An aerial photograph of a large, dark lake situated in a valley. The surrounding landscape consists of rolling hills and valleys covered in green grass and some trees. The sky is overcast with grey clouds. The text is overlaid on the upper portion of the image.

UK Acid Water Monitoring Network: 15 Year Report

**Analysis and interpretation of results:
April 1988 - March 2003**

**Published for the Department for Environment Food
and Rural Affairs by ENSIS Publishing**

Edited by: D.T. Monteith

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**Report available for download from the web site:
www.ukawmn.ucl.ac.uk**

Cover photograph: Llyn Llgi (AWMN Site 15) by E. M. Shilland

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Acknowledgments

The United Kingdom Acid Waters Monitoring Network is funded by the Department for Environment Food and Rural Affairs (DEFRA) and the devolved regions under contract RMP 2036. We thank DEFRA officials Martin Williams, Alison Vipond, John Rea, Tim Williamson and Sam Baker for their continued advice, support and encouragement.

This report represents the work of many individuals from a wide range of organisations (see Appendix 3). In many cases staff have been involved since the onset of monitoring in 1988 and this has helped to ensure long-term consistency in sampling procedures and data quality. We are very grateful to Jo and Mollie Porter, Kevin Solman (University Enterprises Plymouth), Margaret Birch (Environment Agency, Llanelli) and Walter Crozier (Department of Agriculture, Northern Ireland) for local site operations, to John Birks (University of Bergen/UCL) for advice on bio-statistics, to David Moore and Janey Keay (FRS Pitlochry) for data provision, and to Elanor McBay and Miles Irving from the Cartographic Unit, UCL Department of Geography, for their considerable efforts in the design and production of this report. We also recognise the contributions of Steve Warren, Bob Wilson, Ron Harriman, Steve Juggins and Jill Lancaster in the establishment of the Network and early development of field sampling and analytical techniques.

Executive Summary

INTRODUCTION

1) This report summarises the findings of the UK Acid Waters Monitoring Network (AWMN) 15 year data interpretation exercise. The AWMN is funded by the UK Department for Environment Food and Rural Affairs. The report also incorporates an analysis of data collated by the UK Acid Deposition Network (ADN) run by NETCEN.

2) The AWMN was established in 1988 by the UK Department of the Environment in order to determine the efficacy of international acid emissions reduction policy on the ecology of acid sensitive lakes and streams across the UK. The Network comprises 11 lakes and 11 streams covering a gradient of acid deposition and geological sensitivity, and representing a range of altitudes and both forested and non-forested catchments. The water chemistry of run-off is measured monthly for streams and quarterly for lakes. Biological assemblages, epilithic diatoms, aquatic macrophytes, macroinvertebrates and salmonid fish are assessed in annual surveys. Data are collated at the Centre for Ecology and Hydrology, Wallingford and the Environmental Change Research Centre, University College London.

TRENDS IN DEPOSITION

3) There are no trends in the amount of precipitation across the UK over the period of analysis of AWMN data (1988-2003). Inter-annual variability in climate has exerted only a minor effect on the ionic concentration of precipitation, relative to the major trends in concentrations. However, concentrations of pollutant ions tend to be enhanced during drier, more easterly influenced years, when the concentration of marine ions is smaller.

4) On a national scale the deposition of non-marine sulphate ($x\text{SO}_4^{2-}$) declined from 525 kt in 1987 to 205 kt in 2001, a reduction of approximately 60% during a period in which emissions declined by 70%.

5) Trends in the bulk flux of oxidised nitrogen (NO_x) are uncertain due to the short period of nitric acid (HNO_3) monitoring. However, trends in nitrate (NO_3^-) in precipitation are small, and only statistically significant in the English Midlands. Over the UK, the wet deposition of oxidised N has remained fairly constant at about 100 kt N, dry deposition of nitrogen dioxide (NO_2) has declined from about 60 to 30 kt N and the deposition of HNO_3 , which is currently about 60 kt N is unknown earlier than 2000. There appears to have been a small decline in reduced N deposition over a period when emissions fell by about 10%.

6) The concentration of $x\text{SO}_4^{2-}$ in precipitation has declined by approximately 50% across the UK. In central and southeastern England this amounts to a reduction of circa $3 \mu\text{eq l}^{-1} \text{yr}^{-1}$. The magnitude of decline weakens in northerly and westerly directions. In the regions where most AWMN sites occur concentrations of $x\text{SO}_4^{2-}$ have fallen by an average of $0.9 \mu\text{eq l}^{-1} \text{yr}^{-1}$. In contrast with the analysis presented in the previous (10 year) report, significant trends are now detected even in the extreme northwest of the UK although the average rate of decline here is less than $0.5 \mu\text{eq l}^{-1} \text{yr}^{-1}$.

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7) The concentration of NO_3^- in precipitation has also fallen, but trends are only significant in the English Midlands, where current levels are approximately 20% lower than 1986. The concentration of ammonium (NH_4^+) in precipitation has declined by about 10% over the same period over a similar region.

8) Data for the concentration of base cations in precipitation are not available for the entire monitoring period, but differences between early and recent measurements suggest that concentrations have declined by about 50% over central and eastern England.

9) The acidity of precipitation has also declined by approximately 50% across the UK, but once again the magnitude, in both absolute and relative terms falls in a northerly and westerly direction.

10) The contribution of dry deposition, mainly of sulphur dioxide (SO_2), to AWMN sites is relatively small as most sites are located in high rainfall areas of the UK. However, the contribution to acidification is significant even in the uplands and the change in dry deposition of SO_2 over the monitoring period is the largest contributor to changes in the net deposition budget for the country as a whole. Average SO_2 concentrations in the UK have declined from 2 ppb in 1986 to 0.2 ppb in 2001.

11) Although there is considerable uncertainty in estimates for the dry deposition of NO_2 at a national scale it is estimated this represents around a third to a half of the contribution of N from wet deposition. Again this will be much smaller for most AWMN sites.

12) In some areas of southern and especially southeastern England there is evidence for an increased contribution to rainfall acidity from shipping. In some cases this may have negated the small decline in contributions from terrestrial sources in these relatively unpolluted areas.

RELATIONSHIP BETWEEN FLUXES IN DEPOSITION AND RUN-OFF FROM AWMN SITES

13) Trends in xSO_4^{2-} deposition and run-off concentration at AWMN sites have not been linear. At most ADN stations situated near AWMN sites, little change is apparent from the onset of AWMN monitoring in 1988 until 1996. There is also little evidence for trends at most AWMN sites over the same period. Since 1996 there has been a sharp decline in the deposition of xSO_4^{2-} and in concentrations of xSO_4^{2-} in run-off from AWMN lakes and streams. The onset of this decline coincides with the fitting of Flue Gas Desulphurisation (FGD) technology at two major emissions sources in the UK, Drax and Ratcliffe on Soar power stations.

14) The relatively constant levels of S deposition between 1988-1996, over a period of significant declines in emissions, may reflect coincident changes in prevailing weather conditions. A decline in chloride concentrations in surface waters from 1990 to 1995 is indicative of a declining, low-sulphate, Atlantic weather source compensated by an increased contribution from more polluted air trajectories.

15) Catchment processes influencing S retention and release, operating at time scales longer than one year, have been identified elsewhere. However, xSO_4^{2-} concentrations in AWMN streams and lakes have changed at an annual time scale with, and with similar magnitude to, estimated xSO_4^{2-} deposition. This implies relatively limited long-term retention or loss of S from catchments in relation to short-term through-put.

16) Some sites show sulphate flushes in autumn, believed to result from oxidation of sulphides. Although some recovery might be expected by greater immobilisation in succeeding years, this is not immediately apparent from measurements.

17) NO_3^- concentrations in run-off from AWMN sites are not closely related to input concentrations. The biological component of the nitrogen cycle is known to include major storage and release characteristics quite separate from inputs. Sites with high dissolved organic carbon (DOC) concentrations generally show high dissolved organic nitrogen (DON) concentrations. This nitrogen is not thought to be associated with hydrological translation or short-term changes in nitrogen storage.

TRENDS IN THE CHEMISTRY OF RUN-OFF FROM AWMN SITES

18) Geographically, the strength of trends in the concentration of xSO_4^{2-} in run-off (i.e. water samples taken monthly from streams and quarterly from lake outflows) roughly matches those in deposition.

19) The concentration of xSO_4^{2-} has fallen significantly at 18 of 22 sites. Trends are particularly marked at Old Lodge in southeast England and the River Etherow in the Pennines, amounting to approximately $9 \mu\text{eq l}^{-1} \text{yr}^{-1}$ and consistent with their positions close to emission sources. Most other sites show significant declines of between $1\text{-}2 \mu\text{eq l}^{-1} \text{yr}^{-1}$. The sites most remote from sources, Loch Coire nan Arr and Allt na Coire nan Con in northwest Scotland and Coneyglen Burn in northwest Northern Ireland, show very small, statistically insignificant trends.

20) No site shows a significant trend in (NO_3^-) concentration. Although it has been hypothesised that as deposited N continues to accumulate in catchment soils sites will eventually show the characteristics of N saturation and “breakthrough”, there is no evidence for a change in state in nitrogen characteristics at any site.

21) Nitrate concentrations continue to show marked seasonality with highest levels usually recorded in spring. The negative relationship between seasonal peak NO_3^- concentration and the winter North Atlantic Oscillation (NAO) Index, first identified in the 10 year analysis, continues to hold. This suggests a relationship between colder, drier winters and more elevated concentrations. An apparent recent slight increase in NO_3^- concentrations at a minority of sites can be linked to a recent decline in the winter NAO Index over the same period. At Lochnagar, in the Scottish Grampians, the increase has been large enough to balance the decline in the primary acid anion xSO_4^{2-} , thus preventing any decline in acidity.

22) Most sites show significant declines in base cation concentrations. This is expected, as a result of a decline in leaching from catchments with less acidic deposition and, to a much lesser extent, due to a decline in the base cation concentration of deposition. In general, the decline in the sum of the concentration of the two dominant base cations, calcium (Ca^{2+}) and magnesium (Mg^{2+}), amounts to approximately 80% of the decline in the dominant anion (xSO_4^{2-}).

23) Eight sites show significant, although generally slight, declines in hydrogen ion (H^+) concentration. With the exception of Old Lodge in southeast England, these sites are contained within an area of central western UK, covering north Wales, the English Lake District, Galloway, the Mourne Mountains and the Scottish Trossachs. This is some 300 km in latitude and less than 150 km in longitude, and represents the zone where the strongest downward trends in xSO_4^{2-} have been observed. Within this zone, there is no significant trend in H^+ in two relatively well buffered and only weakly acidified sites, two lakes with afforested catchments and three

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strongly episodic streams. Despite the absence of overall trend, the latter three sites do show a tendency for declining H^+ maxima (indicative of the severity of “acid episodes”) which may be of considerable biological importance.

24) Ten sites show a significant decrease in labile (inorganic and biologically toxic) aluminium (Al_{lab}) concentration. Once again these are largely confined to the geographic zone described above.

25) Dissolved Organic Carbon (DOC) concentration has increased significantly at all AWMN sites, representing a near doubling in concentration over 15 years. Similar patterns in DOC have been reported in Scandinavia and areas of North America in recent years. These observations suggest a systematic response to one or more external driver on a large spatial scale. Analyses of AWMN time-series suggest that trends are influenced by a decline in the acidity and/or ionic concentration of deposition. However, comparable trends at essentially unimpacted sites in the northwest of the UK suggest that climatic factors, possibly relating to smoothed responses to rising air temperature and/or increased frequency of drought, may also be important drivers.

26) The Acid Neutralising Capacity (ANC) of run-off has been determined using two alternative approaches. Few trends are apparent when using the conventional determination, i.e. $ANC = \sum [\text{base cations}] - \sum [\text{acid anions}]$. However, it has been argued that this calculation is particularly sensitive to compound errors associated with the seven ions included in the equation. An alternative expression of the same relationship, $ANC (\mu\text{eq l}^{-1}) = [\text{Alkalinity}] (\mu\text{eq l}^{-1}) + x[\text{DOC}] (\text{mg l}^{-1}) - 3*[\text{Labile Aluminium}] (\mu\text{mol}^{-1})$ (where x varies from 4.5 to 5.0 depending on pH), produces substantially different trend results.

27) The alkalinity-based ANC determination (or AB-ANC) shows many large and significant positive trends which are strongly correlated with the trends in xSO_4^{2-} concentration. The geographical distribution of sites showing trends again approximates to the central western UK region, but in this case embraces a total of 14 sites. For all but one of these sites significant trends are also found in one or more of pH, alkalinity or labile aluminium concentration. Change in AB-ANC therefore provides a convenient generic surrogate for changes in acidity. However, the influence of DOC is clear. It would appear that where alkalinity and H^+ trends are small relative to those in AB-ANC, the major shift has been from strong mineral (pollutant) to weaker organic (naturally derived) acidity.

28) Given the clear relationship between changes in DOC and AB-ANC it is essential that the cause of the DOC increase is more thoroughly understood before these trends of apparent improvement can be categorically attributed to decreasing acid deposition.

