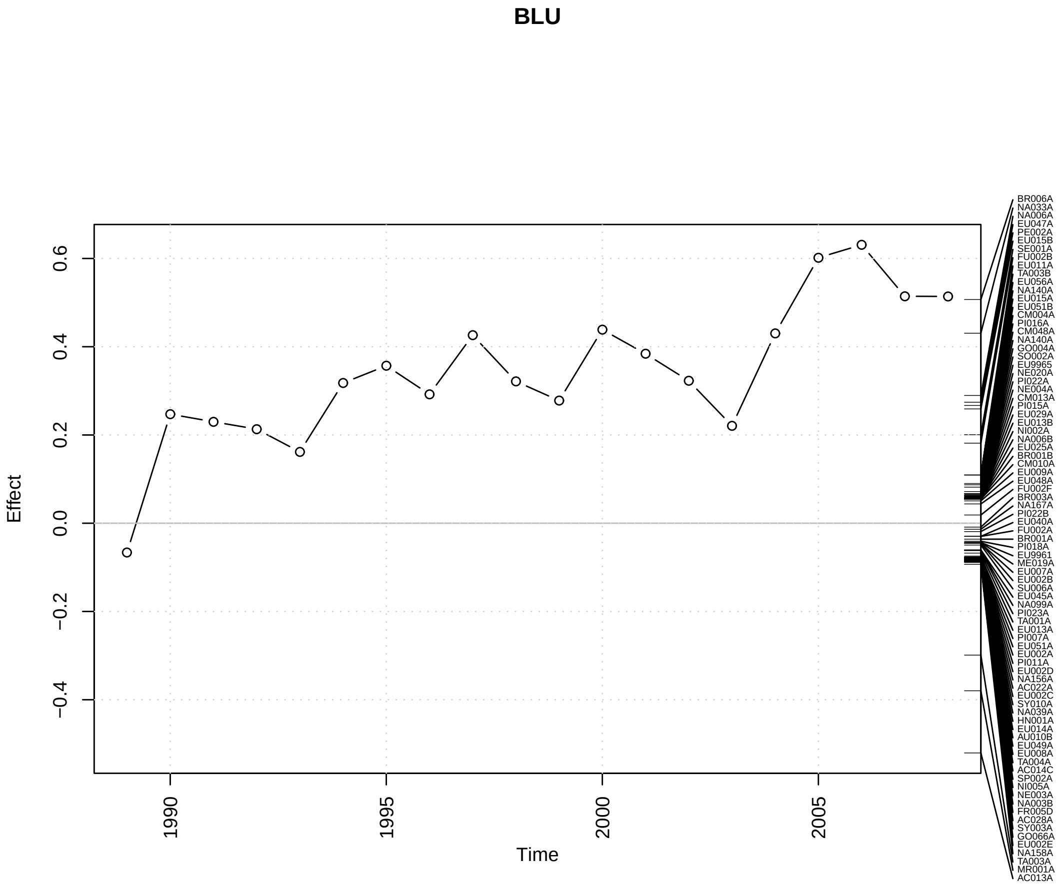

Figure 28: PRC plot of the diatom epilithon data for Blue Lough

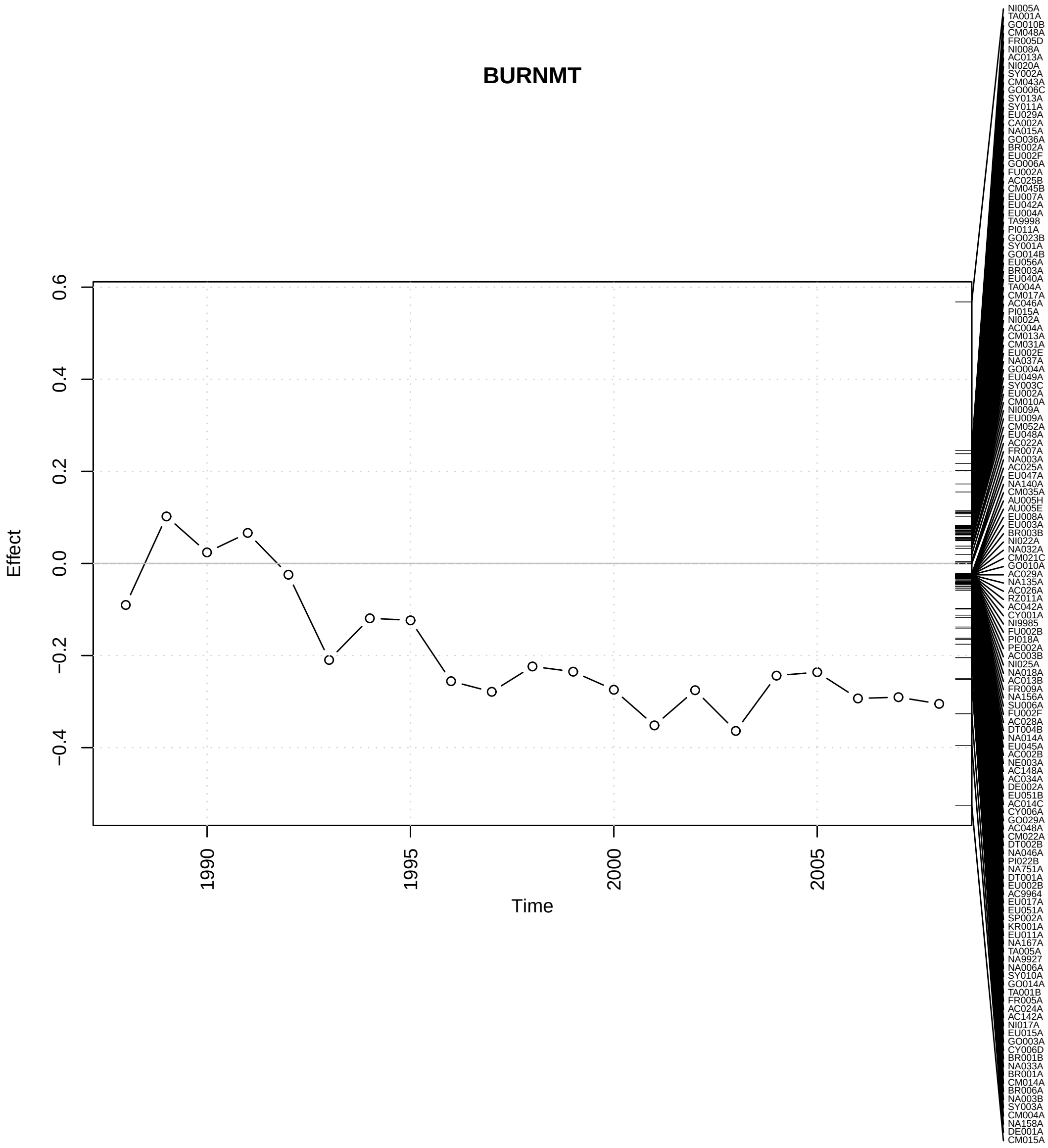

Figure 29: PRC plot of the diatom epilithon data for Burnmoor Tarn

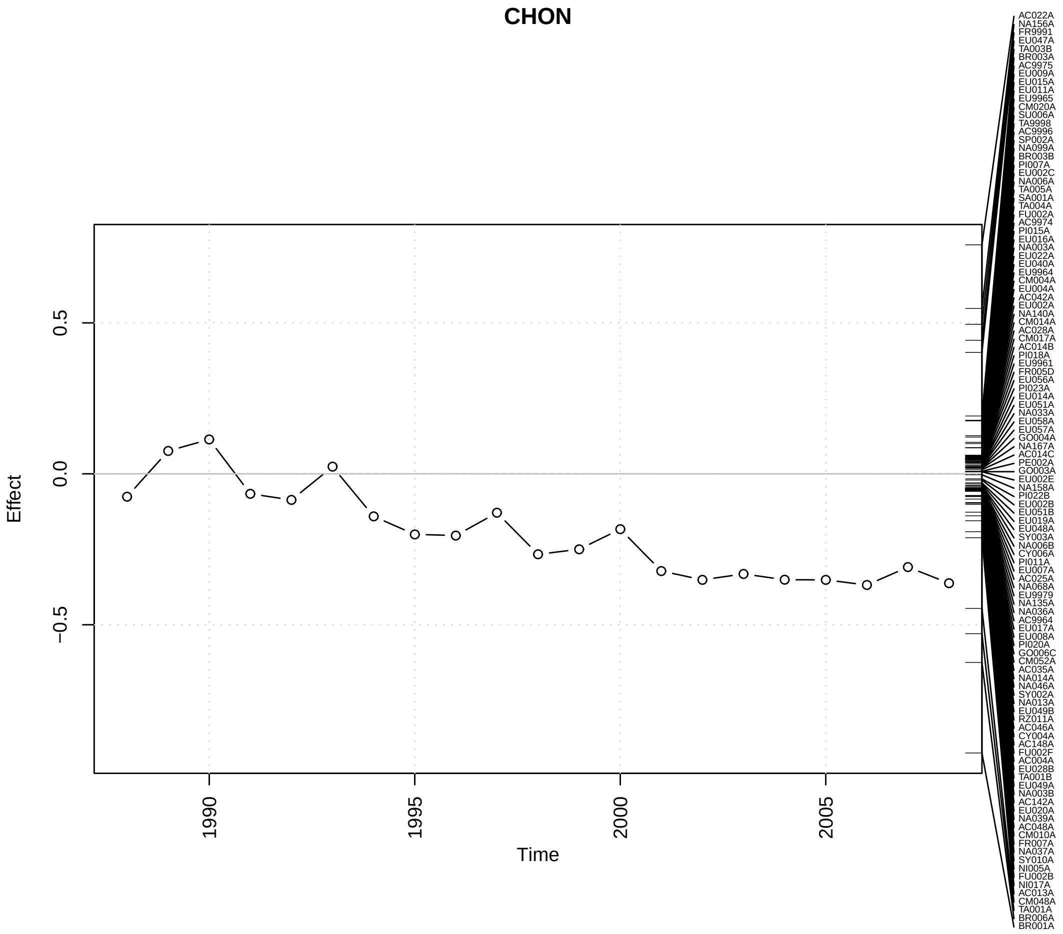

Figure 30: PRC plot of the diatom epilithon data for Loch Chon

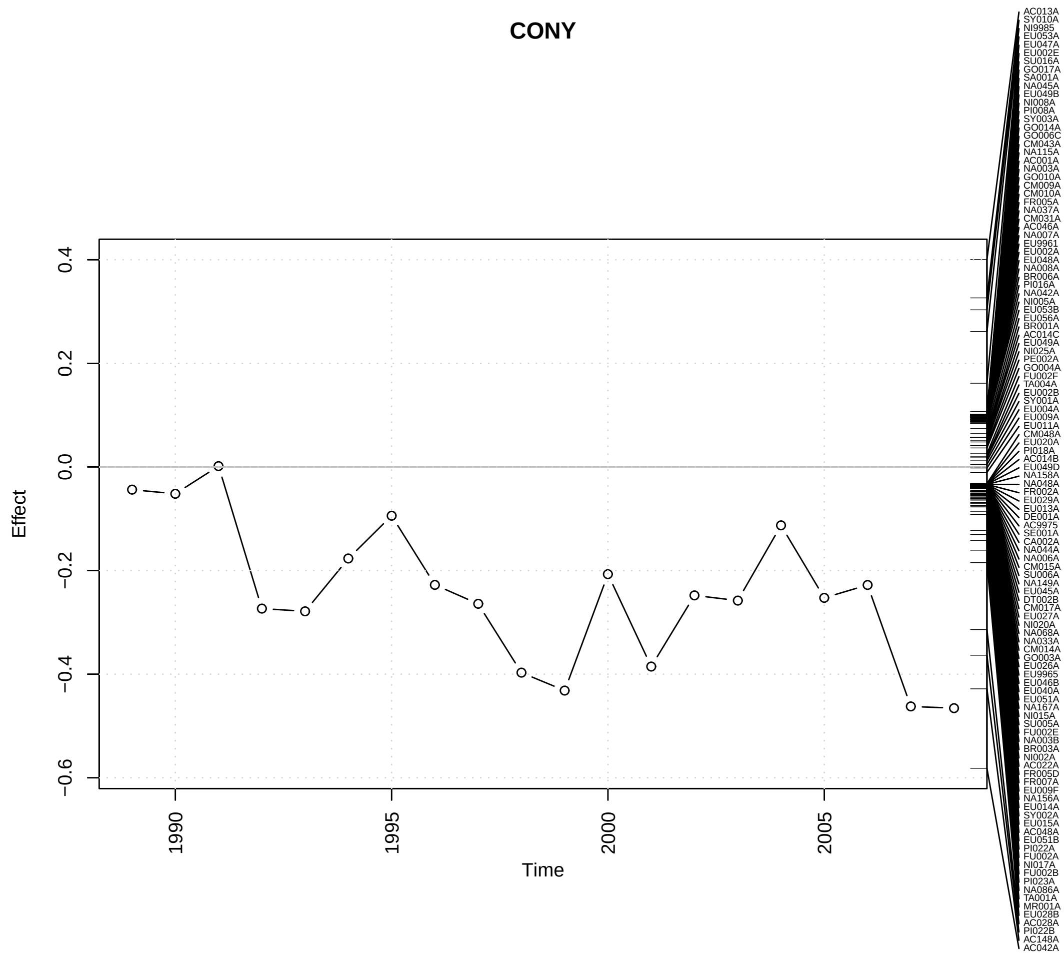

Figure 31: PRC plot of the diatom epilithon data for Coneyglen Burn.

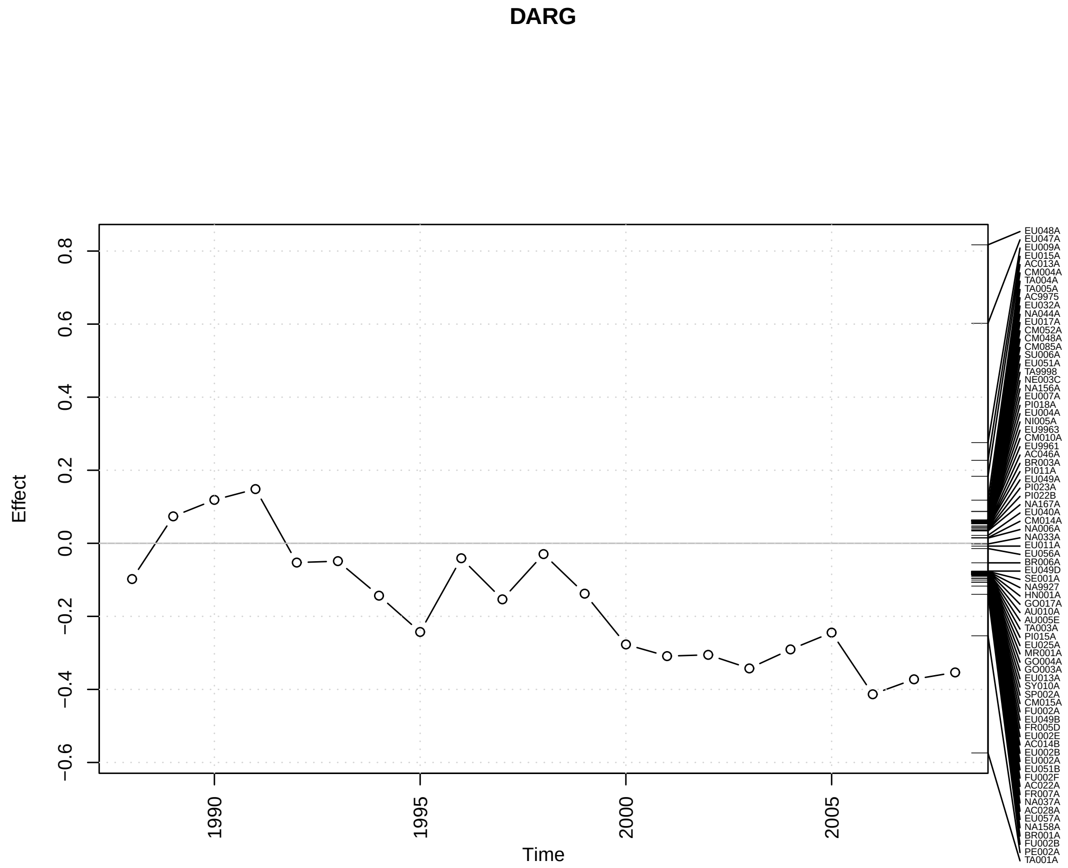

Figure 32: PRC plot of the diatom epilithon data for Dargall Lane.

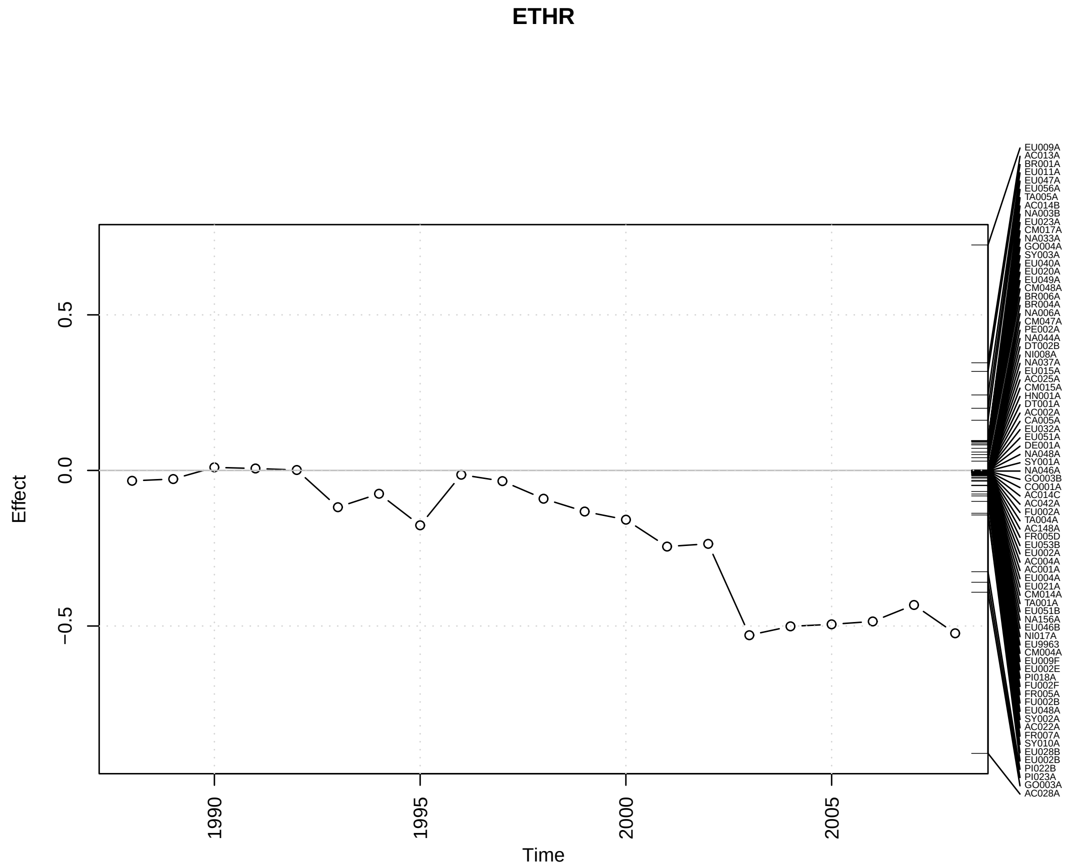

Figure 33: PRC plot of the diatom epilithon data for River Etherow.

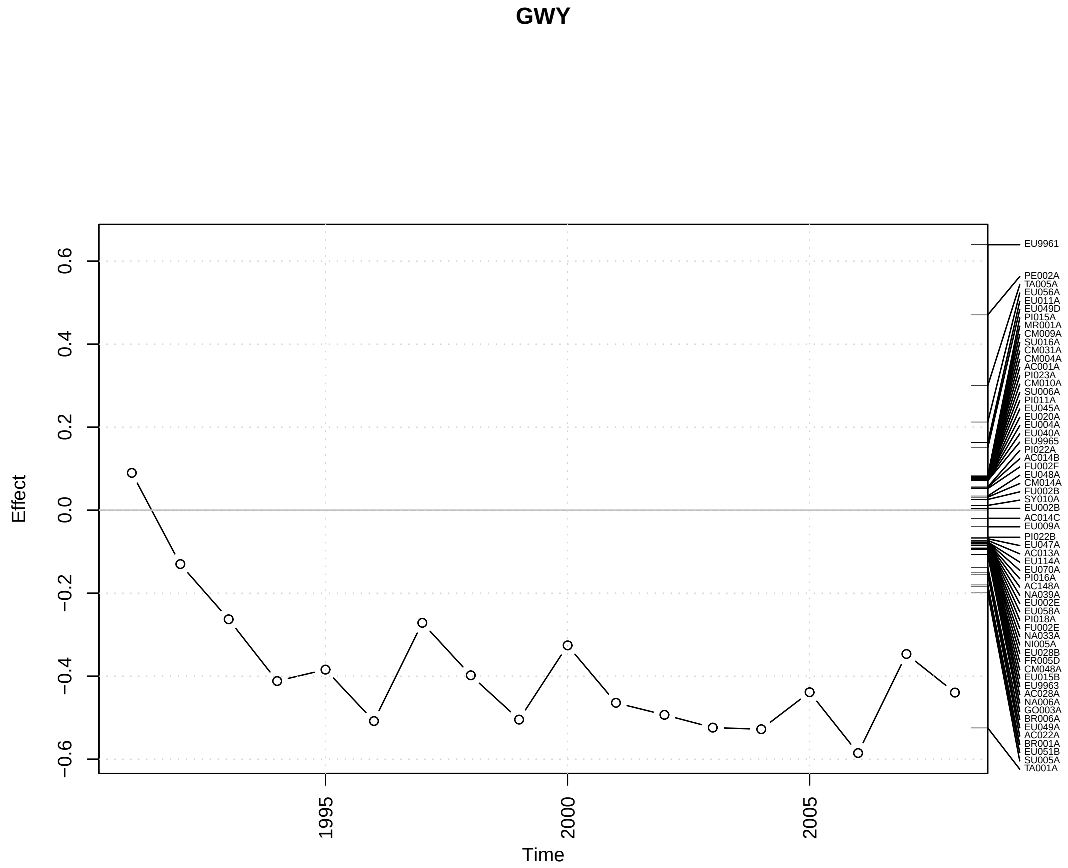

Figure 34: PRC plot of the diatom epilithon data for Afon Gwy

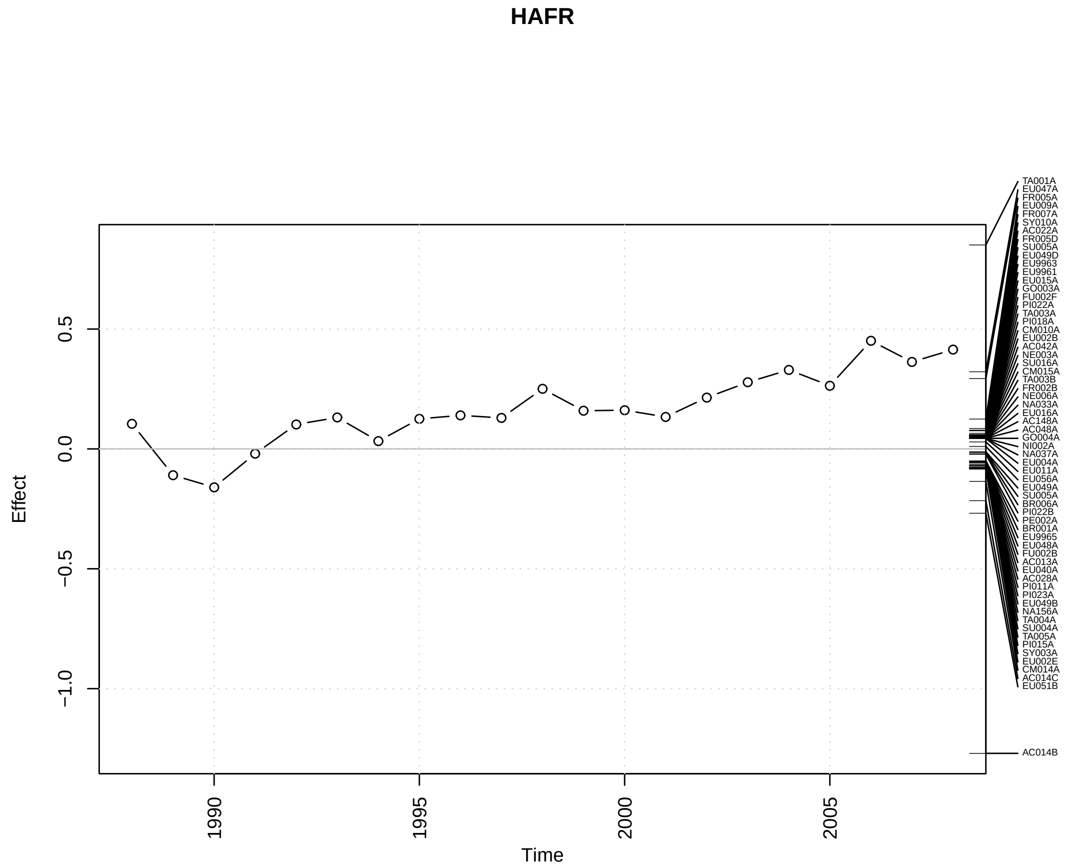

Figure 35: PRC plot of the diatom epilithon data for Afon Hafren.

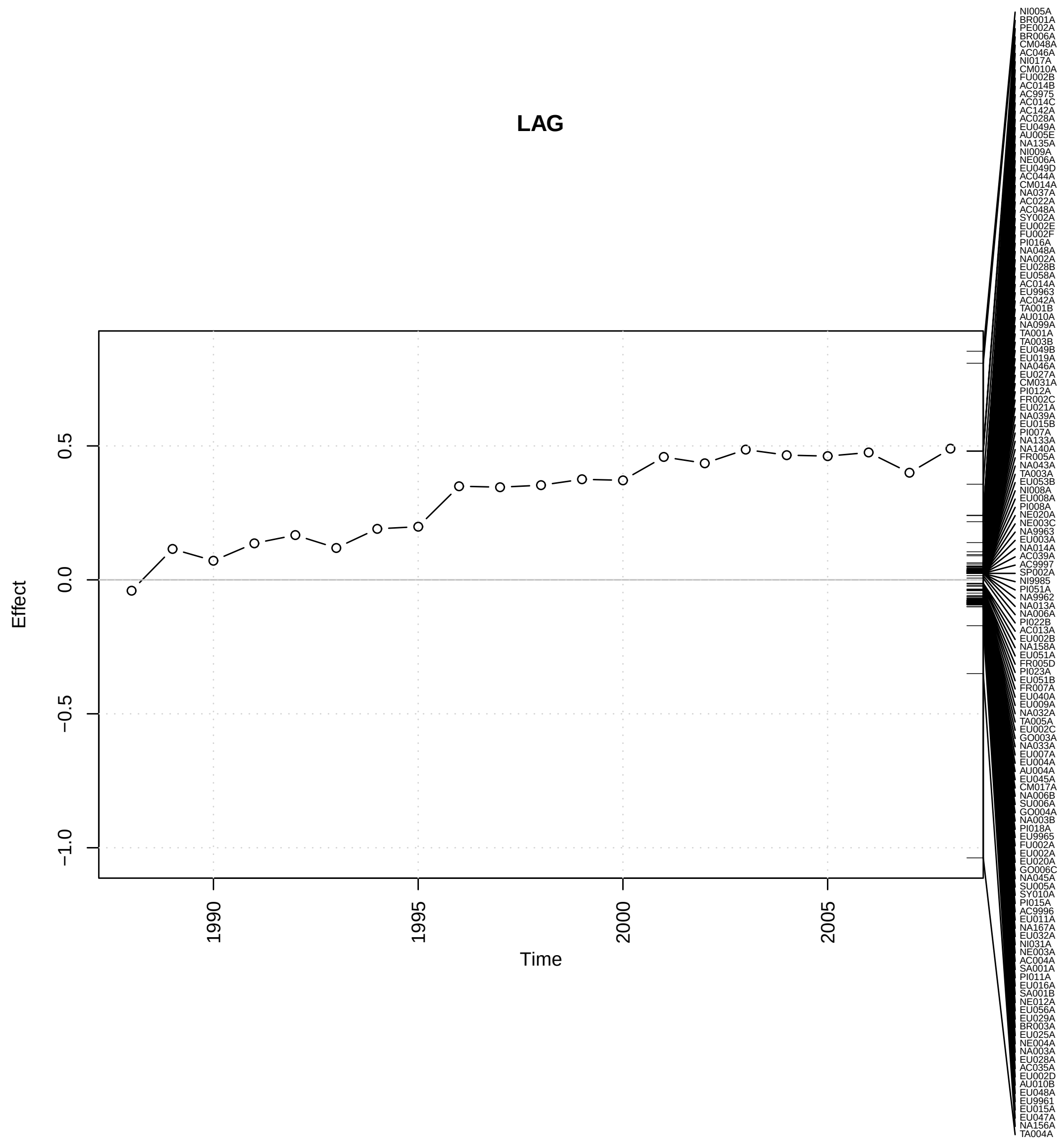

Figure 36: PRC plot of the diatom epilithon data for Llyn Llagi.

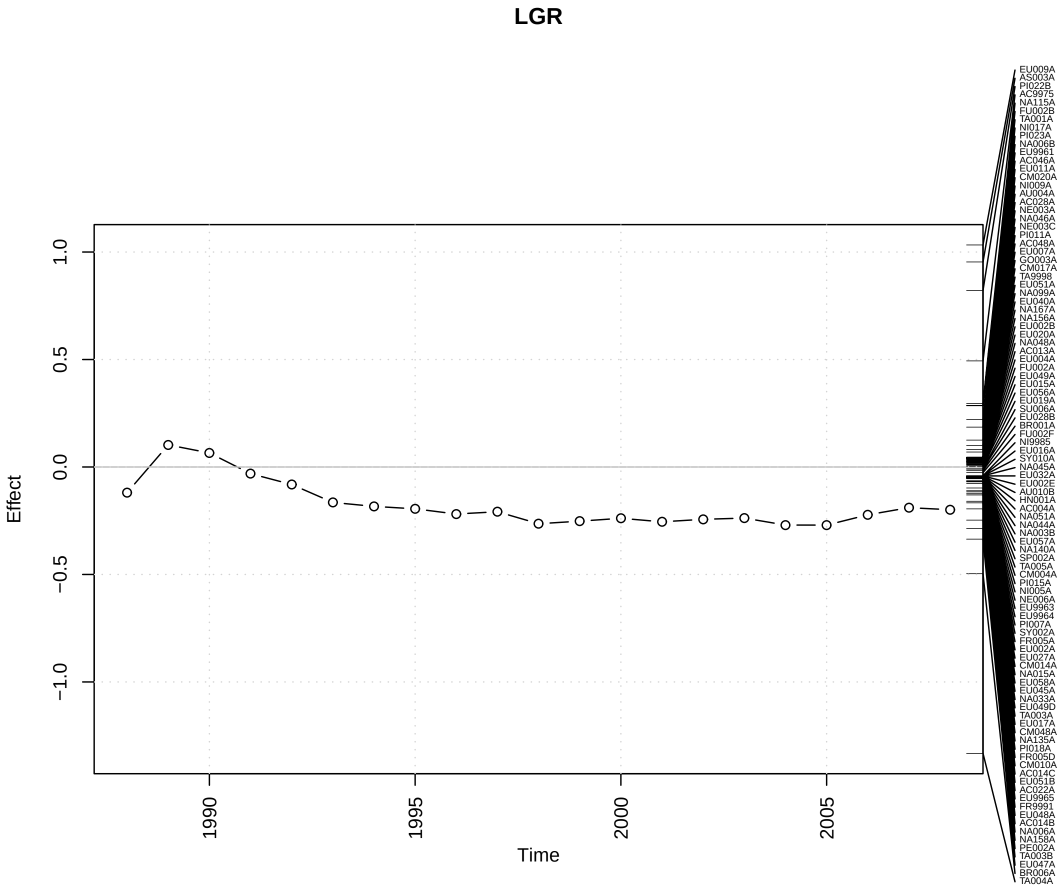

Figure 37: PRC plot of the diatom epilithon data for Loch Grannoch.

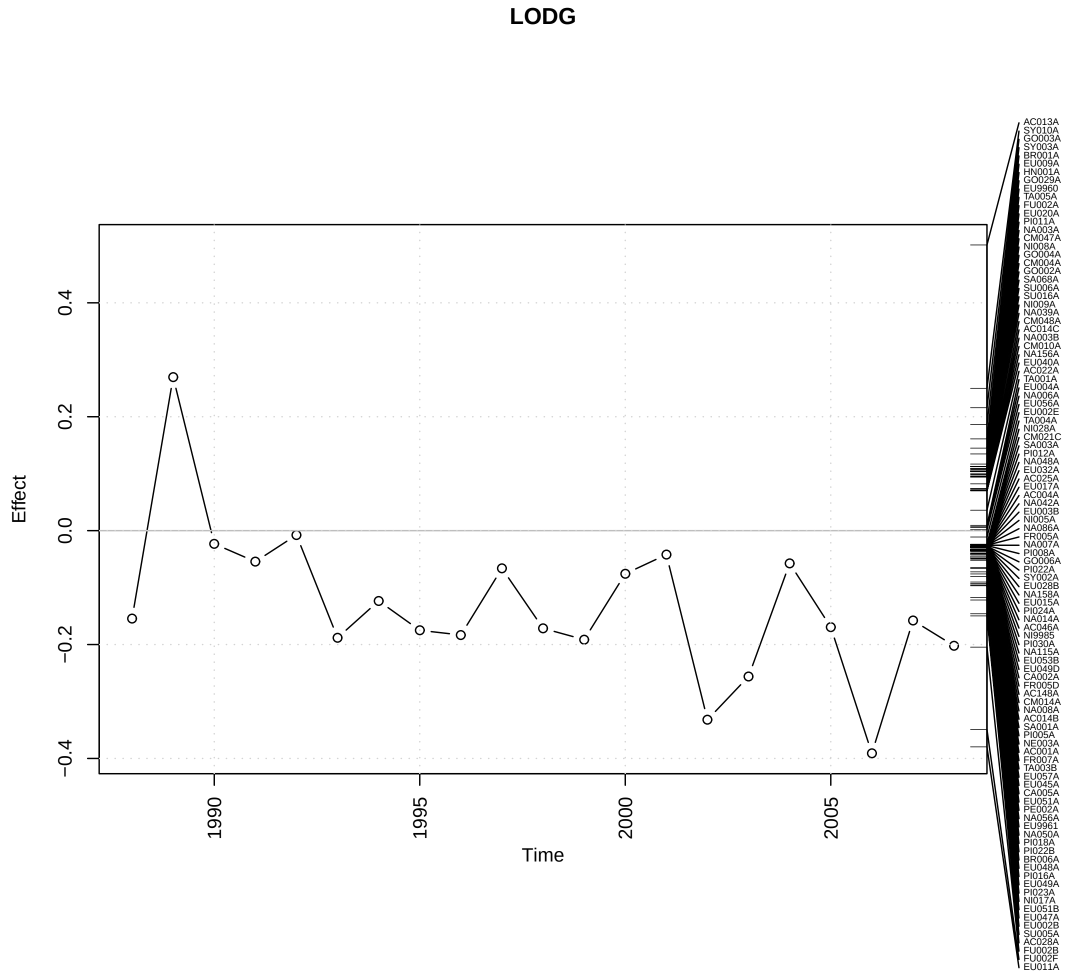

Figure 38: PRC plot of the diatom epilithon data for Old Lodge.

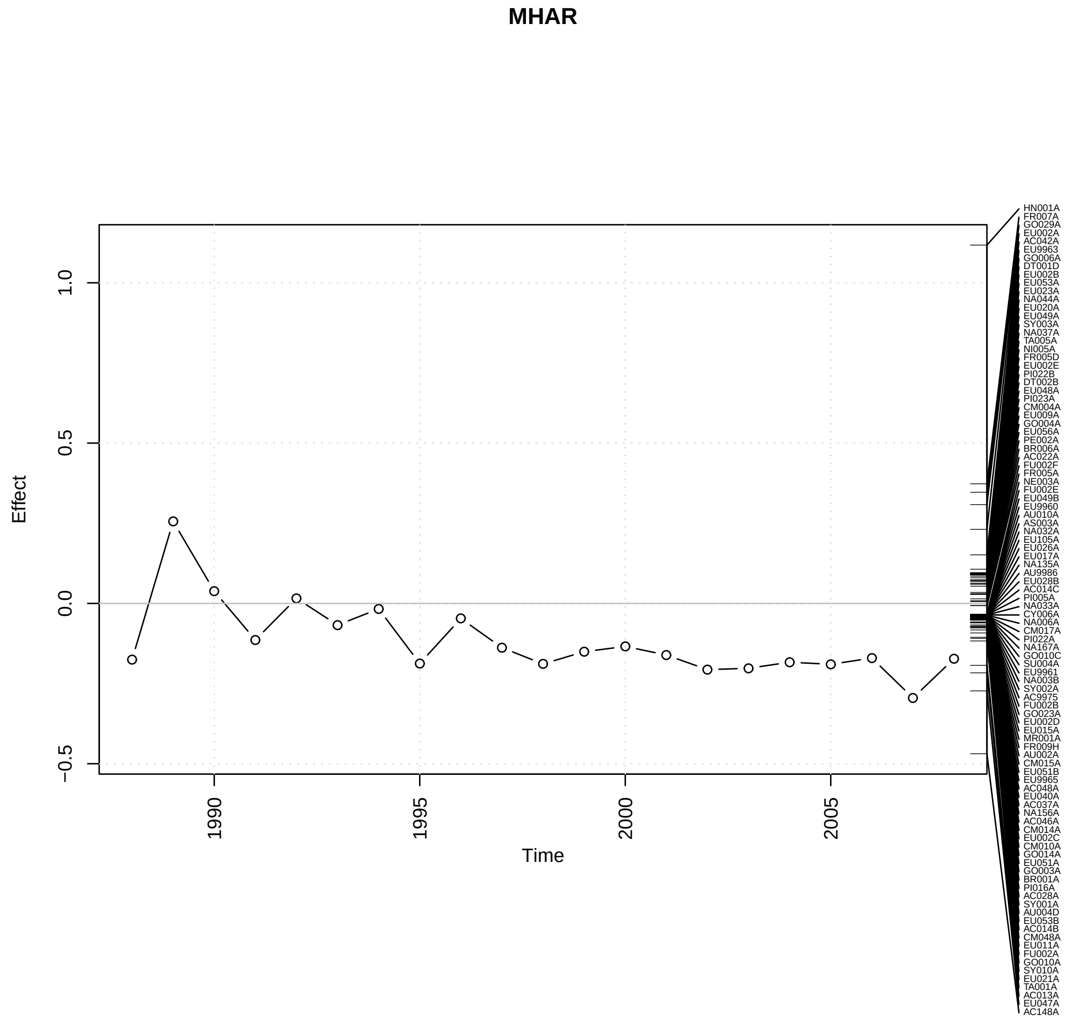

Figure 39: PRC plot of the diatom epilithon data for Allt a' Mharcaidh.

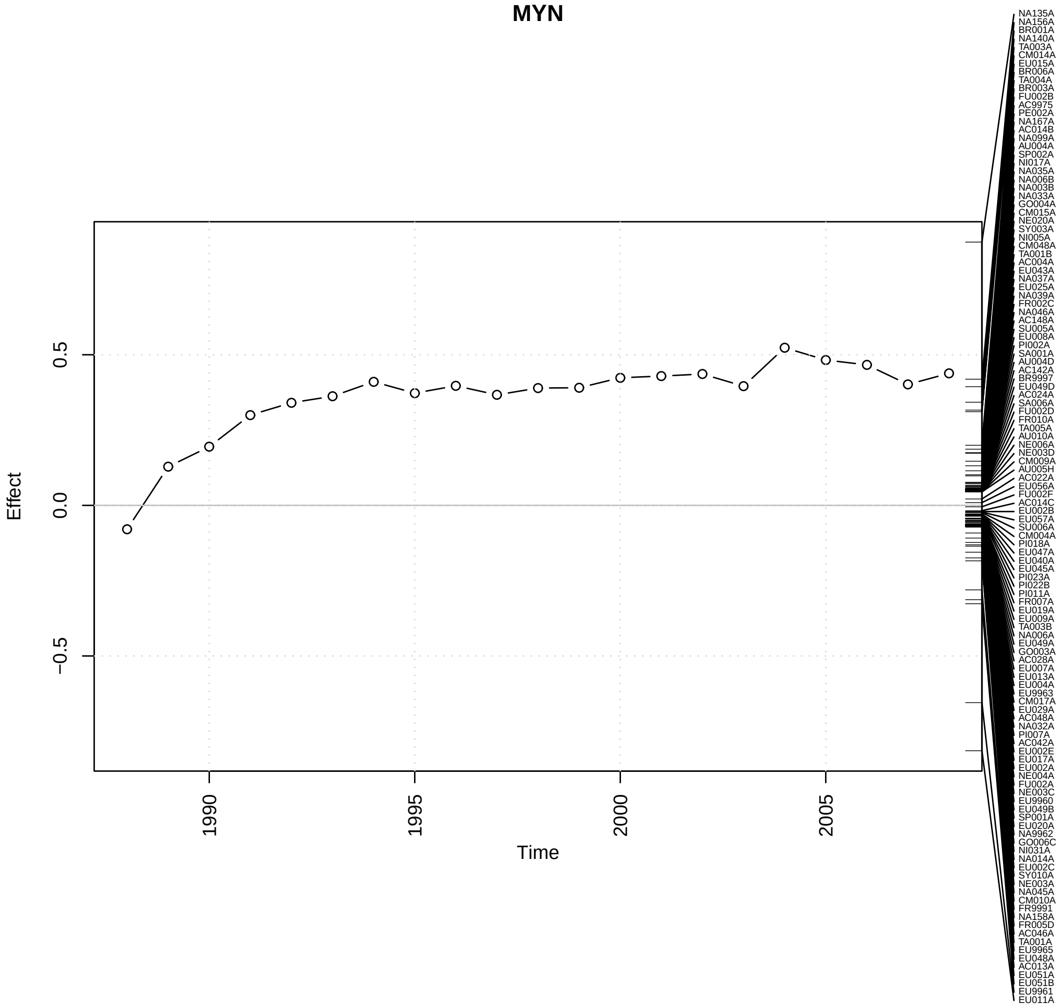

Figure 40: PRC plot of the diatom epilithon data for Llyn Cwm Mynach.

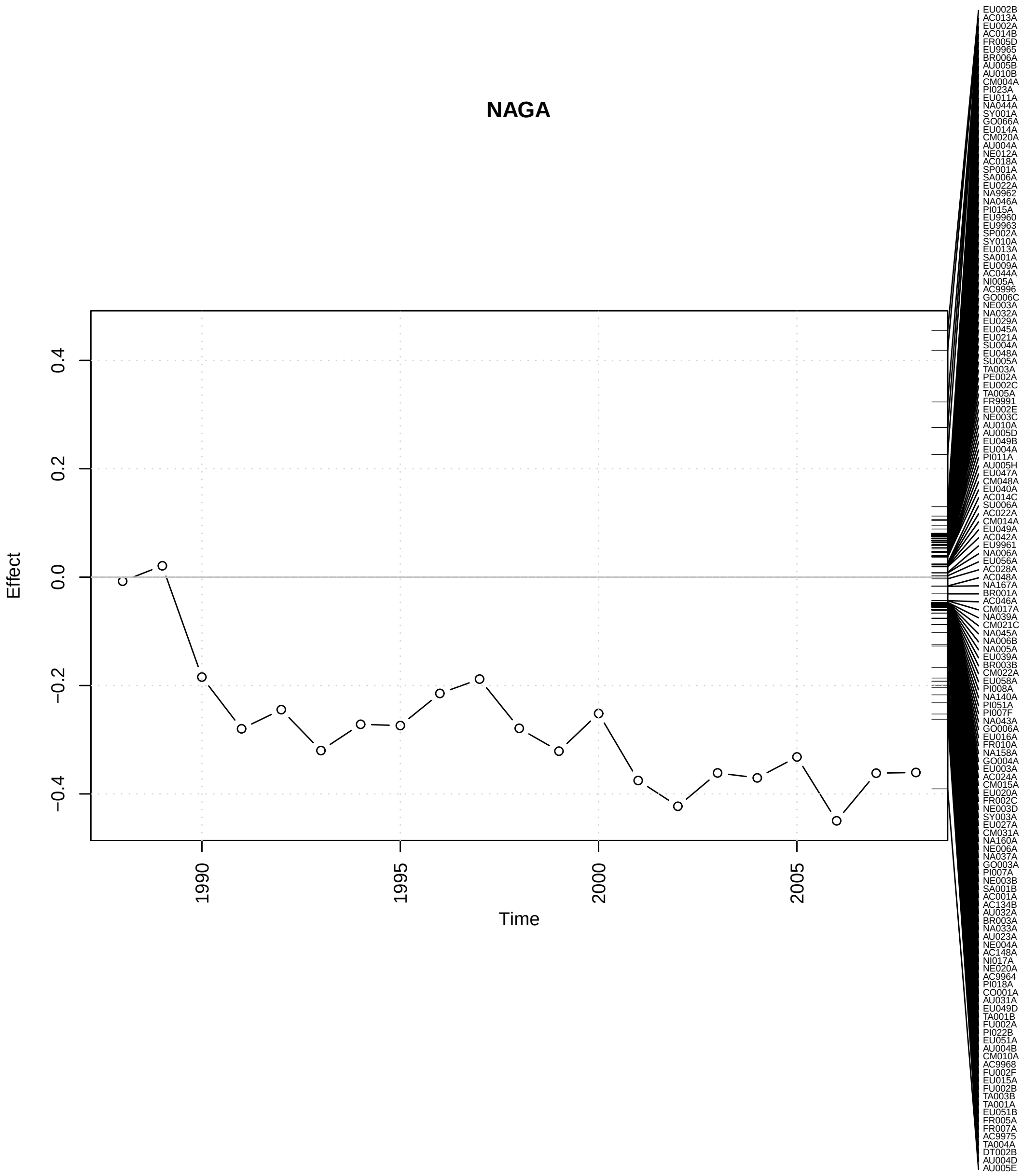

Figure 41: PRC plot of the diatom epilithon data for Lochnagar.

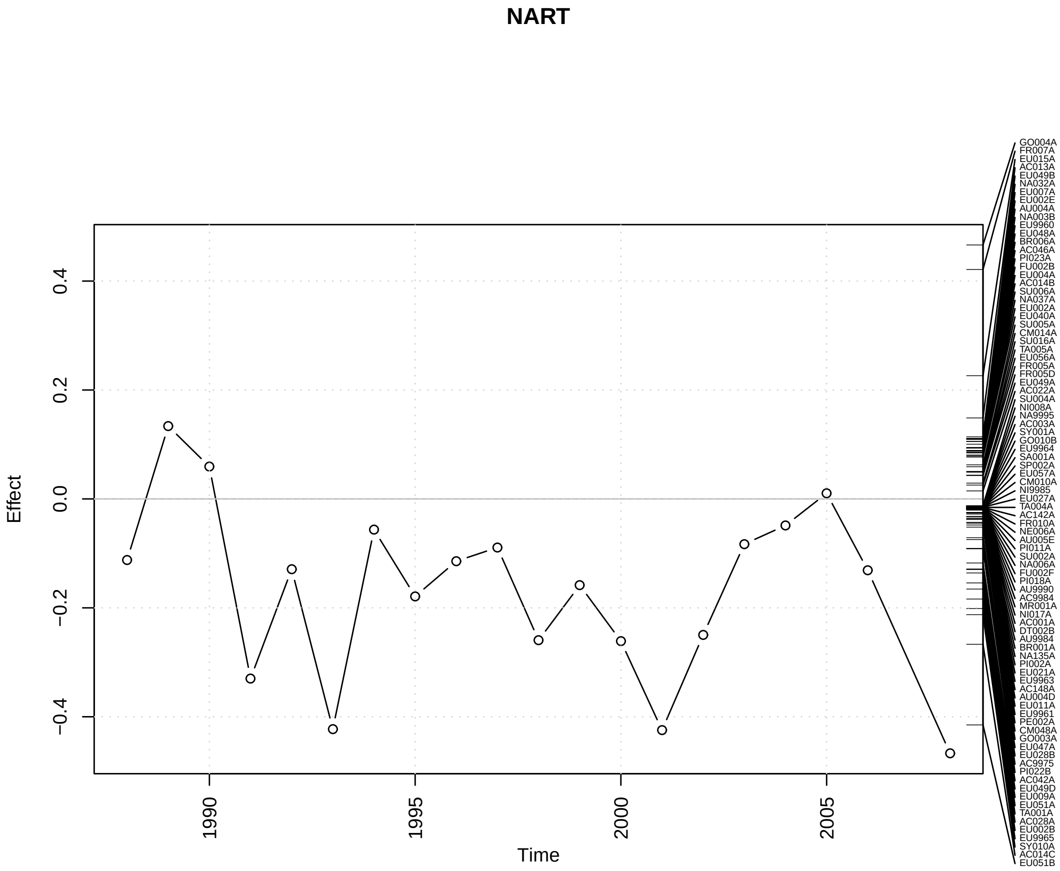

Figure 42: PRC plot of the diatom epilithon data for Narrator Brook.

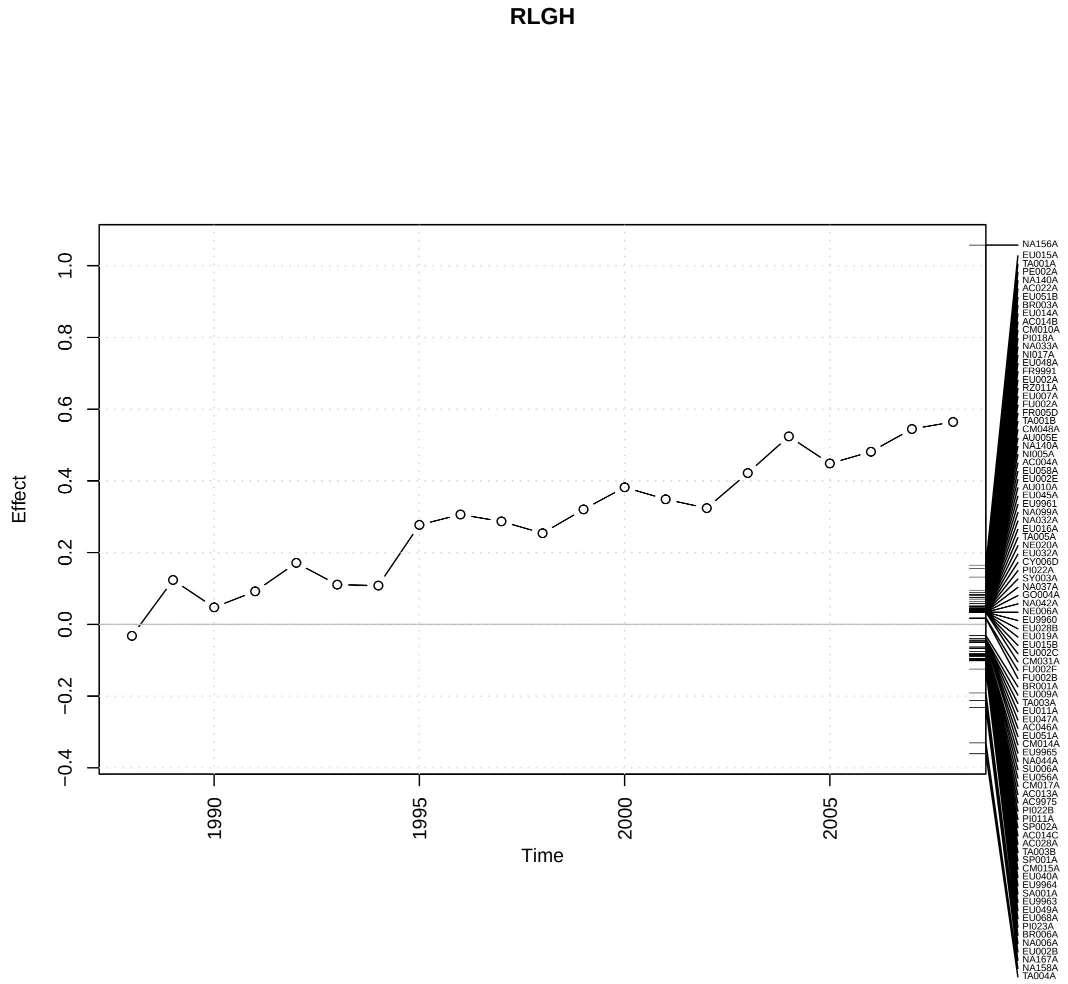

Figure 43: PRC plot of the diatom epilithon data for Round Loch of Glenhead.

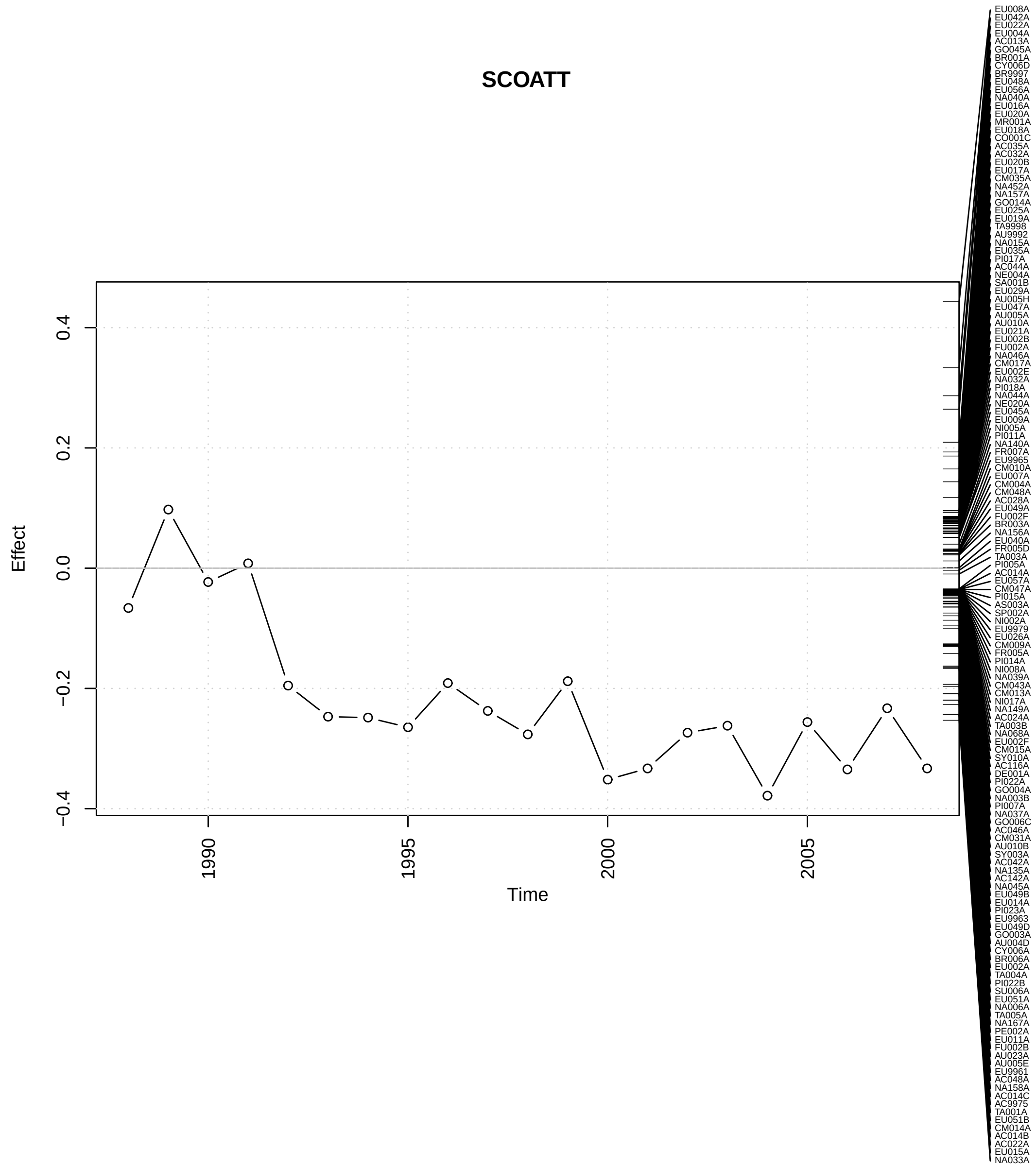

Figure 44: PRC plot of the diatom epilithon data for Scoat Tarn.

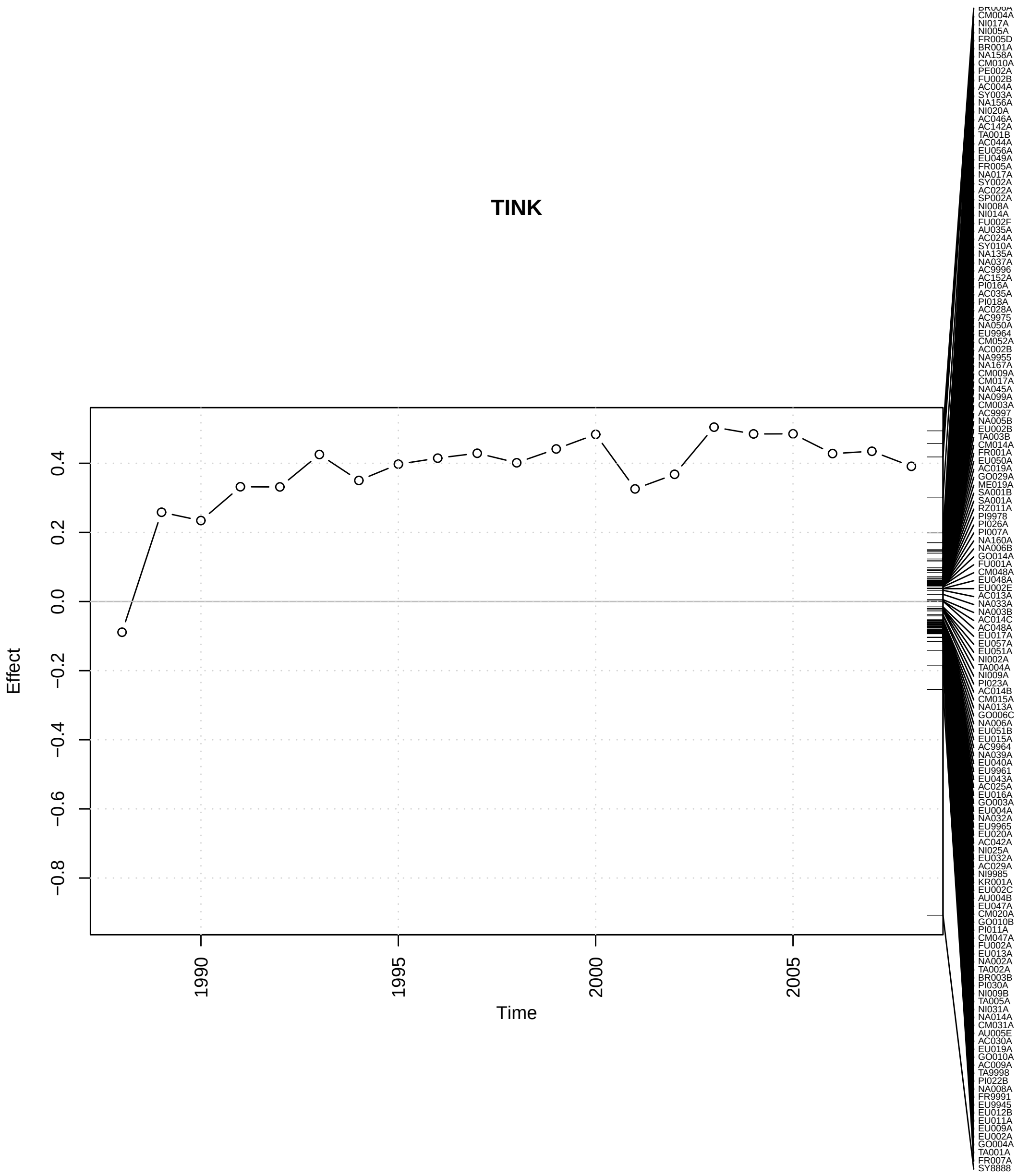

Figure 45: PRC plot of the diatom epilithon data for Loch Tinker.

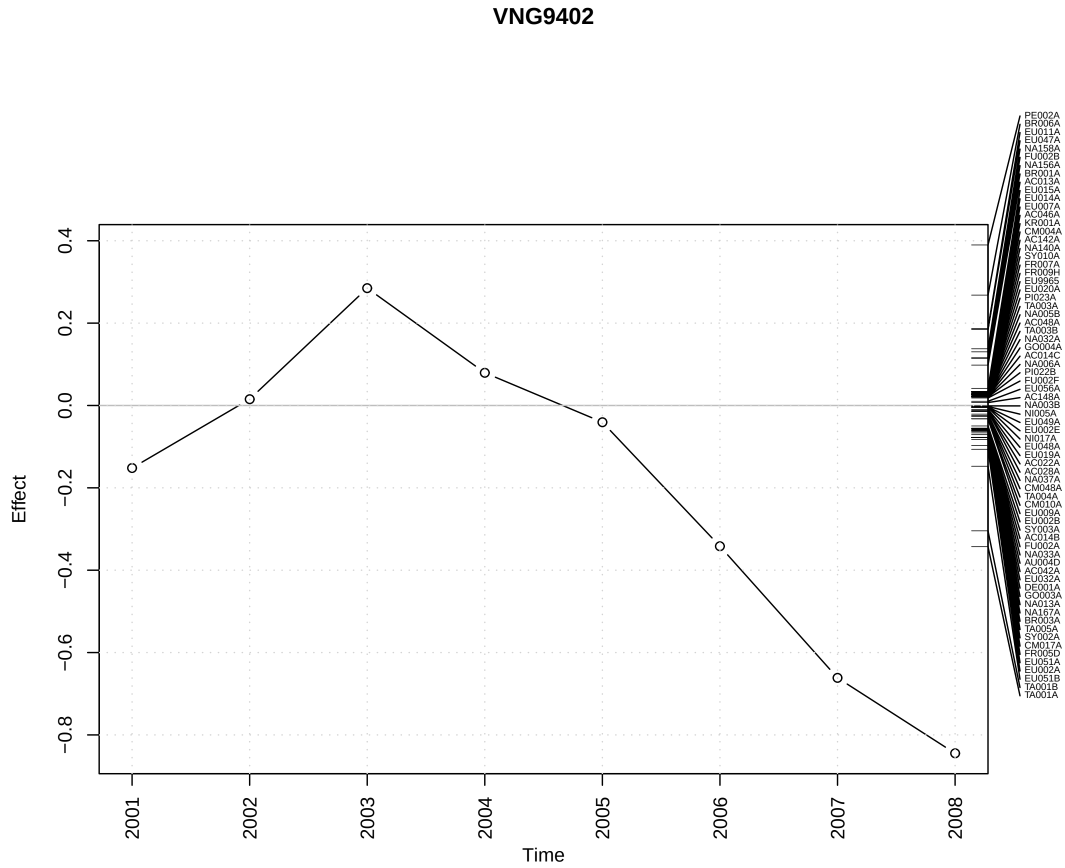

Figure 46: PRC plot of the diatom epilithon data for Loch Coire Fionnaraich

Table 1: Diatom species codes and names used in diagrams

Code	Taxon Name
AC001A	Achnanthes lanceolata
AC002A	Achnanthes linearis
AC002B	Achnanthes linearis f. curta
AC003A	Achnanthes microcephala
AC003B	Achnanthes microcephala var. scotica
AC004A	Achnanthes pseudoswazi
AC009A	Achnanthes recurvata
AC013A	Achnanthes minutissima
AC013B	Achnanthes minutissima var. cryptocephala
AC014A	Achnanthes austriaca
AC014B	Achnanthes austriaca var. minor
AC014C	Achnanthes austriaca var. helvetica
AC018A	Achnanthes laterostrata
AC019A	Achnanthes nodosa
AC022A	Achnanthes marginulata
AC024A	Achnanthes depressa
AC025A	Achnanthes flexella
AC025B	Achnanthes flexella var. alpestris
AC026A	Achnanthes frigida
AC028A	Achnanthes saxonica
AC029A	Achnanthes sublaevis
AC030A	Achnanthes umara
AC032A	Achnanthes hungarica
AC034A	Achnanthes suchlandtii
AC035A	Achnanthes pusilla
AC037A	Achnanthes biasolettiana
AC038A	Achnanthes lapponica
AC039A	Achnanthes didyma
AC042A	Achnanthes detha
AC044A	Achnanthes levanderi
AC046A	Achnanthes altaica
AC048A	Achnanthes scotica
AC116A	Achnanthes rossii
AC134B	Achnanthes helvetica var. alpina
AC142A	Achnanthes kuelbsii
AC148A	Achnanthes modestiformis
AC152A	Achnanthes carissima
AC9961	Achnanthes [cf. minutissima]
AC9964	Achnanthes [minutissima var. scotica]
AC9968	Achnanthes [marginulata] forma. Major
AC9974	Achnanthes [sp. 6 (fine)]
AC9975	Achnanthes altaica var. minor
AC9984	Achnanthes [sp. 2]
AC9996	Achnanthes [cf. levanderi]
AC9997	Achnanthes [cf. lapidosa]
AC9999	Achnanthes sp.
ACZZZZ	Achnanthes [cf. abundans]
AM9999	Amphora sp

AS003A Asterionella ralfsii
AU002A Aulacoseira ambigua
AU004A Aulacoseira lirata
AU004B Aulacoseira lirata var. lacustris
AU004D Aulacoseira lirata var. alpigena
AU005A Aulacoseira distans
AU005B Aulacoseira distans var. nivaloides
AU005D Aulacoseira distans var. tenella
AU005E Aulacoseira distans var. nivalis
AU005H Aulacoseira distans var. alpigena
AU010A Aulacoseira perglabra
AU010B Aulacoseira perglabra var. floriniae
AU023A Aulacoseira tethera
AU031A Aulacoseira alpigena
AU032A Aulacoseira lacustris
AU035A Aulacoseira tenuior
AU9984 Aulacoseira [lirata alpigena (small)]
AU9986 Aulacoseira [subarctica type 2]
AU9990 Aulacoseira [small]
AU9992 Aulacoseira [sp. b cf. tethera]
AU9999 Aulacoseira sp.
BR001A Brachysira vitrea
BR001B Brachysira vitrea var. lanceolata
BR002A Brachysira follis
BR003A Brachysira serians
BR003B Brachysira serians var. modesta
BR004A Brachysira styriaca
BR006A Brachysira brebissonii
BR9997 Brachysira [sp. 1]
BR9998 Brachysira [brebissonii (fine)]
CA002A Caloneis bacillum var. bacillum
CA005A Caloneis bacillaris
CA9999 Caloneis sp.
CM003A Cymbella sinuata
CM004A Cymbella microcephala
CM009A Cymbella naviculiformis
CM010A Cymbella perpusilla
CM013A Cymbella helvetica
CM014A Cymbella aequalis
CM015A Cymbella cesatii
CM017A Cymbella hebridica
CM020A Cymbella gaeumannii
CM021C Cymbella heteropleura
CM022A Cymbella affinis
CM031A Cymbella minuta
CM035A Cymbella angustata
CM043A Cymbella naviculacea
CM045B Cymbella prostrata var. auerswaldii
CM047A Cymbella incerta
CM048A Cymbella lunata
CM052A Cymbella descripta

CM085A Cymbella lapponica
CM9999 Cymbella sp.
CO001A Cocconeis placentula
CO001C Cocconeis placentula var. lineata
CO9999 Cocconeis sp.
CY001A Cyclotella comta
CY004A Cyclotella stelligera
CY006A Cyclotella kuetzingiana
CY006D Cyclotella kuetzingiana var. minor
CY9999 Cyclotella sp.
DE001A Denticula tenuis
DE002A Denticula elegans
DE9999 Denticula sp.
DI9999 Diatomella sp.
DP9999 Diploneis sp.
DT001A Diatoma elongatum
DT001D Diatoma elongatum var. tenue
DT002B Diatoma hyemale var. mesodon
DT004B Diatoma tenue var. elongatum
EU002A Eunotia pectinalis
EU002B Eunotia pectinalis var. minor
EU002C Eunotia pectinalis var. ventralis
EU002D Eunotia pectinalis var. undulata
EU002E Eunotia pectinalis var. minor f. impressa
EU002F Eunotia pectinalis var. minor f. intermedia
EU003A Eunotia praerupta
EU003B Eunotia praerupta var. bidens
EU004A Eunotia tenella
EU007A Eunotia bidentula
EU008A Eunotia monodon
EU009A Eunotia exigua
EU009F Eunotia exigua var. undulata
EU011A Eunotia rhomboidea
EU012B Eunotia robusta var. diadema
EU013A Eunotia arcus
EU013B Eunotia arcus var. curvata
EU014A Eunotia bactriana
EU015A Eunotia denticulata
EU015B Eunotia denticulata var. fennica
EU016A Eunotia diodon
EU017A Eunotia flexuosa
EU018A Eunotia formica
EU019A Eunotia iatriaensis
EU020A Eunotia meisteri
EU020B Eunotia meisteri var. bidens
EU021A Eunotia sudetica
EU022A Eunotia bigibba
EU023A Eunotia polydentula
EU025A Eunotia fallax
EU026A Eunotia praerupta-nana
EU027A Eunotia trinacria

EU028A Eunotia microcephala
EU028B Eunotia microcephala var. tridentata
EU029A Eunotia valida
EU032A Eunotia serra
EU035A Eunotia major
EU039A Eunotia triodon
EU040A Eunotia paludosa
EU042A Eunotia lapponica
EU043A Eunotia elegans
EU045A Eunotia nymanniana
EU046B Eunotia perpusilla var. tridentata
EU047A Eunotia incisa
EU048A Eunotia naegelii
EU049A Eunotia curvata
EU049B Eunotia curvata var. subarcuata
EU049D Eunotia curvata var. attenuata
EU050A Eunotia tibia var. tibia
EU051A Eunotia vanheurckii
EU051B Eunotia vanheurckii var. intermedia
EU053A Eunotia tridentula
EU053B Eunotia tridentula var. perminuta
EU056A Eunotia minutissima
EU057A Eunotia exgracilis
EU058A Eunotia schwabei
EU068A Eunotia bidens
EU070A Eunotia bilunaris
EU105A Eunotia subarcuoides
EU114A Eunotia muscicola
EU9945 Eunotia [microcephala (coarse)]
EU9960 Eunotia [tenella/paludosa]
EU9961 Eunotia [vanheurckii var. 1]
EU9963 Eunotia [sp. 13 (minutissima)]
EU9964 Eunotia [sp. 12 (minor)]
EU9965 Eunotia [sp. 10 (minima)]
EU9979 Eunotia [meisteri var. 1 (pusilla)]
EU9999 Eunotia sp.
FR001A Fragilaria pinnata
FR002A Fragilaria construens
FR002B Fragilaria construens var. Binodis
FR002C Fragilaria construens var. venter
FR003A Fragilaria bicapitata
FR005A Fragilaria virescens
FR005D Fragilaria virescens var. exigua
FR007A Fragilaria vaucheriae
FR009A Fragilaria capucina
FR009H Fragilaria capucina var. gracilis
FR010A Fragilaria constricta
FR9991 Fragilaria [cf. oldenburgiana PIRLA pl 20, 61-2]
FR9999 Fragilaria sp.
FU001A Frustulia vulgaris
FU002A Frustulia rhomboides

FU002B Frustulia rhomboides var. saxonica
FU002C Frustulia rhomboides var. elongatissima
FU002D Frustulia rhomboides var. amphipleuroides
FU002E Frustulia rhomboides var. saxonica f. undulata
FU002F Frustulia rhomboides var. viridula
FU002G Frustulia rhomboides var. crassinervia
GO002A Gomphonema apicatum
GO003A Gomphonema angustatum agg.
GO003B Gomphonema angustatum var. productum
GO004A Gomphonema gracile
GO005A Gomphonema lagerheimei
GO006A Gomphonema acuminatum
GO006C Gomphonema acuminatum var. coronatum
GO010A Gomphonema constrictum
GO010B Gomphonema constrictum var. capitatum
GO010C Gomphonema constrictum var. capitatum f. turgida
GO013A Gomphonema parvulum
GO014A Gomphonema intricatum
GO014B Gomphonema intricatum var. pumilum
GO017A Gomphonema lanceolatum
GO019A Gomphonema augur
GO023A Gomphonema truncatum
GO023B Gomphonema truncatum var. capitatum
GO029A Gomphonema clavatum
GO036A Gomphonema dichotomum
GO045A Gomphonema lacunicola
GO066A Gomphonema tergestinum
GO9999 Gomphonema sp.
HN001A Hannaea arcus
KR001A Krasskella kriegerana
MA9999 Mastogloia sp.
ME019A Melosira arentii
MR001A Meridion circulare
NA002A Navicula jaernefeltii
NA003A Navicula radiosa var. radiosa
NA003B Navicula radiosa var. tenella
NA005A Navicula seminulum
NA005B Navicula seminulum var. intermedia
NA006A Navicula mediocris
NA006B Navicula mediocris var. atomus
NA007A Navicula cryptocephala
NA008A Navicula rhyncocephala
NA013A Navicula pseudoscutiformis
NA014A Navicula pupula var. pupula
NA015A Navicula hassiaca
NA017A Navicula ventralis
NA018A Navicula wittrockii
NA032A Navicula cocconeiformis
NA033A Navicula subtilissima
NA035A Navicula salinarnum
NA036A Navicula perpusilla

NA037A Navicula angusta
NA039A Navicula festiva
NA040A Navicula hoefleri
NA042A Navicula minima
NA043A Navicula subatomoides
NA044A Navicula krasskei
NA045A Navicula bryophila
NA046A Navicula contenta
NA048A Navicula soehrensis
NA050A Navicula clementis
NA051A Navicula cari
NA056A Navicula cuspidada
NA068A Navicula impexa
NA075A Navicula subhamulata
NA086A Navicula tantula
NA099A Navicula bremensis
NA115A Navicula difficillima
NA129A Navicula seminuloides
NA133A Navicula schassmannii
NA135A Navicula tenuicephala
NA140A Navicula madumensis
NA140A Navicula madumensis
NA149A Navicula digitulus
NA156A Navicula leptostriata
NA157A Navicula simsii
NA158A Navicula cumbriensis
NA160A Navicula submolesta
NA167A Navicula hoefleri
NA452A Navicula insociabilis
NA751A Navicula cryptotenella
NA9927 Navicula [subtilissima var. 1]
NA9955 Navicula [cf. vitiosa]
NA9962 Navicula [sp. 2]
NA9963 Navicula [sp. 1]
NA9995 Navicula [sp. a]
NA9999 Navicula sp.
NE003A Neidium affine
NE003B Neidium affine var. longiceps
NE003C Neidium affine var. amphirhynchus
NE003D Neidium affine var. humerus
NE004A Neidium bisulcatum
NE006A Neidium alpinum
NE012A Neidium glaberrimum
NE020A Neidium hercynicum
NE9999 Neidium sp.
NI002A Nitzschia fonticola
NI005A Nitzschia perminuta
NI008A Nitzschia frustulum
NI009A Nitzschia palea
NI009B Nitzschia palea var. tenuirostris
NI014A Nitzschia amphibia var. Amphibia