29) Climate exerts strong effects on temporal patterns in pH, alkalinity and Al_{lab} concentration. Although there are no clear climatic trends over the full monitoring period, these effects increase the amount of “noise” in chemical recovery signals and weaken trend strength. At more remote sites where changes in deposition are relatively slight these may be sufficient to render trends statistically insignificant.

30) Precipitation exerts a major influence on short term variability in acidity as a result of its effect on flow paths within catchments. Run-off tends to be most acidic after prolonged periods of heavy rain when the contribution from groundwater is minimised. Seasalt deposition, which occurs during prolonged westerly winter storms, results in the temporary displacement of H^+ and aluminium ions from soil exchange sites, causing severe acidic pulses. The frequency and intensity of short-term hydrological and seasalt episodes may be extremely important for the viability of biological recovery at sites where there is an overall long-term improvement.

TRENDS IN THE BIOLOGICAL COMPOSITION OF AWMN SITES

31) The species composition of epilithic diatom (unicellular siliceous algae which grow attached to rocks), macroinvertebrate (non-microscopic aquatic invertebrates) and aquatic macrophyte (larger aquatic plants) communities, and the density of salmonid fish (salmon and brown trout) have been monitored annually since 1988.

32) Percentage abundance data for epilithic diatom and macroinvertebrate species have been assessed using a multivariate statistical method (Redundancy Analysis) in order to determine whether these communities show significant linear change over the monitoring period. A similar approach has been applied to aquatic macrophyte % cover scores for streams and 1-5 ordinal abundance data for lakes. Evidence for change in the density of newly recruited brown trout (<1 year old) and those over 1 year old have been assessed using linear regression.

33) Epilithic diatom assemblages have changed significantly at 12 sites. At most sites species changes are subtle and do not represent a large turnover in composition. However, for the majority, changes represent an increase in abundance of species characteristic of sites of higher pH relative to those characteristic of more acidic conditions. While these changes are therefore indicative of recovery, linear change at two sites in northern Scotland suggest a shift to taxa characteristic of slightly more acidic conditions.

34) Evidence for recovery in epilithic diatom communities is clearest in the less acidic sites. Assemblages in the six sites with mean 15 year pH > 5.0 which show significant trends in pH and and/or alkalinity, all show species shifts, while those from the three most acidic sites on the Network (Old Lodge, Blue Lough and the Round Loch of Glenhead) do not, despite these also showing chemical improvement.

35) Inter-annual variation in epilithic diatom species composition can be related to variations in water chemistry representing the summer period prior to biological sampling. While several acidity related parameters show significant relationships with the species data, overall, the strongest links are with DOC and Ca²⁺ concentrations.

36) The species composition of macroinvertebrate communities has changed significantly at twelve sites. Species changes are again subtle and do not represent a large turnover in composition. There is a particularly striking spatial relationship between those sites showing trends in faunal assemblages and those sites which have undergone an increase in AB-ANC and, also, labile aluminium.

37) Several more macroinvertebrate species show significant increases in abundance than show significant declines. This is consistent with a gradual expansion of the recovering community without strong competitive displacement of acid tolerant taxa.

38) Caddisfly species have increased proportionally in five lakes while a decline in a Caddisfly species is only apparent at one site. At four of the lakes the increasing Caddisfly species is predatory. Linear community shifts also reflect increases in the abundance of other predators. Predatory Stonefly species have increased proportionally in three streams, and a predatory Damselfly in one lake. These changes at higher trophic levels suggest a broadening of the aquatic food web.

39) At the four stream sites showing macroinvertebrate trends, taxonomic shifts are consistent with recovery responses according to our understanding of species-acidity relationships.

Executive Summary

40) Inter-annual variability in macroinvertebrate assemblages can often be directly linked to variability in the water chemistry of samples collected during spring and, most frequently, with AB-ANC and labile aluminium concentrations.

41) Most streams, but few lakes, show an apparent increase in the species richness of macroinvertebrates. There is no link with those sites showing trends in acidity. Temporal patterns in species richness in streams are most closely correlated between sites which are geographically close. This suggests an influence of climate, and, more specifically, interannual differences in the amount of precipitation early in the year, with lower number of species recorded after wetter springs.

42) Few sites show significant trends in aquatic macrophyte species composition according to conventional multivariate analysis. However acid sensitive plants have been found for the first time in the last five years at several sites, mostly within the region where AB-ANC has increased. In the majority of cases these are acid-sensitive, and chiefly elodeid species (those with erect and branching growth forms) in lakes, and mosses in streams.

43) The recent appearance of two structurally important elodeid macrophytes, *Myriophyllum alterniflorum* (Water milfoil) and *Callitriche hamulata* (Intermediate Water Starwort), at the Round Loch of Glenhead and Llyn Llgi respectively, coincides with the alkalinity of these sites exceeding zero ($\mu\text{eq l}^{-1}$) for the first time. These species rarely occur in sites with negative alkalinity, and are possibly limited by the availability of dissolved inorganic carbon within the water column (i.e. dissolved CO_2 or bicarbonate). If their appearance is indicative of a threshold response to improving water quality it would suggest that they maintained a non-vegetative presence, i.e. as seeds, while these lakes were in a more acidified condition.

44) The acid sensitive moss *Fontinalis* sp. was detected recently in the survey stretch of the River Etherow in two consecutive years, but was then lost after a particularly heavy spate event and has not been recorded since. Although it is not clear whether its recent loss was due to physical or chemical (episodic) effects, its transient appearance highlights potential limitations on biological recovery of acidified running waters.

45) There is little indication of significant trends in the density of brown trout in most streams and lake outflows. In comparison with the other biological groups, mobility, and particularly the ability to avoid adverse chemical conditions, complicates the assessment of fish density data.

46) A spatial comparison of AWMN fish and chemical data reveals clear relationships between the density of brown trout (both juvenile and >1 year old age classes) and Al_{lab} concentration, with densities particularly restricted at concentrations $> 50 \mu\text{g l}^{-1}$. Relationships are also apparent for AB-ANC. Below $0 \mu\text{eq l}^{-1}$ AB-ANC brown trout densities are invariably low and usually below the limit of detection, whereas a wide range of densities are observed at sites and in years where $\text{AB-ANC} > 0 \mu\text{eq l}^{-1}$.

47) In the Old Lodge stream, and in the outflows of Scoat Tarn and Blue Lough (three of the most acidic sites on the Network), small numbers of juvenile brown trout have been detected after initial years of apparent absence. In Old Lodge there has also been a significant expansion in the density of older fish since 1992. These records can be linked to improving water chemistry; the first detection of this age class roughly coincides with AB-ANC approaching or exceeding zero. However, densities at these three sites are still very low relative to those found in circumneutral sites.

THE ROLE OF THE AWMN

48) The primary purpose of the AWMN is to communicate information on the changing state of acidified waters in the UK to the UK government. This is achieved primarily through annual data reports, five yearly interpretative exercises and the AWMN web page (www.ukawmn.ucl.ac.uk).

49) AWMN data are integral to:

- other acidification related government projects including DEFRA's freshwater acidification programme and the development and application of dynamic acidification models;
- other national and international monitoring initiatives, and particularly the UK Environmental Change Network (ECN) and the UNECE International Cooperative Programme on the Assessment of Acidification of Rivers and Lakes;
- large European Union Research Framework Projects, and most recently those under the 6th Framework, including EURO-LIMPACS (<http://www.eurolimpacs.ucl.ac.uk>) and REBECCA (<http://www.environment.fi/syke/rebecca>).
- AWMN data are requested frequently by scientists from a range of academic and scientific institutions, while the AWMN web page receives over 1000 visits per month.

50) A substantial amount of AWMN research has been reported in the peer-reviewed scientific and the analysis which underpins this report has been developed and recently published in a Special Issue of the journal *Environmental Pollution* (Volume 137 no.1, 2005).

51) Beyond the immediate acidification problem there is also a clear role for the AWMN in developing a better understanding of the wider linkages between atmospheric, terrestrial and aquatic systems, particularly with respect to the likely consequences of future climate change and land use for the quality of the water draining upland areas, and associated fluxes of carbon and other elements.

FUTURE REQUIREMENTS

52) It is clear that emissions reductions are stimulating biological improvement at many trophic levels. However, most sites remain in a significantly acidified condition and biological communities at most sites remain relatively impoverished. Our report reveals a number of issues which require a better understanding. This is particularly important if we are to be able to “scale-up” findings from the AWMN to the wider UK population of acidified lakes and streams.

53) Further work is necessary to ascertain: the likely threat of future N saturation (whereby NO_3^- could rise dramatically and become the dominant acidifying anion); the mechanisms behind the large increase in organic acid concentrations (i.e., DOC) and the wider implications of this change for biota; and the implications of forecast climate change for further chemical and biological recovery.

54) There remains a need for further catchment characterisation, particularly with relation to soils and catchment vegetation, while an expansion of the currently restricted programme of continuous monitoring of conductivity, pH and discharge would benefit the assessment of the relative roles of hydrology, seasalt episodes and rising air temperature in influencing run-off chemistry.

Executive Summary

55) Continued monitoring is clearly vital if we are to ascertain whether the tentative early stages of biological recovery will be sustained, and to what extent the rate of biological change may be being restricted by chemical and/or other biotic and physical factors.

56) Investigations focusing on AWMN and other less acidified sensitive sites are also necessary before we are better able to define biological recovery targets, in terms of the re-establishment of sensitive species and wider ecosystem functioning, and the seasonal dynamics of the monitored biota. An expansion of the range of biological fossil groups in sediment trap and sediment cores would shed more light on appropriate reference conditions while placing current recovery rates in a longer-term context.

57) Clearly, further tracking and understanding of ecological recovery from acidification requires a continuation of the current monitoring programme, ideally in partnership with other acidification projects under the DEFRA "Freshwater Umbrella" and other detailed experimental work linked to AWMN catchments.

Chapter 1

Introduction to the 15 year interpretative report

1.1 The UK Acid Waters Monitoring Network

This report presents the third five-yearly interpretation of data collated by the UK Acid Waters Monitoring Network (AWMN), which is funded by the Department for Environment Food and Rural Affairs (DEFRA). In addition it draws on data collated by the UK Acid Deposition Network (ADN). The previous reports in this series are Patrick *et al.* (1995) and Monteith and Evans (2000). The AWMN also produces annual data reports which are available via the AWMN web site (www.ukawmn.ucl.ac.uk).

The AWMN was established in 1988, by what was then the Department of the Environment, with the remit of assessing the ecological impact of acid emissions reduction strategy on acidified lakes and streams in the UK. The Network encompasses 22 sites (see Figure 1.1) representing many of the regions which are known to be vulnerable to the effects of acidification. Chemical monitoring comprises the assessment of monthly and seasonal water samples taken from streams and lake outflows respectively. Biological monitoring consists of annual surveys of diatoms (unicellular algae), macroinvertebrates (non-microscopic invertebrates), salmonids (brown trout and Atlantic salmon - based on electrofishing of streams and lake outflows) and stream aquatic macrophytes (mosses and liverworts). Lake aquatic macrophytes (including a range of mosses, liverworts, and higher plants) are assessed bi-annually. A detailed description of sites and sampling and analytical methodologies is available from the AWMN web site.

1.2 Acidification: processes and consequences

The processes and ecological impacts of acidification are explained in more detail elsewhere (see for example NEG-TAP, 2001). A brief summary is presented here in order to put the following chapters into context.

Even in relatively “clean” regions, such as in the far northwest of Scotland, precipitation is naturally slightly acidic due to carbonic acid content. As precipitation filters through organic soils its acidity is further enhanced by naturally occurring organic acids before it reacts with minerals in underlying substrata in a process known as weathering. Weathering generates base cations, such as calcium and magnesium, and dissolved inorganic carbon (DIC). As water leaves the soil in such a hypothetically “pristine” region, a reduction in partial pressure leads to a degassing of CO₂ and subsequently to run-off characterised by bicarbonate and base-cations.

Historically, acidic pollutants, chiefly sulphurous and nitrogenous compounds, were derived primarily from heavy industry, and particularly coal and oil burning power stations. Increasingly, however, vehicular and agricultural sources have become more important as older power stations have been decommissioned and other large plant have been fitted with particle arrestor and, more recently, flue gas desulphurisation, technology. These compounds form oxides in the atmosphere, which then react with water droplets to form “acid rain”, or are

deposited directly onto surfaces. Deposited ammonium can be a source of acidity if it is nitrified to nitrate by soil bacteria and / or assimilated by vegetation .

As acidified rainwater filters through soil, hydrogen ions displace base cations from soil exchange sites so increasing the acidity of the soil while increasing the base cation concentration of run-off. As the soil acidifies, aluminium is mobilised in a biologically toxic form (referred to in this report as labile aluminium). The potential chemical sensitivity of run-off to acid deposition is determined by the weathering rate which, in turn, is largely dependent on geology. Weathering rates for granites, sandstones, schists, gneisses, shales and volcanic rocks, which dominate much of the UK uplands where AWMN sites occur, are relatively restricted. If the rate of base cation displacement from the soil exceeds the weathering rate, the run-off which feeds streams and lakes becomes enriched in hydrogen and aluminium cations and the acid anions sulphate and nitrate, while acidity may increase to a level where all DIC remains as CO₂, and all bicarbonate is lost.

These changes to water chemistry can have a profound impact on aquatic biota. Some aquatic plants depend on bicarbonate as the source of carbon for photosynthesis, while free aluminium may complex with phosphorus in soils, thus restricting the availability of this essential nutrient which is often at limiting concentrations in upland systems anyway. As a result, only those plant species which can utilise CO₂ and are adapted to low nutrient levels are able to survive in more acidified waters. Elevated levels of hydrogen and aluminium have various toxic effects on aquatic animals and particularly gill users such as insect larvae, other macroinvertebrates and fish. Problems include disruption to ion-balance mechanisms and the precipitation of aluminium on gill filaments which can lead to potentially lethal hypoxia. Physiological impacts at the species level may result in a decline in biodiversity and changes in ecosystem functioning and food web interactions; for example many specialised macroinvertebrate grazers are unable to survive in acidified waters. Shrinkage of the food web may influence food chain length and the ecosystem may cease to be able to support higher predators, including certain dragonflies, fish and bird species.

1.3 The international response to the problem and the requirement to monitor

In 1979, at a time of growing evidence of the anthropogenic acidification of Scandinavian lakes, the UNECE (United Nations Economic Commission for Europe) set up the Convention on Long Range Transboundary Air Pollution. Since then the international community has agreed a range of protocols to cut emissions. Of these the most recent is the "Multi-pollutant, Multi-effect Protocol" (1999) which set emissions targets, or ceilings, for the year 2010 for four pollutants, sulphur dioxide, nitrogen dioxide, ammonia and volatile organic compounds (VOCs). The UK is committed to annual emissions ceilings of 625 ktonnes for sulphur dioxide, 1,181 ktonnes for nitrogen oxides and 297 ktonnes for ammonia. Since the implementation of the UNECE directives, sulphur dioxide emissions have fallen substantially, while those for nitrogen oxides and ammonia have declined at a much lower rate.

Signatories to these directives are required to monitor the effects of their emission controls on sensitive "target" environments, including acid-sensitive freshwater ecosystems. In the UK this has been achieved by the establishment and operation of the ADN and the AWMN. In addition to informing on the national situation, these networks also contribute data to international networks sponsored by the UNECE, the most pertinent of these to acidification studies being the International Cooperative Programme on Assessment of Acidification of Rivers and Lakes (or ICP Waters), managed by NIVA in Oslo.

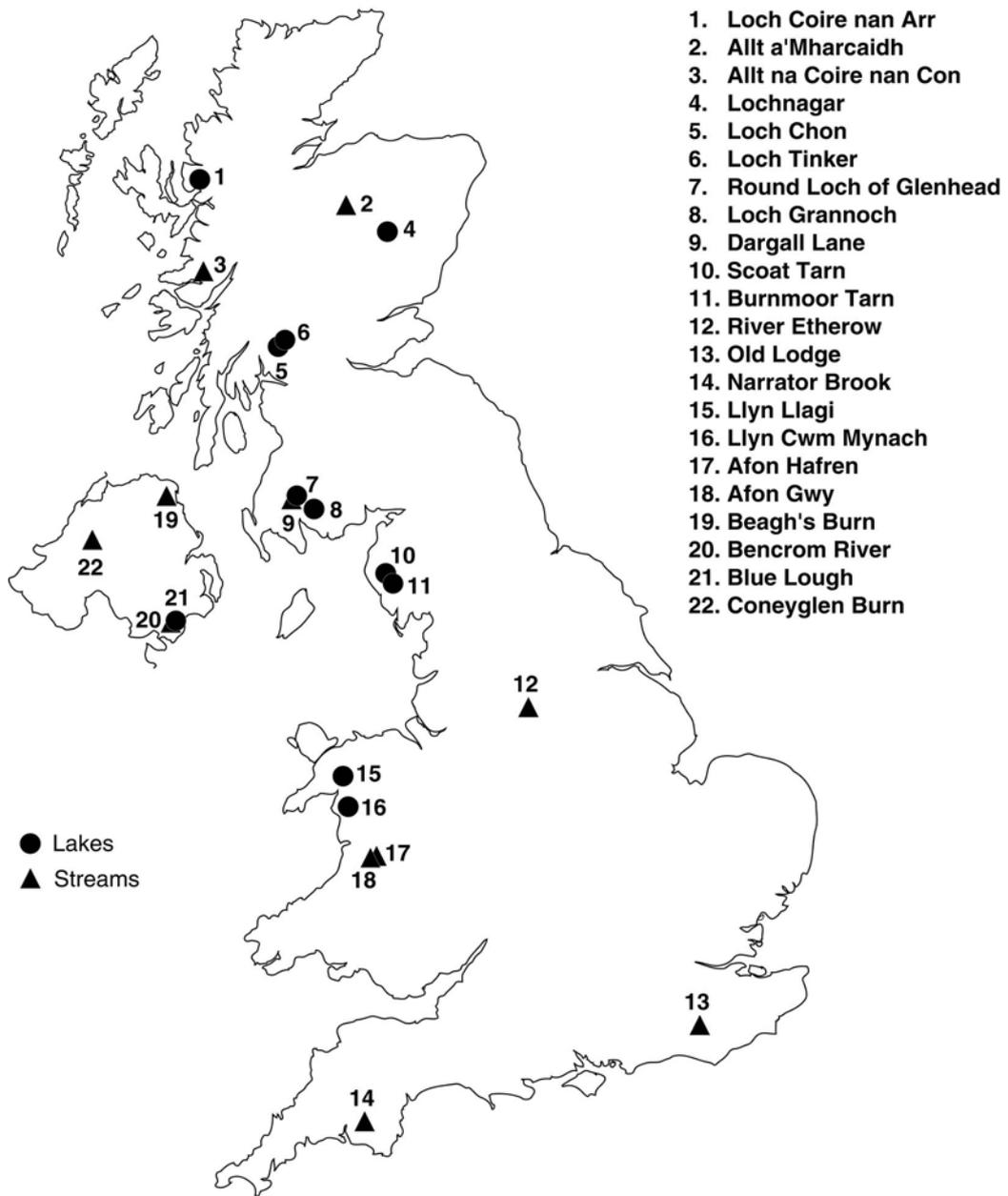


Figure 1.1 Location of AWMN sites.

1.4 Contents of this report

In our 10 Year Interpretative Report (Monteith and Evans, 2000) we proposed that a series of causal links had to be demonstrated in order to support the hypothesis that acid emissions reductions were having a beneficial impact on acid sensitive ecosystems. These provide the basis for the structure of this report, with chapters as follows:

- the impact of emissions control on acid deposition (Chapter 2);
- the relationship between the acid anion content of deposition and catchment run-off at AWMN sites (Chapter 3);
- trends in run-off chemistry (Chapter 4);
- possible links between acid deposition, climate and rising dissolved organic carbon concentrations (Chapter 5);
- relationships between changes in water chemistry and biota (Chapter 6); and,
- a summary of results (Chapter 7).

The analysis which underpins this report has since been developed in a substantially broader and more detailed series of papers, recently published by the journal *Environmental Pollution* (Volume 137, no. 1, 2005). In addition to the themes covered by the report chapters, the *Environmental Pollution* papers also include:

- a consideration of the importance of nitrate leaching as a confounding factor for the recovery of AWMN sites (Curtis *et al.*, 2005);
- an assessment of herbivore-algal linkages across a pH gradient of AWMN streams (Ledger and Hildrew, 2005);
- a demonstration of the use of a palaeoecological technique, Analogue Matching, to identify modern ecological reference analogues for AWMN lakes (Simpson *et al.*, 2005);
- a comparison of palaeolimnological and modelling approaches for the historical reconstruction of the pH of the AWMN site, the Round Loch of Glenhead (Battarbee *et al.*, 2005);
- an assessment of trends in carbonaceous particle fluxes to sediment traps in AWMN lakes (Rose and Monteith, 2005); and,
- a review of regional chemical trends in surface water chemistry across the ICP Waters network, providing a wider context for observations made at the national scale (Skjelkvåle *et al.*, 2005).

Most of the raw data used in these papers is presented in the Appendices of this report, while more recent updates are now available in the latest annual report (Shilland *et al.*, 2005) which may be also be downloaded from the AWMN web page.

Chapter 2

Have emission controls influenced the deposition of acidic pollutants across the UK over the period covered by the UK Acid Waters Monitoring Network?

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2.1. Introduction

The ionic composition of air and precipitation in the UK is monitored by the UK Acid Deposition Monitoring Network (ADN). Using a consistent sampling protocol and chemical analysis for over 16 years, the record is long enough to overcome most of the inter-annual variability in weather. It provides very clear, and in some cases very large, trends with time in concentration and deposition since 1986. During this period, substantial changes in emissions of sulphur dioxide (SO₂) in the UK and more widely in Europe have occurred, but there have also been climatological changes including shifts in the North Atlantic Oscillation (NAO). In this chapter the observed changes in air and precipitation chemistry are presented along with concurrent trends in emissions of sulphur (S) and nitrogen (N) compounds and indices of trends in atmospheric circulation over NW Europe.

The original network (Table 2.1; Figure 2.1A) contained 59 stations but this was reduced to 32 in 1989 before being recently increased again to 39. The sites are located away from major local sources of contamination (small industry, roads, intensive farming activity, etc.) and are in rural locations, primarily at low altitude to avoid losing samples in snowy weather and also to minimize sample loss resulting from exposure to wind of the collectors.

Data from the ADN were first analysed for trends on behalf of the UK Acid Waters Monitoring Network (AWMN) by Fowler and Smith (2000), covering the period 1986-1997. They used a hierarchical clustering technique to classify four geographical groups of sites (Figure 2.1B) representing a declining gradient of trend slope in sulphur deposition. Trend strength in sulphate (SO₄²⁻) varied from circa 3 $\mu\text{eq l}^{-1} \text{yr}^{-1}$ in Group 1 to statistically insignificant change in Group 4. The same grouping is used throughout this Chapter.

Group	Site	Ref Number	Easting (km)	Northing (km)
1	Stoke Ferry	5004	570.0	298.8
1	High Muffles	5009	477.6	493.9
1	Preston Montford	5023	343.2	314.3
1	Flatford Mill	5024	607.7	233.3
1	Thorganby	5117	467.6	442.8
1	Jenny Hurn	5118	481.6	398.6
1	Wardlow Hay Cop	5120	417.7	373.9
1	Bottesford	5121	479.7	337.6
1	Woburn	5127	496.4	236.1
1	Compton	5129	451.2	180.4
1	Driby	5136	538.6	374.4
2	Barcombe Mills	5007	543.7	114.9
2	Glen Dye	5011	364.2	786.4
2	Whiteadder	5106	366.4	663.3
2	Redesdale	5109	383.3	595.4
2	Bannisdale	5111	351.5	504.3
2	Cow Green Reservoir	5113	381.7	529.8
2	Hillsborough Forest	5149	136.9	515.6
3	Yarner Wood	5008	278.6	78.9
3	Goonhilly	5003	172.3	21.4
3	Eskdalemuir	5002	323.5	603.2
3	Loch Dee	5107	246.8	577.9
3	Beddgelert (closed 1996)	5119	255.6	351.8
	Llyn Llydaw (started 1996)	5153	263.8	354.9
3	Balquhidder (closed 1994)	5200	252.1	720.6
	Balquhidder 2 (started 1994)	5152	254.5	720.7
3	Pumlumon	5150	282.3	285.4
3	Tycanol Wood	5123	209.3	236.4
3	Llyn Brianne	5124	280.7	249.2
3	Achanarras	5140	315.1	955
4	Polloch	5151	179.2	768.9
4	Lough Navar	5006	19.2	521.2
4	River Mharcaidh	5103	287.6	805.2
4	Strathvaich Dam	5010	234.7	875
	<i>Crai Reservoir</i>	5154	288.2	221.9
	<i>Beaghs Burn</i>	5155	156.7	643.2
	<i>Loch Chon</i>	5156	242.9	708.4
	<i>Lochnagar</i>	5157	325.2	785.9
	<i>River Etherow</i>	5158	412.5	398.6
	<i>Scoat Tarn</i>	5159	315.8	510.3
	<i>Llyn Llagi</i>	5160	264.7	348.3

Table 2.1 - Acid deposition sites (n = 32 (with 2 substitutes)) with a record of rain ion composition for over 10 years. Sites in italics were established in 1999.

2.2. Wet deposition monitoring and trends

2.2.1 Changes in concentration and deposition 1986 to 2001

It is convenient to consider trends in each of the major ions and rainfall before examining the UK budgets. Trends for individual sites are given in Appendix 1.