NI015A Nitzschia dissipata
NI017A Nitzschia gracilis
NI020A Nitzschia angustata
NI022A Nitzschia navicularis
NI025A Nitzschia recta
NI028A Nitzschia capitellata
NI031A Nitzschia linearis
NI140A Nitzschia palustris
NI9985 Nitzschia [cf. palea]
NI9986 Nitzschia [cf. palea]
NI9999 Nitzschia sp.
PE002A Peronia fibula
PI002A Pinnularia acuminata
PI005A Pinnularia major
PI007A Pinnularia viridis
PI007F Pinnularia viridis var. rupestris
PI008A Pinnularia divergens
PI011A Pinnularia microstauron
PI012A Pinnularia borealis
PI014A Pinnularia appendiculata
PI015A Pinnularia abaujensis
PI016A Pinnularia divergentissima
PI017A Pinnularia carminata
PI018A Pinnularia biceps
PI020A Pinnularia undulata
PI022A Pinnularia subcapitata
PI022B Pinnularia subcapitata var. hilseana
PI023A Pinnularia irrorata
PI024A Pinnularia stomatophora
PI026A Pinnularia tenuis
PI030A Pinnularia acoricola
PI051A Pinnularia lata
PI9978 Pinnularia [rupestris sensu Renberg 1976]
PI9999 Pinnularia sp.
RZ011A Rhizosolenia eriensis var. eriensis
SA001A Stauroneis anceps
SA001B Stauroneis anceps f. gracilis
SA003A Stauroneis smithii var. smithii
SA006A Stauroneis phoenicenteron
SA068A Stauroneis thermicola
SA9999 Stauroneis sp.
SE001A Semiorbis hemicyclus
SO002A Scolioneis brunkseiensis
SP001A Stenopterobia intermedia
SP002A Stenopterobia sigmatella
SP002B Stenopterobia sigmatella
SU002A Surirella ovata
SU004A Surirella biseriata
SU005A Surirella linearis
SU005A Surirella linearis
SU006A Surirella delicatissima

SU016A Surirella minuta
SU9999 Surirella sp.
SY001A Synedra ulna
SY002A Synedra rumpens
SY003A Synedra acus
SY003C Synedra acus var. angustissima
SY010A Synedra minuscula
SY011A Synedra delicatissima
SY013A Synedra tenera
SY8888 Synedra acus agg.
SY9999 Synedra sp.
TA001A Tabellaria flocculosa
TA001B Tabellaria flocculosa var. flocculosa f. IIIp
TA002A Tabellaria fenestrata
TA003A Tabellaria binalis
TA003B Tabellaria binalis f. elliptica
TA004A Tabellaria quadriseptata
TA005A Tabellaria kuetzingiana
TA9998 Tabellaria [flocculosa (long)]
TA9999 Tabellaria sp.
UN9999 Unknown
ZZZ997 Temporary sp. 3
ZZZ999 Temporary sp. 1

APPENDIX 5 Macroinvertebrate Analyses – Figures and Tables

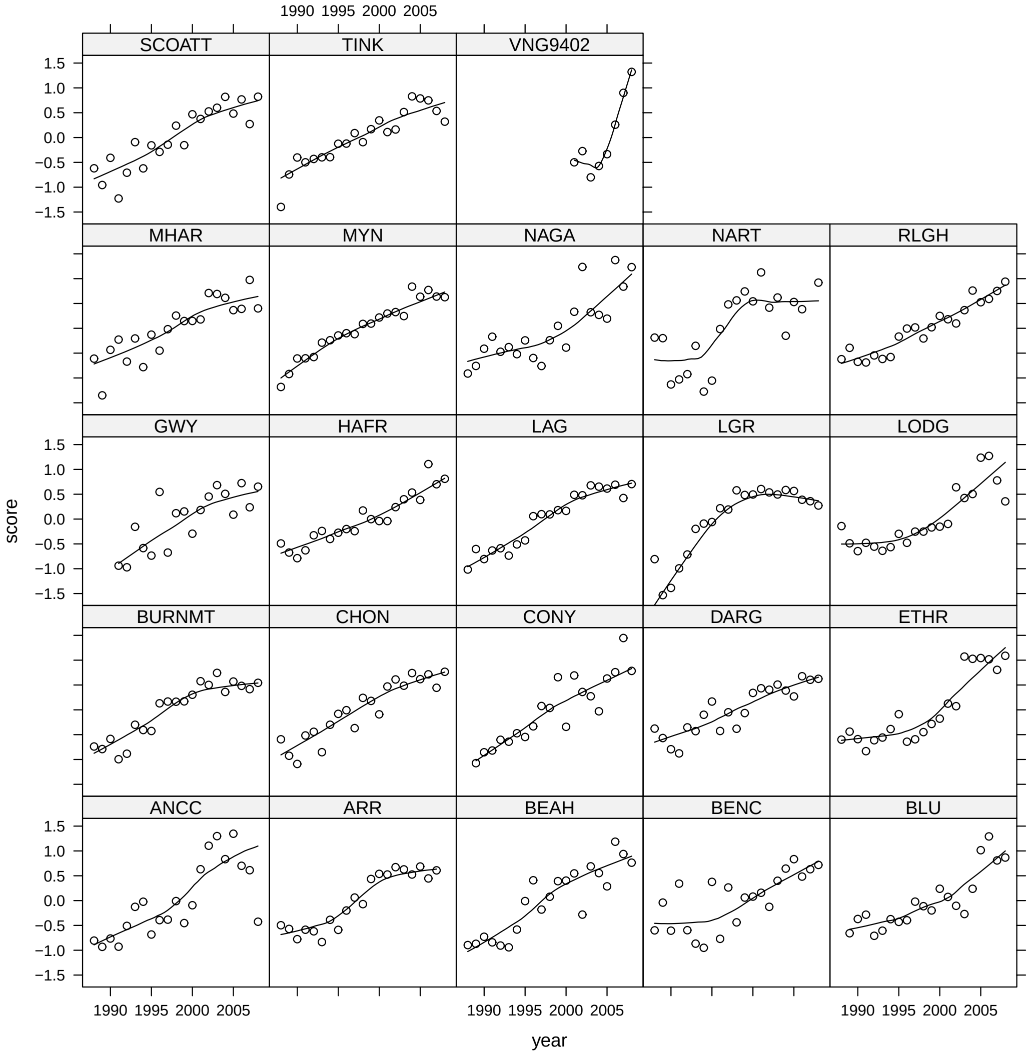

Figure 1: Axis 1 scores from RDA fitted to the macro-invertebrate data constrained by sampling year. The solid line in each plot is a LOESS smoother.

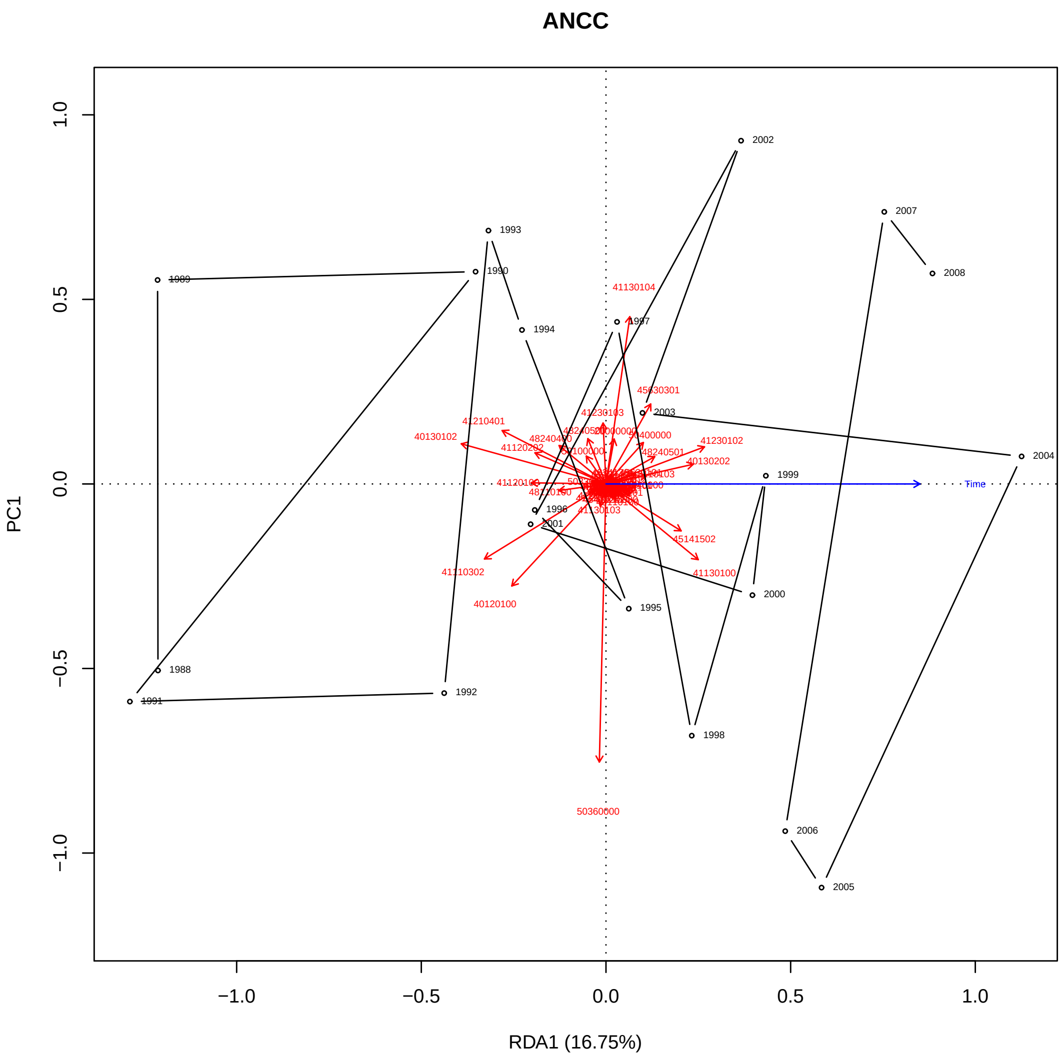

Figure 2: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Allt na Coire nan Con

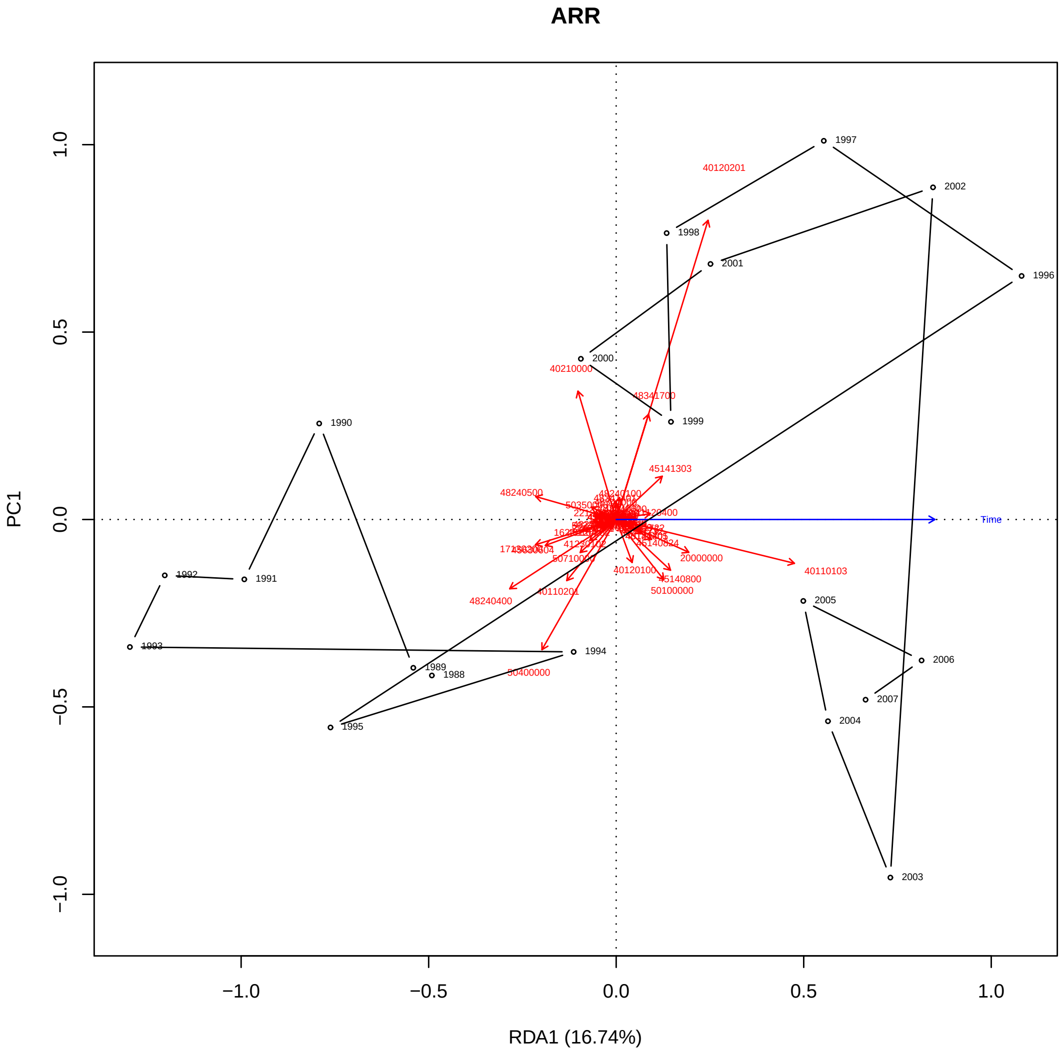

Figure 3: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Loch Coire nan Arr

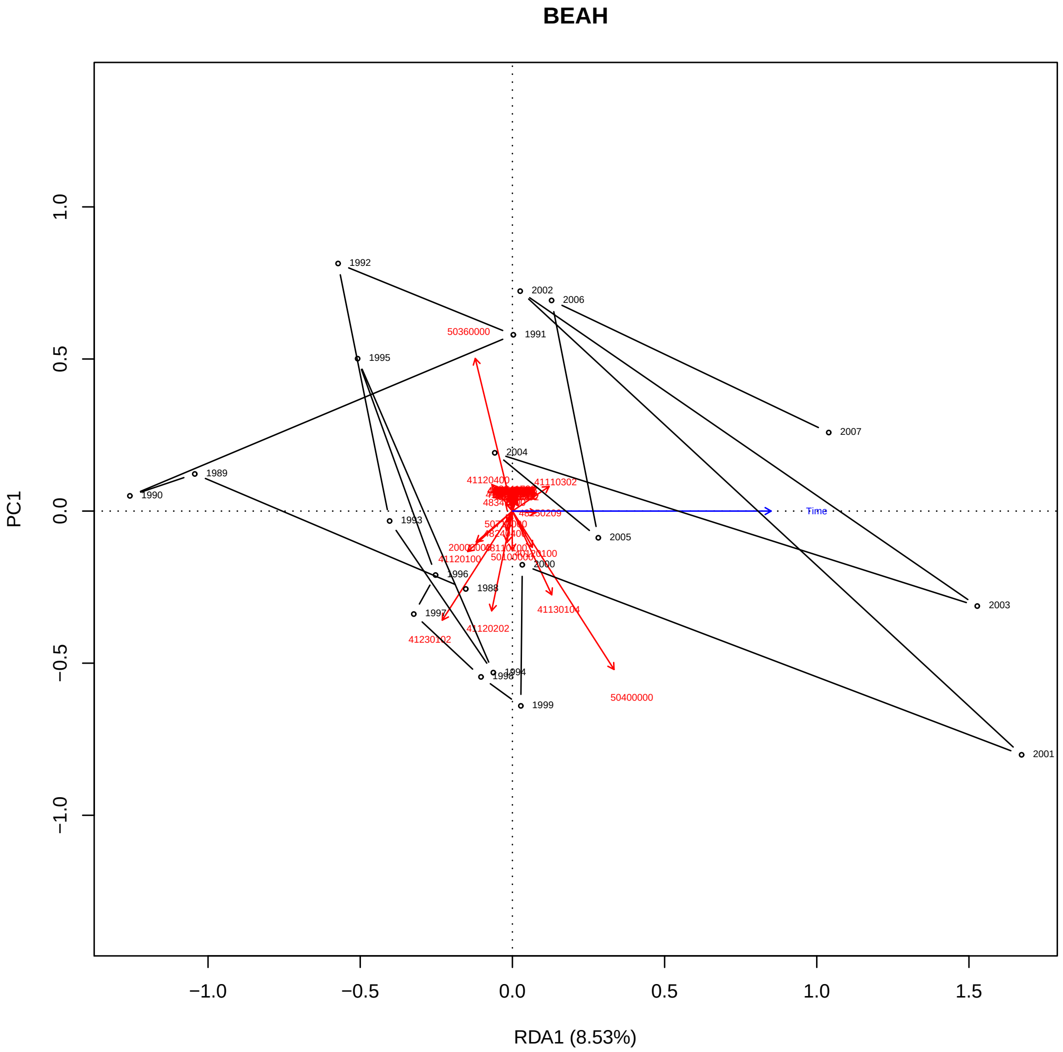

Figure 4: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Beagh's Burn

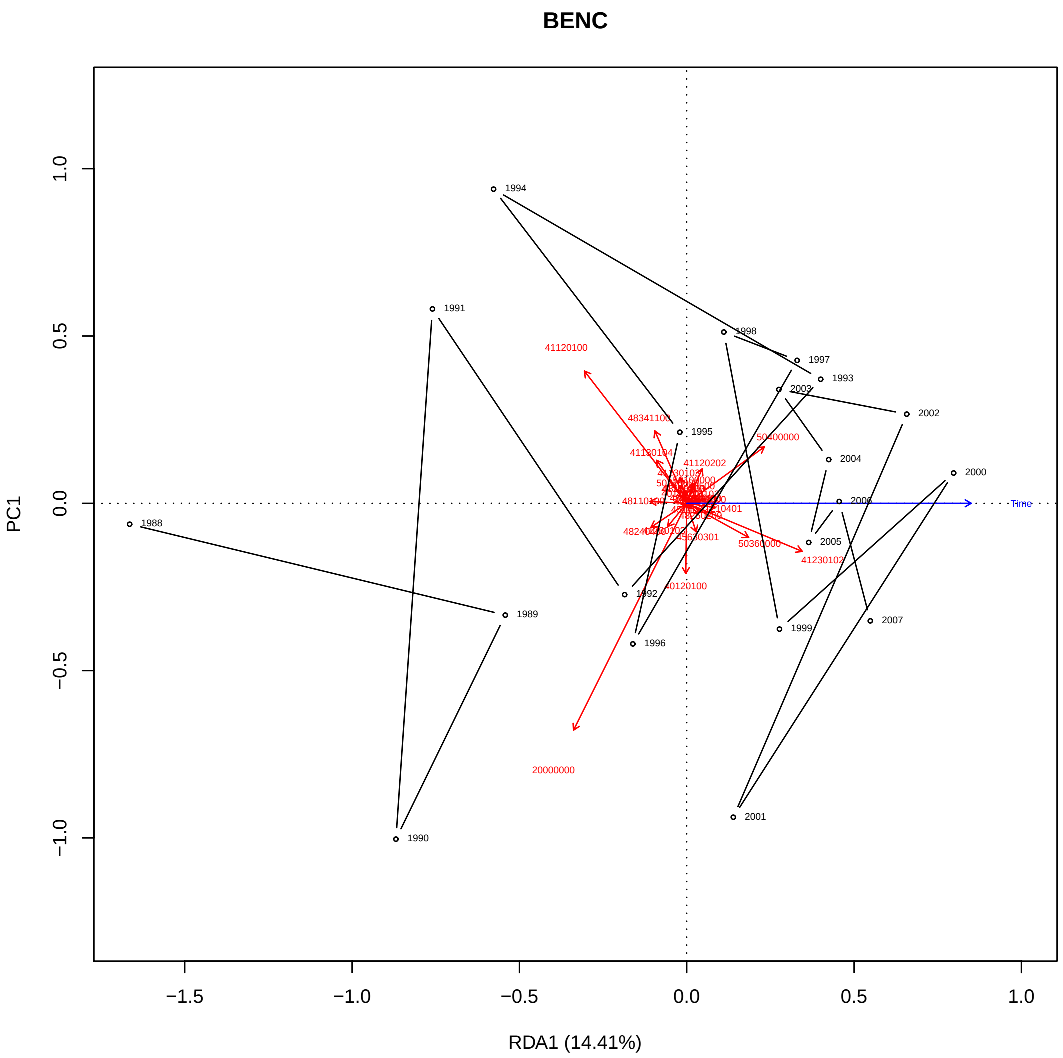

Figure 5: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Bencrom River

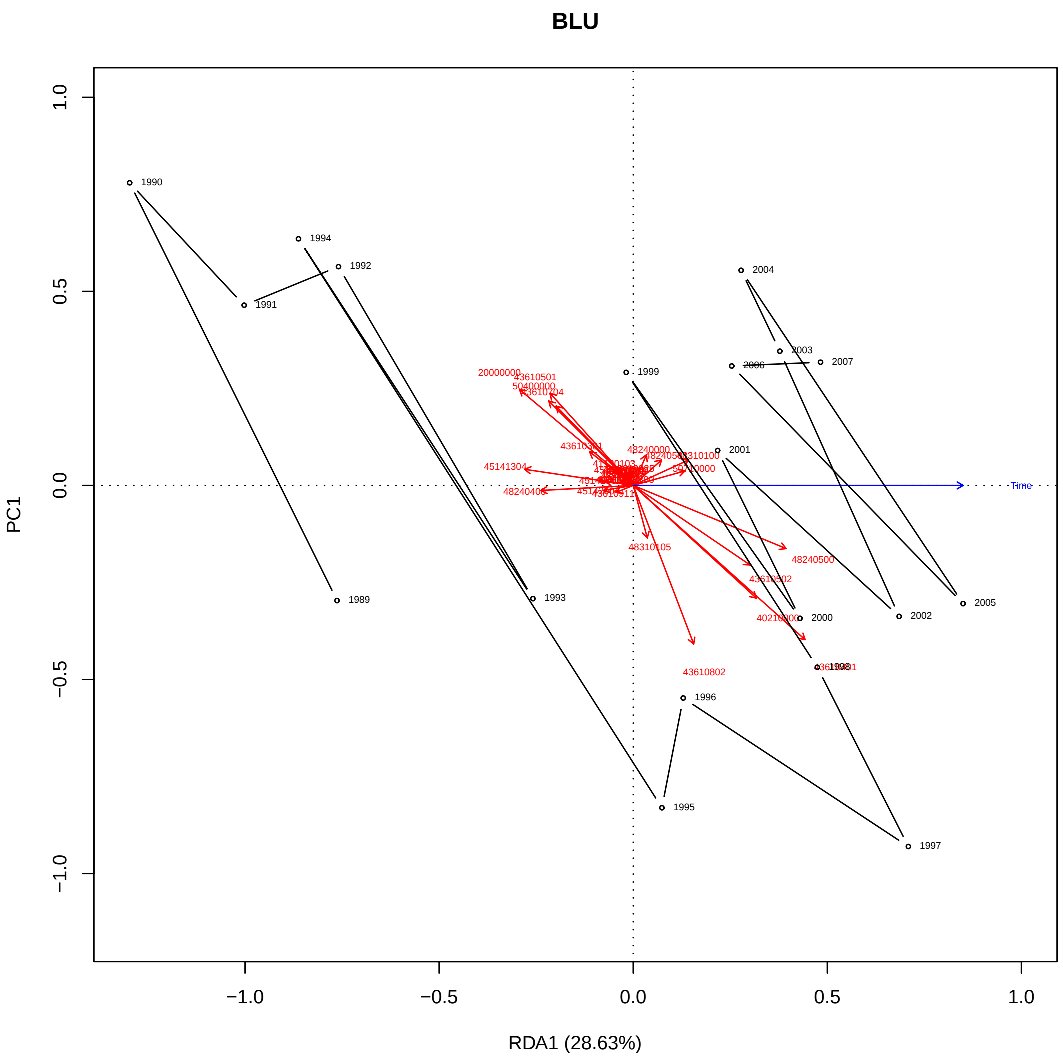

Figure 6: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Blue Lough

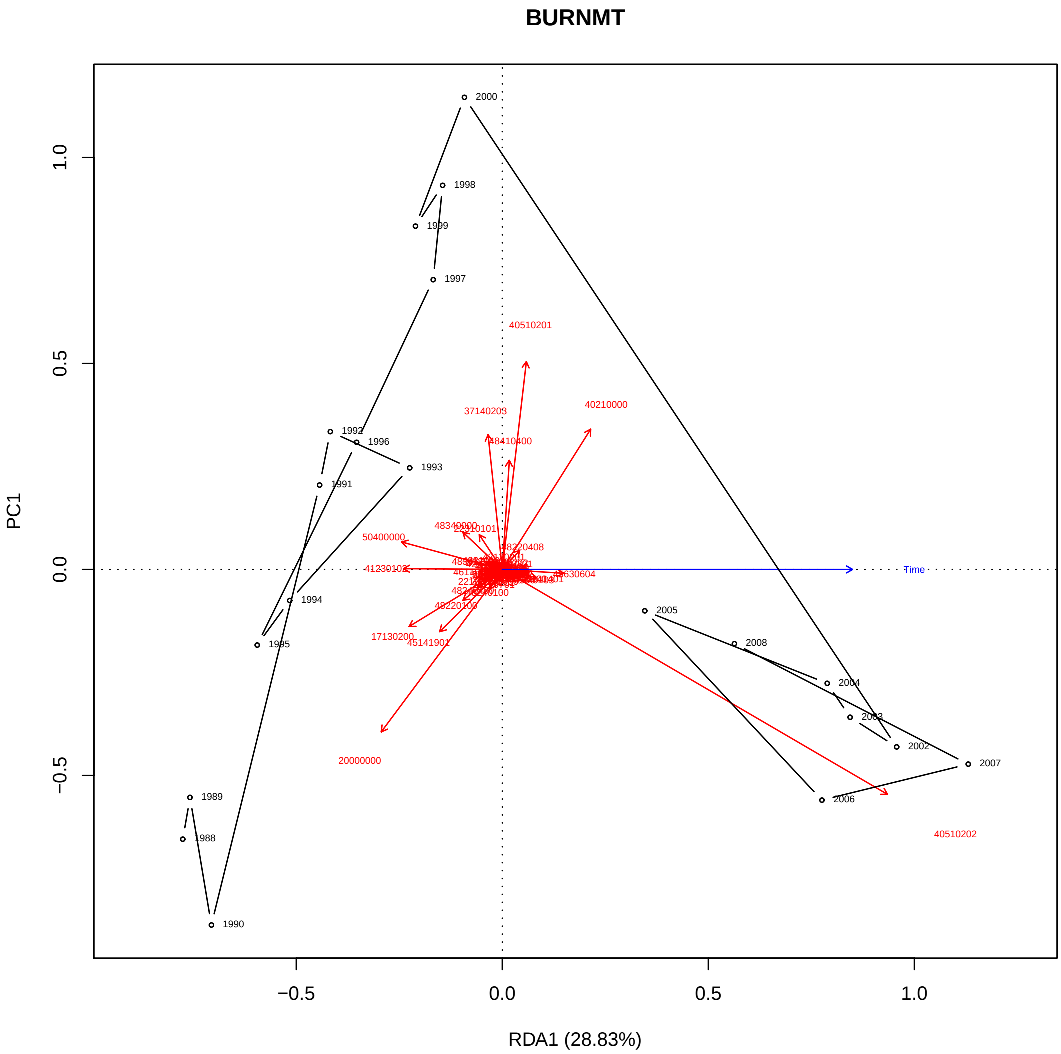

Figure 7: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Burnmoor Tarn

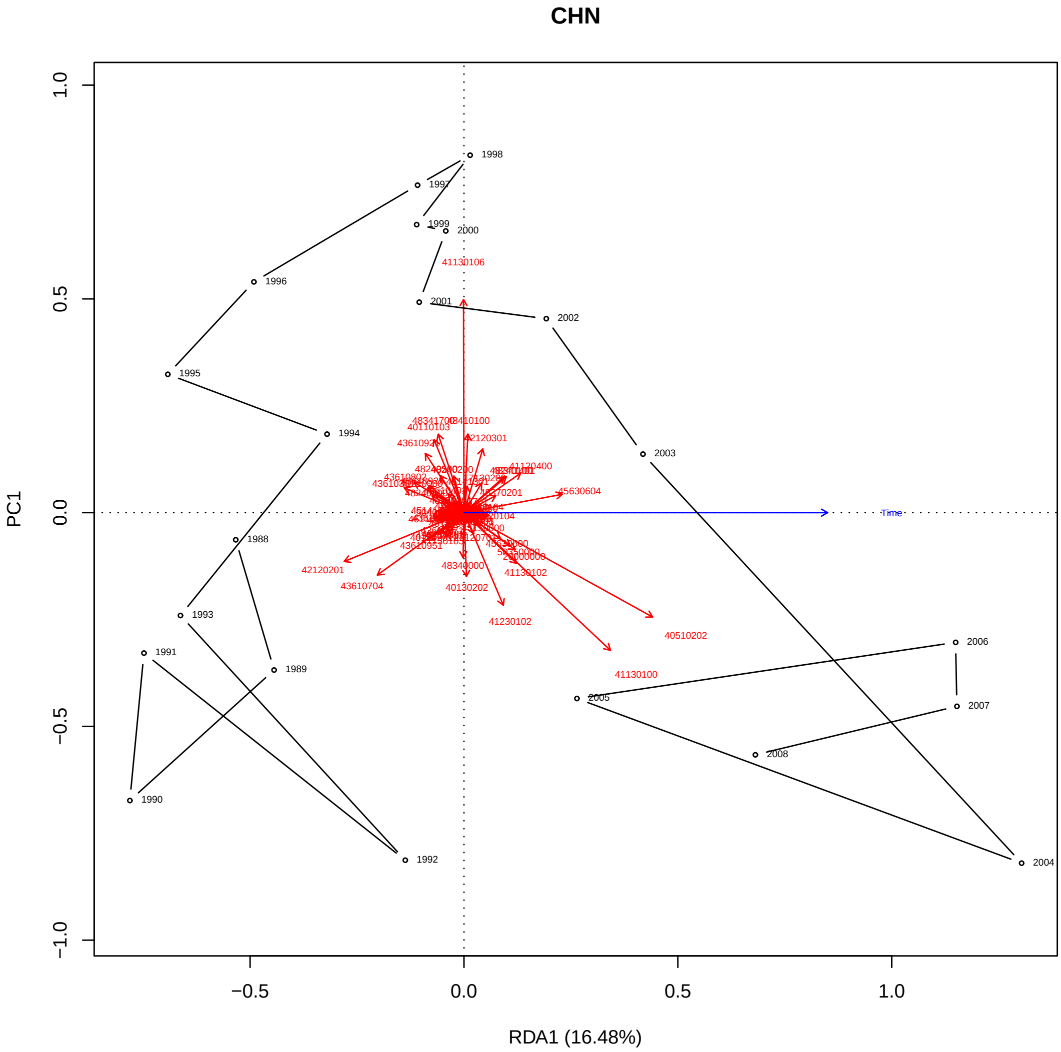

Figure 8: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Loch Chon

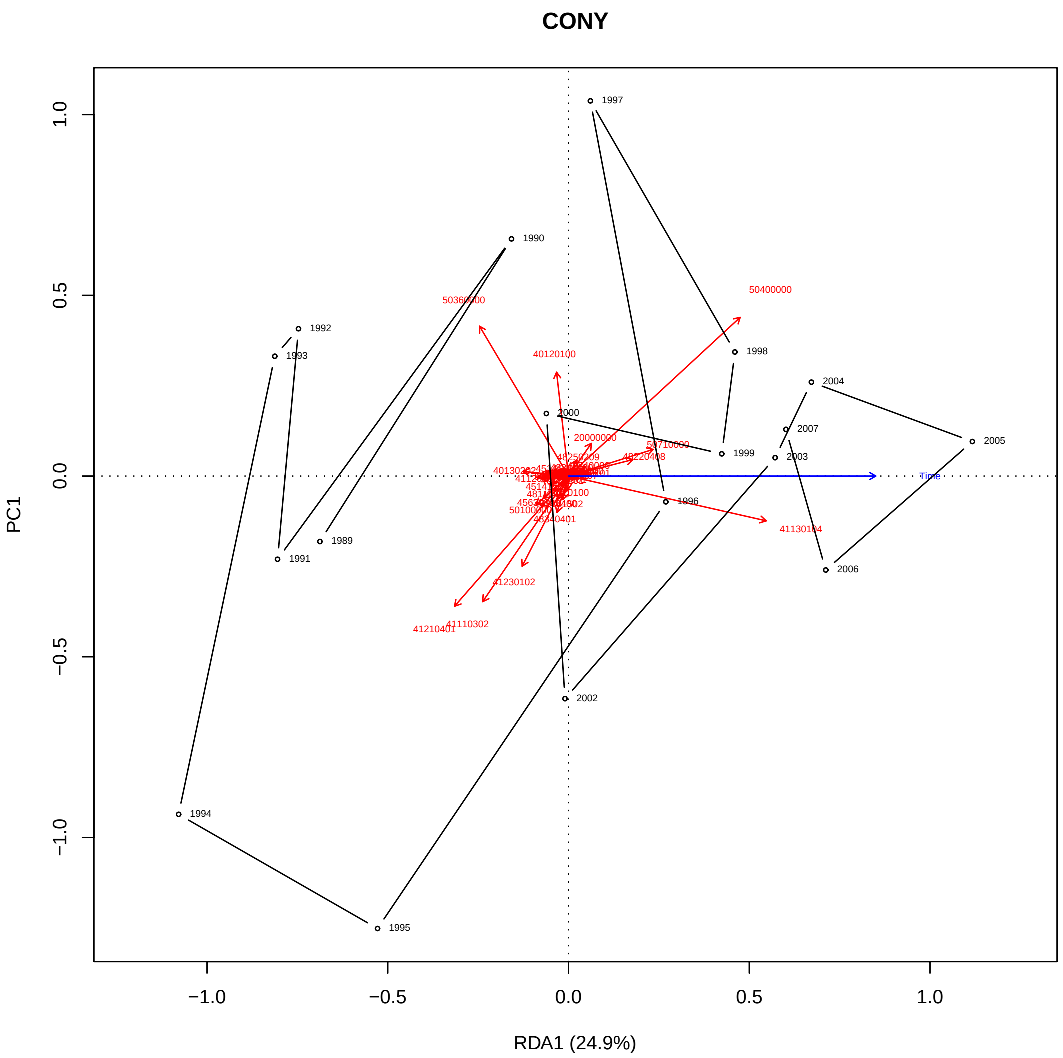

Figure 9: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Coneyglen Burn.

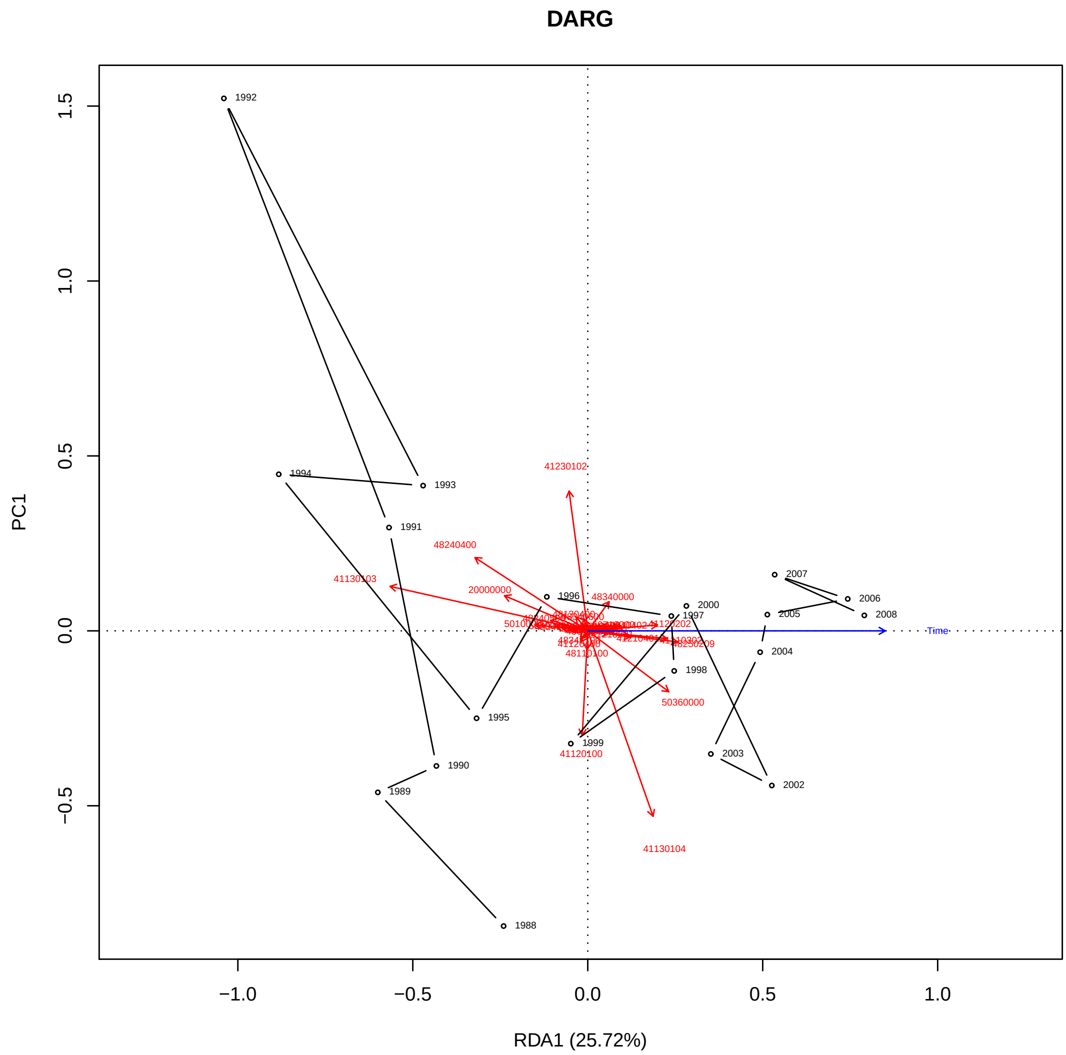

Figure 10: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Dargall Lane.