2.2.2 Climate

Precipitation trends

The 28 stations with 15 or 16 years data show no significant trend in precipitation over the

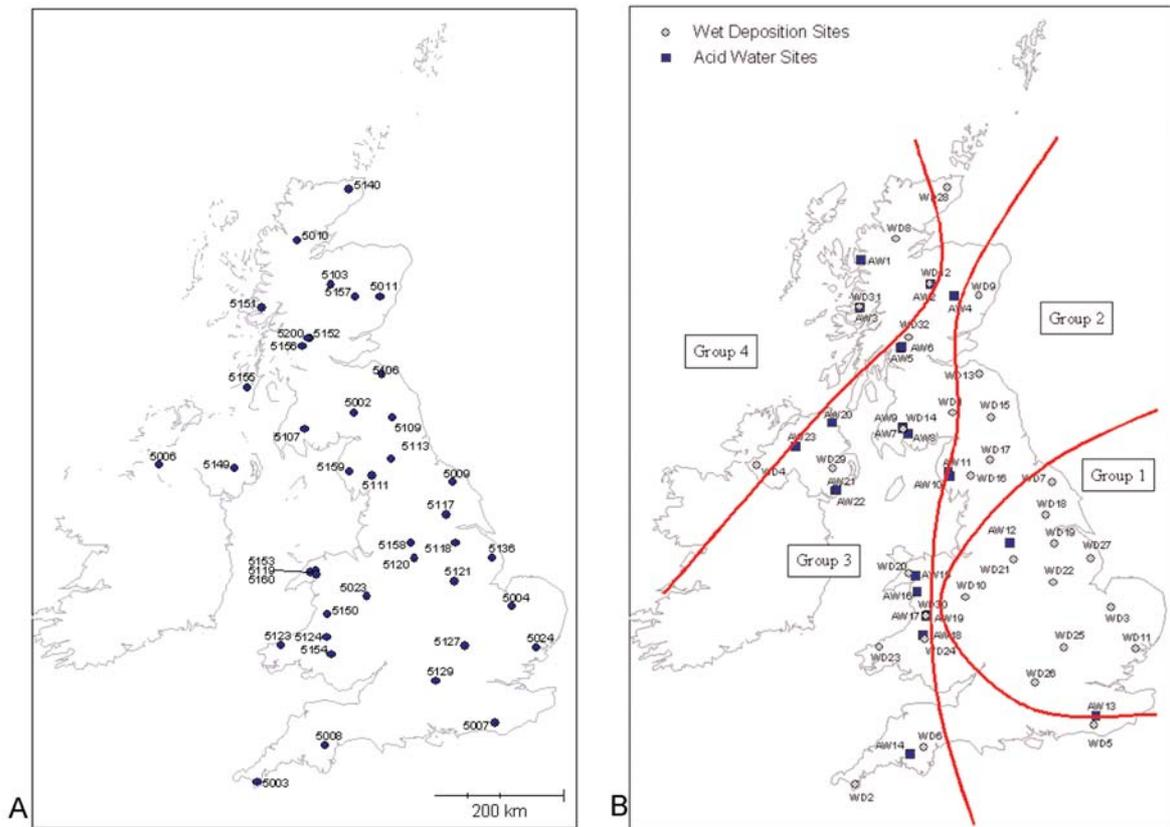


Figure 2.1 (A) Acid Deposition Sites and (B) the geographical locations of groups as in Table 2.1

sampling period (Table 2.2), although the year-to-year variability is considerable, as expected in precipitation data (Figure 2.2). The years 1992, 1998 and 2000 were wet years while 1996 was dry, relative to the mean for the period.

There is an expected and widely observed relationship between precipitation and concentration, with concentration declining as precipitation increases. However, there have been large changes over time in the ionic composition of UK rainfall and these tend to dominate the time-series. Statistically significant relationships between annual rainfall and ion concentration is only apparent for nitrate (NO_3^-) and ammonium (NH_4^+) (Table 2.3). Trends in these determinands are very small, and higher rainfall years clearly show the expected smaller concentrations.

	equation	R ²	p-value
Group 1	$y = 3.83x - 7057$	0.034	0.495
Group 2	$y = 3.17x - 5324$	0.010	0.715
Group 3	$y = -8.42x + 18131$	0.094	0.249
Group 4	$y = -2.45x + 6034$	0.050	0.795
Mean	$y = -1.01x + 2972$	0.020	0.859

Table 2.2 Grouped precipitation statistics (Trends in precipitation (y - mm) with time (x - years))

	Slope	R ²	p-value
Na^+	-0.0208	0.013	0.669
SO_4^{2-}	-0.0197	0.037	0.478
Cl^-	-0.0241	0.012	0.690
non-marine SO_4^{2-}	-0.0169	0.031	0.517
non-marine Cl^-	0.0002	0.000	0.987
NO_3^-	-0.0181	0.360	0.014
NH_4^+	-0.0323	0.499	0.002

Table 2.3 Relationship between mean annual ion concentrations in rain ($\mu\text{eq l}^{-1}$) and mean precipitation amount (mm) in the UK

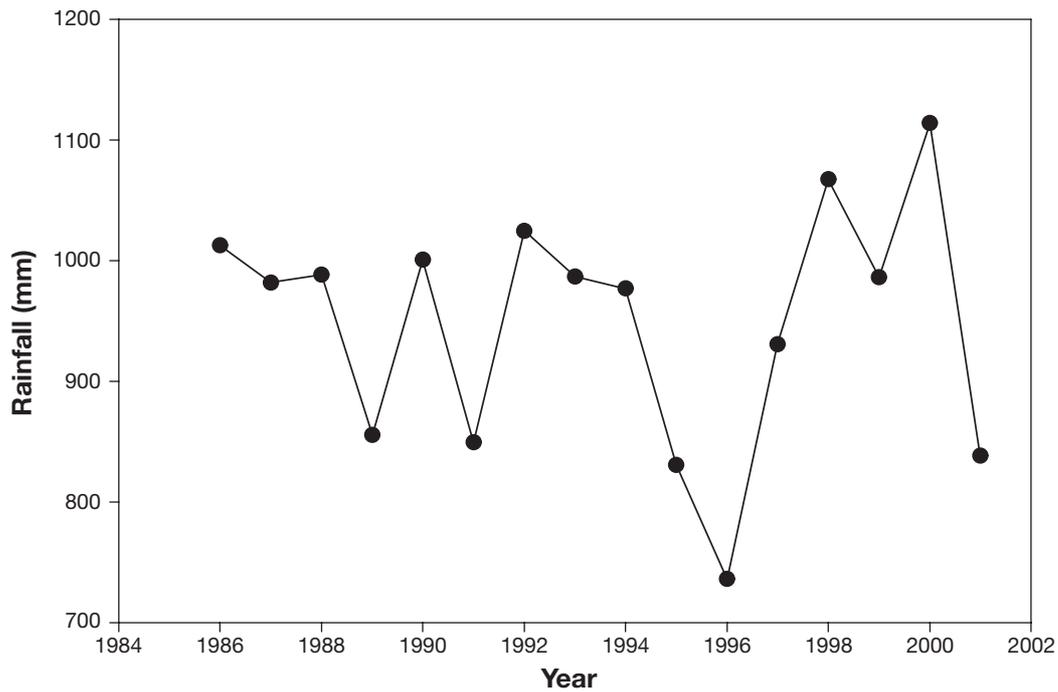


Figure 2.2 Mean annual precipitation for acid deposition sites (n = 28)

Effects of global circulation on wet deposition

The location of the UK at the NW boundary of Europe, and with the Atlantic Ocean to the west and Europe to the south and east, makes the air chemistry very sensitive to air mass trajectories

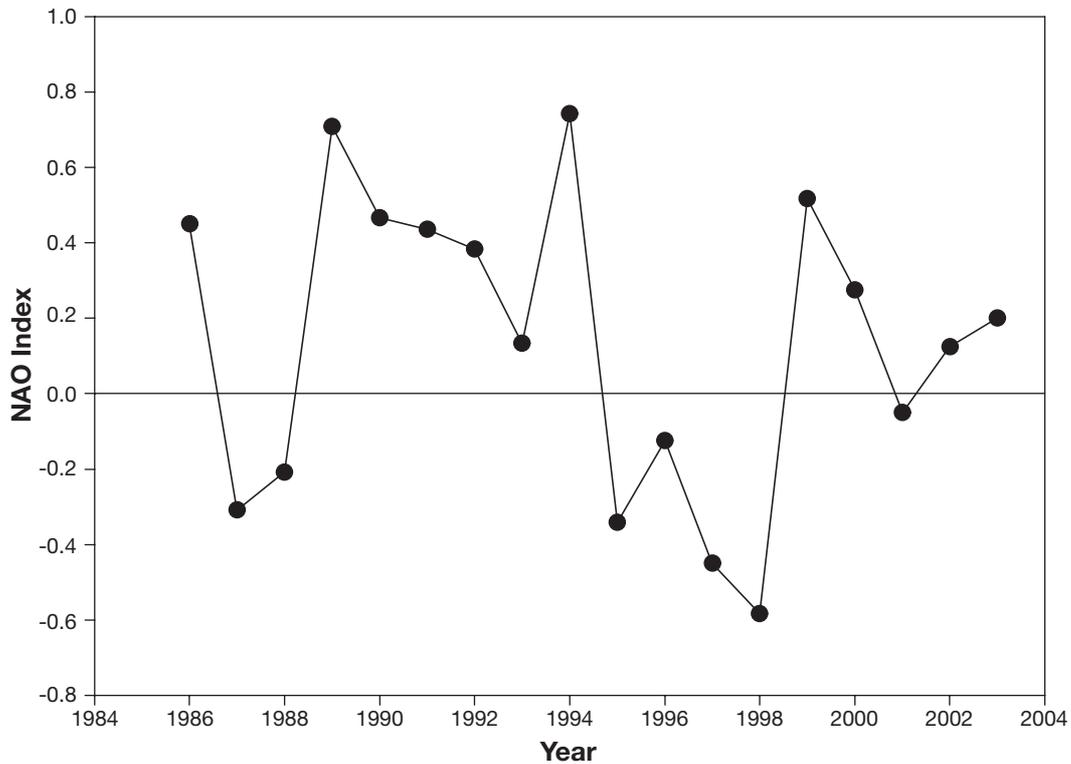


Figure 2.3 Mean annual NAO index

associated with the precipitation. Thus the degree of 'westerlyness' for individual years is expected to significantly influence the annual deposition pattern of both marine and anthropogenic ions, as described in the AWMN 1988-1998 Interpretative Report (Monteith and Evans, 2000). Peaks in positive values of the NAO, due to a larger than average pressure gradient between the Azores and Iceland, are associated with southwesterly airflow over the UK, higher wind speeds and the potential for larger marine ion contribution to precipitation chemistry over the UK. While relationships between the NAO and weather are most apparent during Winter and Spring, an annual average of monthly indices should provide an approximation for average synoptic conditions over the year.

As this broad overview concentrates on the annual statistics of precipitation chemistry and fluxes of acidifying ions we have focussed on the relationship between annual chemistry and the annual mean NAO index (Figure 2.3). There is evidence, however, that the most significant seasalt deposition events occur during Winter and we have therefore also analysed the relationship between mean annual marine salt concentrations at sites on the west coast and the mean January to March NAO Index. To take this analysis further, it would be necessary to examine individual events throughout the monitoring period and the relative frequencies of trajectories over different sources to show the extent to which the relative frequencies have changed with time. Such an exercise is not possible using the current two weekly sampling protocols.

Ion	Equation	R ² (%)	p-value
Na ⁺ - mean 1	y=63.4+9.06x	0.069	0.327
Na ⁺ - mean 2	y=101+9.7x	0.061	0.358
Na ⁺ - mean 3	y=132+26.8x	0.217	0.069
Na ⁺ - mean 4	y=128+32.3x	0.202	0.080
Na ⁺ - overall mean	y=99.9+17.9x	0.179	0.102
NH ₄ ⁺ - mean 1	y=49.6+2.81x	0.026	0.548
NH ₄ ⁺ - mean 2	y=28.1+0.77x	0.006	0.777
NH ₄ ⁺ - mean 3	y=19.2-0.63x	0.007	0.759
NH ₄ ⁺ - mean 4	y=6.84-0.225x	0.006	0.776
NH ₄ ⁺ - overall mean	y=25.9+0.67x	0.006	0.767
Cl ⁻ - mean 1	y=85.3+12.7x	0.064	0.346
Cl ⁻ - mean 2	y=118+11.8x	0.064	0.343
Cl ⁻ - mean 3	y=153+31.7x	0.215	0.071
Cl ⁻ - mean 4	y=148+34.4x	0.176	0.106
Cl ⁻ - overall mean	y=120+21.4x	0.167	0.116
xSO ₄ ²⁻ - mean 1 (*)	y=59.9+7.19x	0.039	0.463
xSO ₄ ²⁻ - mean 2	y=37.4+2.31x	0.014	0.663
xSO ₄ ²⁻ - mean 3	y=23.8+0.53x	0.002	0.867
xSO ₄ ²⁻ - mean 4	y=14.4+1.01x	0.015	0.655
xSO ₄ ²⁻ - overall mean	y=38.3+3.12x	0.019	0.611
H ⁺ - mean 1	y=35.4+4.08x	0.025	0.575
H ⁺ - mean 2	y=27.5+0.13x	0.000	0.977
H ⁺ - mean 3	y=17.4+0.65x	0.010	0.724
H ⁺ - mean 4	y=12.9+1.00x	0.035	0.505
H ⁺ - overall mean	y=25.1+1.64x	0.013	0.688
NO ₃ ⁻ - mean 1	y=37.2+2.45x	0.067	0.332
NO ₃ ⁻ - mean 2	y=25.9+0.03x	0.000	0.986
NO ₃ ⁻ - mean 3	y=16.6-1.58x	0.068	0.329
NO ₃ ⁻ - mean 4	y=9.01-0.001x	0.000	0.999
NO ₃ ⁻ - overall mean	y=22.2+0.21x	0.001	0.889

Table 2.4 Relationship of mean annual NAO Index (x) and annual ion concentrations (y) in precipitation (grouped as in Table 2.1 as overall means) between 1986-2001

There are no significant relationships between individual ion concentrations and the annual mean NAO Index in the 16 year dataset (Table 2.4), although there appears to be some association between this index and the concentrations of chloride (Cl^-) and sodium (Na^+) at sites in groups 3 and 4. The relationship becomes statistically significant if the average January to March NAO index is used (Table 2.5). This is consistent with observations of Evans *et al.* (2001a) and Hindar *et al.* (2004) who have linked the extent of seasalt deposition to this feature of global circulation. However it should be noted that the low value for the average January to March NAO index in 1987 has a major influence on the significance of this interpretation, as illustrated by removing 1987 from the fitted regression (Table 2.5).

Ion	Equation	R ²	p-value
Fit of regression lines including data for 1987:			
Na ⁺ - mean 3	y = 117+31.6x	0.472	0.003
Na ⁺ - mean 4	y = 110+37.4x	0.425	0.006
Cl ⁻ - mean 3	y = 135+37.1x	0.461	0.004
Cl ⁻ - mean 4	y = 128+43.1x	0.433	0.006
Fit of regression lines excluding data for 1987:			
Na ⁺ - mean 3	y = 118+30.6x	0.338	0.023
Na ⁺ - mean 4	y = 115+31.7x	0.250	0.058
Cl ⁻ - mean 3	y = 134+38.3x	0.358	0.018

Table 2.5 Relationship of mean January-March NAO Index and annual ion concentrations in precipitation (grouped as in Table 2.1 as overall means) between 1986-2001

For acidifying components, any effect from climate, as quantified by the NAO Index, is small and currently negligible compared to changes in concentrations resulting from the changes in emissions over the period. However, while not the major process generating variability in precipitation chemistry in the period 1986 to 2001, it may be that climate effects are a much larger contributor to future trends when changes in emissions are likely to be much smaller.

2.2.3 Acidity (hydrogen ion concentration)

The acidity of precipitation is not a conserved quantity and is controlled by the presence of other ions in solution. While the initial focus of the work on acid deposition was acidity *per se*, the ions associated with the acidity were the primary scientific focus, these being non-marine SO_4^{2-} (xSO_4^{2-}) and NO_3^- and, for some areas of the UK, non-marine Cl^- . The acidity in UK precipitation has declined dramatically over the monitoring period at most of the monitoring stations. Considering the 28 sites with 14 years or more data, 22 show a statistically significant reduction in acidity over the monitoring period, varying from $-4 \mu\text{eq l}^{-1} \text{yr}^{-1}$ in the East Midlands of England to $<-0.5 \mu\text{eq l}^{-1} \text{yr}^{-1}$ in Wales. These reductions in acidity in the most polluted regions of Eastern England vary from 40% to 60% of the values of the late 1980s. In the high rainfall regions of Wales, Cumbria and Western Scotland the absolute reductions in acidity are much smaller, but at many sites there is still a statistically significant decline. There are 8 sites with records of over 10 years but no significant change in acidity. These are located either in the west and north (Hillsborough Forest, Balquhiddy, Polloch, Glen Dye, Achanarras), remote from major source areas and never receiving highly acid rainfall, or along the south coast of England (Barcombe Mills, Yarner Wood and Goonhilly), where shipping sources contribute to rainfall acidity. In these areas of southern and especially southwest England, the contribution to wet deposition from shipping is steadily increasing as the terrestrial sources decline.

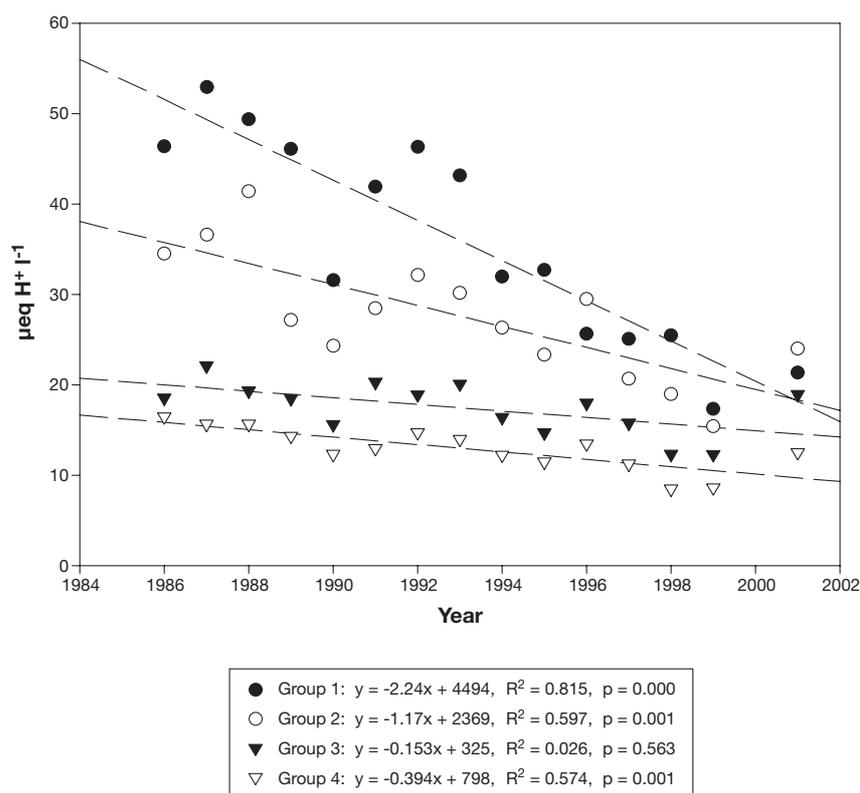


Figure 2.4 Trends of hydrogen ion concentration in precipitation with time (x - years) (sites grouped as in Table 2.1)

Mean acidity across the ADN between 1986 to 2001 is shown in Figure 2.4. By the year 2001 acidity had halved over the country, with larger reductions in the most polluted regions. The regional variability is interesting. Sites in Group 1, the region in the UK which has changed most during the monitoring period, show a decline in acidity from 52 to 18 $\mu\text{eq l}^{-1} \text{yr}^{-1}$. There were concerns in earlier reports on rainfall acidity trends that no reduction in acidity was evident in parts of Western Britain. The longer data series is now revealing reductions in acidity in Wales, but, while trends are generally clearer in other western regions, there remain areas of the country where the acidity in precipitation has not declined despite very large reductions in emissions at the national scale.

2.2.4 Marine derived ions: sodium and chloride

The physical and chemical meteorology of the UK reflect its oceanic climate. Precipitation chemistry, especially close to the coast, is often dominated by marine derived ions and SO_4^{2-} , sodium (Na^+) and magnesium (Mg^{2+}) in particular. The trends in Na^+ over the monitoring period (Figure 2.5) are not statistically significant at most sites, but it is notable that three sites, in central England and the East Midlands, show a significant decline in Na^+ over the 16 years of about 2 $\mu\text{eq l}^{-1} \text{yr}^{-1}$, which is a significant fraction of the concentration at these locations in 1986 (between 70 and 100 $\mu\text{eq l}^{-1}$). As the decline is statistically significant at a few sites where the marine influence is small, an explanation is called for. At most of the remaining sites the changes in Na^+ are negative, but, while non-significant, it is interesting that for many in inland areas the trend is of a similar magnitude, i.e. 1 to 2 $\mu\text{eq l}^{-1} \text{yr}^{-1}$.

One possible cause is a reduction in the application of road salt, which is re-suspended by vehicles, and may have declined in the recent, mild and wet winters. However, so far, it has been

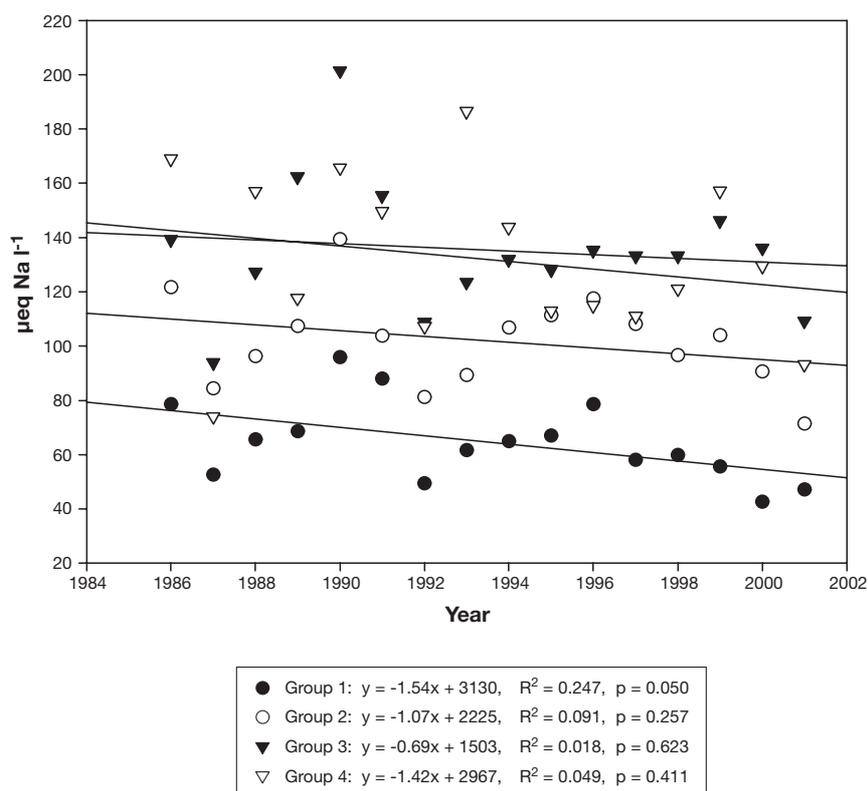


Figure 2.5 Trends in sodium in precipitation with time (x - years) (sites grouped as in Table 2.1)

difficult to find supporting data to check the application of road salt on UK roads during the last 20 years.

For Cl^- the story is more complex, due to additional sources of emission to the atmosphere from the combustion of coal and waste containing Cl^- (Lightowlers and Cape, 1988). Trends in total Cl^- in precipitation (Figure 2.6.) are very similar to Na^+ , confirming the importance of marine

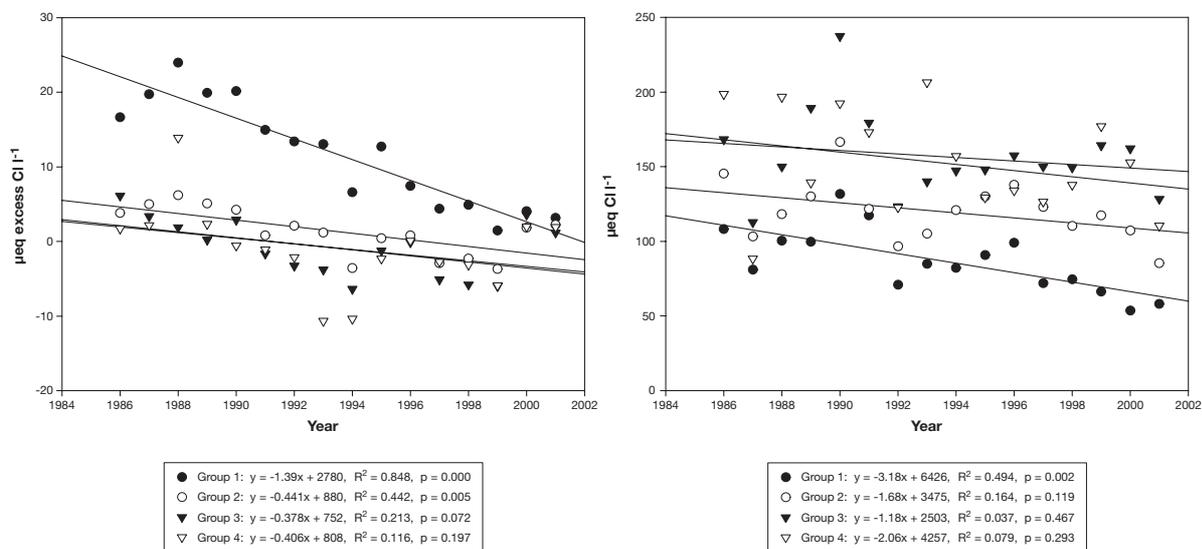


Figure 2.6 Trends of non-marine chloride and total chloride in precipitation with time (x - years) (sites grouped as in Table 2.1)

sources for these ions in UK precipitation. Again there is a significant decline in concentration in the Group 1 sites in central England, but in this case the magnitude of the decline (i.e. about $3 \mu\text{eq l}^{-1} \text{yr}^{-1}$) is larger than that for Na^+ because non-marine Cl^- from coal combustion has also declined appreciably during this period. Non-marine Cl^- concentrations show a very large decline, from about $20 \mu\text{eq l}^{-1}$ in 1986 to current values close to $5 \mu\text{eq l}^{-1}$ in the English Midlands. The area in which statistically significant declines in non-marine Cl^- are observed include both Group 1 and Group 2 sites, therefore covering almost all of southern England, and extending into eastern Scotland.