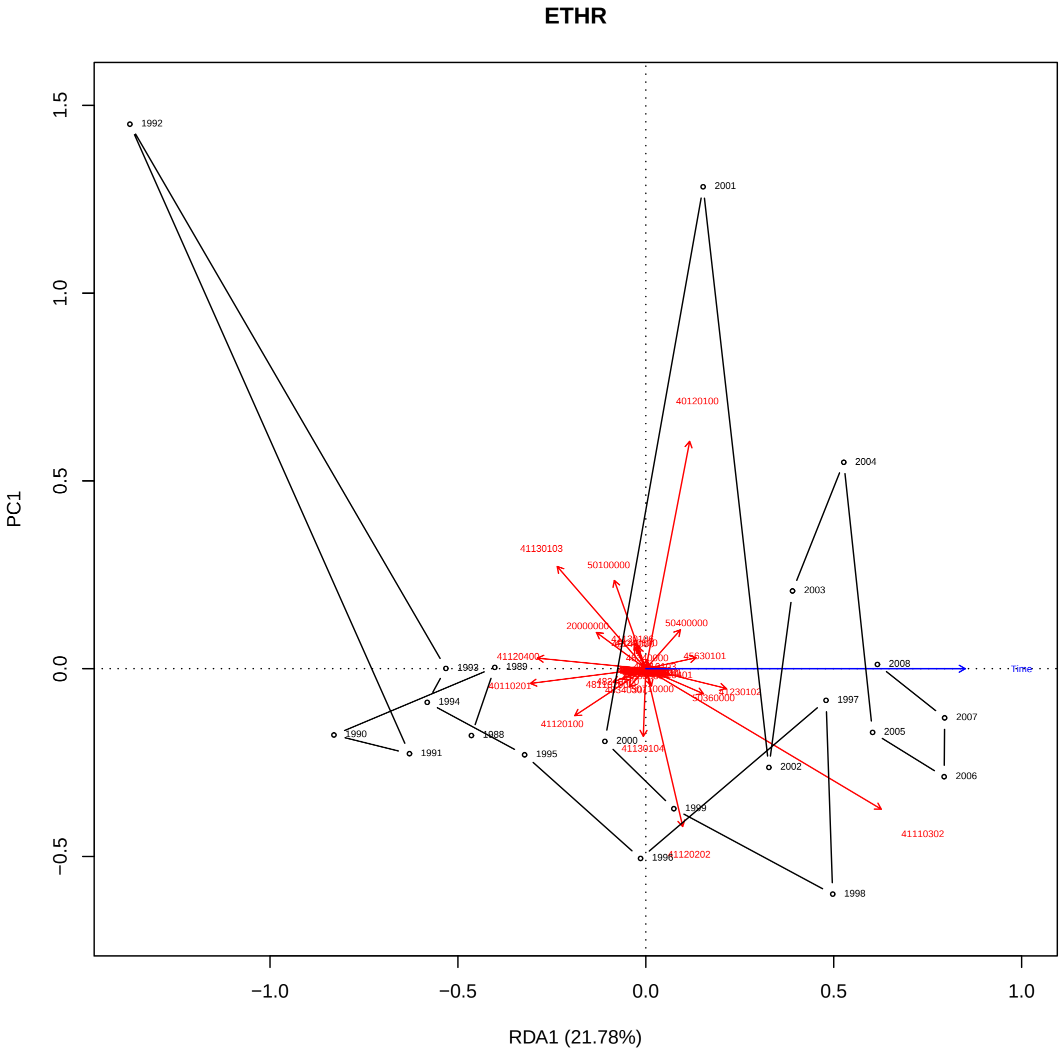

Figure 11: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at River Etherow.

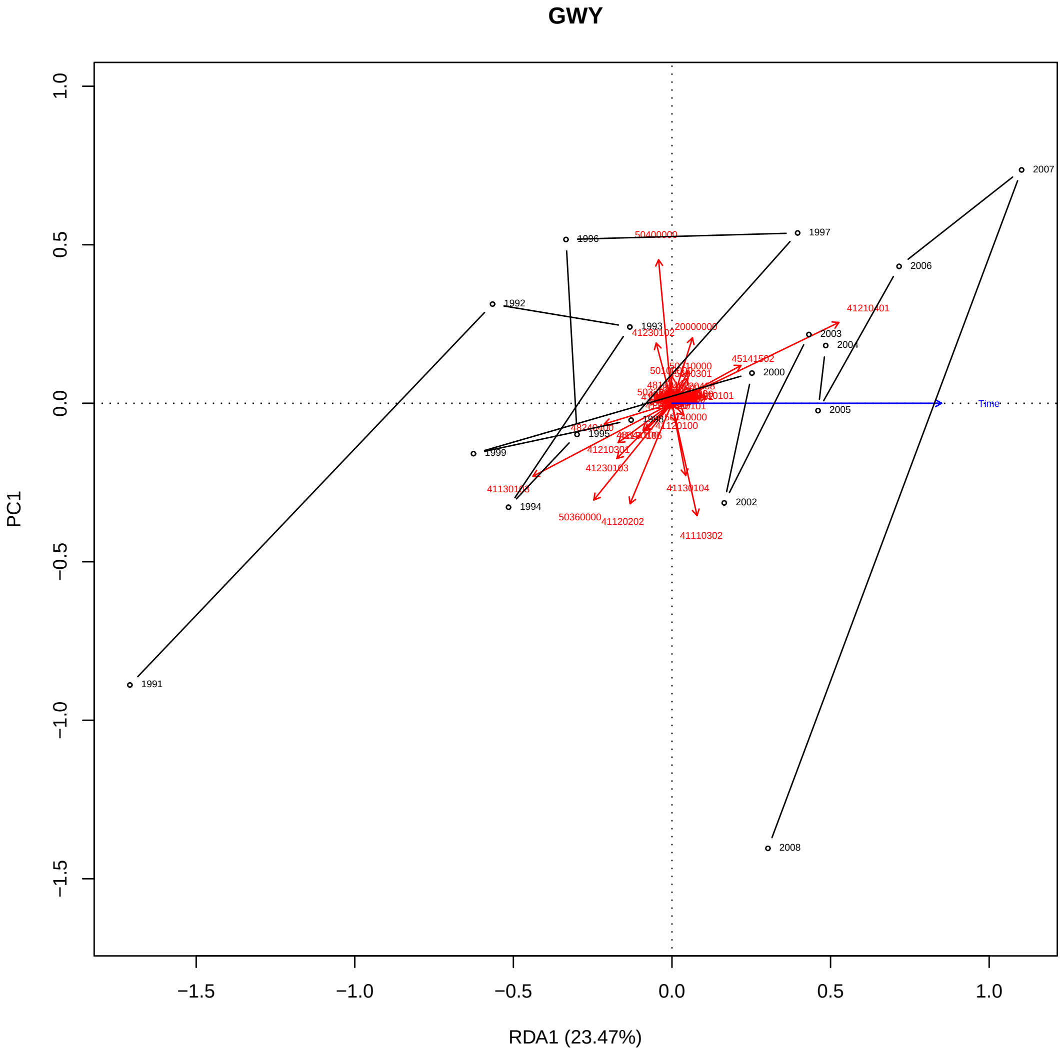

Figure 12: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Afon Gwy

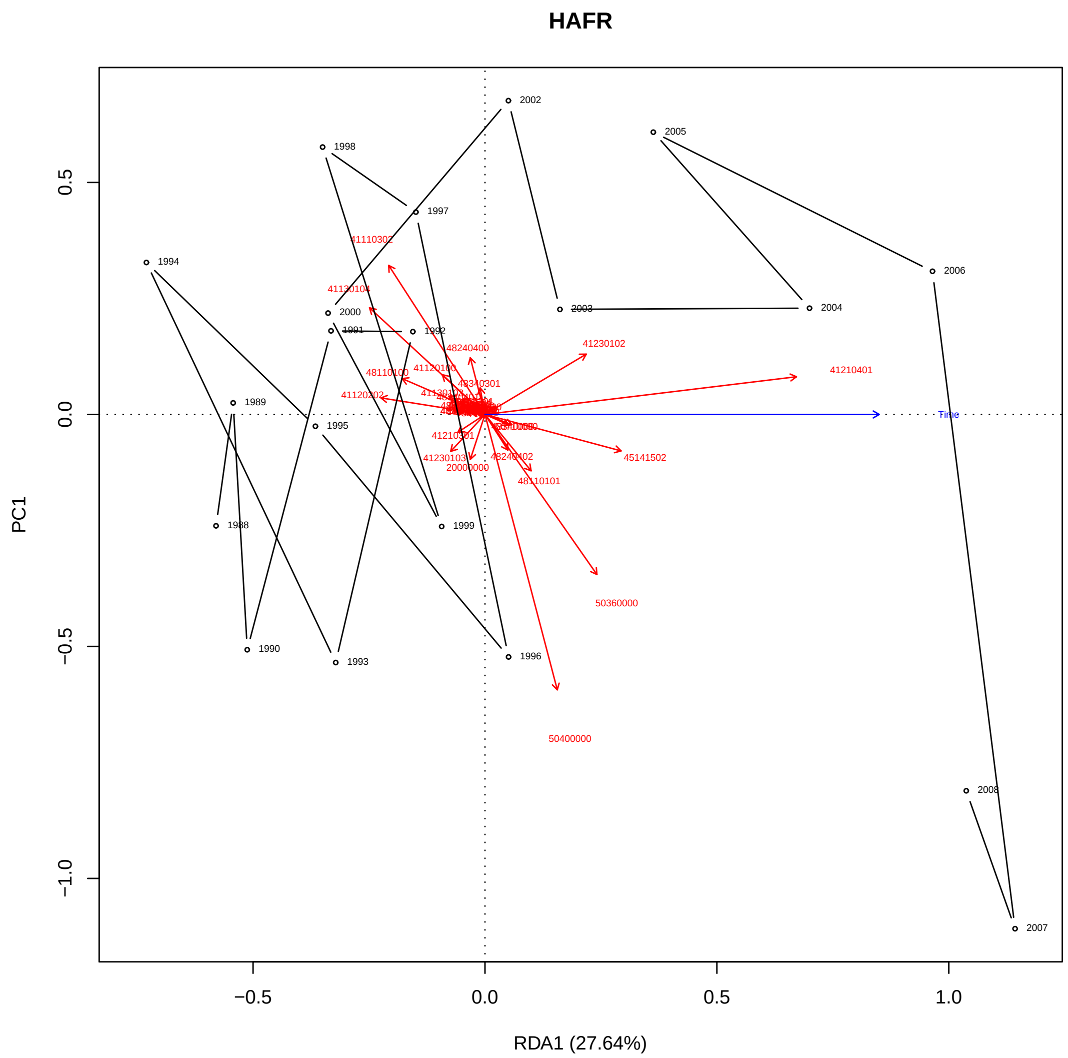

Figure 13: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Afon Hafren.

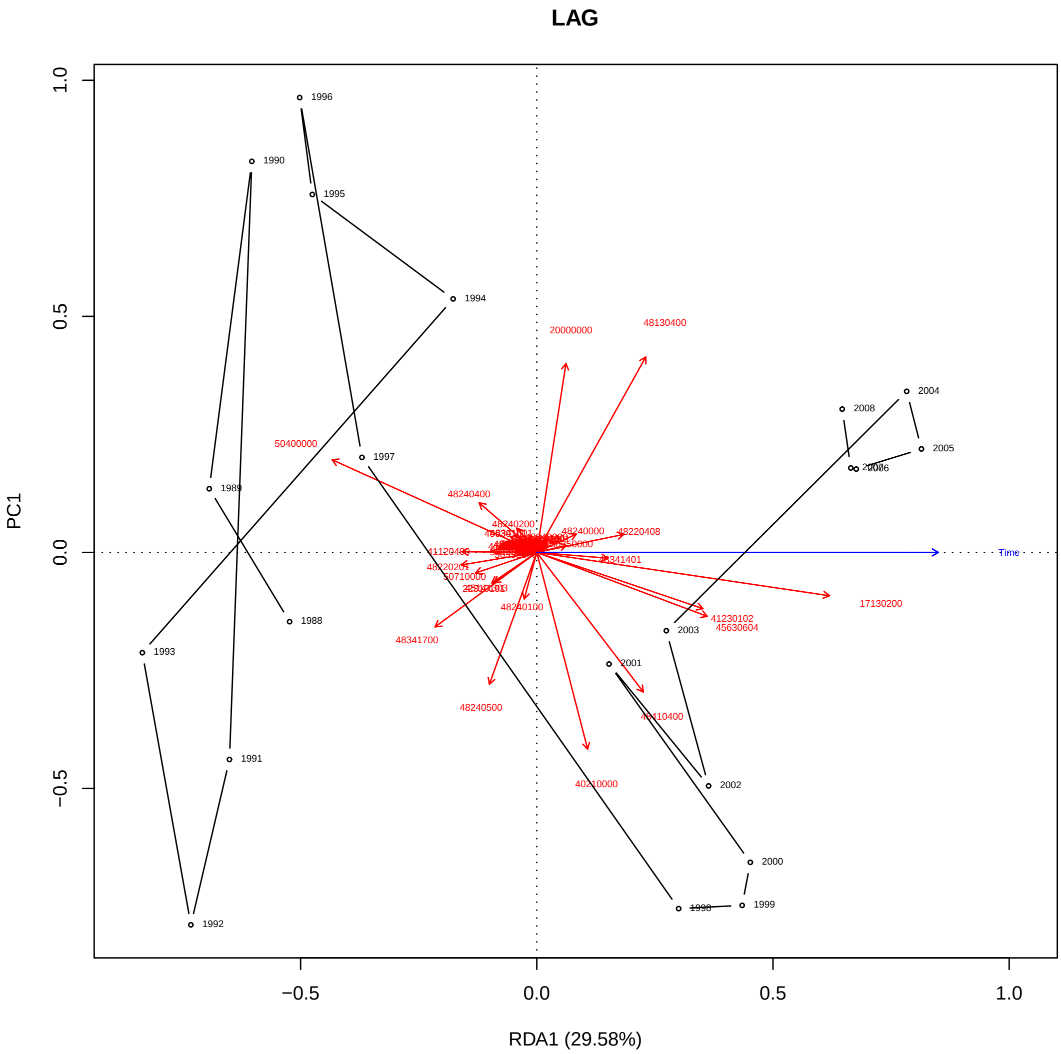

Figure 14: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Llyn Llagi.

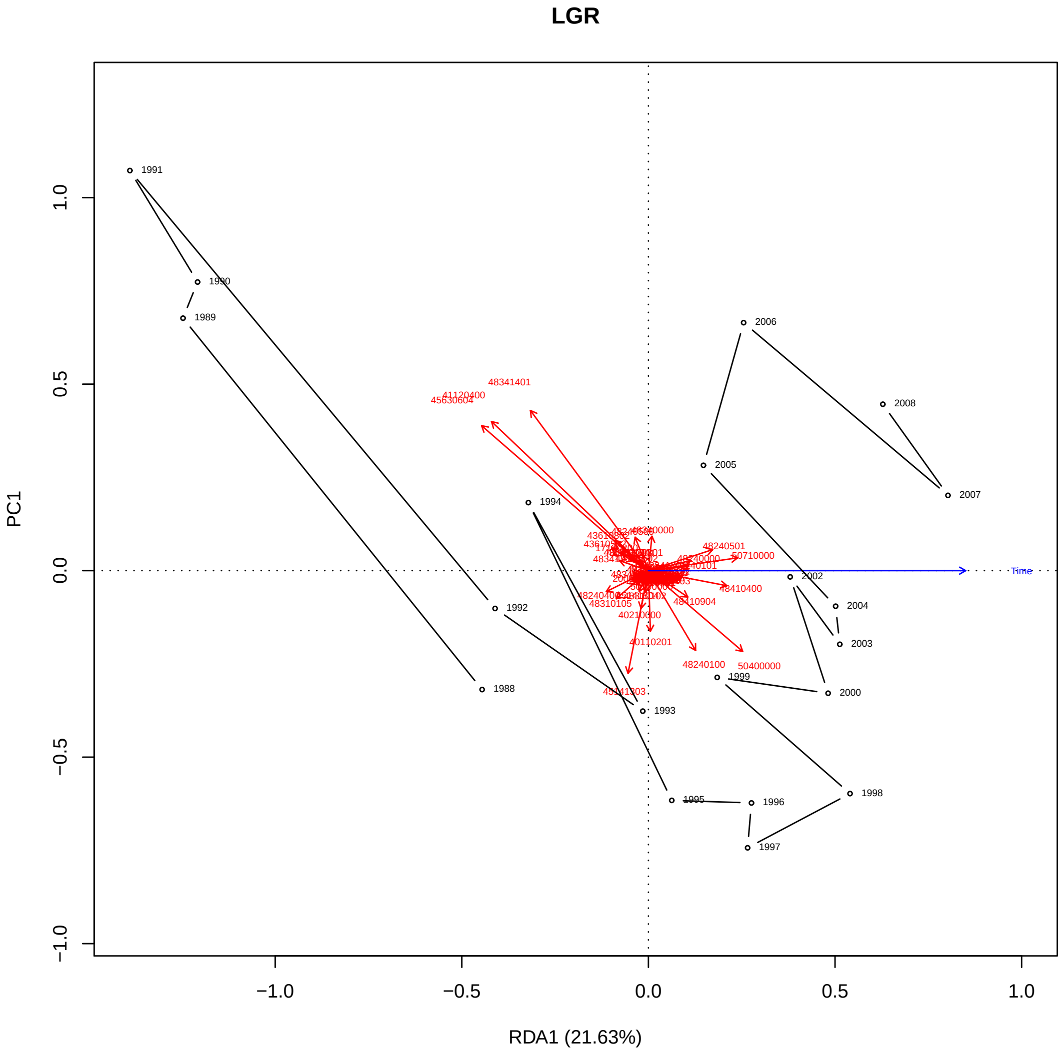

Figure 15: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Loch Grannoch.

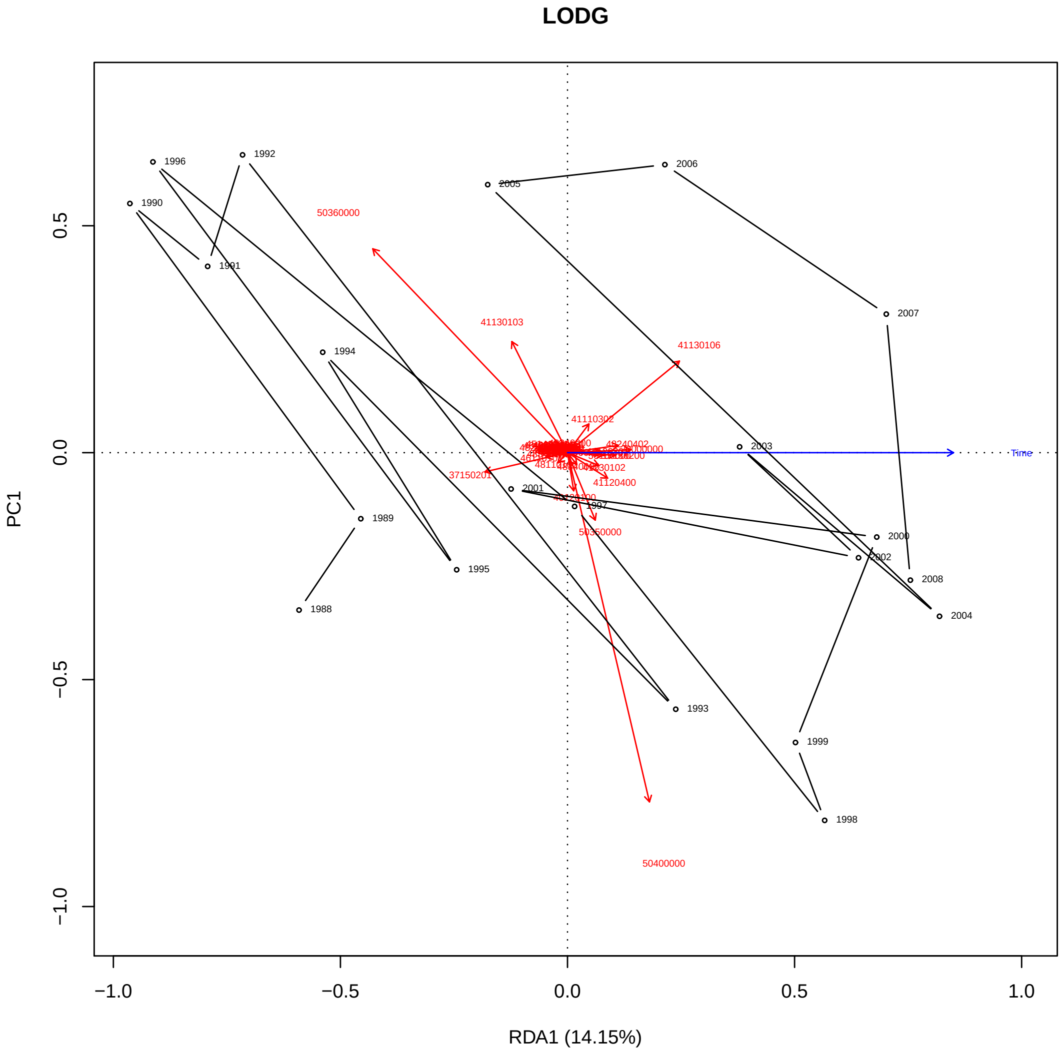

Figure 16: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Old Lodge.

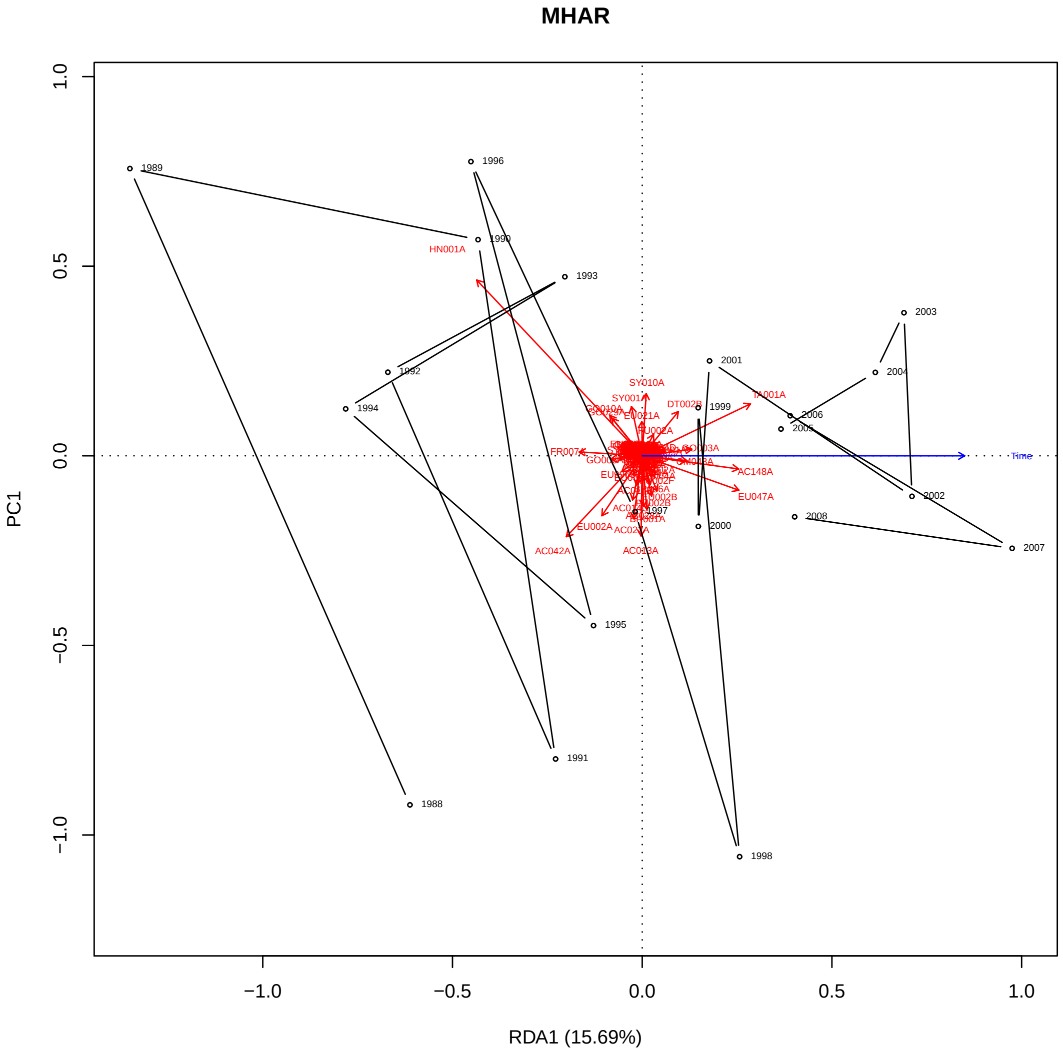

Figure 17: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Allt a' Mharcaidh.

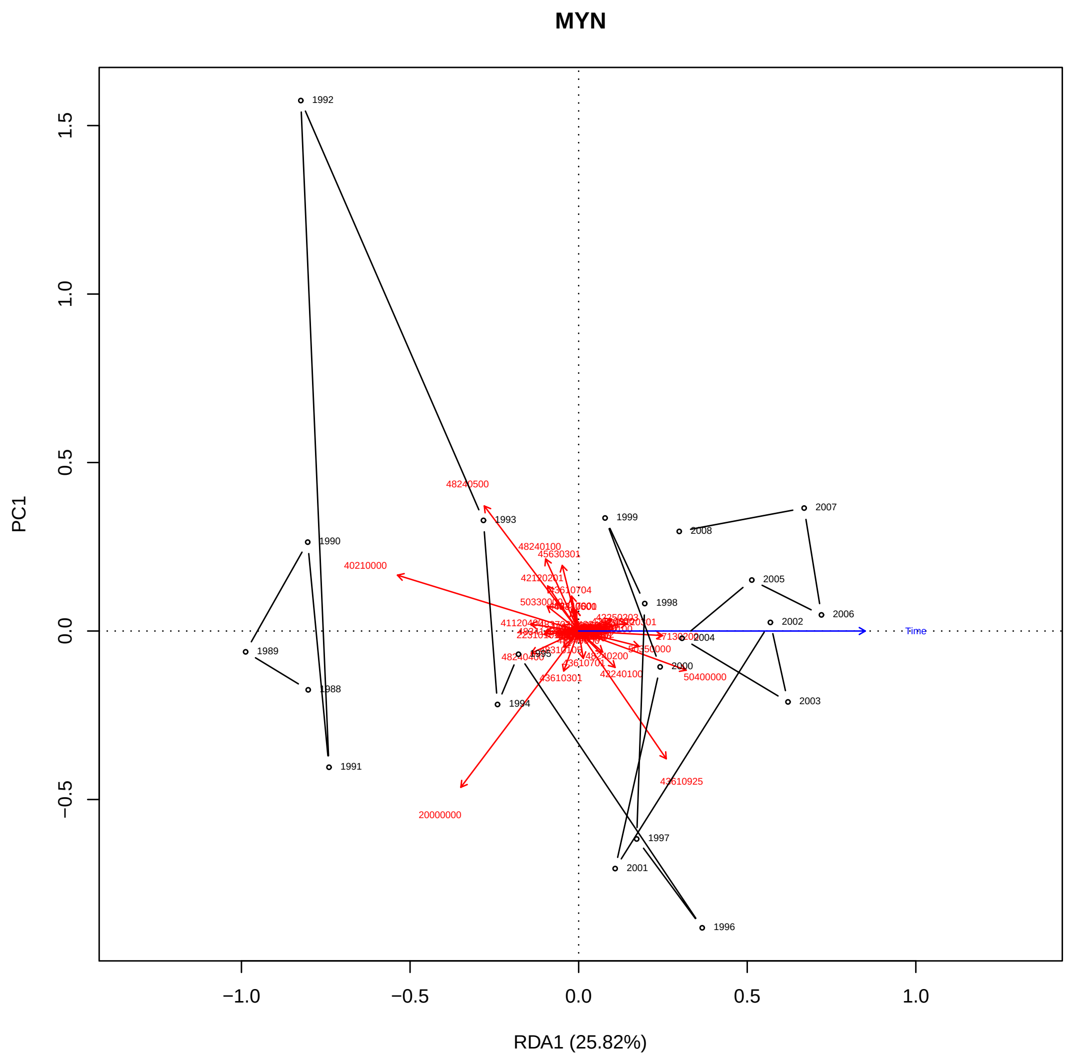

Figure 18: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Llyn Cwm Mynach.

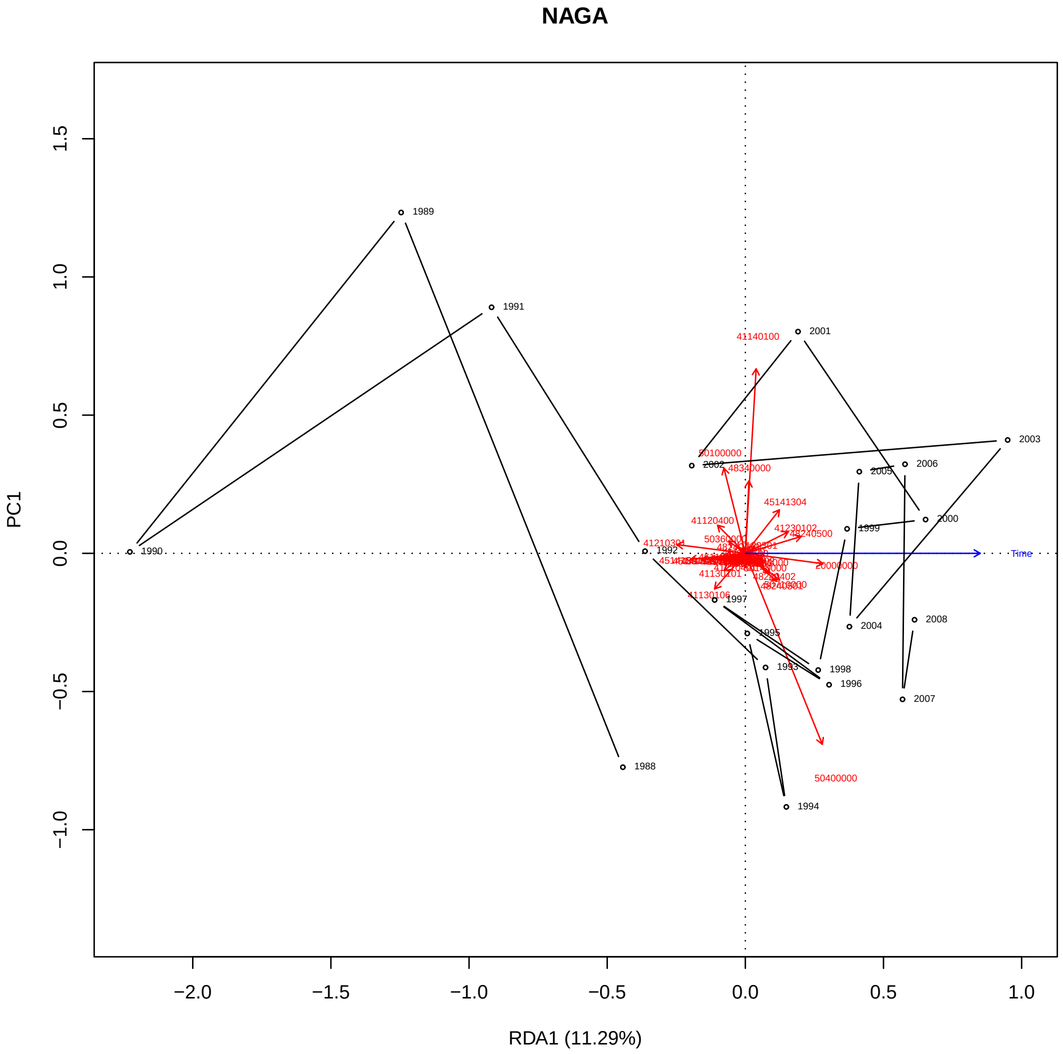

Figure 19: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Lochnagar.

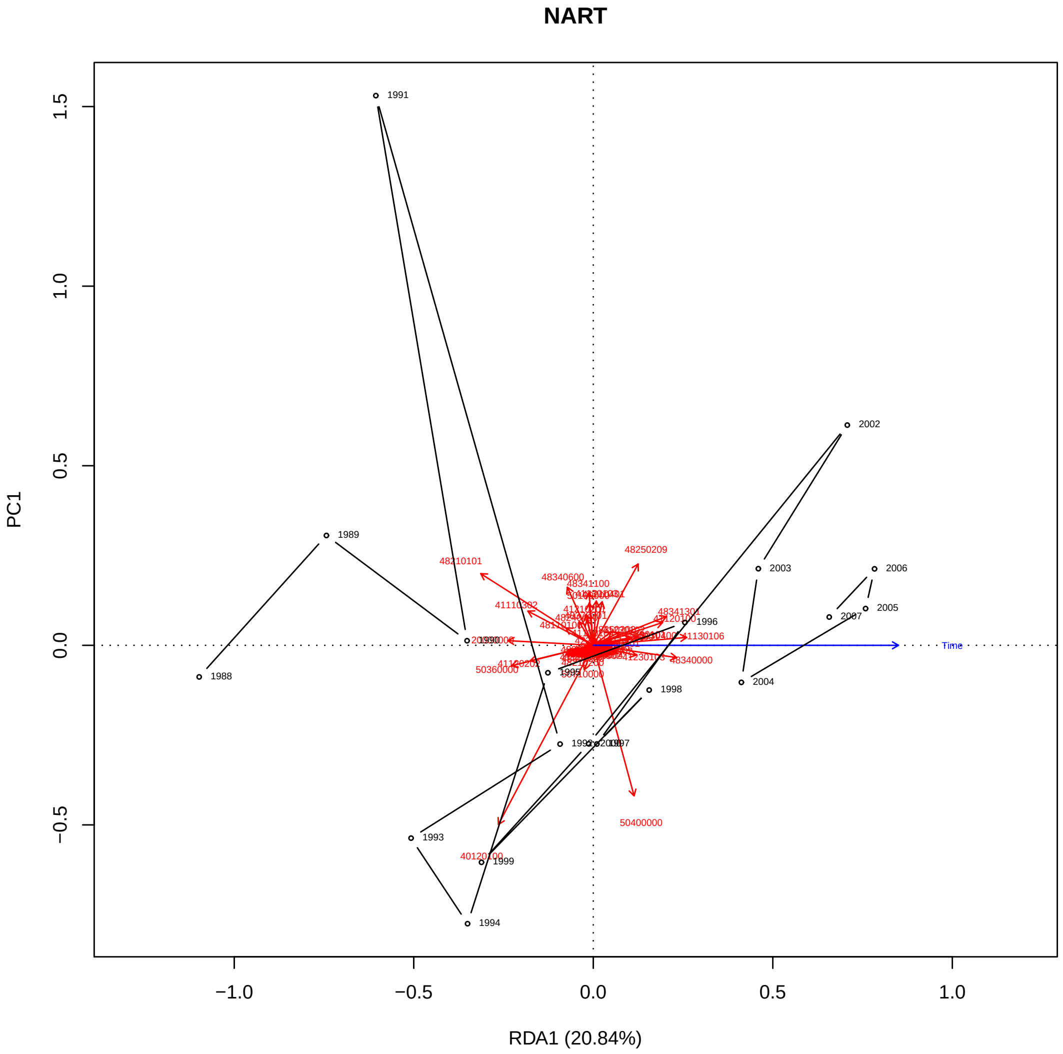

Figure 20: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Narrator Brook.

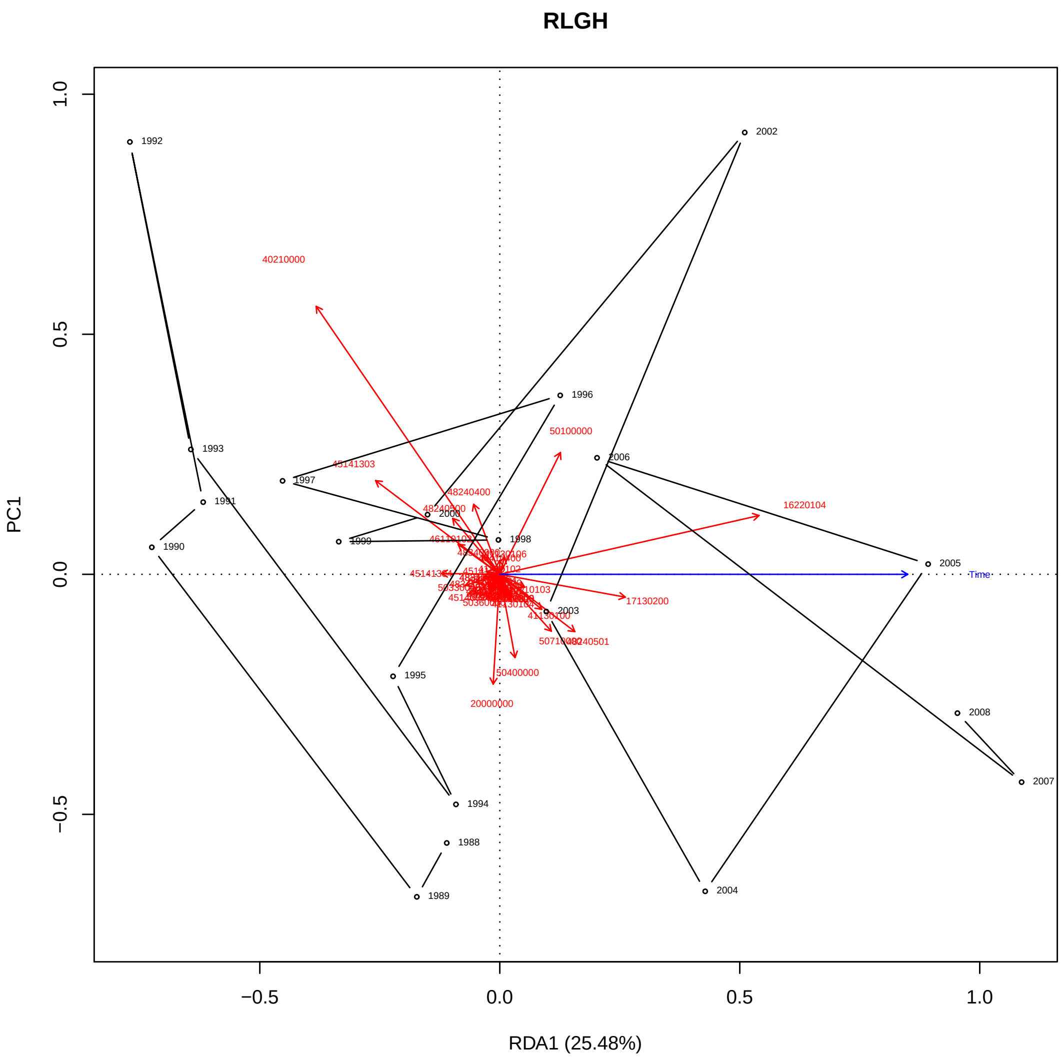

Figure 21: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Round Loch of Glenhead.

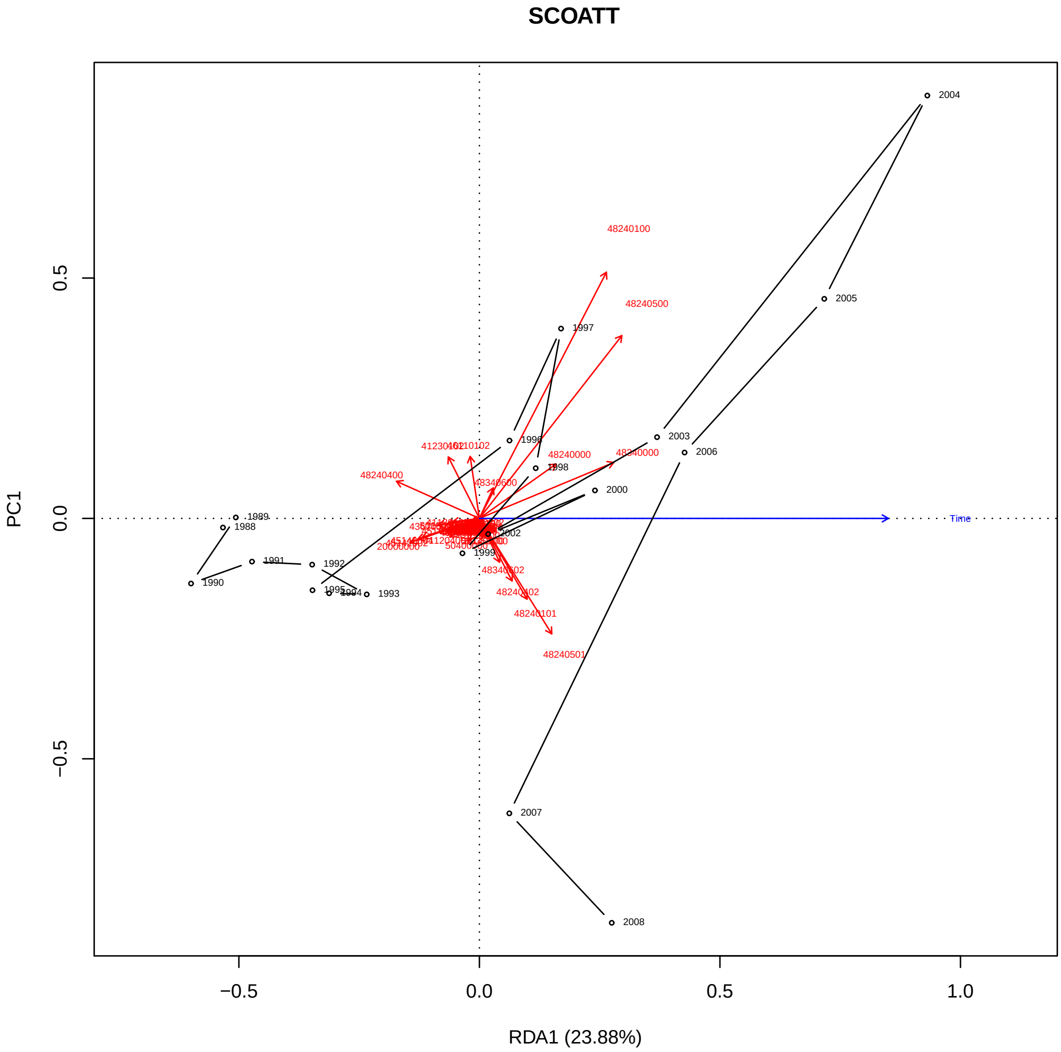

Figure 22: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Scoat Tarn.

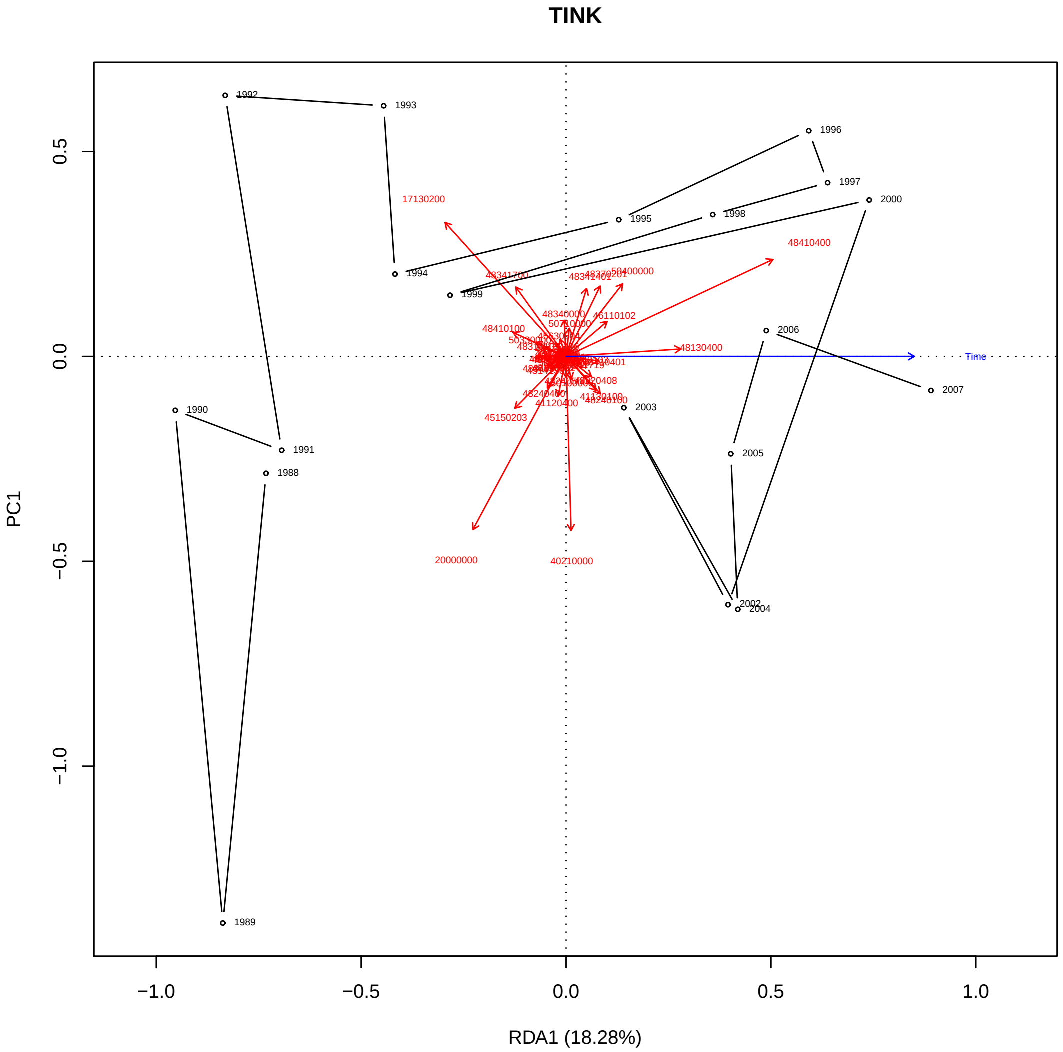

Figure 23: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Loch Tinker.

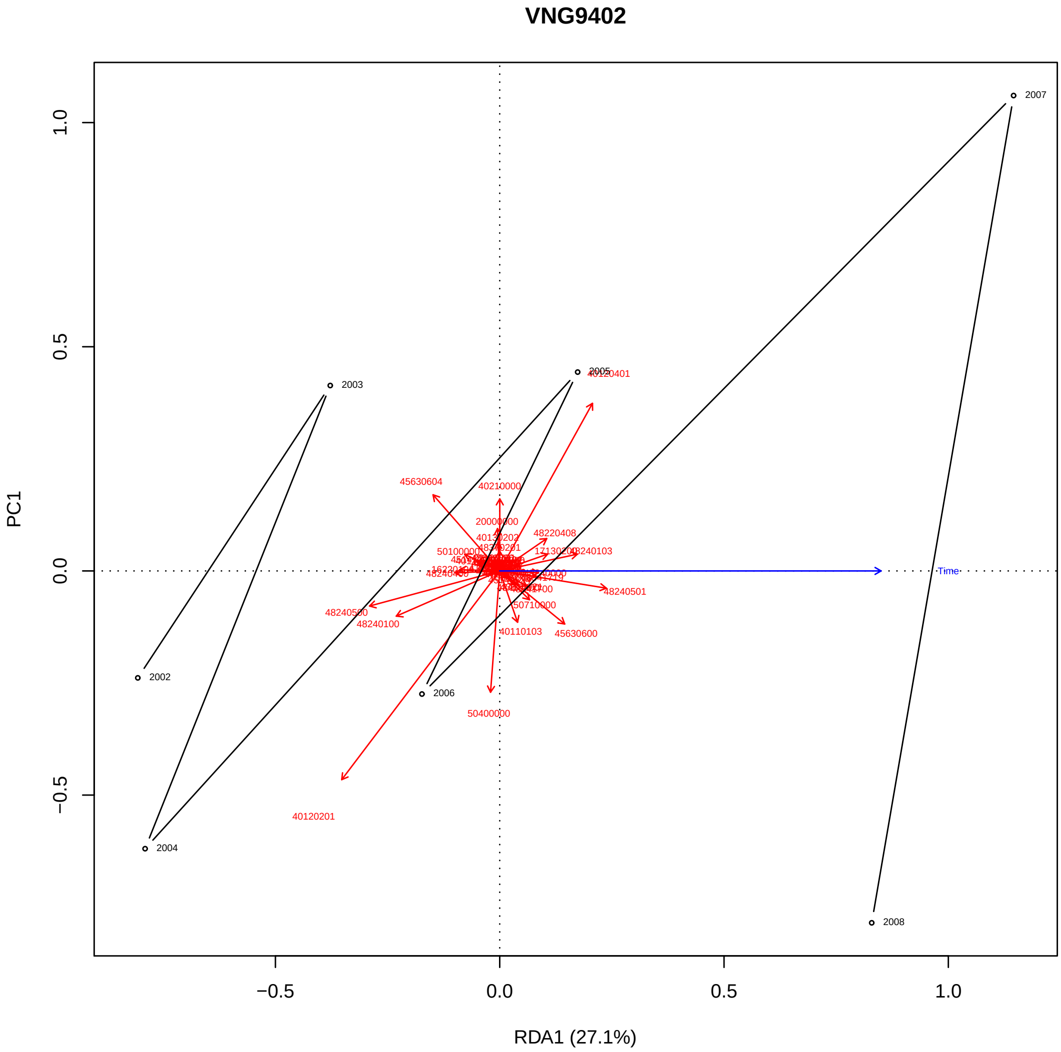

Figure 24: RDA time tracks showing axis 1 and 2 scores for the macro-invertebrate data at Loch Coire Fionnaraich

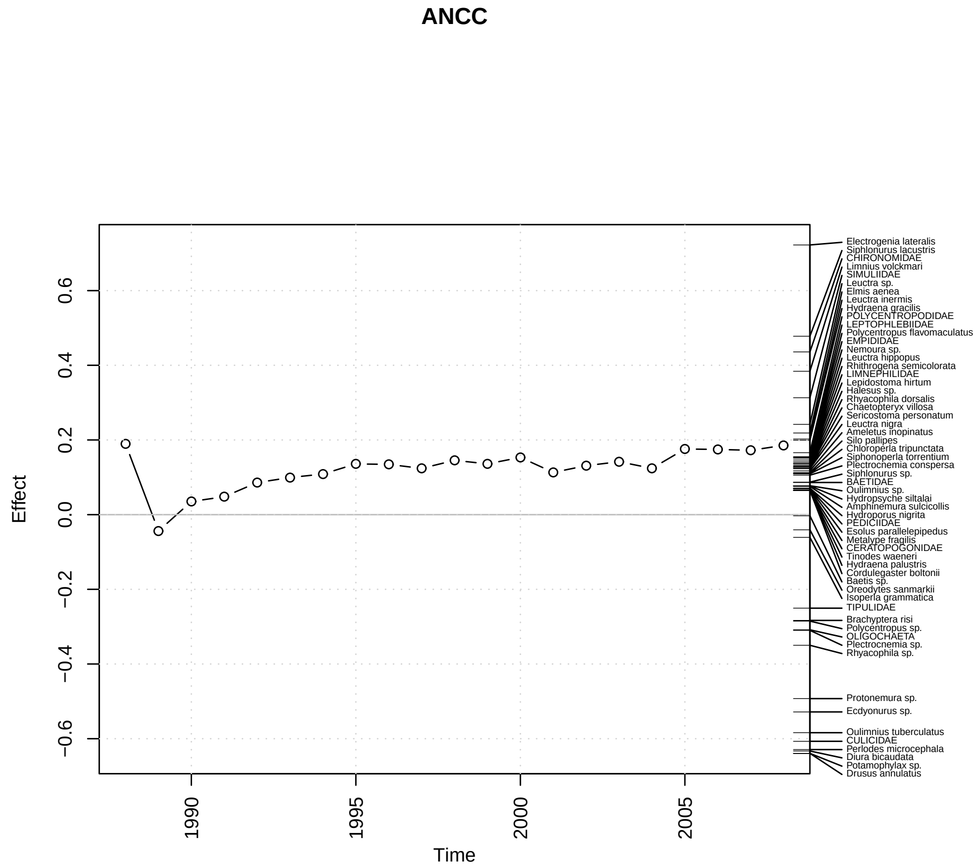

Figure 25: PRC plot of the macroinvertebrate data for Allt na Coire nan Con

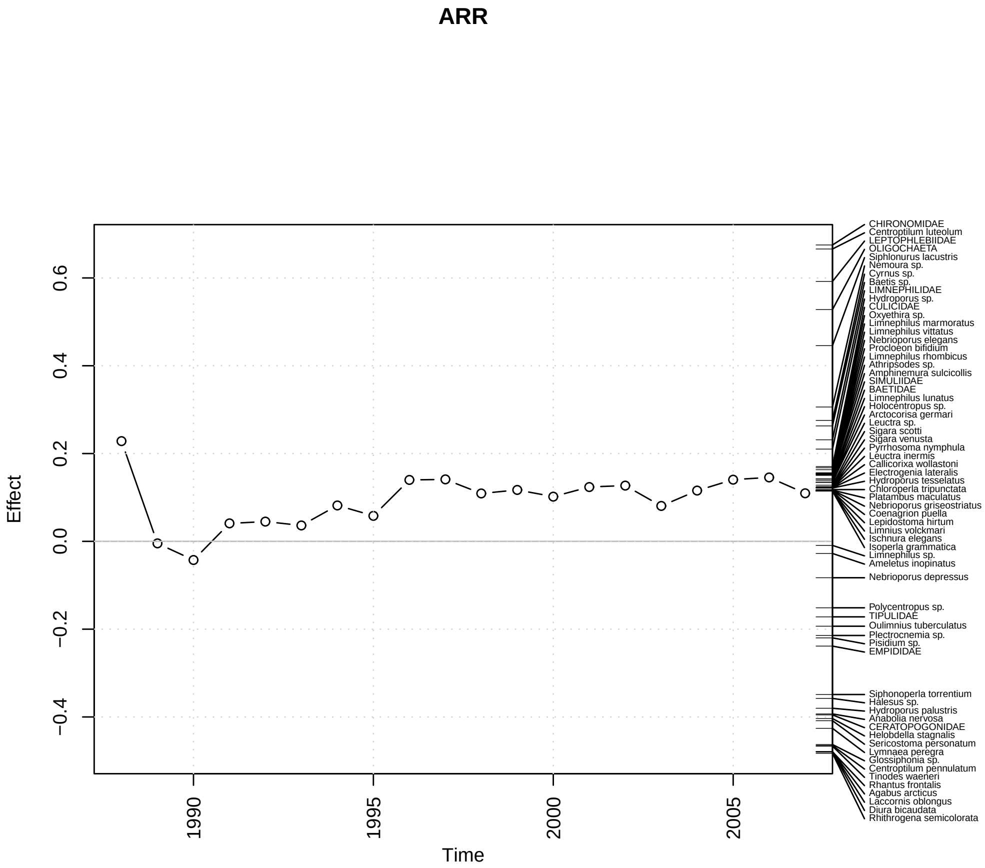

Figure 26: PRC plot of the macroinvertebrate data for Loch Coire nan Arr

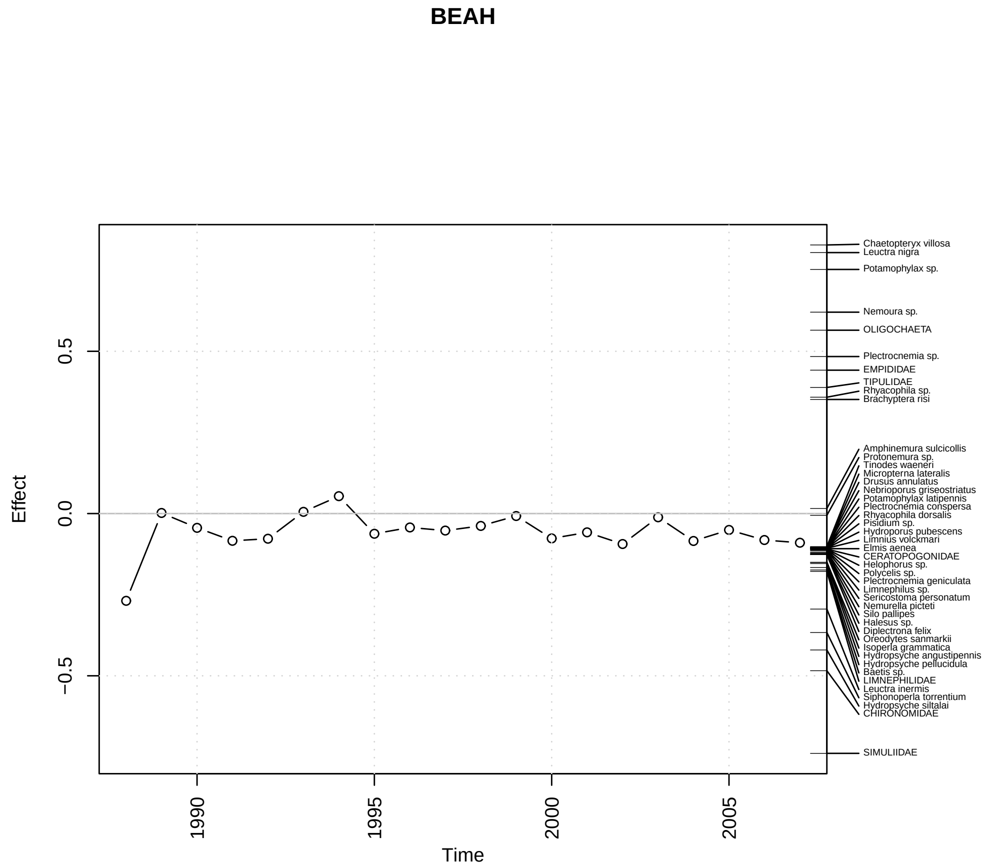

Figure 27: PRC plot of the macroinvertebrate data for Beagh's Burn

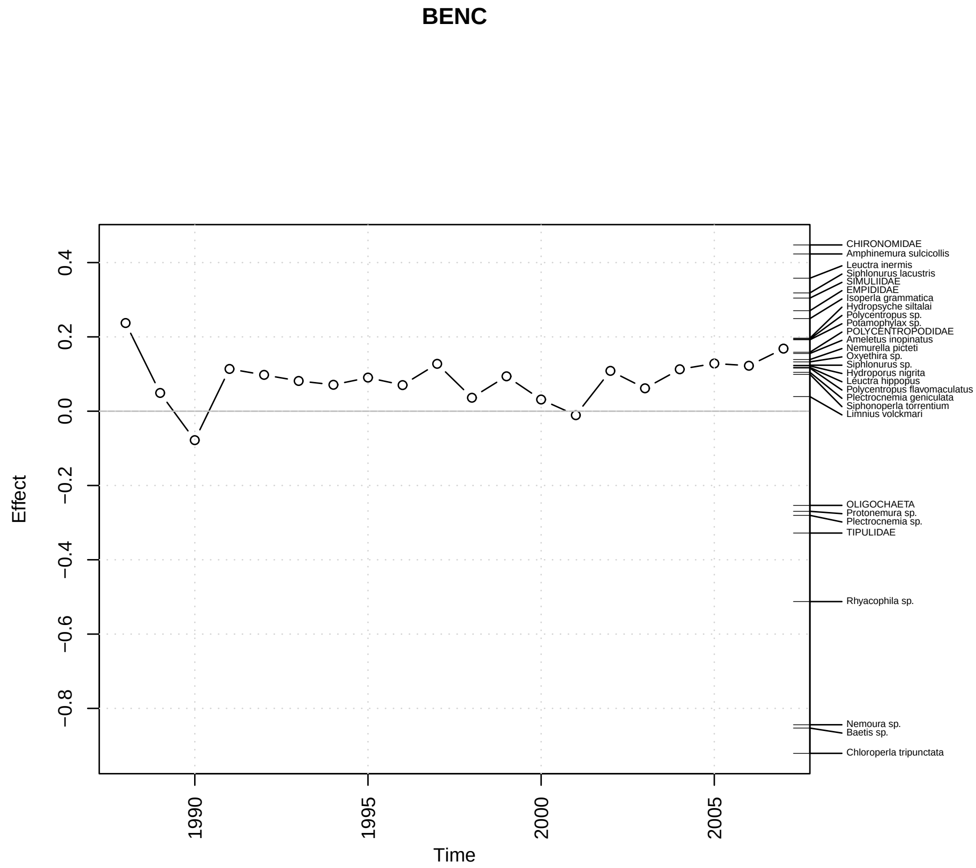

Figure 28: PRC plot of the macroinvertebrate data for Bencrom River

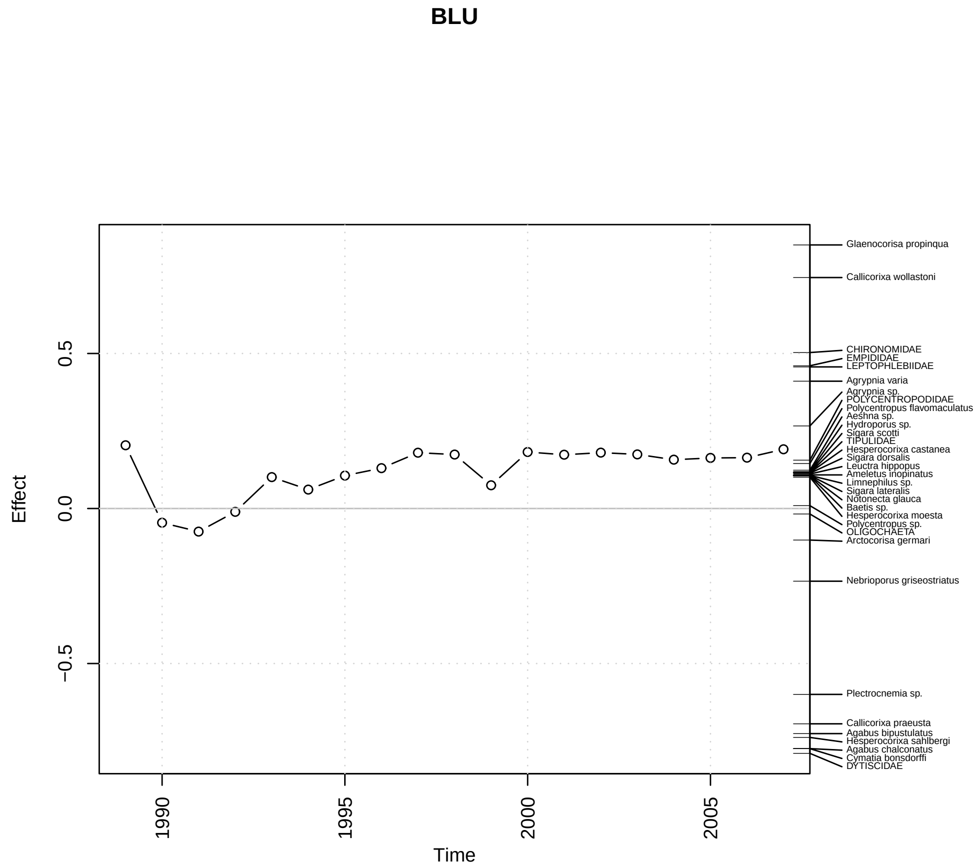

Figure 29: PRC plot of the macroinvertebrate data for Blue Lough

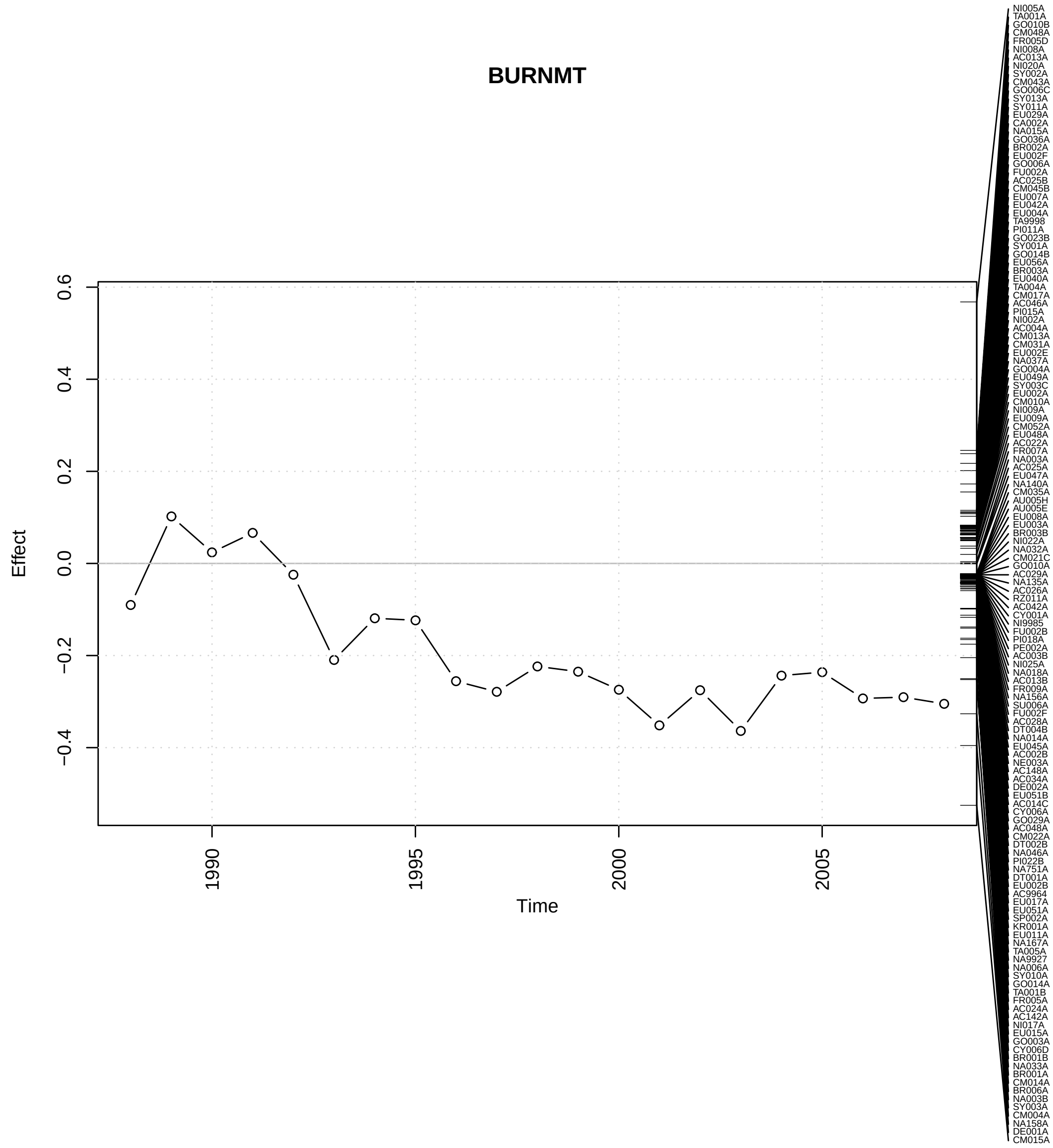

Figure 30: PRC plot of the macroinvertebrate data for Burnmoor Tarn

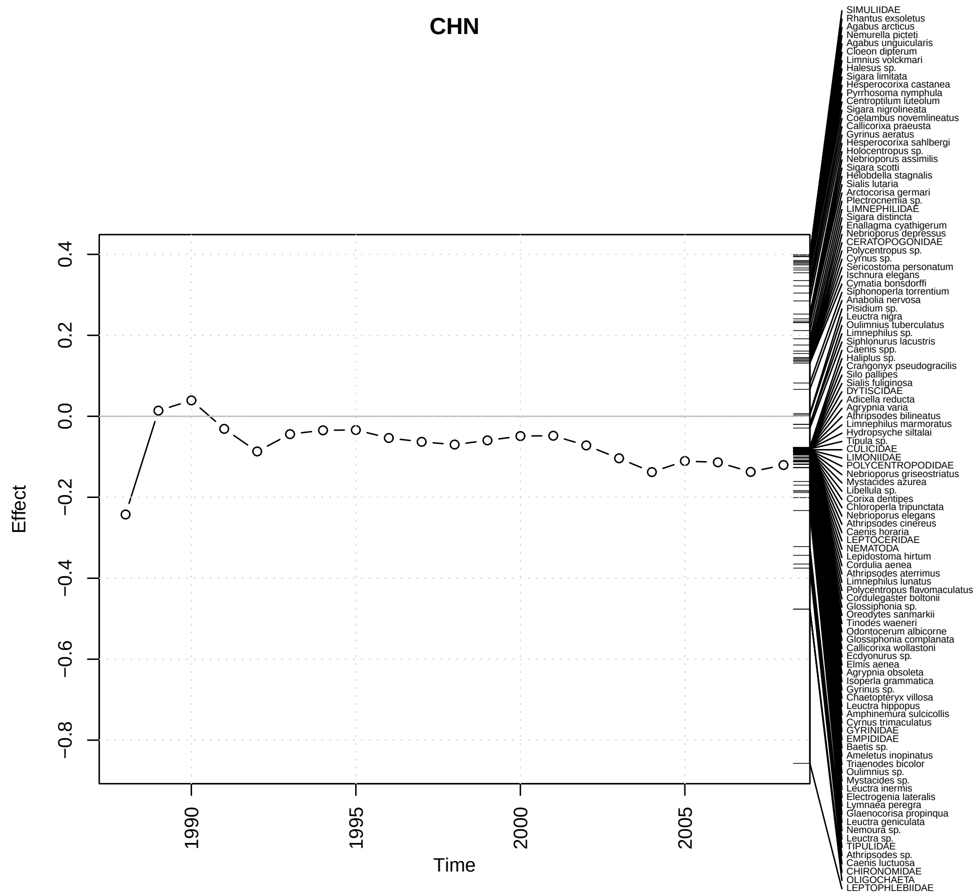

Figure 31: PRC plot of the macroinvertebrate data for Loch Chon

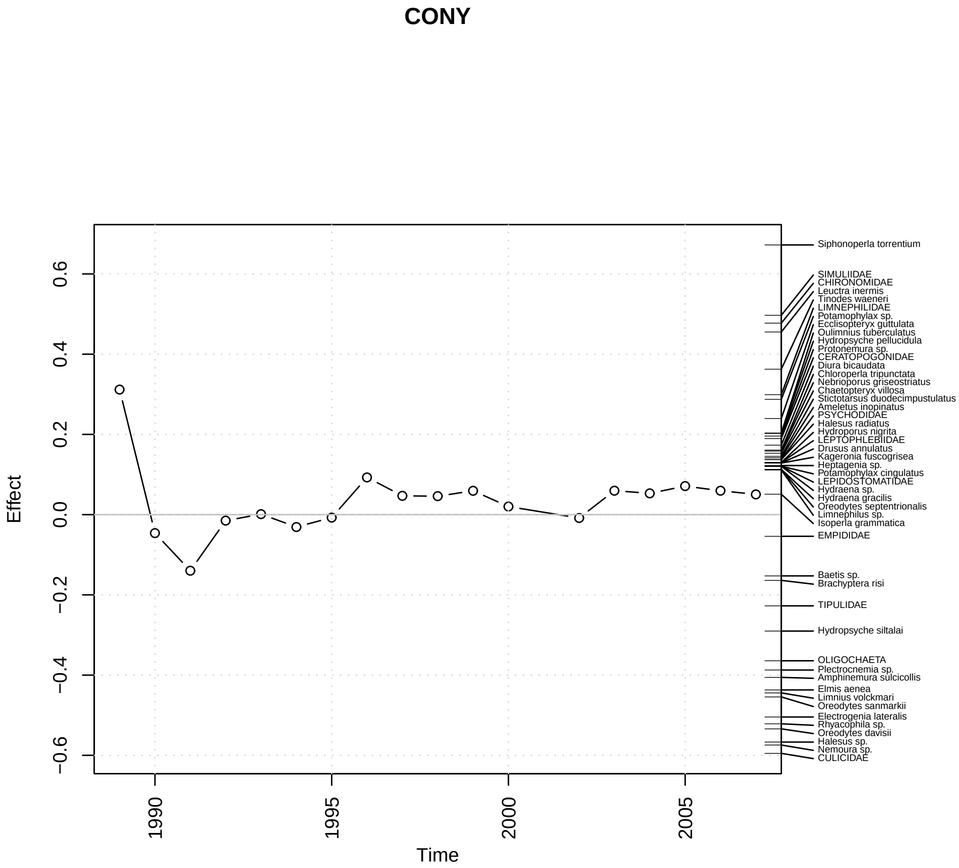

Figure 32: PRC plot of the macroinvertebrate data for Coneyglen Burn.

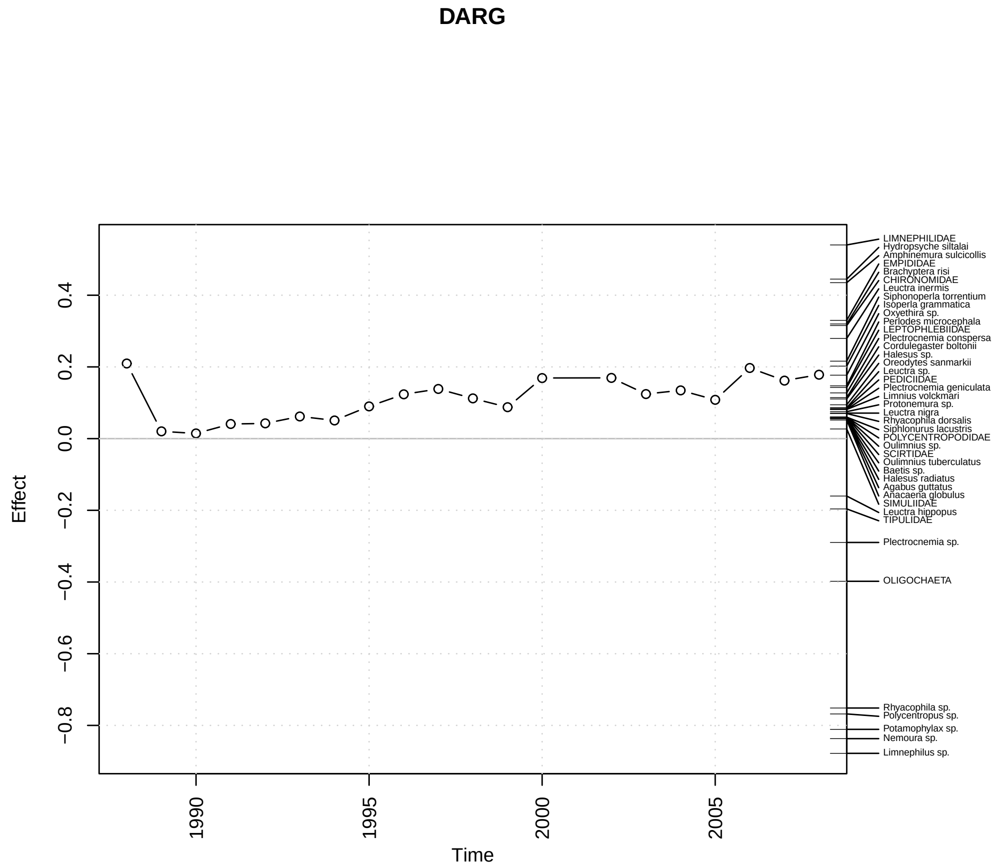

Figure 33: PRC plot of the macroinvertebrate data for Dargall Lane.