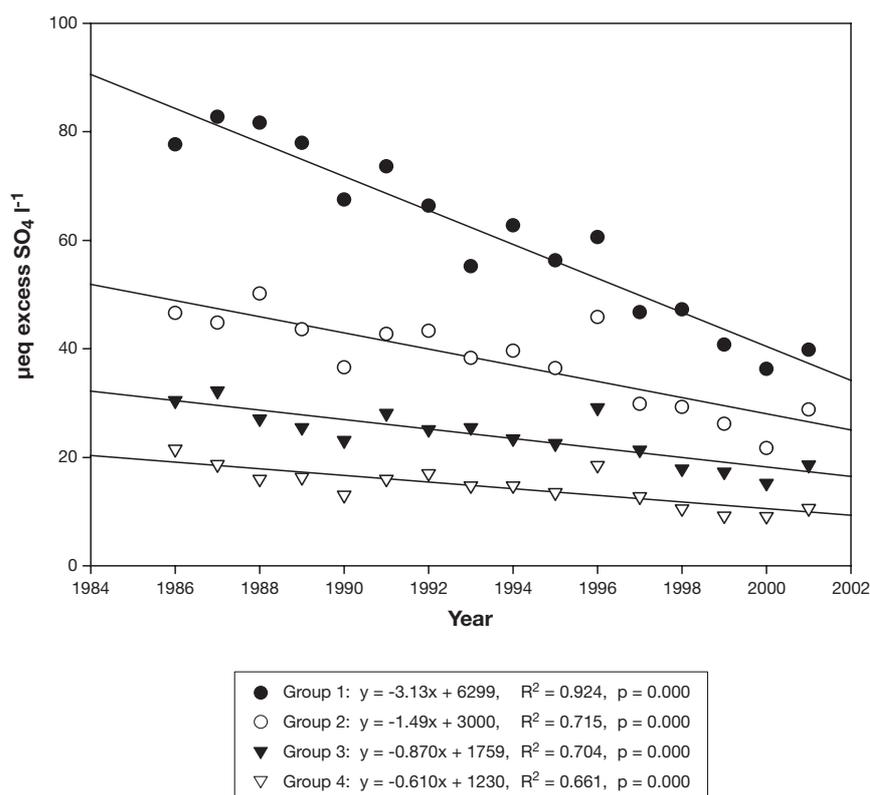


Figure 2.7 Trends in non-marine sulphate in precipitation (sites grouped as in Table 2.1)

2.2.5 Non-marine sulphate

As the major source of acidity in precipitation during the 1970s and 1980s, xSO_4^{2-} was the ion on which most attention was focussed. Trends in xSO_4^{2-} in UK precipitation between 1986 and 1997 were clear at Group 1 and 2 sites in the NEG-TAP report (NEG-TAP, 2001), but west coast sites showed non-significant trends, in part due to shipping emissions. With the longer time series, trends in xSO_4^{2-} are now statistically significant in all the groups (Figure 2.7). The magnitude of the decline is notable, amounting to 50% at Group 1 sites. Even at the remote sites in Group 4 the decline approaches 50% over the 16-year monitoring period. The data for the last 4 years has clearly made an appreciable difference to the countrywide picture and show a recovery of the precipitation chemistry, at least in the respect of xSO_4^{2-} , to values not recorded in the UK since 1950s (Stevenson, 1986). Earlier data exist from the work of Smith (1872), and Lawes *et al.* (1883), but the protocols for collection and analysis are not described in sufficient detail to allow direct comparisons with contemporary data.

2.2.6 Nitrate

Changes in UK concentrations of NO_3^- in precipitation are shown in Figure 2.8. The data show a reduction in concentration over substantial areas of England with the grouped data showing a significant trend only in Group 1, amounting to a reduction in NO_3^- of 20% in the 16 year record. This compares with a reduction in emissions of nitrous oxides (NO_x) in the UK and the EU of 35% and 25% respectively over the monitoring period. The trends at individual sites are generally statistically significant for those in Group 1 (7 out of the 11 sites) along with Barcombe Mills on the south coast of England, Whiteadder in the Scottish Borders and one site, Polloch, on the west coast of Scotland.

Concentrations of NO_3^- , from the oxidation of NO_x in the atmosphere, are not complicated by significant marine sources. They should therefore reflect the official reduction in regional (European) emissions, providing that the latter has not been over-estimated and that there is no additional contribution to the NO_x budget over the UK from non-European sources.

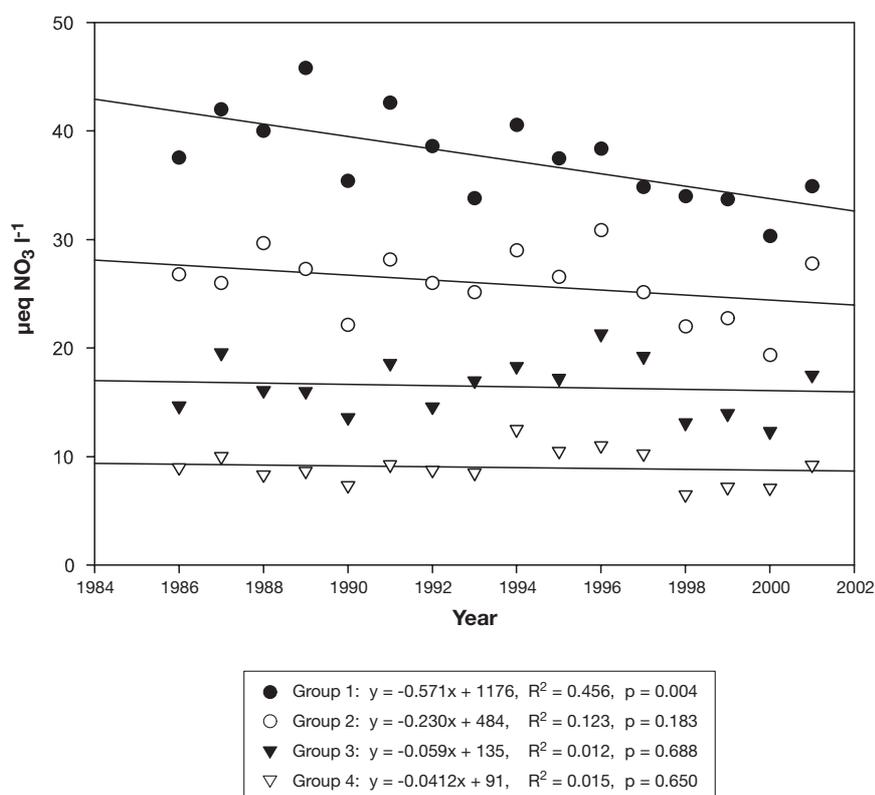


Figure 2.8 Trends of nitrate in precipitation with time (x - years) (sites grouped as in Table 2.1)

2.2.7 Ammonium

Along with SO_4^{2-} and NO_3^- , the other major ion in precipitation with an anthropogenic source is NH_4^+ . In the early days of the ADN, concentrations of NH_4^+ were among the largest of the three and, especially in the source regions of the English Midlands, NH_4^+ concentrations were generally larger than NO_3^- . The main sources are agricultural, with intensive production of livestock and beef and dairy cattle, in particular, being the largest contributors. The data show a decline in NH_4^+ concentration at seven of the long-term sites, and as five of these are in Group 1, this group shows a statistically significant decline (Figure 2.9) of more than 20% over the 16

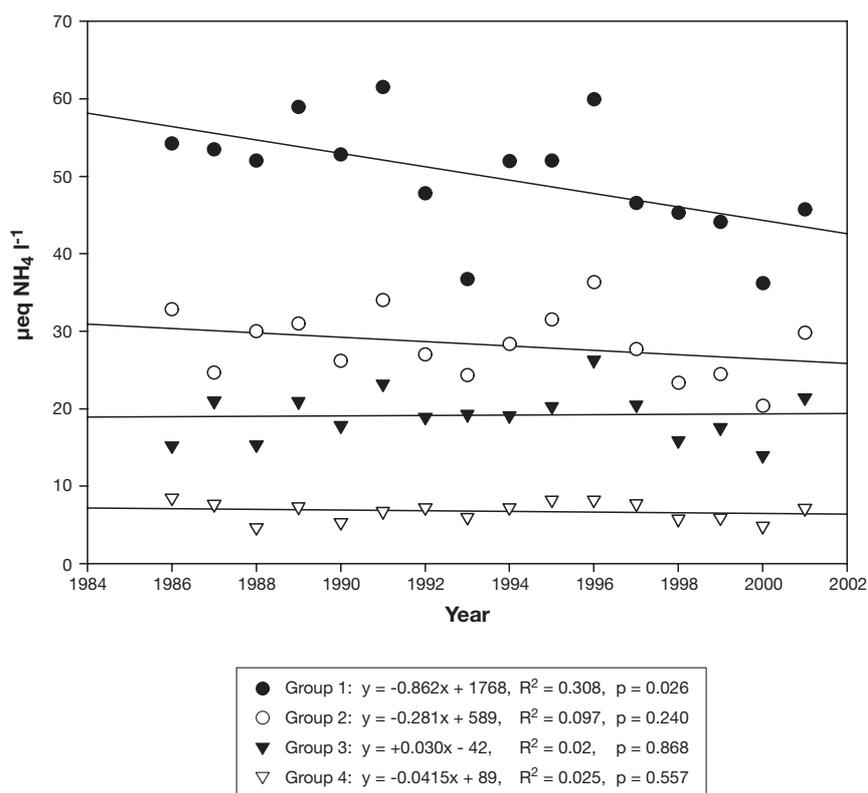


Figure 2.9 Trends of ammonium in precipitation with time (x - years) (sites grouped as in Table 2.1)

years. Many sites show non-significant declines but most changes over the monitoring period are negative rather than positive.

Given the very large decline in non-marine SO_4^{2-} concentrations and the reduction in acidic aerosol concentrations with which it was associated, the scavenging of NH_4^+ would be expected to change. In particular we might expect an increase in travel distance of NH_4^+ and a gradual change in the partitioning of ammonia (NH_3)/ NH_4^+ . Emissions of NH_3 have declined by about 15% since 1986, and the larger reductions in NH_4^+ concentration are broadly consistent with the change expected through the combination of the emission reduction and the changing atmospheric sinks in the source region.

2.2.8 Base cations: calcium and magnesium

The base cations are generally minor contributors to the ionic strength of precipitation, but are important in the overall acid deposition story as they contribute acid neutralising ions to the surface. As such, base cations are very important contributors to the recovery of fresh waters in catchments with very slow weathering soil and parent mineralogies.

Calcium and magnesium are primarily from marine sources over most of the UK, but anthropogenic sources, primarily related to combustion plant or quarrying activities, are very important in certain areas. As it is assumed that marine sourced ions are neutral overall when input to a catchment, the components of most interest for acidification studies are the non-marine base cations.

Both total and non-marine Ca^{2+} and Mg^{2+} show a clear decline at almost all sites over the monitoring period, but the record is limited to the period 1986 to 1991 and 2000 to 2001. The

missing years have been deleted due to analytical problems. There are significant and substantial declines in concentration of both total and non-marine Ca^{2+} at 4 sites in Group 1 (Flatford Mill, Woburn, Bottesford and Jenny Hurn). Here, reductions of between 1.0 and 2.5 $\mu\text{eq l}^{-1} \text{yr}^{-1}$ amount to a fall of around 50% over the period. The cause of the decline is most likely a consequence of reduced emissions of non-marine Ca^{2+} from combustion plant. There are related reductions in non-marine Mg^{2+} at some of these sites but, as the estimation of non-marine Mg^{2+} is prone to error, other smaller significant reductions may be an artefact of data analysis.

For the recovery of freshwaters from the effects of acidification, base cation deposition is an important source of alkalinity, and these substantial reductions in base cation deposition may be very important in determining the trajectory of the recovery process in catchments with very limited weathering rates. It will be important to improve the estimates of wet (and dry) deposition of base cations in order to refine recovery models.

2.3 Dry and total deposition

2.3.1 Dry deposition

The contribution of dry deposition, mainly of SO_2 , to AWMN sites is relatively small, as the sites are mainly located in the high rainfall areas of the UK. However the contribution to acidification is significant, even in the uplands, and the change in dry deposition of SO_2 over the monitoring period is the largest contributor to the changes in the UK deposition budget. There are reductions in the estimated dry deposition of non-marine base cations over the period, but this is a small component of the total deposition of base cations and estimates are relatively uncertain. There are insufficient data at present to allow precise quantification of any changes in dry deposition of nitric acid (HNO_3) or NH_3 over the period 1986-2001. The current estimate of dry deposition of nitrite (NO_2) to the UK is 30 kt N yr^{-1} while a previous report (RGAR, 1987) used a different methodology to indicate a UK budget of 60 kt N yr^{-1} in the mid 1980s. These estimates amount to around a third to a half of the wet deposition nationally, but dry deposition will represent a much smaller fraction of the total at most AWMN sites.