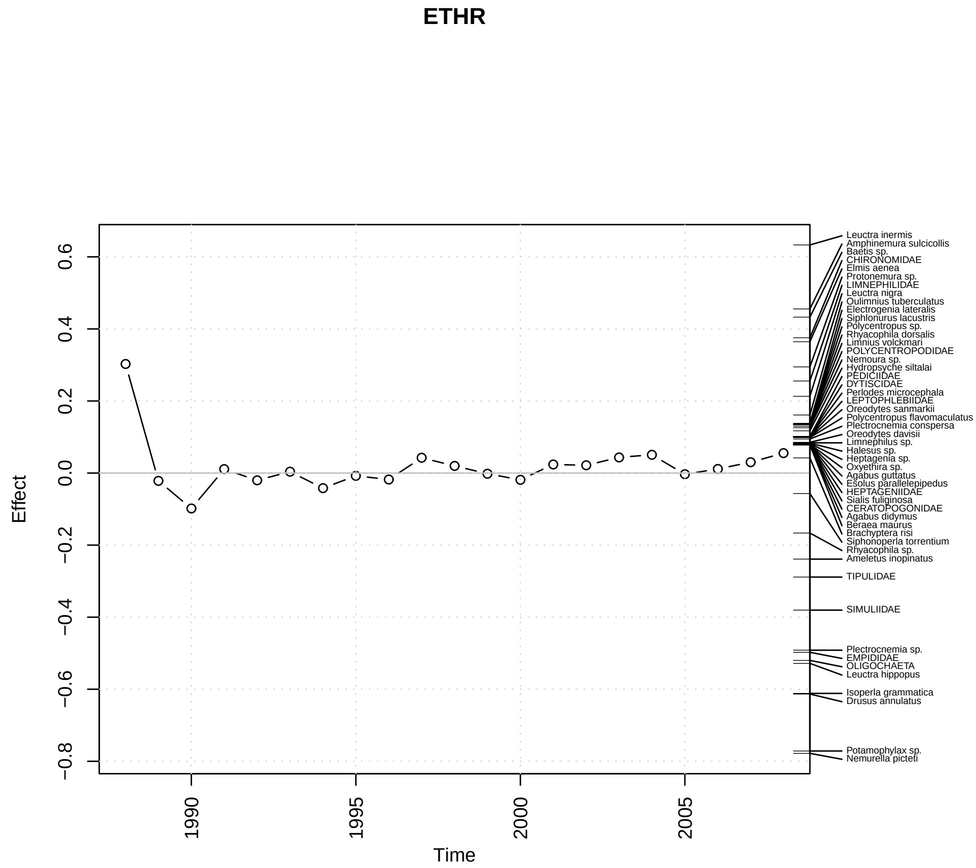

Figure 34: PRC plot of the macroinvertebrate data for River Etherow.

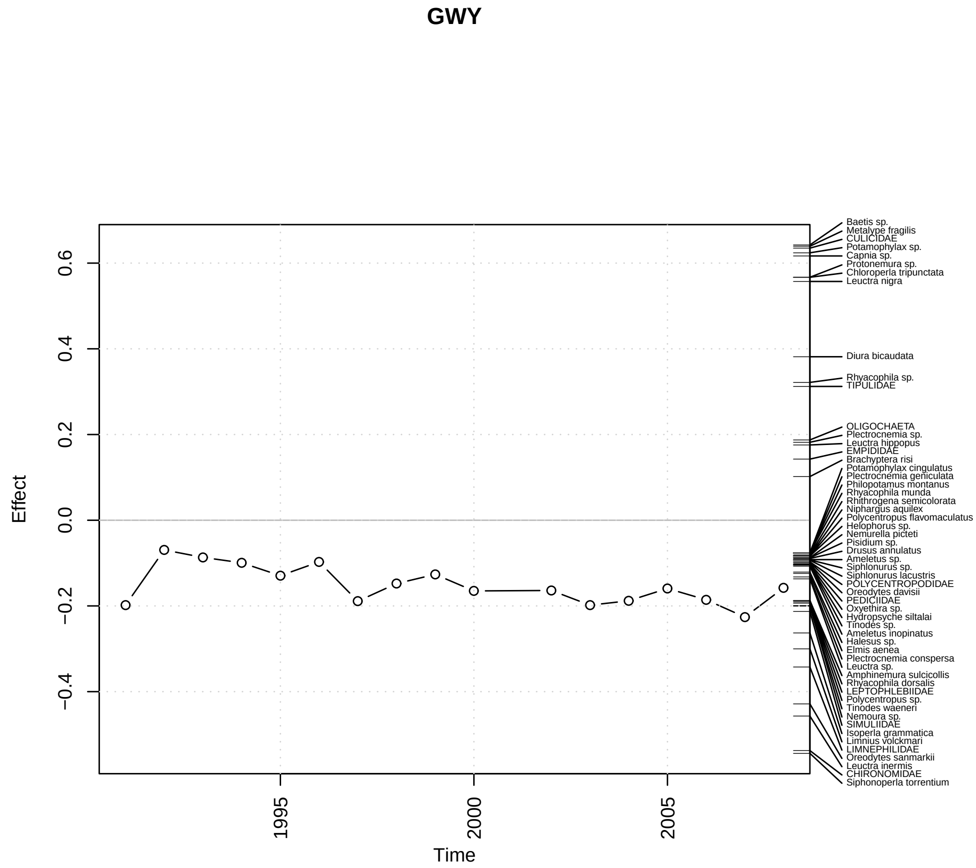

Figure 35: PRC plot of the macroinvertebrate data for Afon Gwy

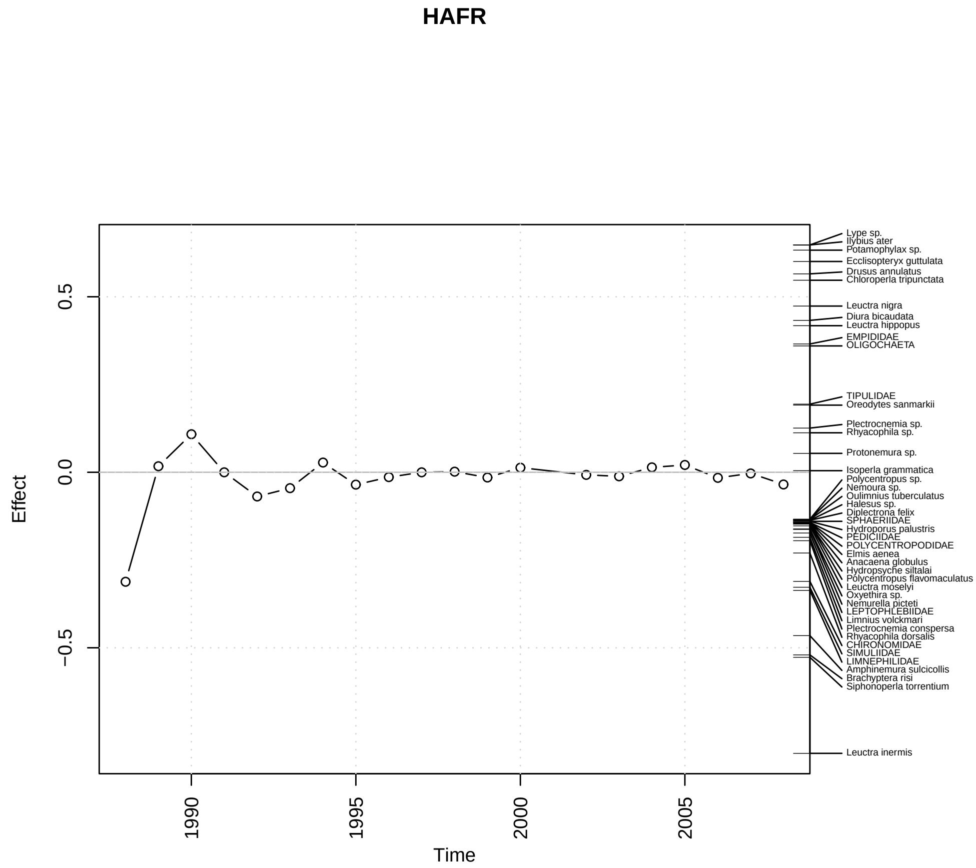

Figure 36: PRC plot of the macroinvertebrate data for Afon Hafren.

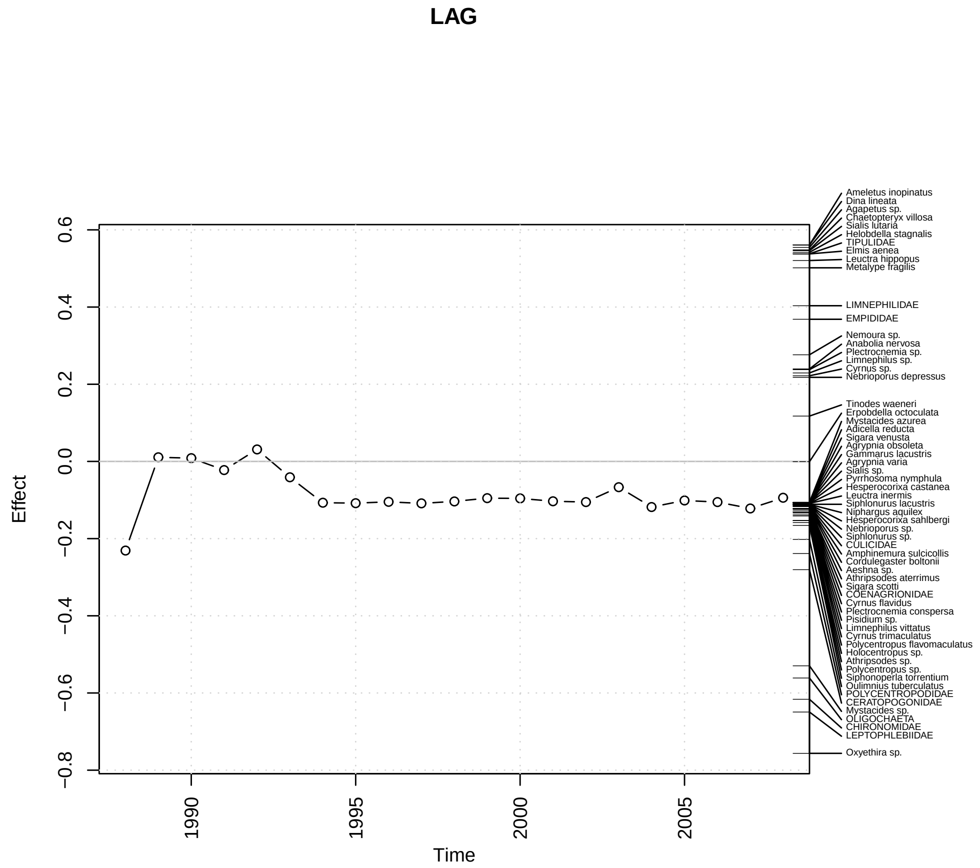

Figure 37: PRC plot of the macroinvertebrate data for Llyn Llagi.

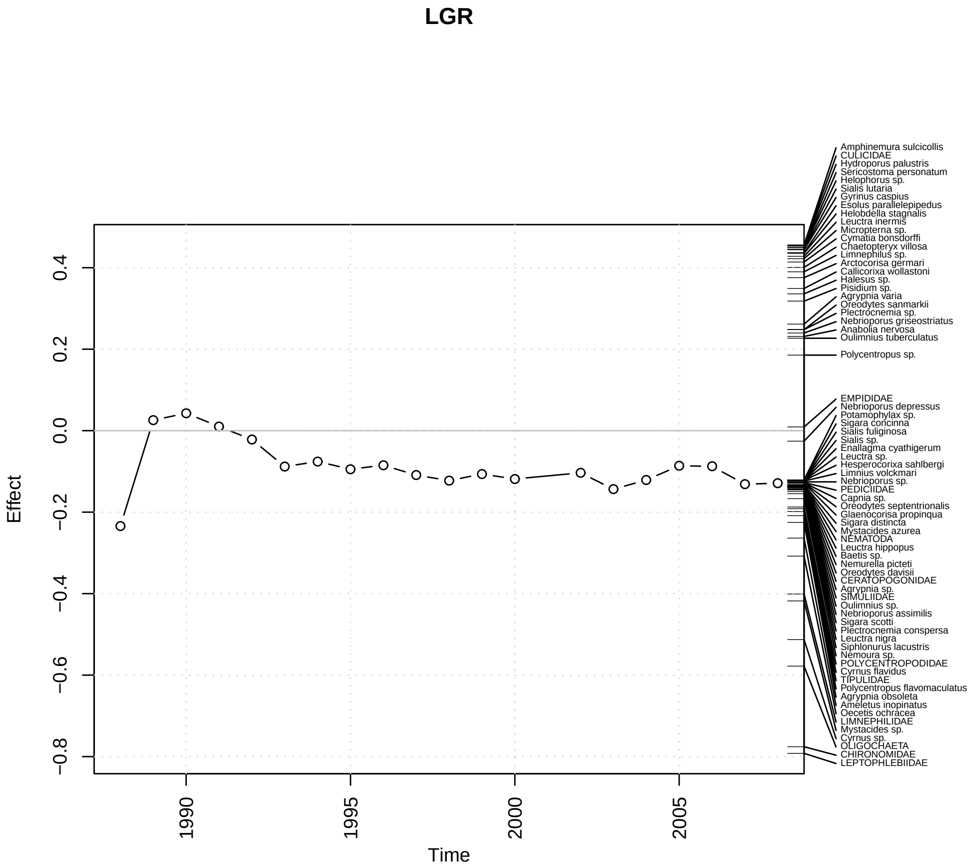

Figure 38: PRC plot of the macroinvertebrate data for Loch Grannoch.

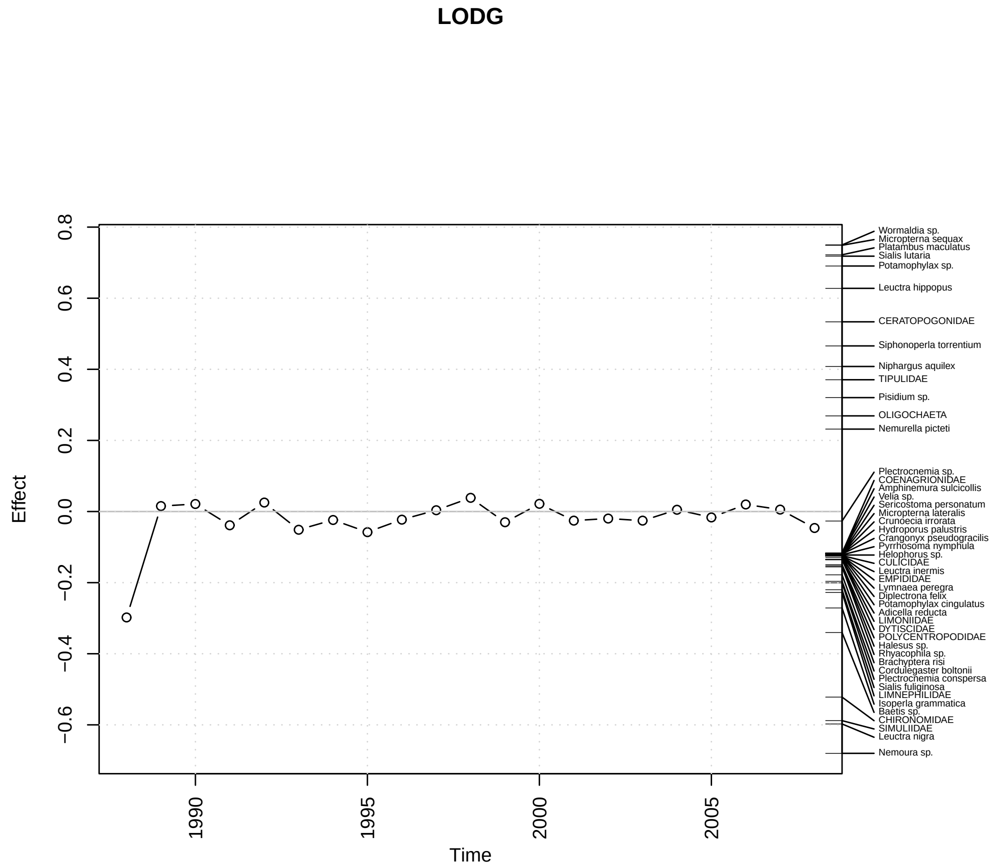

Figure 39: RDA PRC plot of the macroinvertebrate data for Old Lodge.

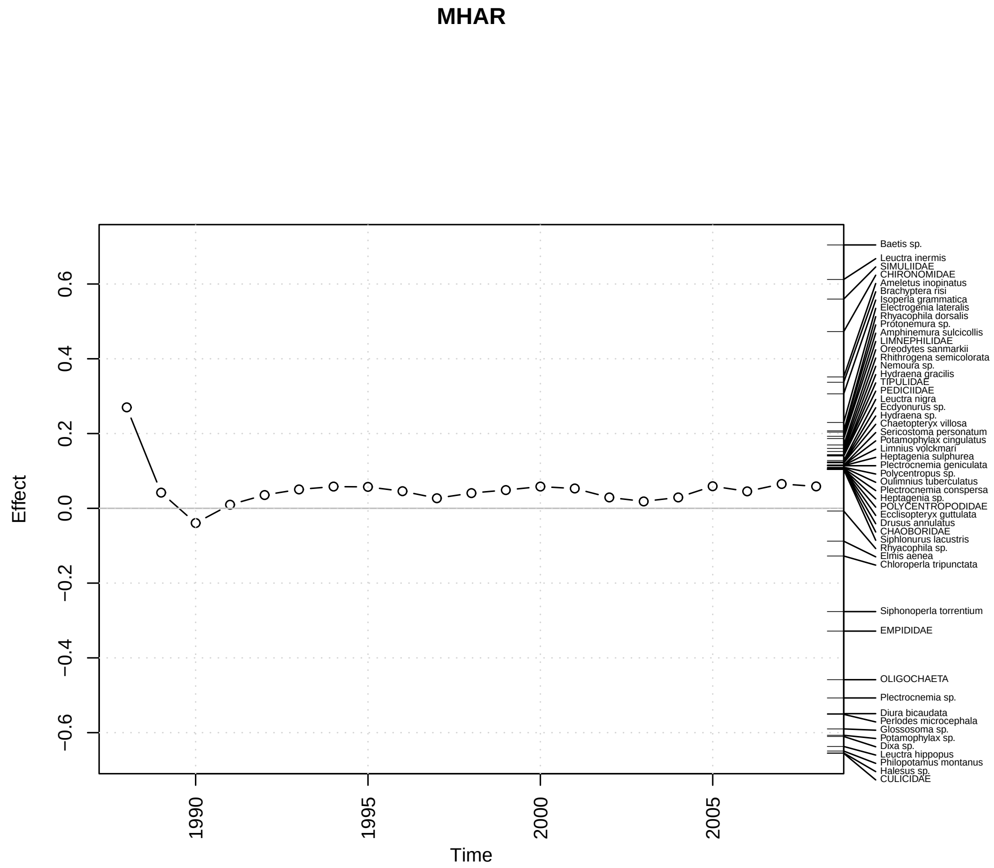

Figure 40: PRC plot of the macroinvertebrate data for Allt a' Mharcaidh.

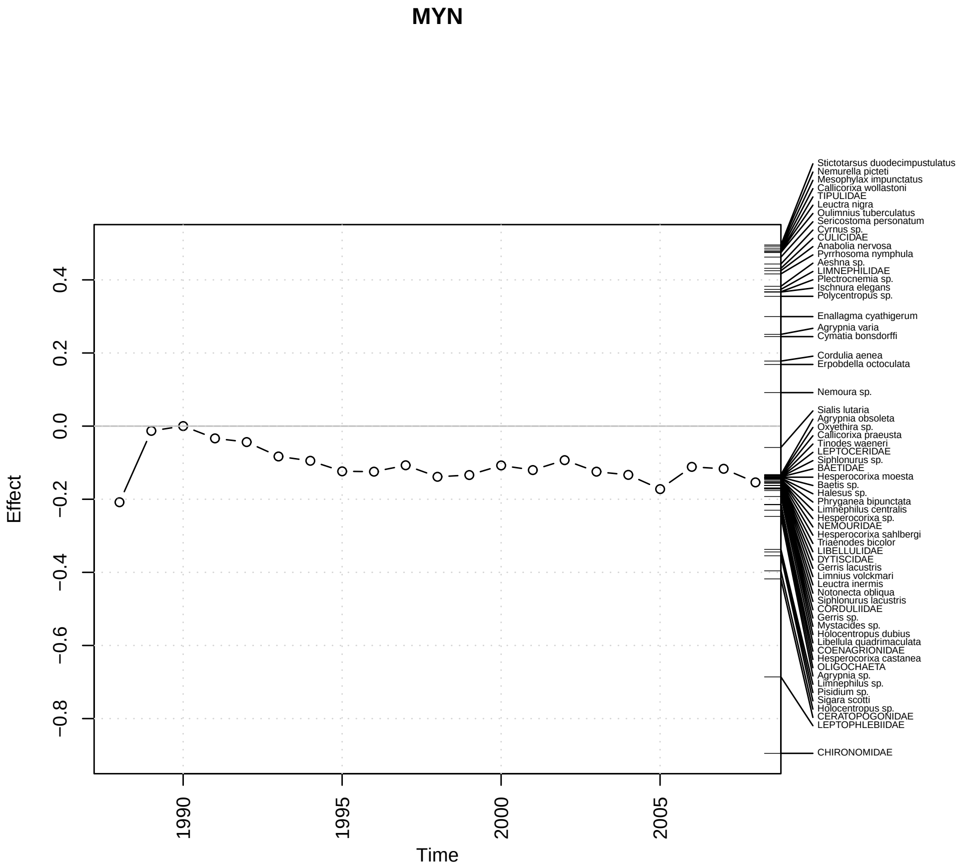

Figure 41: PRC plot of the macroinvertebrate data for Llyn Cwm Mynach.

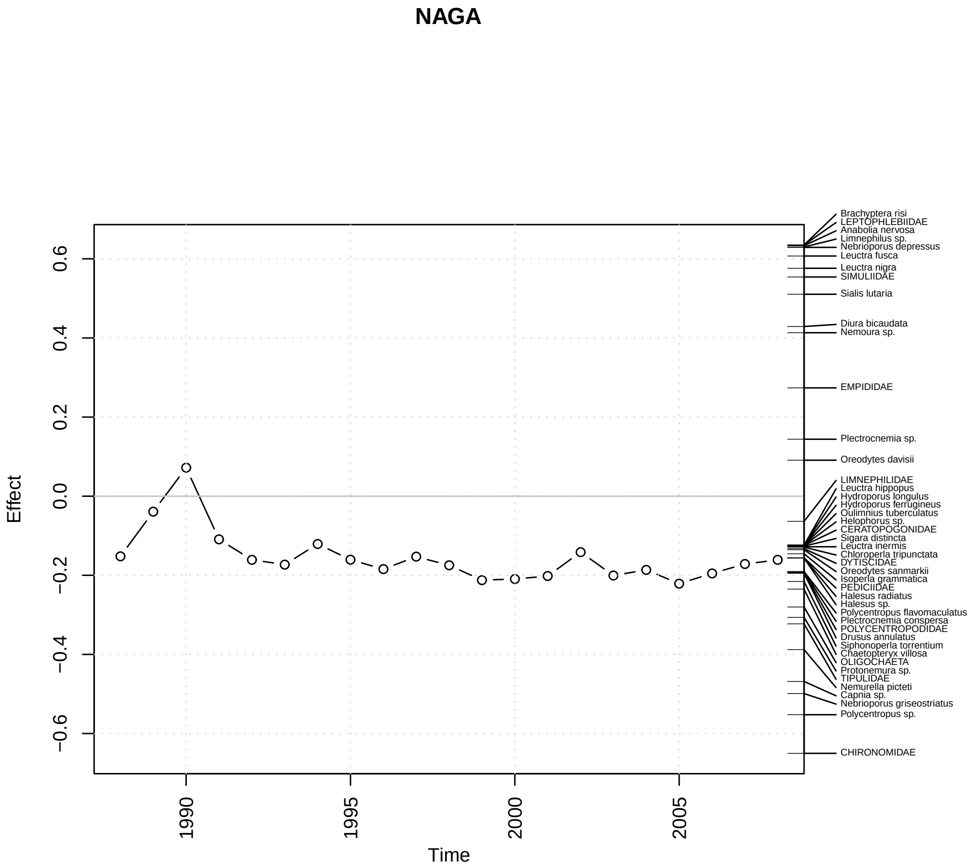

Figure 42: PRC plot of the macroinvertebrate data for Lochnagar.

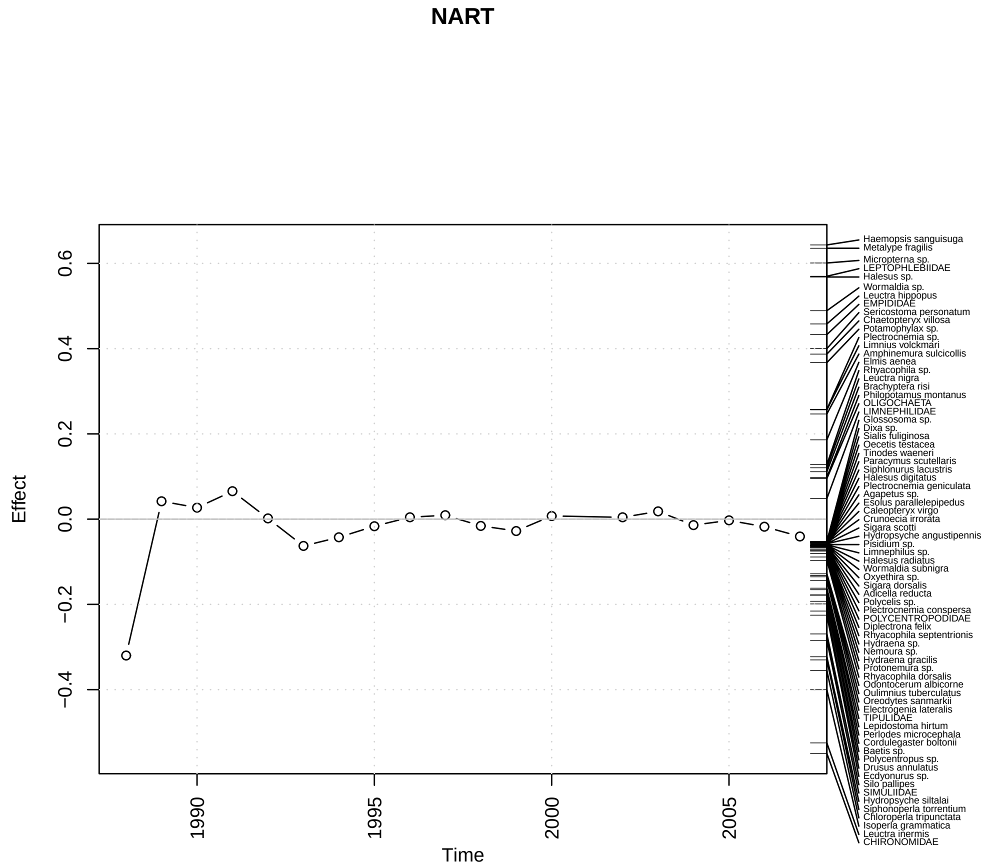

Figure 43: PRC plot of the macroinvertebrate data for Narrator Brook.

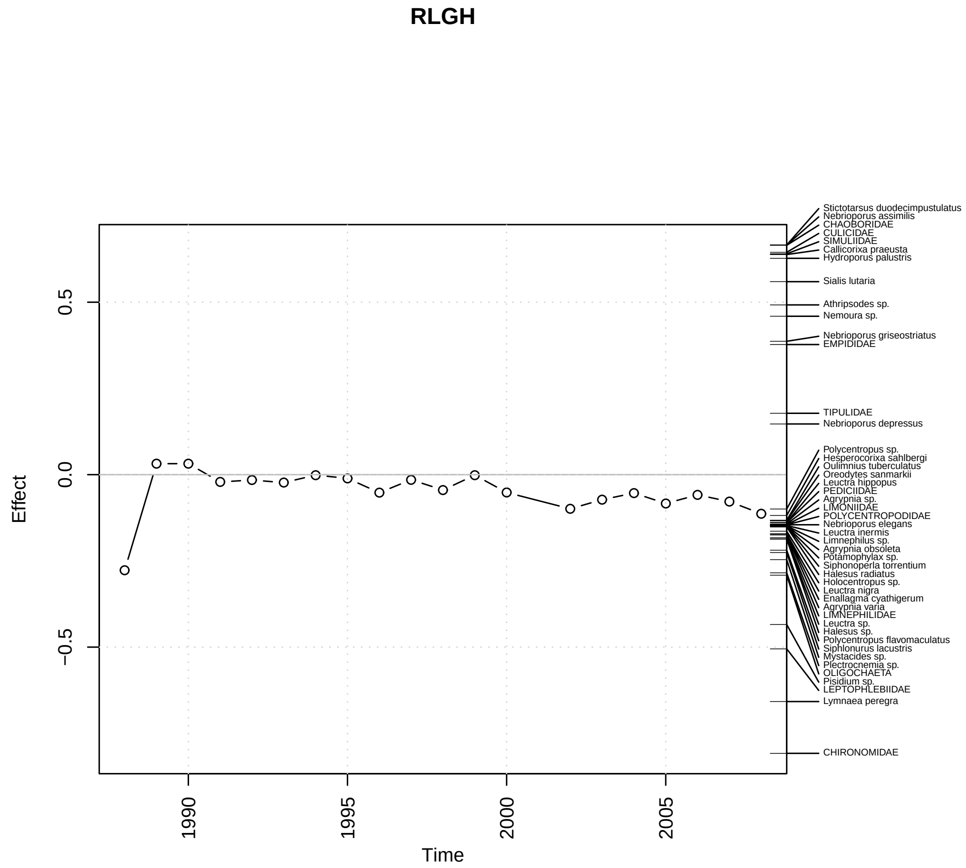

Figure 44: PRC plot of the macroinvertebrate data for Round Loch of Glenhead.

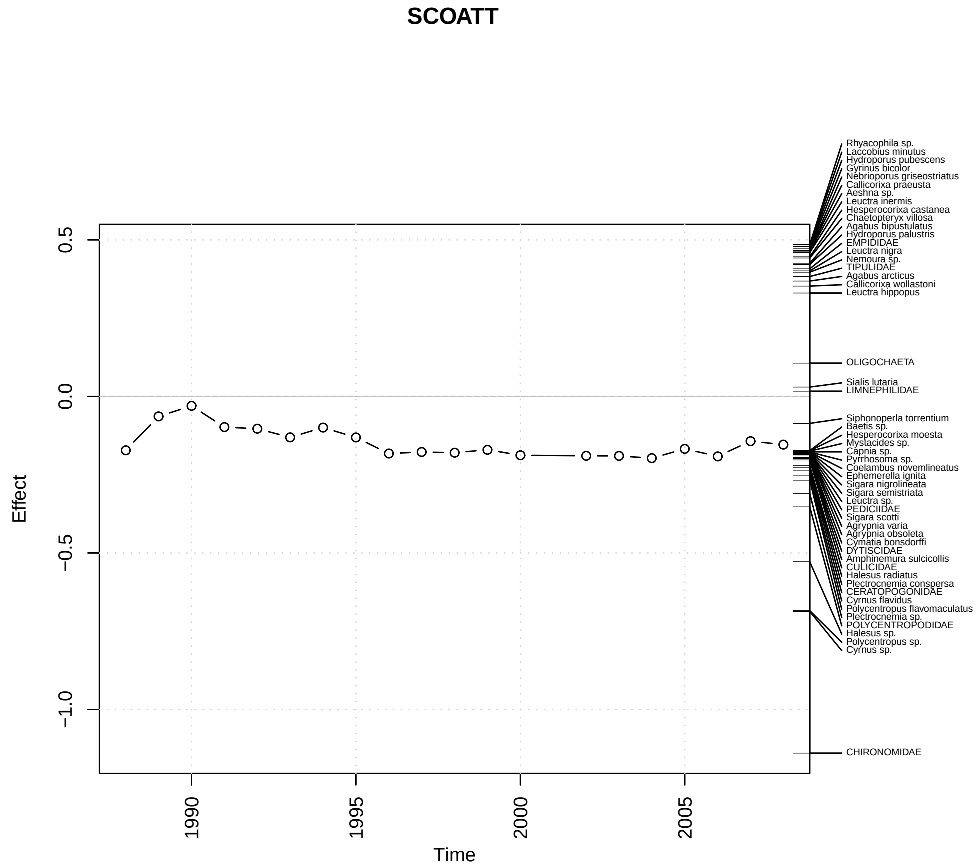

Figure 45: PRC plot of the macroinvertebrate data for Scoat Tarn.

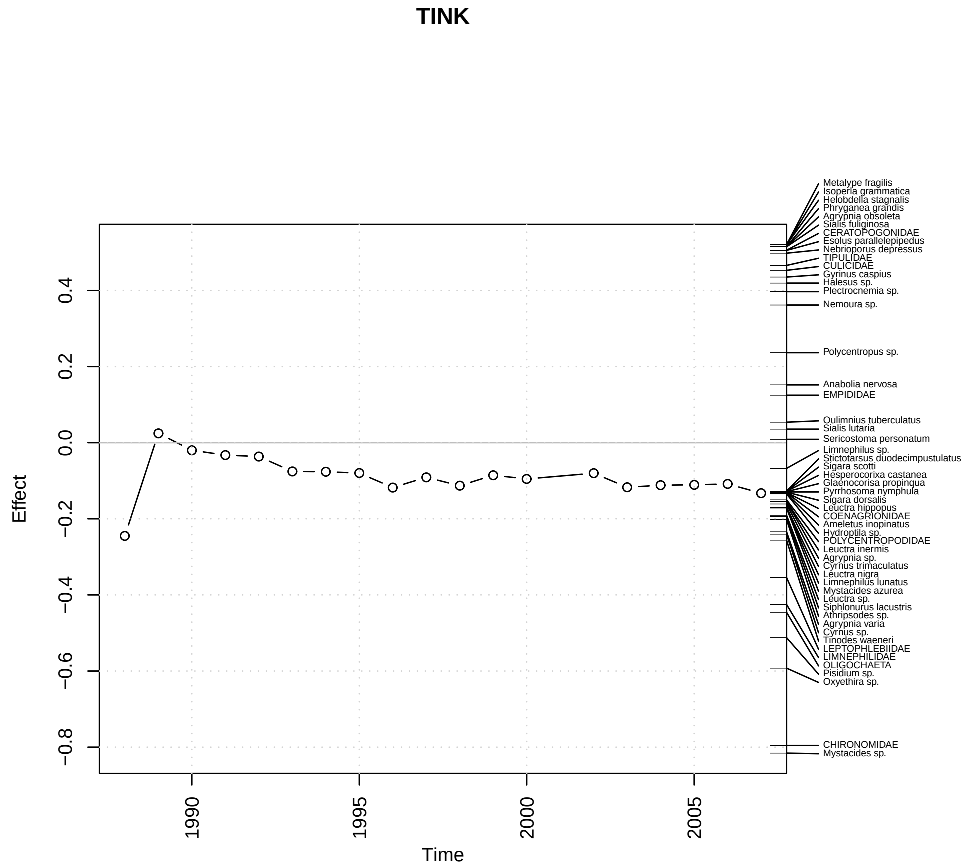

Figure 46: PRC plot of the macroinvertebrate data for Loch Tinker.

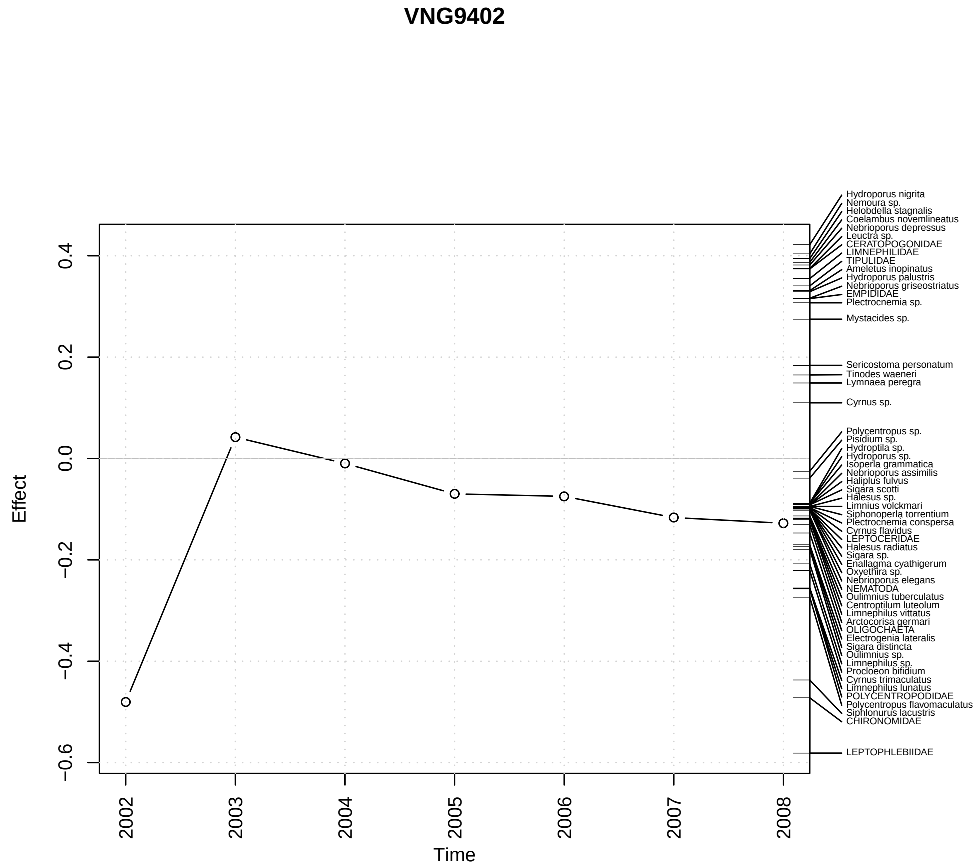

Figure 47: PRC plot of the macroinvertebrate data for Loch Coire Fionnaraich

Table 1: Macroinvertebrate species codes and names used in the diagrams

Code	ECN Code	Taxon Name
3120200	5110200	Polycelis sp.
10000000	10000000	NEMATODA
13070000	16220000	LYMNAEIDAE
13070107	16220104	Lymnaea peregra
13100101	16250101	Acroloxus lacustris
13100201	16240101	Ancylus uviatilis
14030000	17130000	SPHAERIIDAE
14030200	17130200	Pisidium sp.
16000000	20000000	OLIGOCHAETA
17020000	22120000	GLOSSIPHONIIDAE
17020300	22120400	Glossiphonia sp.
17020302	22120401	Glossiphonia complanata
17020501	22120701	Helobdella stagnalis
17030101	22210101	Haemopsis sanguisuga
17040102	22310101	Erpobdella octoculata
17040201	22310201	Dina lineata
28070101	37130101	Crangonyx pseudogracilis
28070303	37140203	Gammarus lacustris
28070501	37150201	Niphargus aquilex
30010100	40110100	Siphlonurus sp.
30010102	40110103	Siphlonurus lacustris
30010200	40110200	Ameletus sp.
30010201	40110201	Ameletus inopinatus
30020000	40120000	BAETIDAE
30020100	40120100	Baetis sp.
30020201	40120201	Centroptilum luteolum
30020202	40120202	Centroptilum pennulatum
30020301	40120301	Cloeon dipterum
30020401	40120401	Procloeon bidium
30030000	40130000	HEPTAGENIIDAE
30030101	40130102	Rhithrogena semicolorata
30030200	40130200	Heptagenia sp.
30030201	40130204	Heptagenia sulphurea
30030203	40130601	Kageronia fuscogrisea
30030204	40130202	Electrogenia lateralis
30030400	40130400	Ecdyonurus sp.
30040000	40210000	LEPTOPHLEBIIDAE
30050101	40410101	Ephemerella ignita
30080200	40510200	Caenis spp.
30080204	40510201	Caenis horaria
30080206	40510202	Caenis luctuosa
31010302	41110302	Brachyptera risi
31020000	41120000	NEMOURIDAE
31020100	41120100	Protonemura sp.
31020202	41120202	Amphinemura sulcicollis
31020301	41120301	Nemurella picteti
31020400	41120400	Nemoura sp.
31030100	41130100	Leuctra sp.

31030101 41130102 Leuctra geniculata
31030102 41130104 Leuctra inermis
31030103 41130103 Leuctra hippopus
31030104 41130106 Leuctra nigra
31030105 41130101 Leuctra fusca
31030106 41130105 Leuctra moselyi
31040100 41140100 Capnia sp.
31050201 41210201 Perlodes microcephala
31050301 41210301 Diura bicaudata
31050401 41210401 Isoperla grammatica
31070101 41230102 Siphonoperla torrentium
31070102 41230103 Chloroperla tripunctata
32020000 42120000 COENAGRIONIDAE
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32040102 42140102 Caleopteryx virgo
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32070200 42230200 Aeshna sp.
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32090000 42250000 LIBELLULIDAE
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33040100 43220100 Velia sp.
33050100 43230100 Gerris sp.
33050106 43230114 Gerris lacustris
33090101 43510101 Notonecta glauca
33090103 43510103 Notonecta obliqua
33110201 43610301 Cymatia bonsdor
33110301 43610401 Glaenocorisa propinqua
33110401 43610501 Callicorixa praeusta
33110402 43610502 Callicorixa wollastoni
33110501 43610602 Corixa dentipes
33110600 43610700 Hesperocorixa sp.
33110602 43610704 Hesperocorixa sahlbergi
33110603 43610701 Hesperocorixa castanea
33110604 43610703 Hesperocorixa moesta
33110702 43610802 Arctocorisa germari
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33110803 43610921 Sigara distincta
33110807 43610925 Sigara scotti
33110808 43610941 Sigara lateralis
33110809 43610951 Sigara nigrolineata
33110810 43610961 Sigara concinna
33110811 43610971 Sigara limitata
33110812 43610972 Sigara semistriata
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35030928 45140831 Hydroporus tesselatus
35030930 45140807 Hydroporus ferrugineus
35031001 45141701 Laccornis oblongus
35031101 45142011 Agabus guttatus
35031107 45142022 Agabus unguicularis
35031108 45142009 Agabus didymus
35031115 45142002 Agabus arcticus
35031117 45142006 Agabus chalconatus
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35031502 45142203 Rhantus exsoletus
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35051001 45311302 Anacaena globulus
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38080510 48341719 Limnephilus lunatus
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38081200 48340600 Halesus sp.

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38081504	48341002	Micropterna sequax
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38081901	48341301	Chaetopteryx villosa
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38120107	48410104	Athripsodes cinereus
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38120601	48410904	Oecetis ochracea
38120605	48410905	Oecetis testacea
38130201	48350202	Silo pallipes
38140000	48330000	LEPIDOSTOMATIDAE
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40010008	50130000	LIMONIIDAE
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40020000	50210000	PSYCHODIDAE
40040100	50310100	Dixa sp.
40050000	50320000	CHAOBORIDAE
40060000	50330000	CULICIDAE
40080000	50350000	CERATOPOGONIDAE
40090000	50400000	CHIRONOMIDAE
40150000	50360000	SIMULIIDAE
40170000	50710000	EMPIDIDAE
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50140000	50140000	PEDICIIDAE

APPENDIX 6 Time trajectory for each AWMN lake showing the post-1850 changes in diatom assemblages

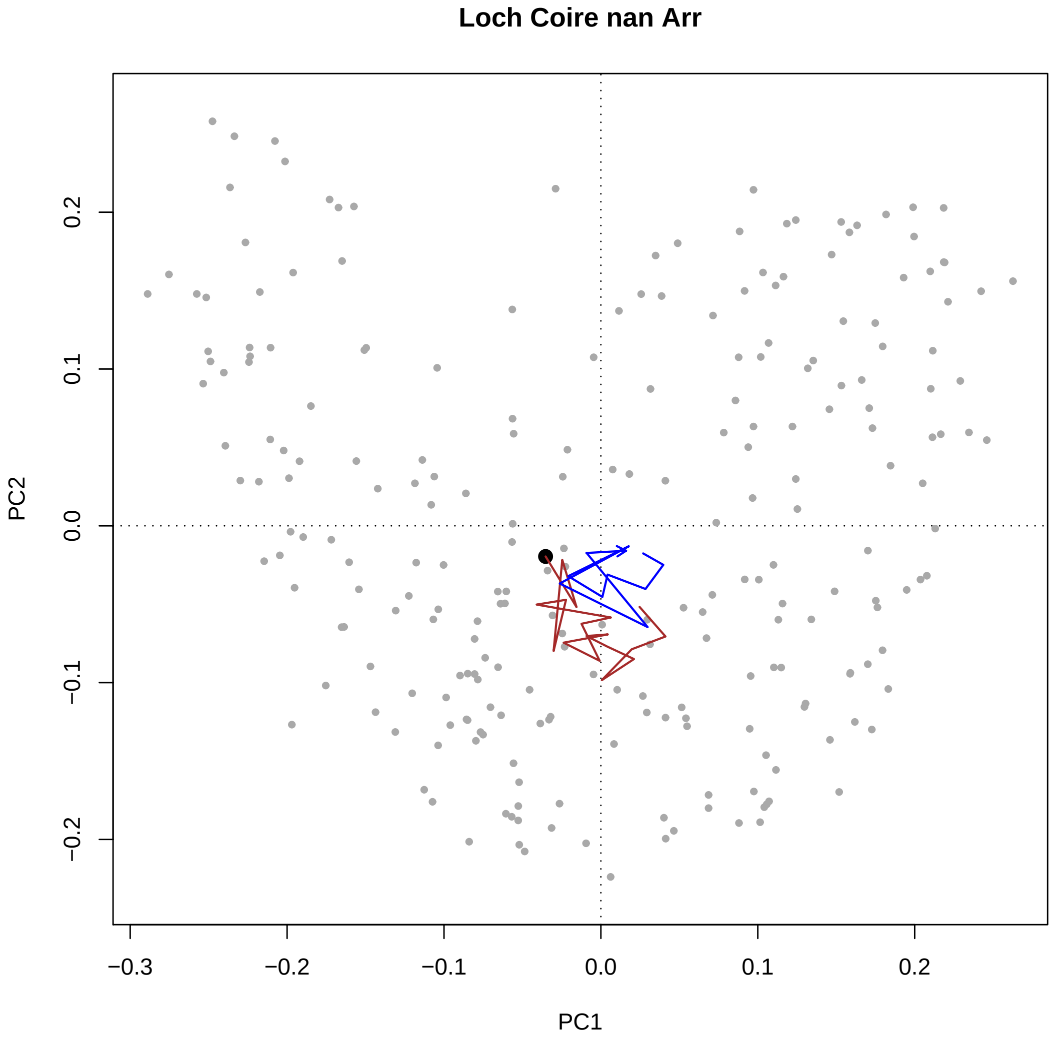

Figure 1: "Recovery" trajectories for diatom assemblages at Loch Coire nan Arr based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

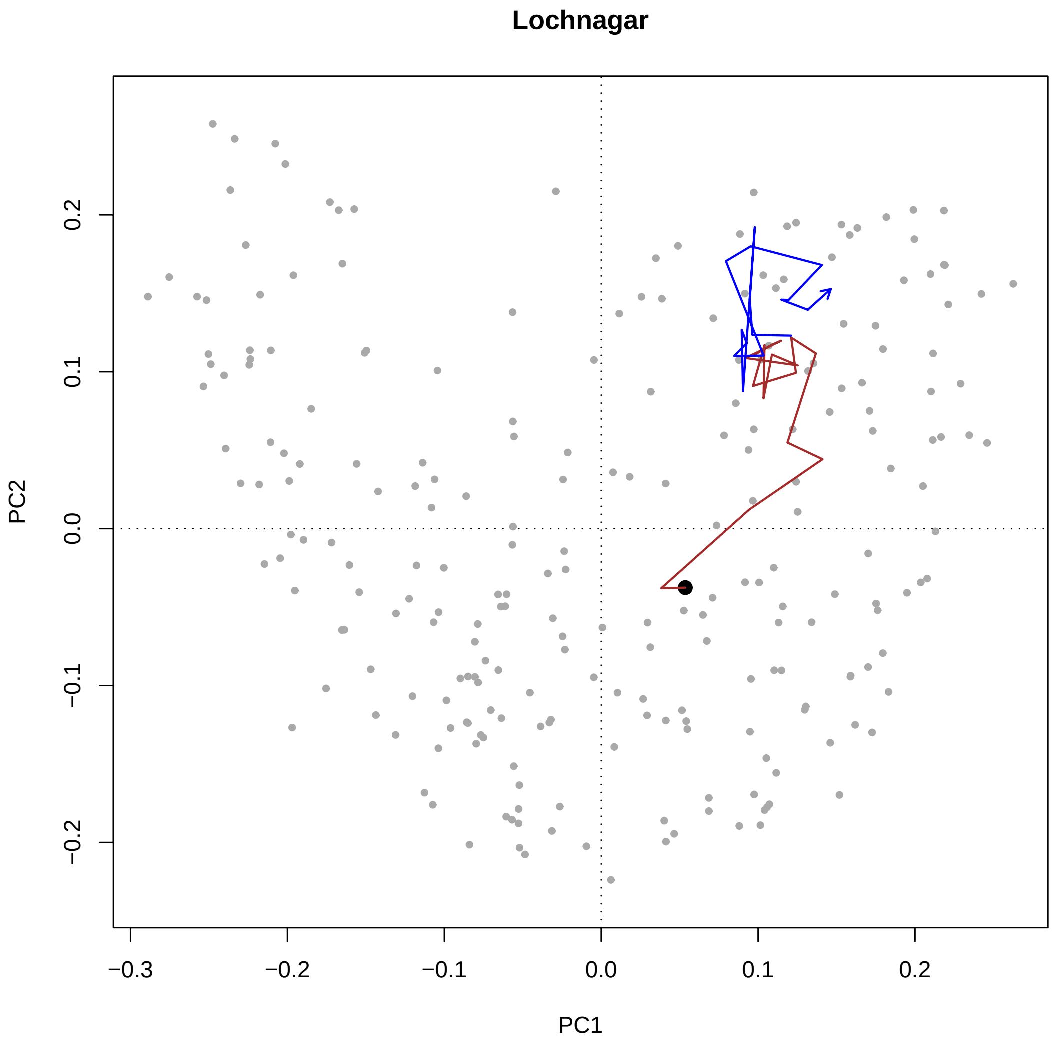

Figure 2: "Recovery" trajectories for diatom assemblages at Lochnagar based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

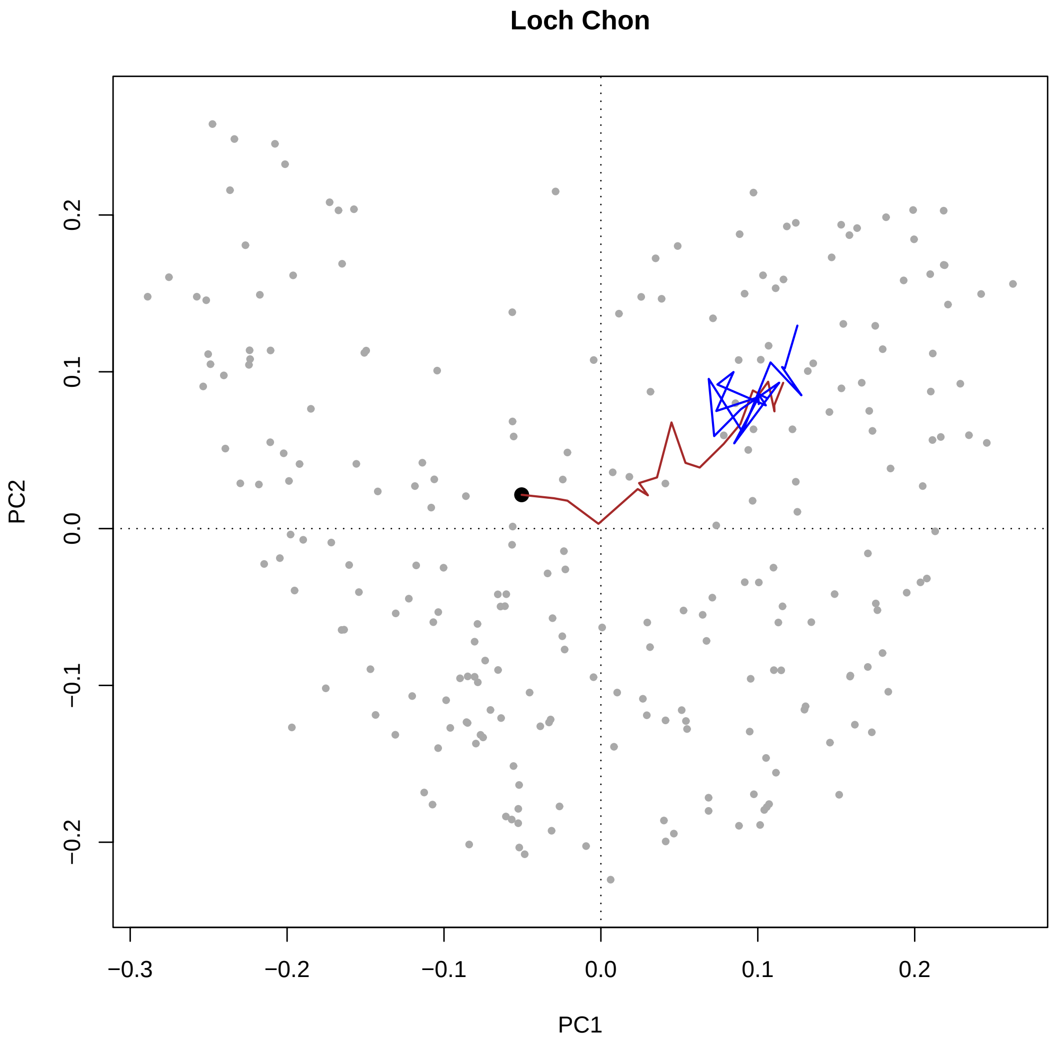

Figure 3: "Recovery" trajectories for diatom assemblages at Loch Chon based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

Loch Tinker

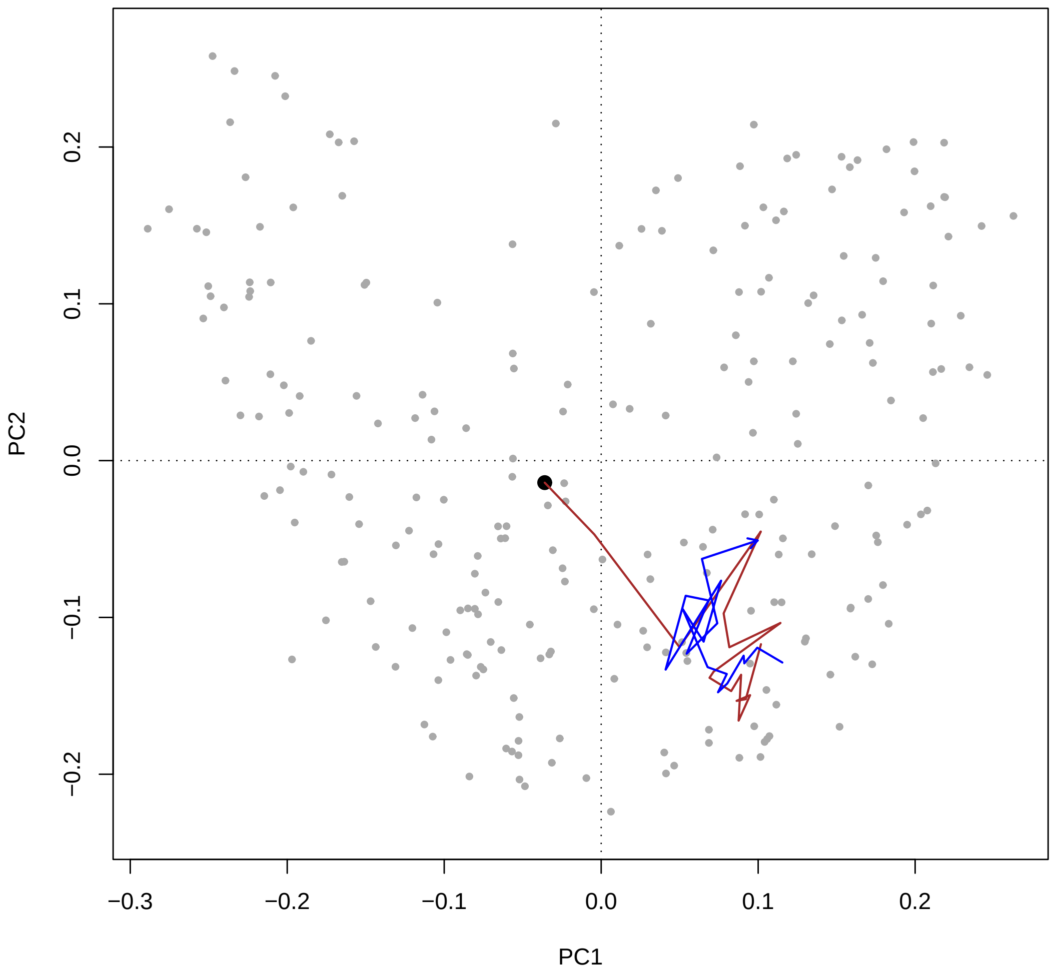

Figure 4: "Recovery" trajectories for diatom assemblages at Loch Tinker based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

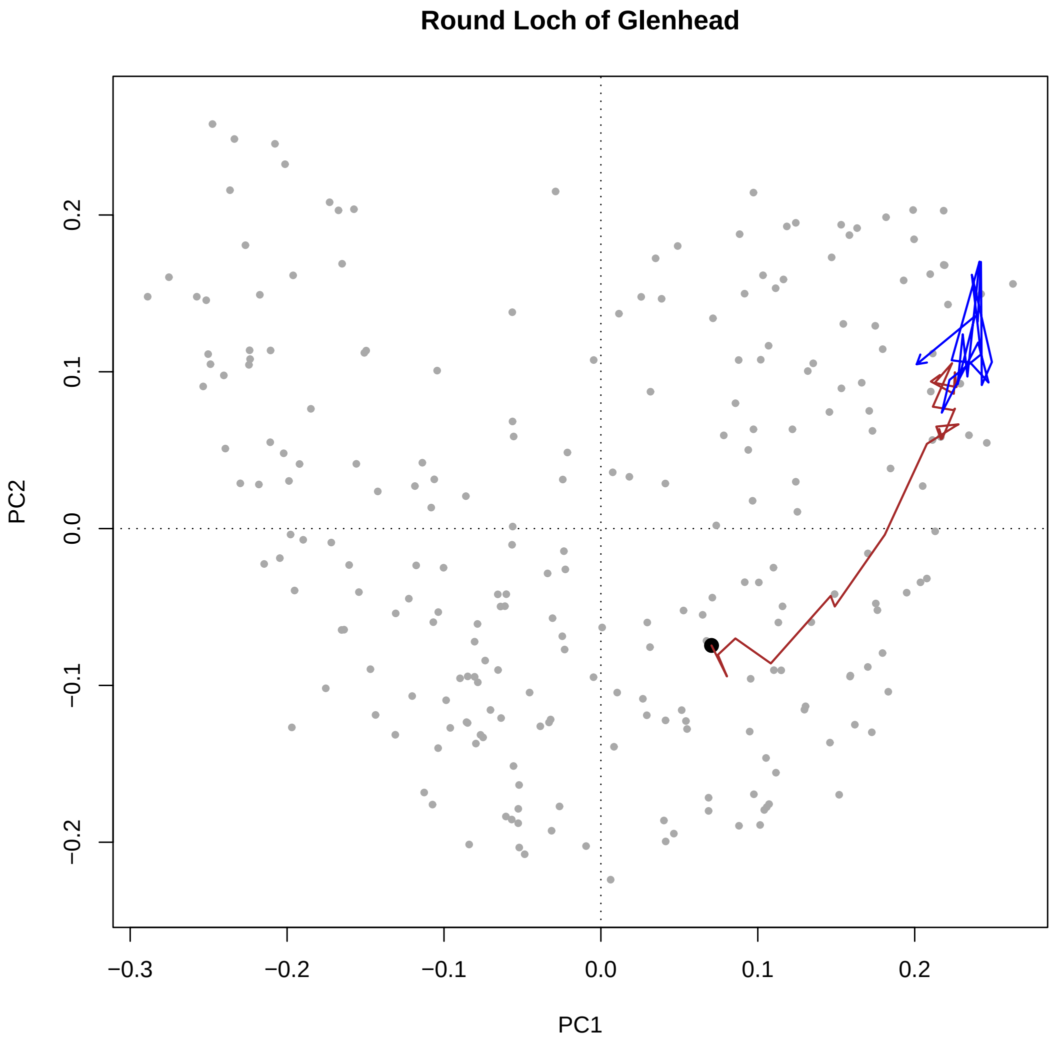

Figure 5: "Recovery" trajectories for diatom assemblages at Round Loch of Glenhead based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

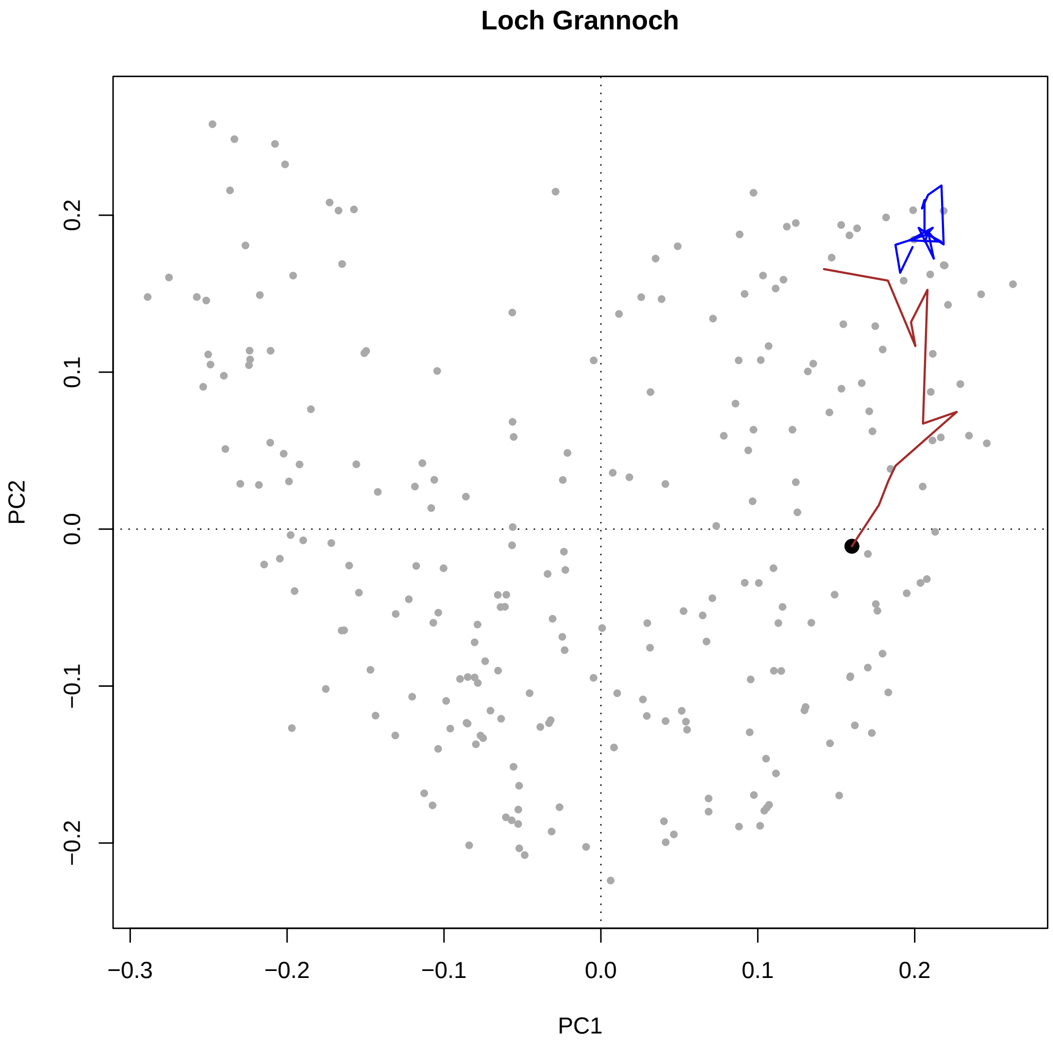

Figure 6: "Recovery" trajectories for diatom assemblages at Loch Grannoch based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

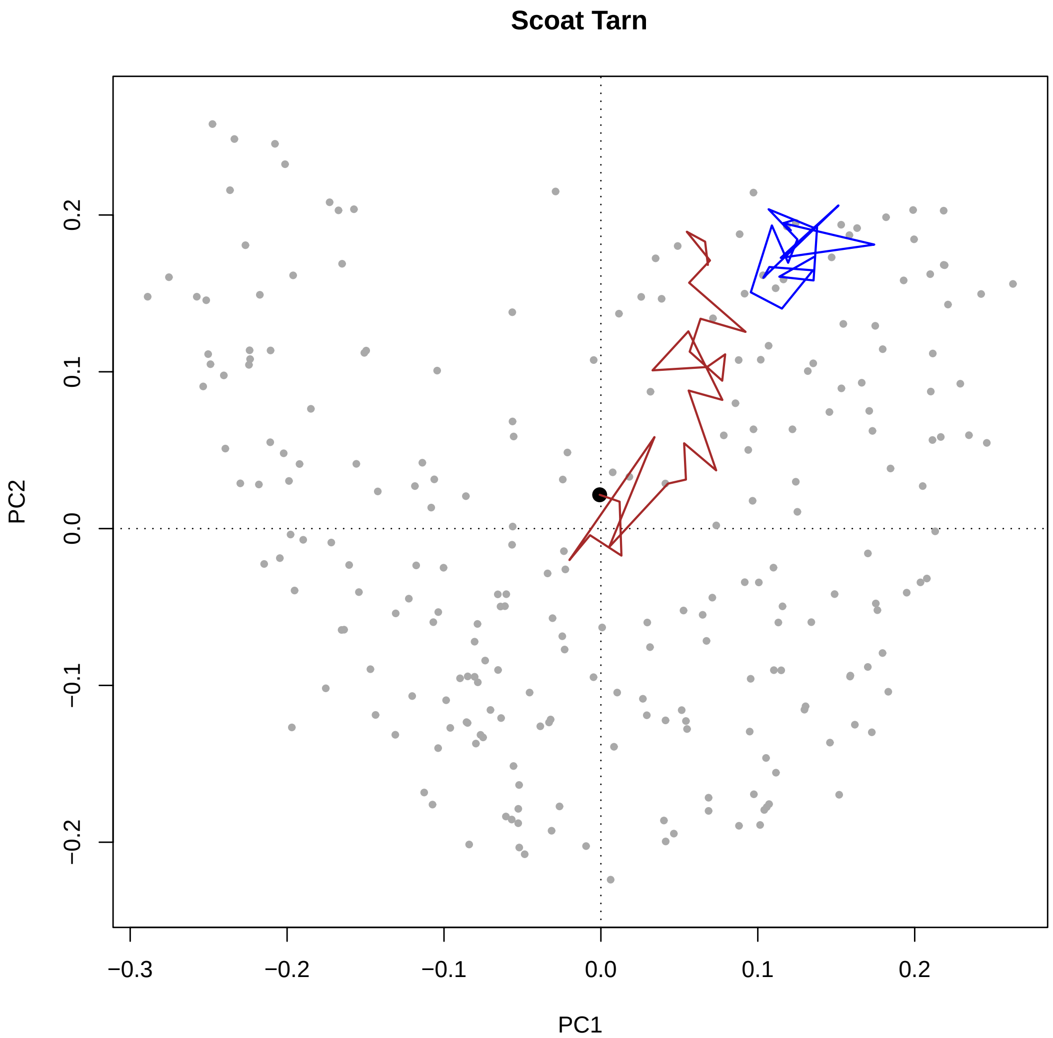

Figure 7: "Recovery" trajectories for diatom assemblages at Scoat Tarn based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

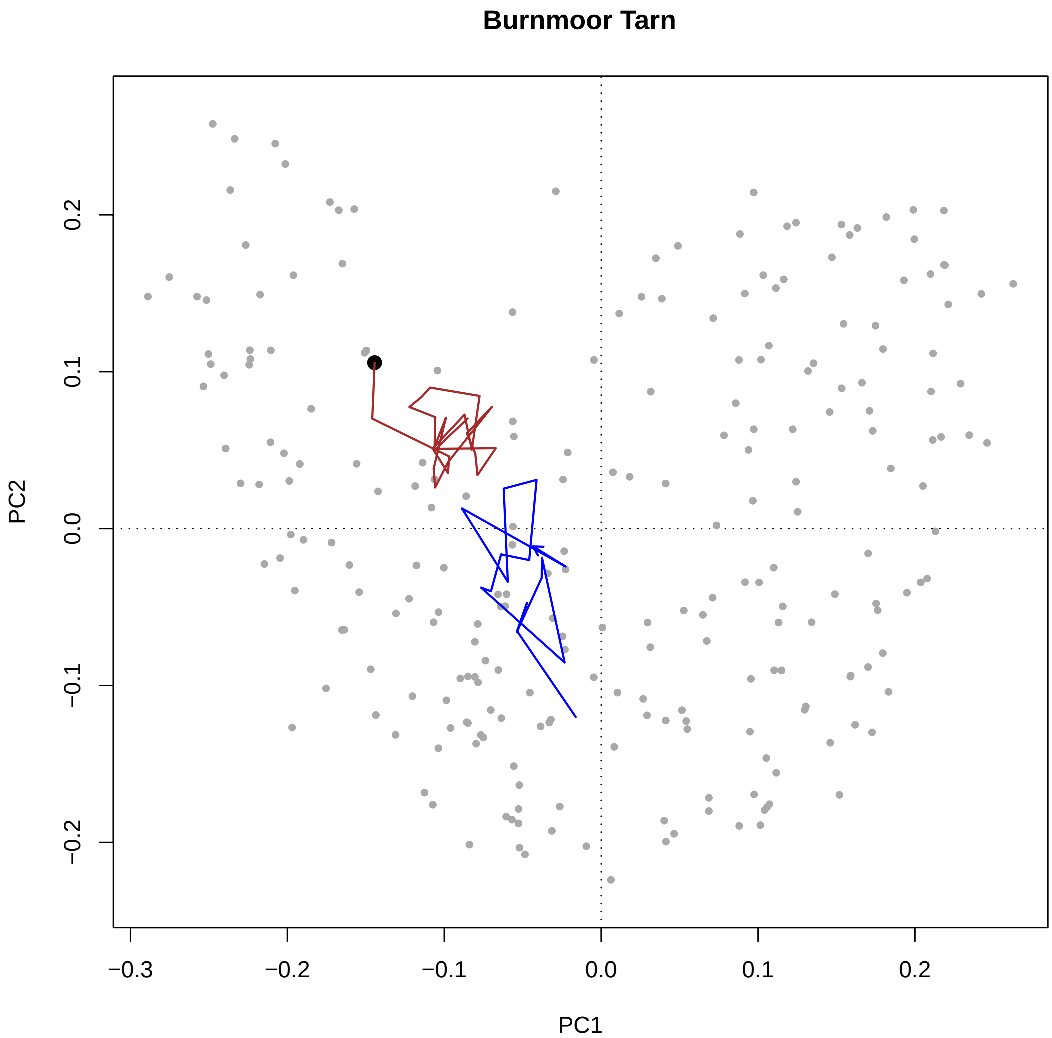

Figure 8: "Recovery" trajectories for diatom assemblages at Burnmoor Tarn based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

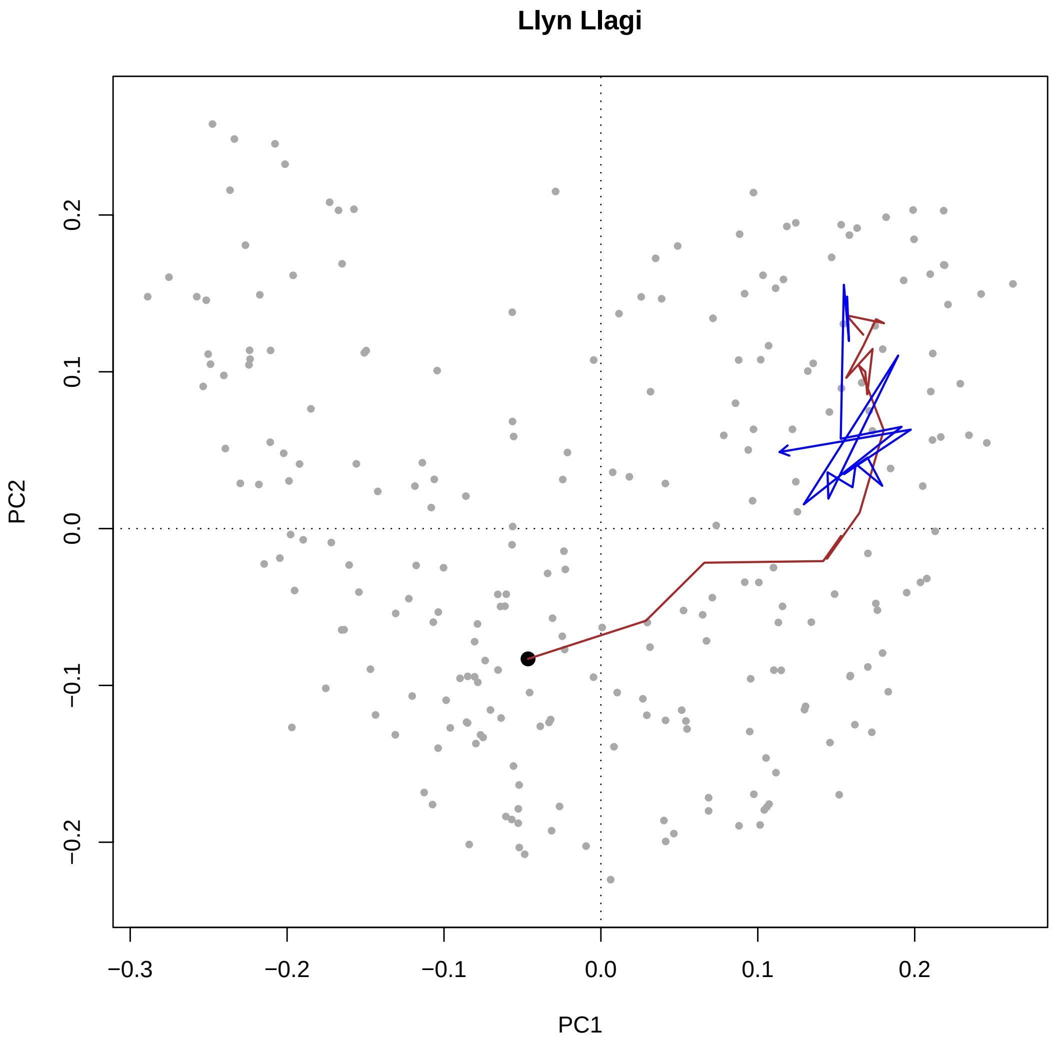

Figure 9: "Recovery" trajectories for diatom assemblages at Llyn Llagi based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