Year	Emissions	Wet deposition	Dry deposition	Total deposition
1987	1937	233	291	524
1988	1905	240	233	473
1989	1848	195	223	418
1990	1860	192	199	391
1991	1768	191	232	423
1992	1731	220	188	408
1993	1558	189	167	356
1994	1338	204	156	360
1995	1183	159	146	306
1996	1015	178	145	323
1997	835	147	110	258
1998	804	163	93	256
1999	615	146	82	227
2000	594	136	73	209
2001	563	129	76	205

Table 2.6 UK sulphur budget (kilotonnes) from the network measurements 1987-2001

In summary, changes in total deposition at the sites in the Acid Waters Monitoring Network are essentially driven by changes in wet deposition. However, the change in relative importance of the dry deposition of SO_2 to the wet deposition of SO_4^{2-} has implications for the recovery from acidification of freshwater systems.

2.3.2 Changes in the wet/dry deposition partitioning in the UK 1986-2001 and the consequence for recovery of acidified upland freshwaters

At the UK scale, changes in total deposition, for the period 1987-2001, are clear in the deposition budget for S, with a much larger reduction in dry deposition (74%) than wet deposition (45%) (Table 2.6). The reduction in dry deposition is greater than the reduction in emissions (71%) over the monitoring period. The relative magnitude of these changes in wet and dry deposition is important in illustrating geographical variability and has implications for recovery from acidification.

The benefits of the reduction in emissions with time have therefore been much greater in the regions of the UK in which dry deposition dominates the inputs of S, primarily across the

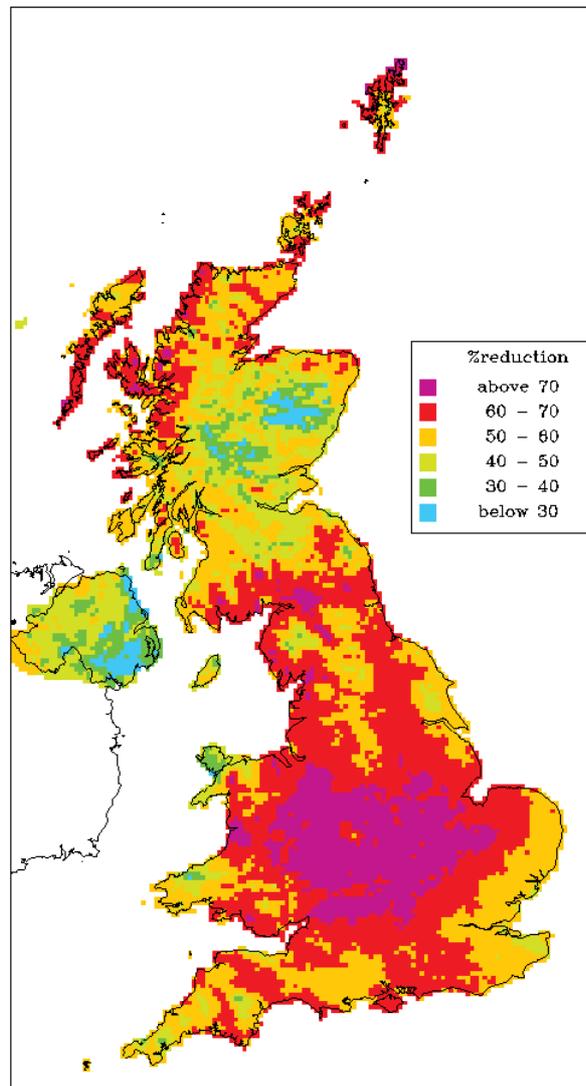


Figure 2.10 Relative reduction from 1987 to 2001 in the total deposition of non-marine sulphur (total deposition is the sum of dry, wet and cloud droplet deposition)

English Midlands (Figure 2.10). Many areas of the UK, including many upland regions, show reductions in deposition of less than 60% over the period, and therefore a considerably smaller improvement in deposition than expected from the 71% reduction in emissions.

At the time of the last review of deposition trends as a part of the AWMN 10 year report (Monteith and Evans, 2000), there were regions of the UK in which trends in S deposition were non-significant. The result was a surprise, especially given the magnitude of the emission reduction at the time. The data presented in this report demonstrate that all regions of the UK are now showing a reduction in sulphur deposition, and reduced acidity in precipitation. However, the magnitude of the reduction in S deposition in the some high rainfall areas of Cornwall and Devon, Wales, the Pennines, Cumbria and Scotland is small relative to the reduction in S emissions in the UK, or even in Europe as a whole. In part this is a consequence of a significant increase in the delivery of S from shipping sources to the west of the UK, and to changes in the atmospheric processing of emitted S over the 16 years.

2.3.3. Changes in the UK deposition budget

The absence of change in precipitation over time implies that the trends in the wet deposition budget reflect the changes in concentration described above, and so these trends are not explicitly discussed here.

Deposition of $x\text{SO}_4^{2-}$ in the UK has declined from 525 kt in 1987 to 205 kt in 2001, a reduction of approximately 60%, during a period in which emissions declined by 70%.

Trends in the deposition of oxidised N are uncertain due to the short period of HNO_3 monitoring. However, trends in precipitation NO_3^- are small, and only statistically significant in the English Midlands. Over the UK, the wet deposition of oxidized N has remained fairly constant at about 100 kt N, dry deposition of NO_2 has declined from about 60 to 30 kt N, while the deposition of HNO_3 , which is currently about 60 kt N is unknown earlier than 2000.

Dry deposition of reduced N appears to have declined by about 10% over the period 1996 to 2000 while wet deposition has declined by about 10% between 1986 and 2001. Overall there does therefore appear to be a small decline in reduced N deposition over a period in which emissions fell by about 10%.

Deposition of non-marine Cl^- has declined by about 80% between 1986 and 2001, but the absolute values are subject to substantial uncertainty due to analytical problems.

The wet deposition of base cations in the UK is estimated to have declined by between 30% and 40% over the period 1986-2001, but this is subject to substantial uncertainty. The extent of decline in dry deposition is also uncertain but probably amounts to a similar magnitude.

2.4 Summary

- As there is no trend in rainfall over the period 1986 to 2001, trends in wet deposition reflect the changes in concentrations of ions in rainfall. Wet deposition is the predominant input at most Acid Waters Monitoring Network sites.
- The North Atlantic Oscillation (NAO), when averaged over the year, has a minor effect on the rainfall and ion concentrations. The dry years (negative NAO Index) tend to have larger concentrations of the pollutant ions and smaller concentrations of marine ions. Significant

relationships are, however, apparent between a Winter NAO Index and annual marine ion deposition, although, relative to the major trends in ionic concentrations, this is not a dominant effect.

- Acidity in rain has declined by about 50% over the UK since 1986. The decline is detectable even in the remote regions of the country, but the magnitude in both absolute and relative terms is smaller in the remote areas.
- The trend in xSO_4^{2-} concentration is large and significant throughout the UK and current concentrations are about 50% of the values in the late 1980s. Even the west coast sites now show clear trends. However, the decline in concentration and wet deposition is still less than that expected given the decline in emissions of SO_2 over the UK and Europe and many sites are affected by an increase in emissions of S from shipping.
- Concentrations of NO_3^- in rain have declined but significant trends are largely restricted to the English Midlands where they are 20% smaller than 1986. Over this period, emissions declined by 40%. Concentrations of NH_4^+ in rain declined about 10%, in line with the decline in UK emissions over the 16 years.
- The data for base cations are of poorer quality, and analytical problems during the mid 1990s have reduced the length of the record. However, there is a clear decline in concentrations amounting to about 50% over central and eastern England.

Chapter 3

Are sulphur and nitrogen deposition signals seen in freshwater run-off?

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3.1 Introduction

Previous AWMN reports have eluded to possible discrepancies between trends in sulphur (S) deposition and concentrations in surface waters. This has prompted concern that catchment soils may impose a lag on the leaching of S, thereby delaying the onset of chemical recovery. Now, with an extended dataset, a recent decline in non-marine sulphate ($x\text{SO}_4^{2-}$) concentration is evident at many AWMN monitoring sites and this has coincided with a period of reduced atmospheric deposition of S. There is every reason to expect a direct causal link between these two downward trends. This can be investigated by estimating catchment budgets and comparing inputs and outputs at a suitable time scale. There is less clear evidence of changes in nitrogen (N) deposition or in surface water concentrations of N. Nevertheless, the estimation of a budget can indicate whether catchments appear to be gaining or losing N, and suggest the magnitude of any net annual change. This may have implications for future N loss, if catchments are becoming saturated.

To compute a budget which is useful for detecting a response to changed deposition, a suitable time scale needs to be selected. This should be long enough to integrate short-term variation due to differences between storms, hydrological travel times and regular seasonal factors, but short enough to retain information on trends. We need to consider first the processes influencing concentrations. Soluble chemical components in atmospheric deposition ultimately reach surface waters along a variety of hydrological pathways. Concentrations in surface waters are influenced by the delay as water moves along these pathways and by evaporative loss. There may also be concentration changes during transit due to immobilisation and release processes. The net effect of these transformation processes is superimposed on the translational delay to generate a “signal” characterising the response of surface water concentrations to changes in atmospheric deposition.

In catchments at equilibrium over some characteristic time scale, the net change in storage of a chemical component over the time period is zero, and the total input matches the total output.

Correspondingly, if measured changes in input and output are of a similar magnitude over successive time intervals at this scale, a reasonable hypothesis is that the system is at equilibrium at that time scale, and that the change in inputs is driving the change in outputs in a causal fashion. Under these circumstances this simple mass-balance model can be used for prediction at this time scale. At a finer temporal resolution short-term disequilibrium might need to be modelled explicitly to derive useful predictions.

3.2 Hydrological and storage processes influencing sulphur and nitrogen in catchments

The purpose here is to determine a suitable time scale for approximate chemical equilibrium in the AWMN catchments, and compute budgets at that time scale.

The AWMN catchments vary in size from around 1 to 17 km². With the exception of one site (Old Lodge) net annual rainfall exceeds 1000 mm, and none of the catchments has extensive groundwater storage. These are almost exclusively small, wet, quickly-responding catchments with most of the hydrological translation effect of storms operating at a time scale much less than a year. Winter residence times for lakes are of the order of a few weeks at most, although some lakes are unlikely to see a complete throughput of water during dry summers. On the basis of hydrology alone, and in the absence of storage changes due to chemical change, we would expect inputs and outputs at the AWMN catchments to approximately balance at an annual time scale.

Sulphur budget studies in wet, upland acid catchments have drawn varying conclusions (Evans *et al.*, 1997), with net retention or loss reported depending on conditions. Sulphur is a minor nutrient, with Carbon:Sulphur (C:S) ratios typically of the order 100:1 (Whitehead, 1964), so that the breakdown of organic matter releases some S, and some will be a component of any accumulating organic matter. These processes are believed to have a minor influence in the AWMN catchments. More importantly, S is readily reduced to sulphides or oxidised to sulphates under changing redox potential, influenced, for example, by soil water conditions. Major short-term changes in storage have been associated with drying soils, with a release of sulphate (SO₄²⁻) (Evans *et al.*, 1997). Sulphur can also be adsorbed by organics or iron oxides. Geological weathering sources may be present and drainage from former improved agricultural land may also result in long-lasting raised S concentrations from fertiliser residuals, although this is not a factor of concern for these remote catchments. While several of these processes may be significant, their effects on S release and immobilisation in the soil are likely to be seasonal or related to short term weather effects. In view of this, a working hypothesis is that, in the absence of geological weathering, the S budget balances at an annual time scale in AWMN catchments.

In AWMN catchments, most N in surface waters is present as nitrate (NO₃⁻) or dissolved organic N (DON), although much of the input of N to catchments is in the form of ammonium (NH₄⁺). Since N is a major nutrient, its concentration in surface waters is strongly dependent on seasonal biological activity in the catchment. N is therefore not conservative along hydrological pathways, and concentrations of dissolved N in surface waters are not expected to be closely related to input concentrations simply through translocation by water flow. Nitrogen storage as organic N is immense in most soils, and far larger than the annual input or output of N. This store is capable of changing under changed inputs without a commensurate change in N losses. There may also be significant gaseous losses of N. It is possible that any response to changed deposition will either not be observed as a change in NO₃⁻ loss, or will only appear after other significant changes in catchment ecology have occurred.

In addition to long-term responses to short-term changes in deposition, concentrations of both sulphate and N may be influenced by other longer-term effects. These include climate effects

such as long-term temperature change, or the consequences of the decadal-scale variation in the North Atlantic Oscillation (NAO; Monteith *et al.*, 2000; Evans *et al.*, 2001a). Several AWMN catchments are forested, and the changing age structure of the forest, felling and logging operations also have the potential to change stream water quality. Other possible influences are a change in stocking rates of those catchments which are grazed.