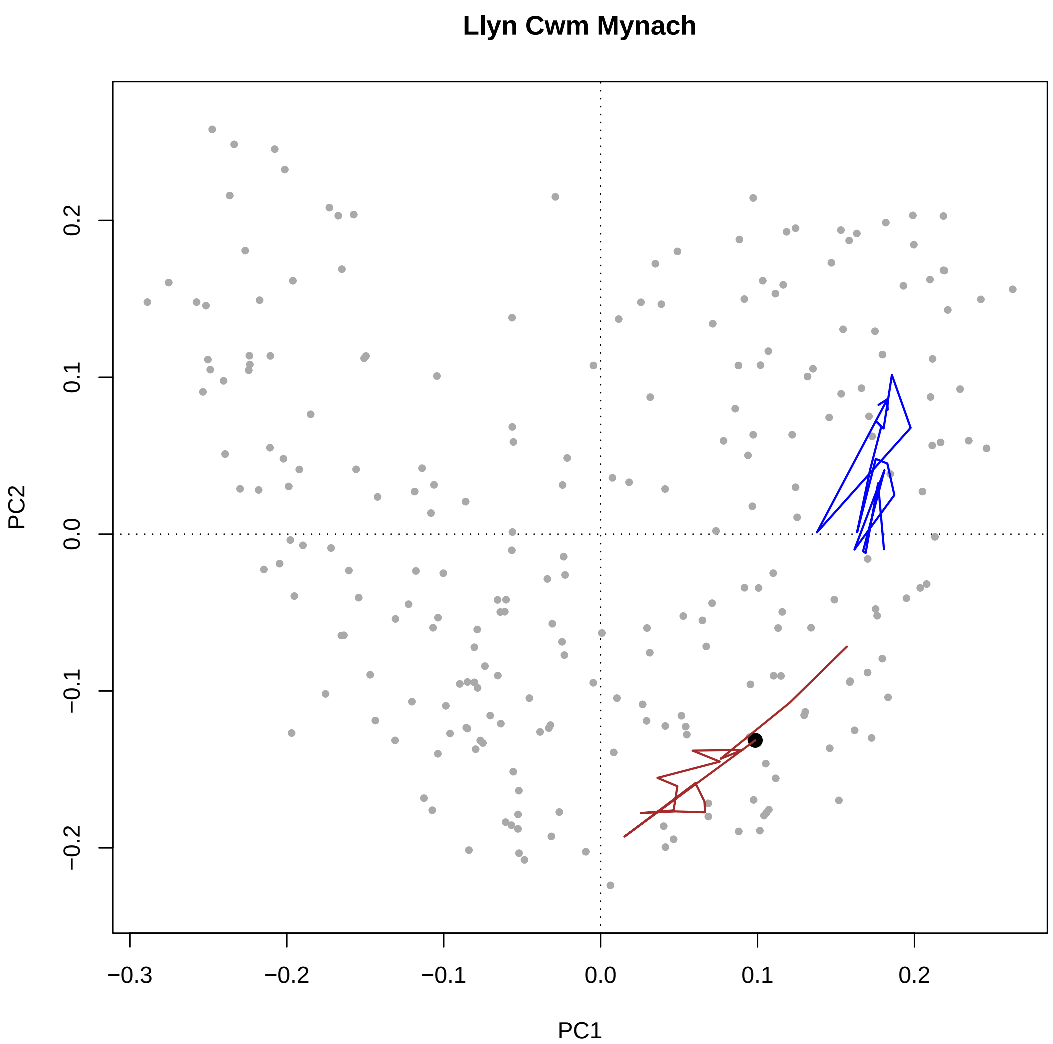

Figure 10: "Recovery" trajectories for diatom assemblages at Llyn Cwm Mynach based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

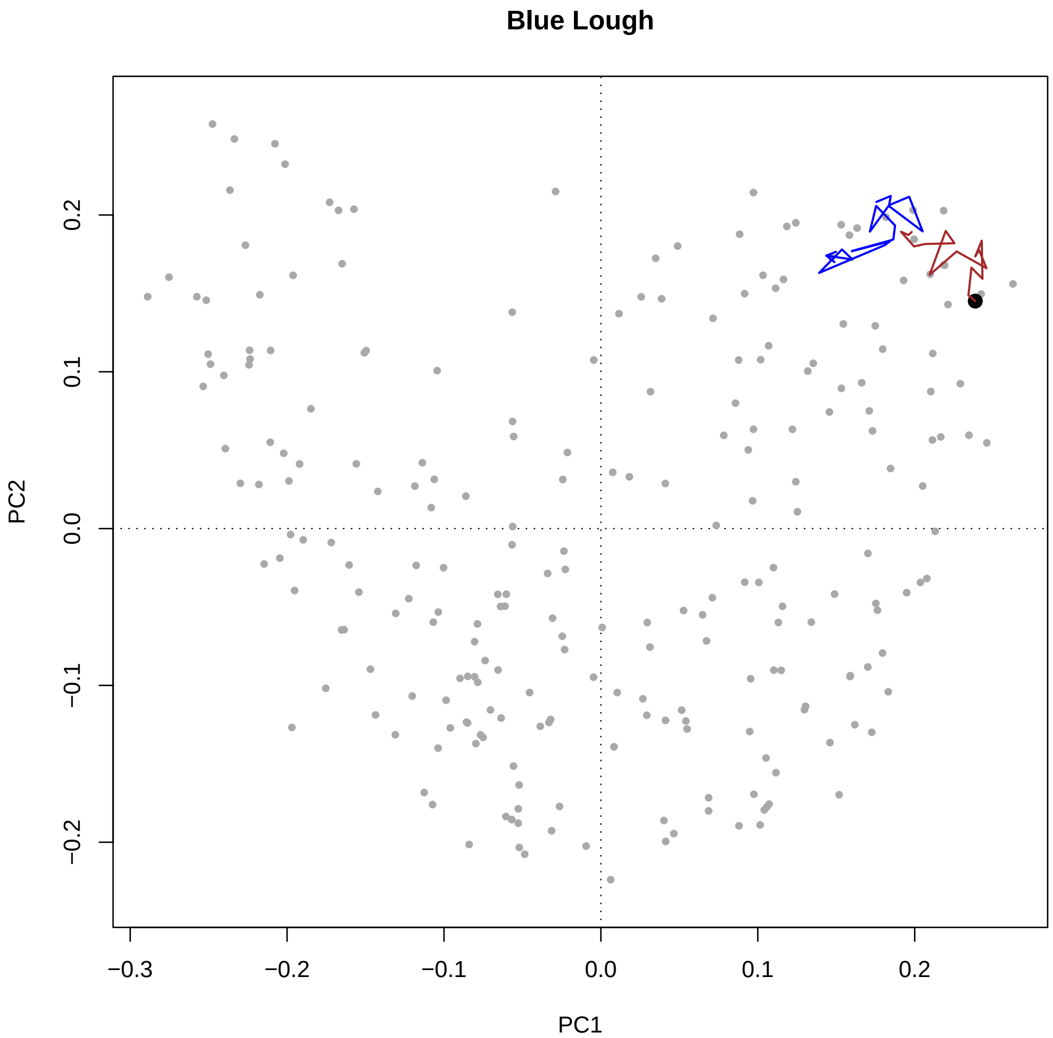

Figure 11: "Recovery" trajectories for diatom assemblages at Blue Lough based on differences between species composition diatom floras of the reference period, the period of maximum acidity and the present day.

APPENDIX 7 AWMN Reference List

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APPENDIX 8 AWMN Afforested Site Maps: Current and Projected

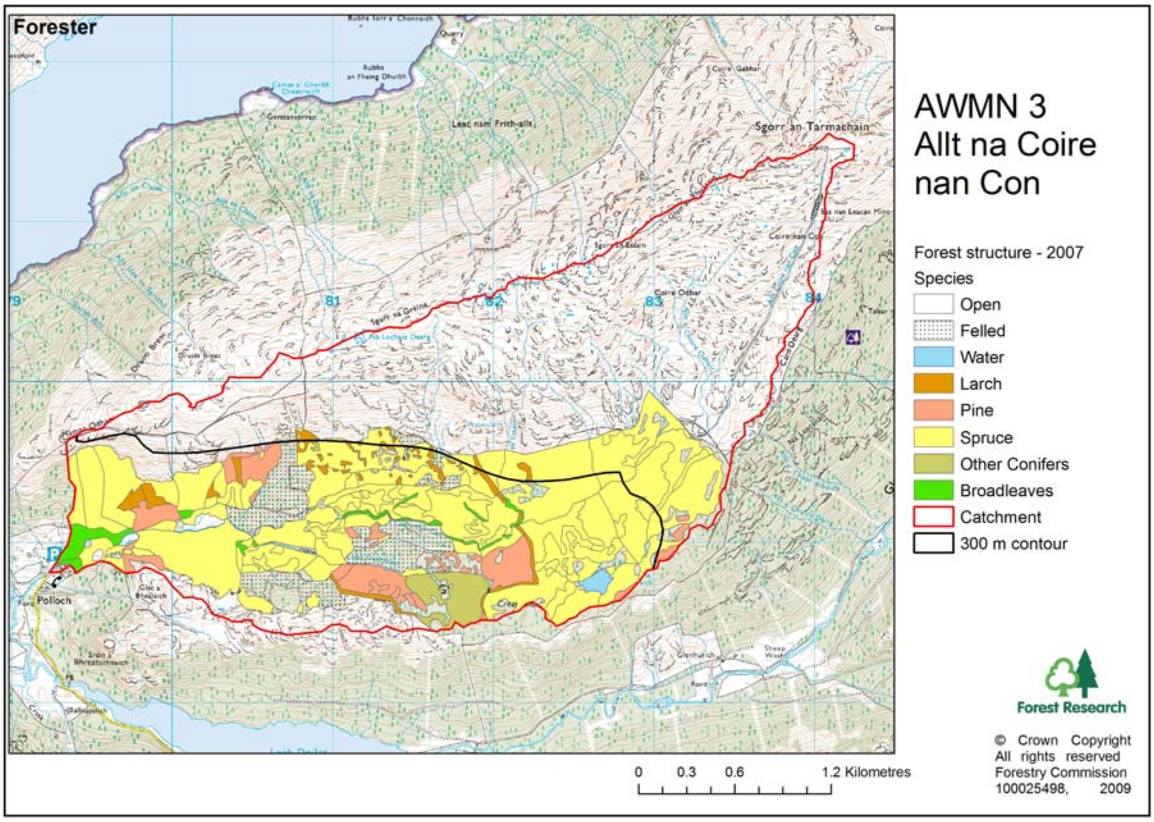

Figure 1 Allt na Coire nan Con Forest Structure 2007

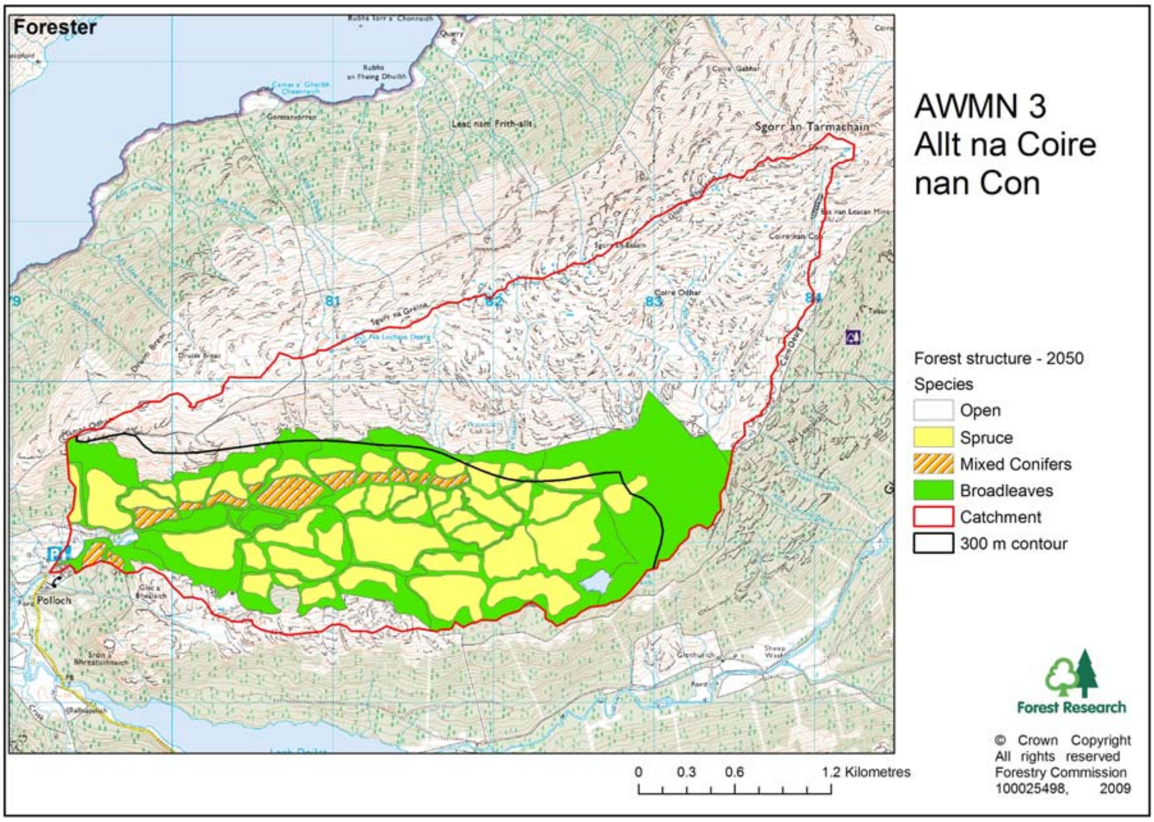

Figure 2 Allt na Coire nan Con Forest Structure 2050

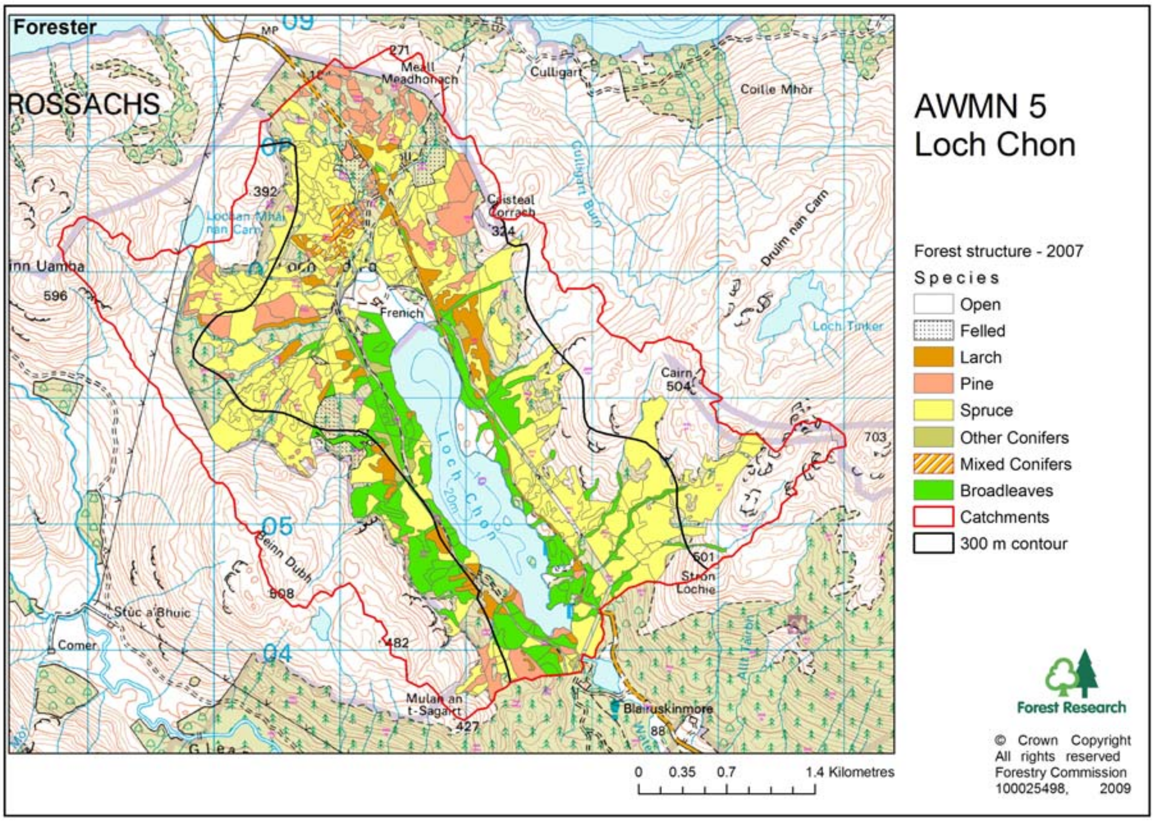

Figure 3 Loch Chon Forest Structure 2007

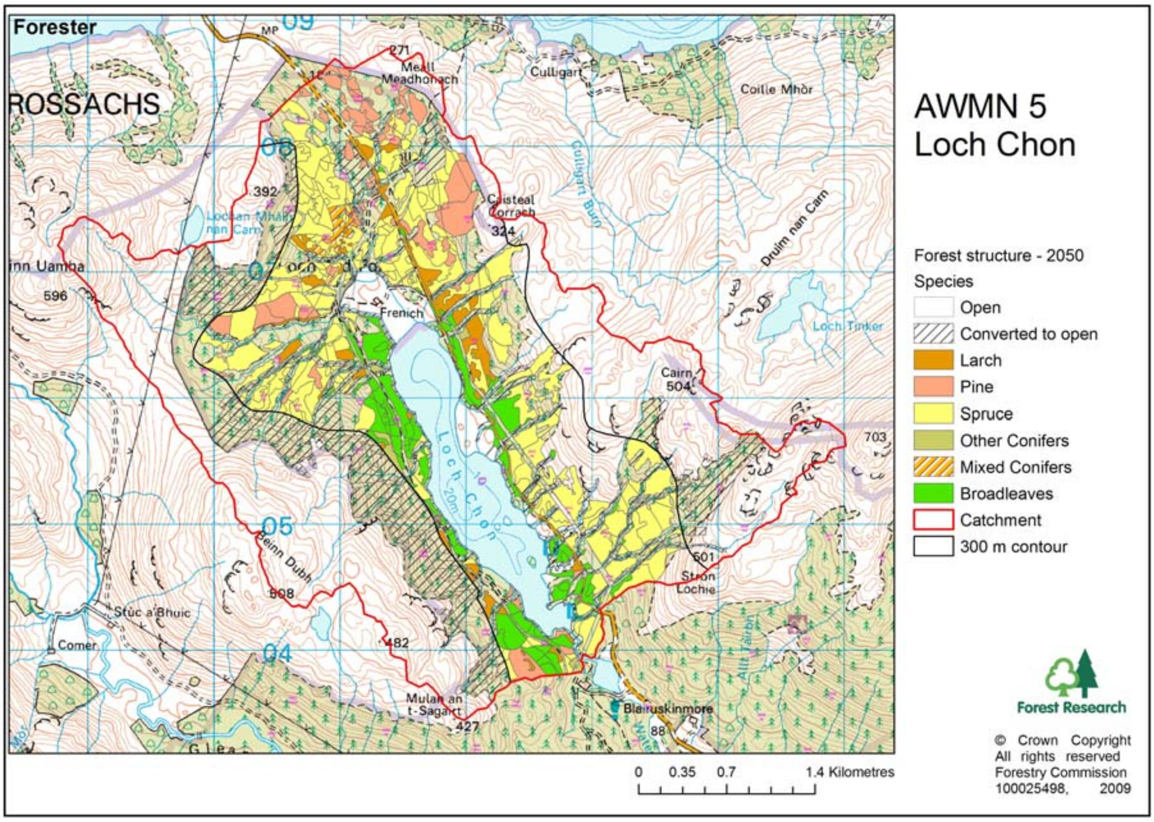

Figure 4 Loch Chon Forest Structure 2050

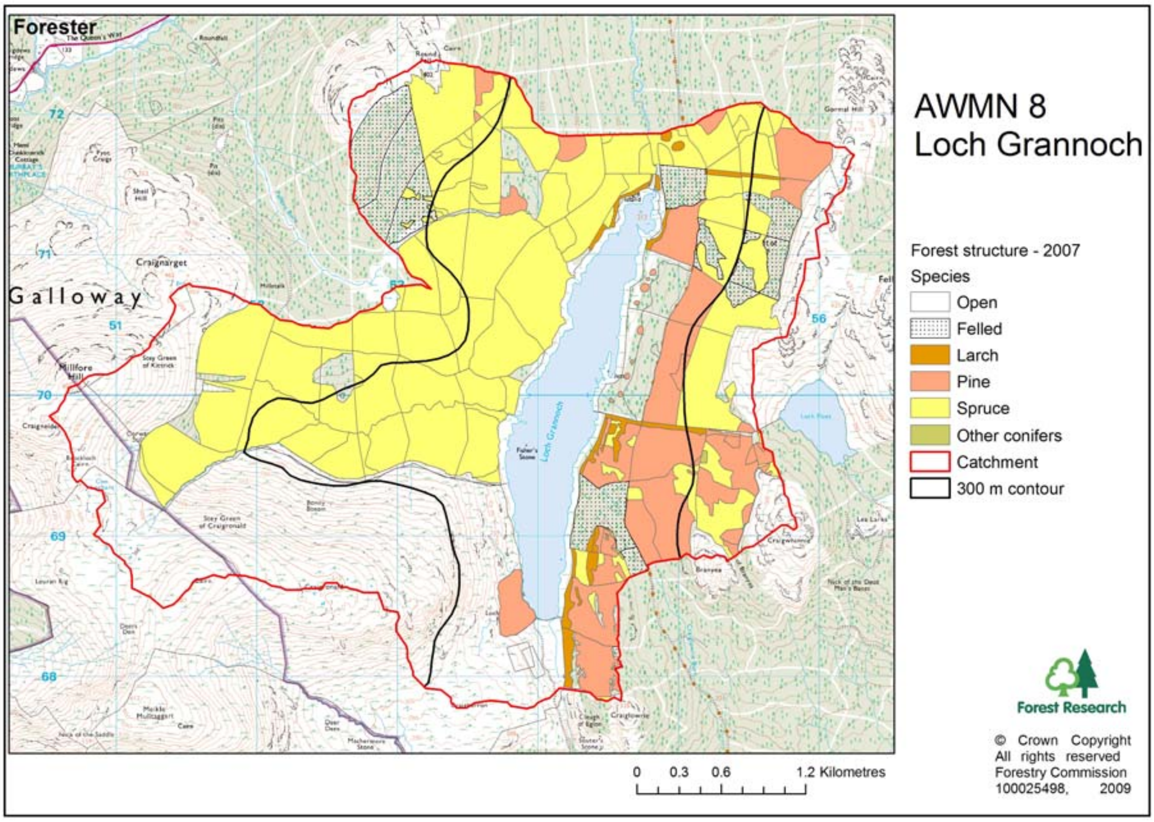

Figure 5 Loch Grannoch Forest Structure 2007

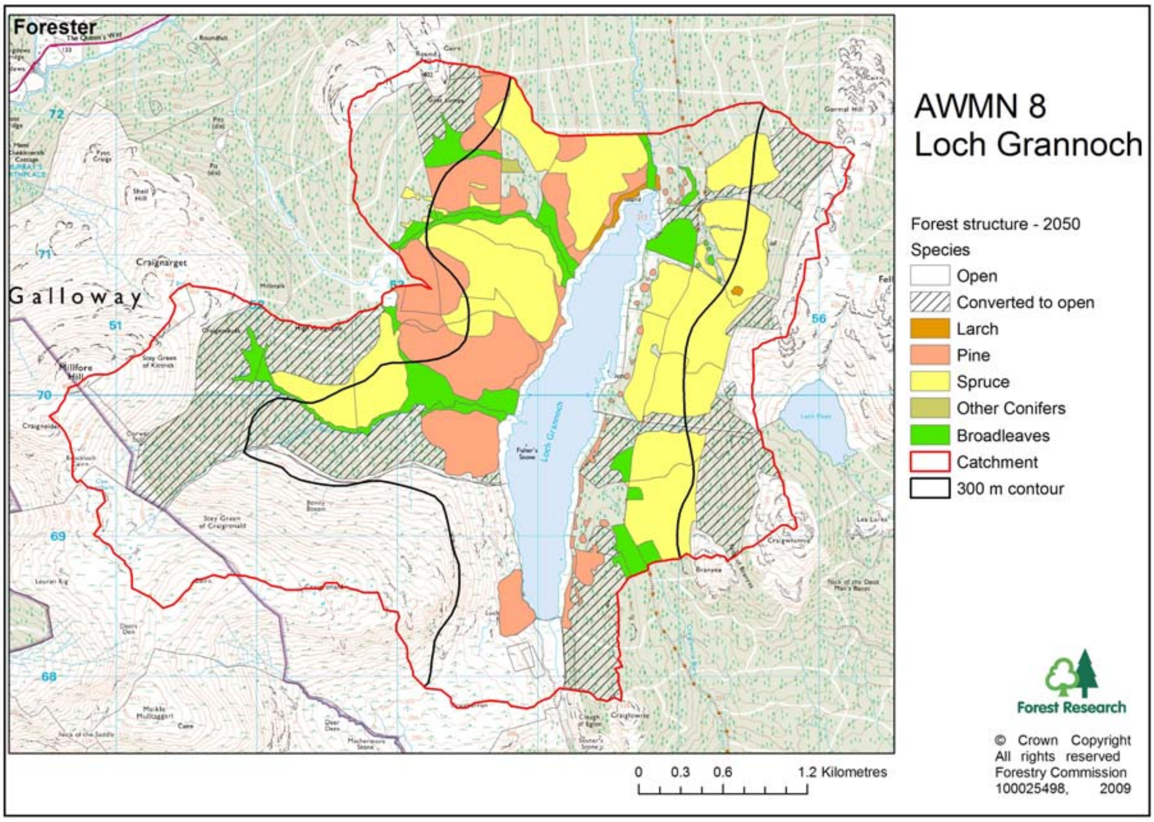

Figure 6 Loch Grannoch Forest Structure 2050

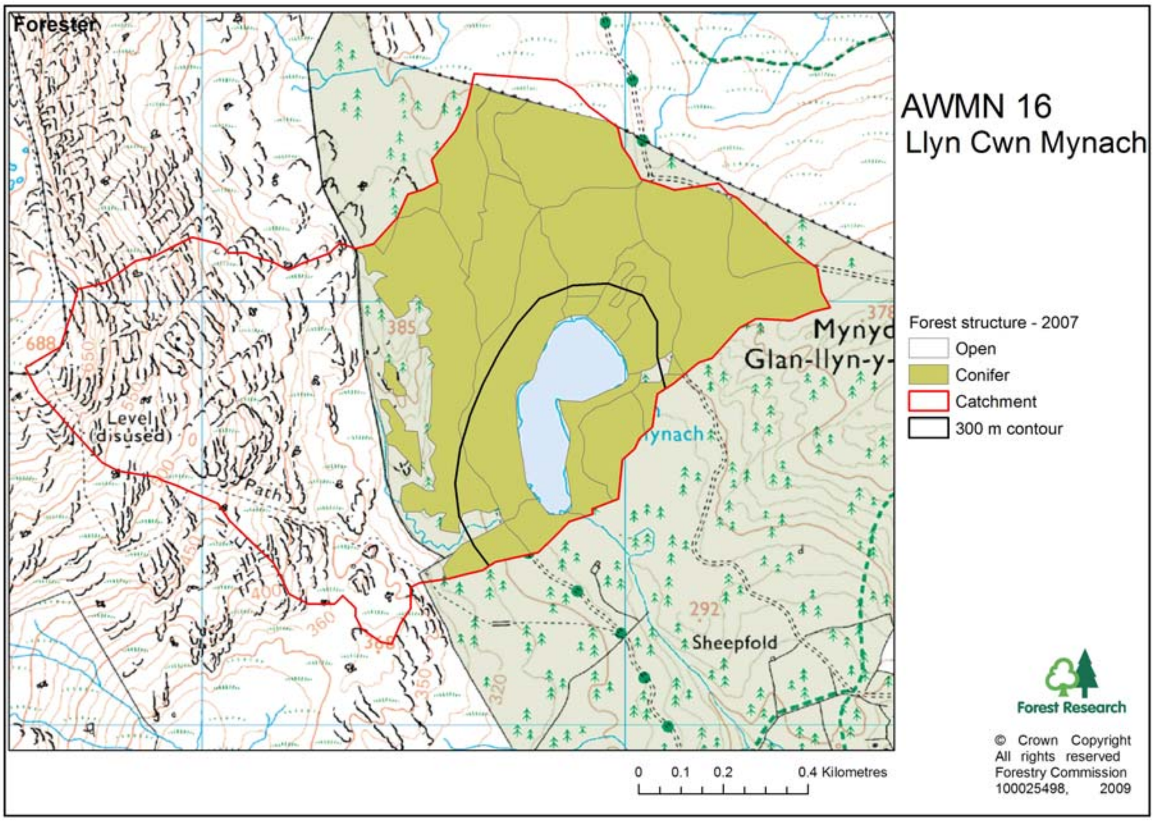

Figure 7 Llyn Cwm Mynach Forest Structure 2007

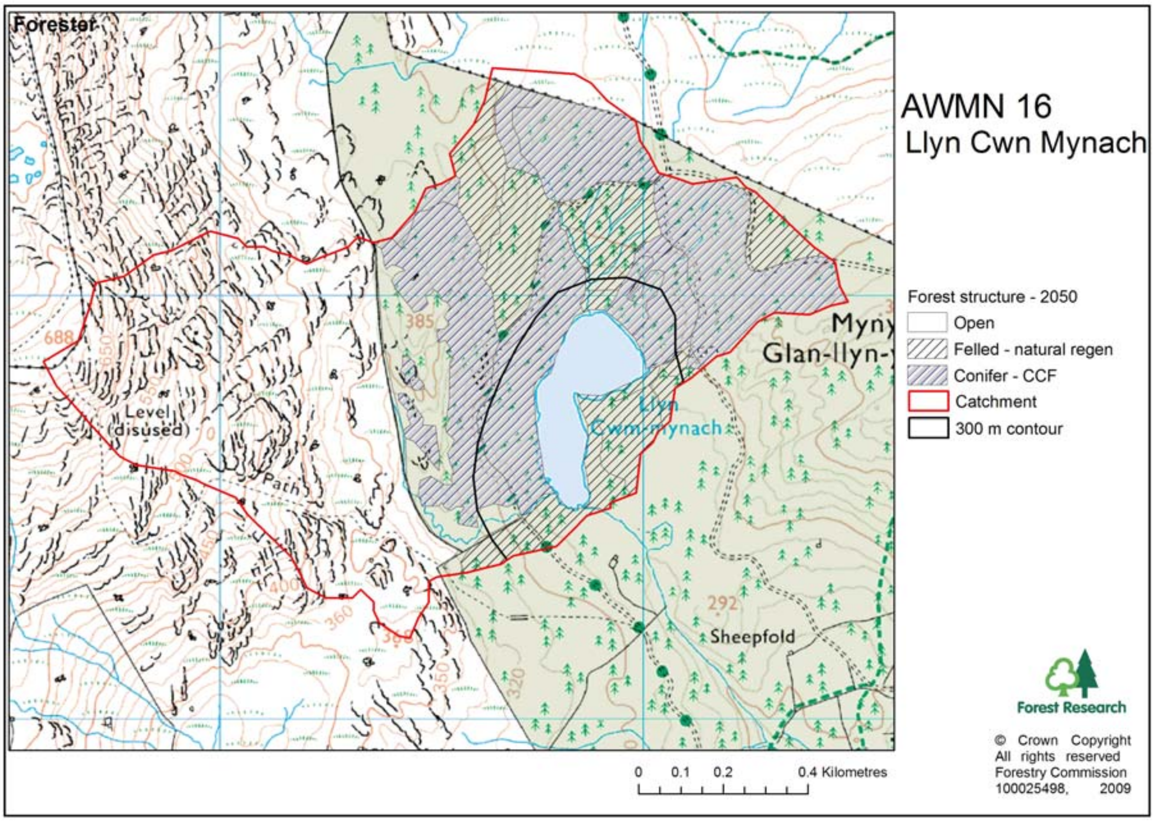

Figure 8 Llyn Cwm Mynach Forest Structure 2050

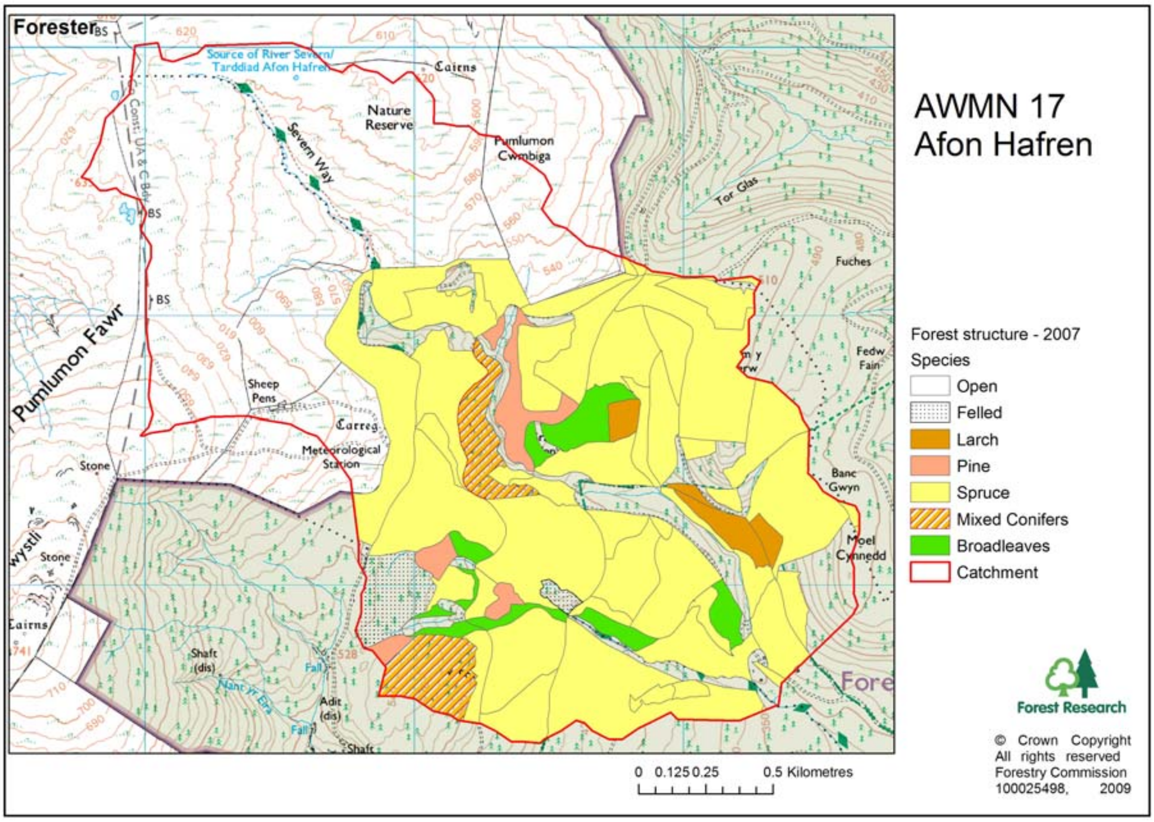

Figure 9 Afon Hafren Forest Structure 2007

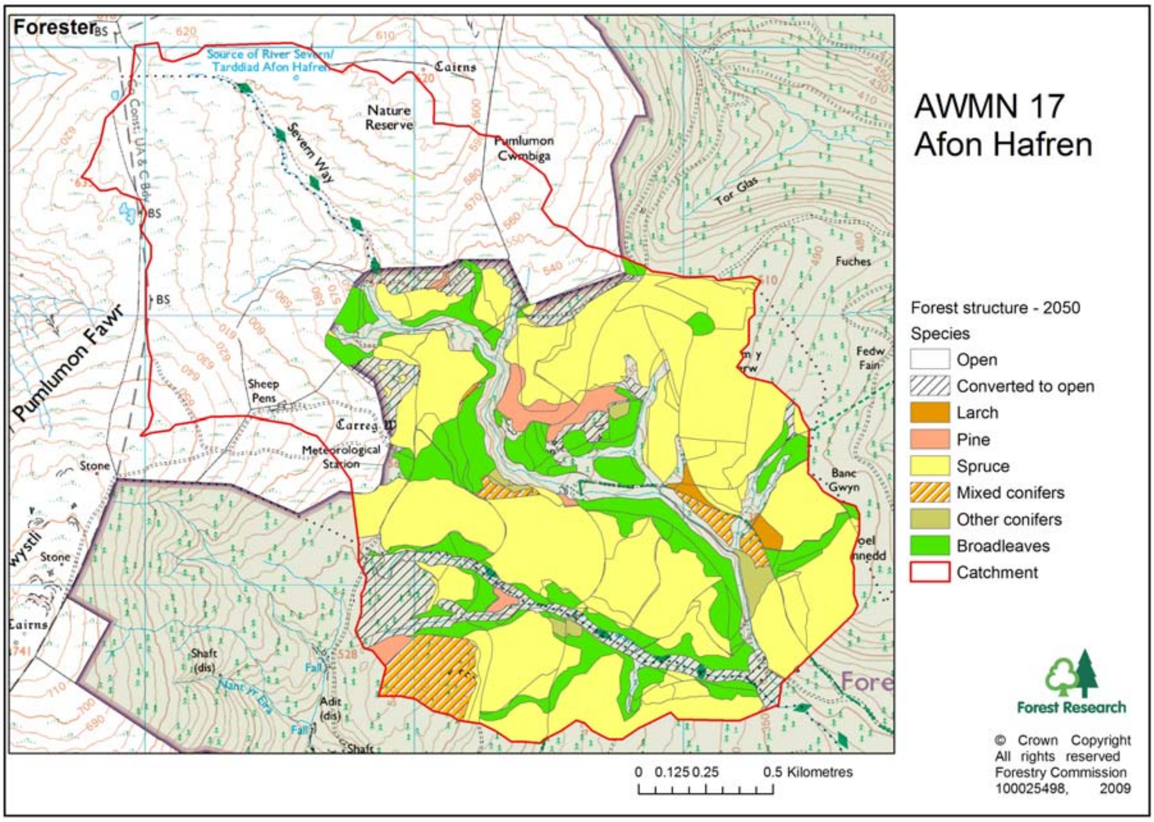

Figure 10 Afon Hafren Forest Structure 2050