3.3 Catchment budget

The working hypothesis for SO_4^{2-} is that stream water concentrations at an annual time scale are determined primarily by hydrological translation. Sulphur inputs are assumed to comprise wet deposition of SO_4^{2-} and dry deposition of S as sulphur-dioxide (SO_2) or SO_4^{2-} particles. Outputs are assumed to be as SO_4^{2-} in drainage water. While it is recognised that subsurface processes are present, the net effect of these on the catchment budget at an annual time scale is assumed, as a first approximation, to be small. For N there is no expectation of a direct hydrological transfer with only a minor influence of storage processes. It is nevertheless useful to estimate catchment budgets to determine whether there is net gain or net loss. The budget for the AWMN sites is based on estimated inputs from wet and dry deposition of NO_3^- and NH_4^+ . Output is measured as NO_3^- and total N, which comprises essentially NO_3^- and DON.

If the hypothesis of a balanced annual S budget were not rejected, this would add weight to the belief that there was a causal link between changes in deposition at this time scale and changes in surface water concentrations. It would nevertheless remain possible that confounding effects were acting coincidentally, and that prediction based on the chosen model might break down if the true mechanism subsequently led to deviation from the hypothesis.

3.4 Measurements of input and output

The catchment budget estimation procedure adopted essentially follows Cooper and Jenkins (2003). The input and output budgets can be estimated in terms of loads, but this is difficult for lake catchments where discharge is not measured. The alternative taken here is to estimate the annual mean concentration in surface water leaving the catchment from sample measurements in the AWMN streams and lakes. These annual mean concentrations are also simulated by accounting for the combined effect of annual precipitation, evaporation and S or N deposition.

Output SO_4^{2-} , NO_3^- and total N concentrations in drainage from the AWMN catchments are measured as single monthly values in streams at a single site, and single seasonal values at lake outflows. At most stream sites there is an accompanying discharge measurement, in which case a flow-weighted mean annual concentration can be found from the 12 monthly values of concentration and flow. This method gives an approximately unbiased estimate, but where only 12 values are available the variance of the estimate is high. Single extreme events can have apparent undue influence in individual years, while years with no extreme events sampled may show bias. This is not a major issue for SO_4^{2-} at most AWMN catchments since the concentration of the non-marine component, at least, is not strongly correlated with discharge.

For the River Etherow, flow measurement is believed unreliable and the mean annual concentration has been estimated by taking a simple average of the concentrations. For the Allt Coire nan Con, the continuous flow record maintained by SEPA has been used rather than the spot measurements made at the time of water quality sampling. The spot data showed step changes through the monitoring period due to uncertainty in updating calibration. These step changes were absent from the SEPA record, although these data may have some calibration drift.

For lakes the concentration estimate is to some extent, depending on recent residence times, an

integrated measure of concentration averaged over several previous storm responses. Ideally each three-monthly measurement would represent a completely mixed sample from the whole response of the previous three months, and the precipitation volume would be the same for each 3-month period. The mean of the four measurements would then be a theoretically perfect value. In practice, a simple mean of four values will tend to bias estimation towards summer concentrations. Theoretically better estimates might be obtained using a weighted mean, with the weights depending not only on the distribution of precipitation, but also on the volume of the lake. For present purposes this is not attempted. A comparison of these aggregated values implies a conceptual model with an approximate time lag of between 2 and 3 months. This is because the first annual lake measurement was made in March, and the last in December.

Estimates of wet deposition inputs are taken from the UK atmospheric deposition network (ADN; <http://www.aeat.co.uk/netcen/airqual/data/nonauto/raindata.html>; Campbell *et al.*, 1994) site data. CEH and HARM model estimates are used for dry deposition (NEG-TAP, 2001). The co-located ADN site for each AWMN site is given in Table 3.1. In most cases they are some distance (>10 km) apart, and this is a potential source of significant error in budget estimation. The recent addition of co-located ADN sites at Lochnagar, Loch Chon, Scoat Tarn, River Etherow, Llyn Llagi and Beagh's Burn will permit improved trend estimation in coming years, but at present the records from these sites are too short to make a significant contribution to the analysis.

Data from ADN sites comprise measurements of concentration and precipitation collected at two-week intervals. Wet deposition of S is taken to be entirely SO_4^{2-} , and a non-marine component is computed by removing the fixed sea-salt ratio to the chloride concentration, taken to be the marine component. Wet deposition of N is estimated as the sum of the contributions from NH_4^+ and NO_3^- . The mean annual concentration at each ADN site is computed as the precipitation-weighted average of the two-weekly concentration values. This mean concentration is used unadjusted at the co-located AWMN site.

AWMN site	ADN site ref.	ADN site name	Rainfall site
1	5010	Strathvaich Dam	Plockton
2	5103	River Mharcaidh	Aviemore
3	5010	Strathvaich Dam	Inverailort
4	5011	Glen Dye	Balmoral
5	5152	Balquhidder 2	Loch Venachar
6	5152	Balquhidder 2	Loch Venachar
7	5107	Loch Dee	Clatteringshaws
8	5107	Loch Dee	Clatteringshaws
9	5107	Loch Dee	Clatteringshaws
10	5111	Bannisdale	Eskmeals
11	5111	Bannisdale	Eskmeals
12	5120	Wardlow Hay Cop	Emley Moor
13	5007	Barcombe Mills	Edenbridge
14	5008	Yarner Wood	Princetown North Hessary
15	5150	Pumlumon	Nantmor
16	5150	Pumlumon	Buarthre Newydd
17	5150	Pumlumon	CefnBrwyn
18	5150	Pumlumon	CefnBrwyn
19	5006	Lough Navar	Ballycastle
20	5107	Loch Dee	Annalong Valley
21	5107	Loch Dee	Annalong Valley
22	5006	Lough Navar	Lough Fea

Table 3.1 - Collocated sites used in calculating simulated surface water concentrations

Where individual annual estimates of dry deposition are not available, these have been computed by linear interpolations based on NEG-TAP tabulated values between 1988 and 2003. These estimates were supplemented by CEH 5 km² estimates for 1995-97, used for checking at some sites. Where the AWMN catchment is forested, the NEG-TAP values have been multiplied by 1.5 to account for additional interception by the canopy. The values used for linear interpolation are shown in Table 3.2. Although linear interpolation has been used to estimate annual dry deposition values, measurements of SO₂ and particulate SO₄²⁻, available at some ADN sites, show that concentrations of these determinands have not in fact declined uniformly over the monitoring period. Since these are the sources of dry deposited S, it is unlikely that dry deposition declined uniformly over the monitoring period either. The dry deposition estimates are therefore viewed as very approximate, and the catchment mass-balance would benefit greatly from better annual estimates of dry S and N deposition.

ADN site ref	ADN site name	1988 S	2003 S	1988 NO ₃ -N	2003 NO ₃ -N	NH ₄ -N All years
5002	Eskdalemuir	7	3.5	1.8	1.5	2
5006	Lough Navar	2	1.5	0.8	0.8	2
5007	Barcombe Mills	8	4	2.5	2.5	3
5008	Yarner Wood	5	3.5	2	2	5
5010	Strathvaich Dam	2	1.5	0.5	0.5	1
5011	Glen Dye	4	2	0.8	0.8	2
5103	River Mharcaidh	3	1.5	0.7	0.7	1.5
5107	Loch Dee	6	3	1.5	1.5	2
5111	Bannisdale	7	3.5	1.8	1.8	3
5120	Warlow Hay Cop	12	6	2.3	2.3	5
5150	Pumlumon	9	5	2.2	1.9	5
5152	Balquhidder	5	2.5	1.3	1.3	3

Table 3.2 - Estimated dry deposition of sulphur and nitrogen in kg ha⁻¹ yr⁻¹ (based on NEG-TAP, 2001)

Annual rainfall at each AWMN site has been estimated from a nearby raingauge (Table 3.1), adjusted by standard-period average annual rainfall (SAAR) value. SAAR values, available on a 1 km grid, give long-term annual mean rainfall. Rainfall estimates at co-located gauging sites have been adjusted to the AWMN catchment values using the SAAR ratio. Annual evaporation has been estimated from the value for the MORECS 40 km square (Thompson *et al.*, 1981), adjusted for land use, with a fixed annual value used for each site. At all sites except Old Lodge, evaporation is a small fraction of rainfall, and estimation errors an even smaller fraction.

The simulated annual concentration in runoff is computed using the estimated mass-balance equation:

$$C_R = \frac{k_1 P C_w + k_2 L_D}{P - E} \quad (1.1)$$

In equation (1.1) the terms are:

- C_R Simulated concentration in runoff
 P Estimated annual precipitation at AWMN site, from Met. Office raingauge and SAAR data

Chapter 3

- C_W Estimated mean annual wet deposition concentration from co-located ADN site
- L_D Estimated annual dry deposition, from CEH and HARM model values
- E Estimated annual evaporation from Met Office MORECS data
- k_1, k_2 Conversion factors

For SO_4^{2-} , non-marine values are computed directly. Equation (1.1) may exclude some occult deposition. Note that there is no model fitting in the sense of adjusting simulations to fit measured values. The simulations are computed without reference to surface water concentrations. This contrasts with techniques such as regression analysis which rely on measurements to estimate unknown parameters.

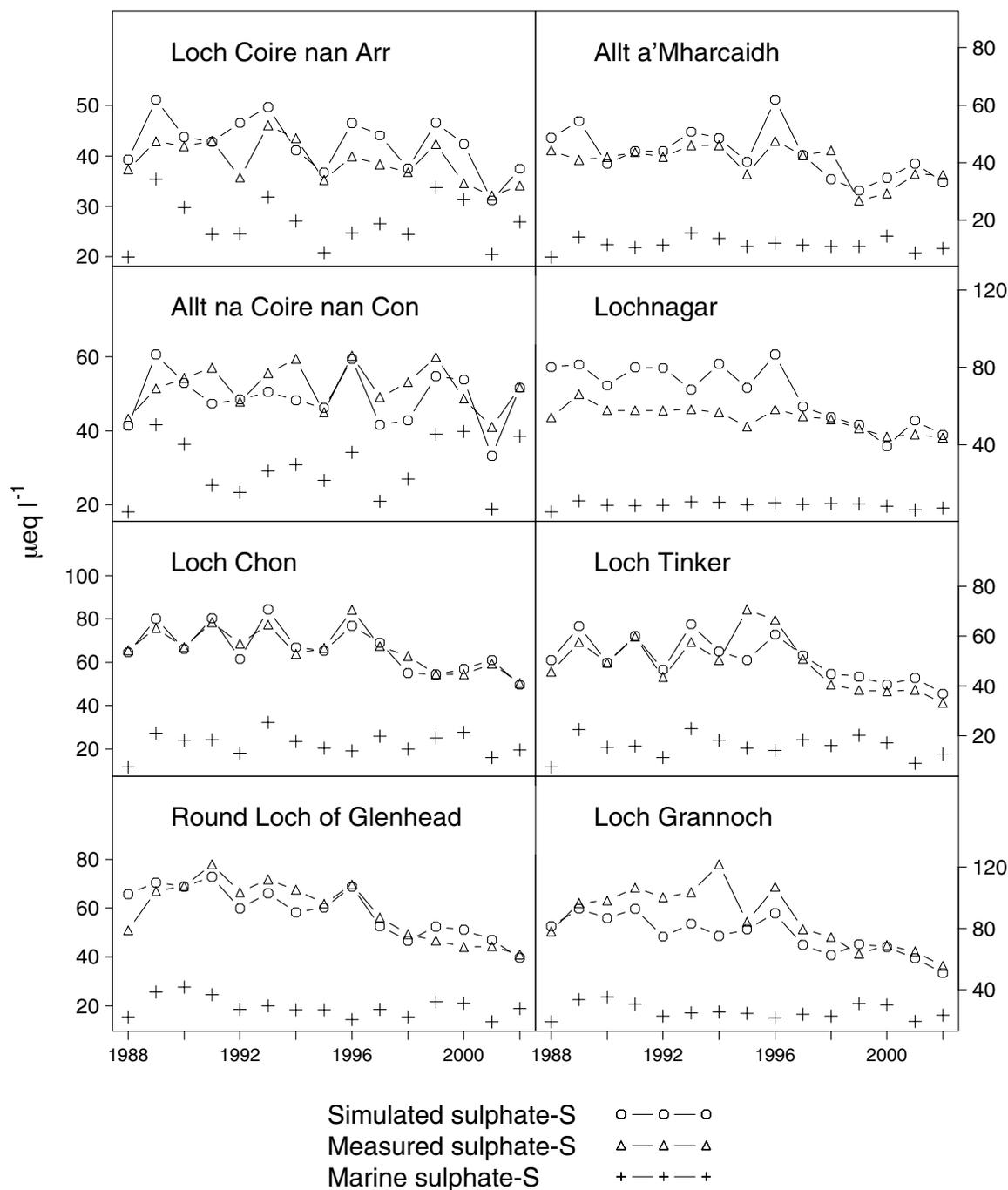


Figure 3.1a - AWMN sites sulphur budget 1988-2002

3.5 Results

3.5.1 Sulphur

Figure 3.1 shows simulated and estimated annual SO_4^{2-} concentrations for each site. Three series are plotted. The annual means of measured concentrations presented have been computed as described. The marine S component is estimated from the measured annual mean chloride concentration, assuming a $\text{Cl}:\text{SO}_4^{2-}$ ratio in terms of equivalents of 1.0:0.104. The simulated sulphate concentration which is plotted is the sum of the marine component and an estimate of the non-marine component found as described. The marine sulphate component is therefore not estimated from deposition measurements, but from surface water concentrations.

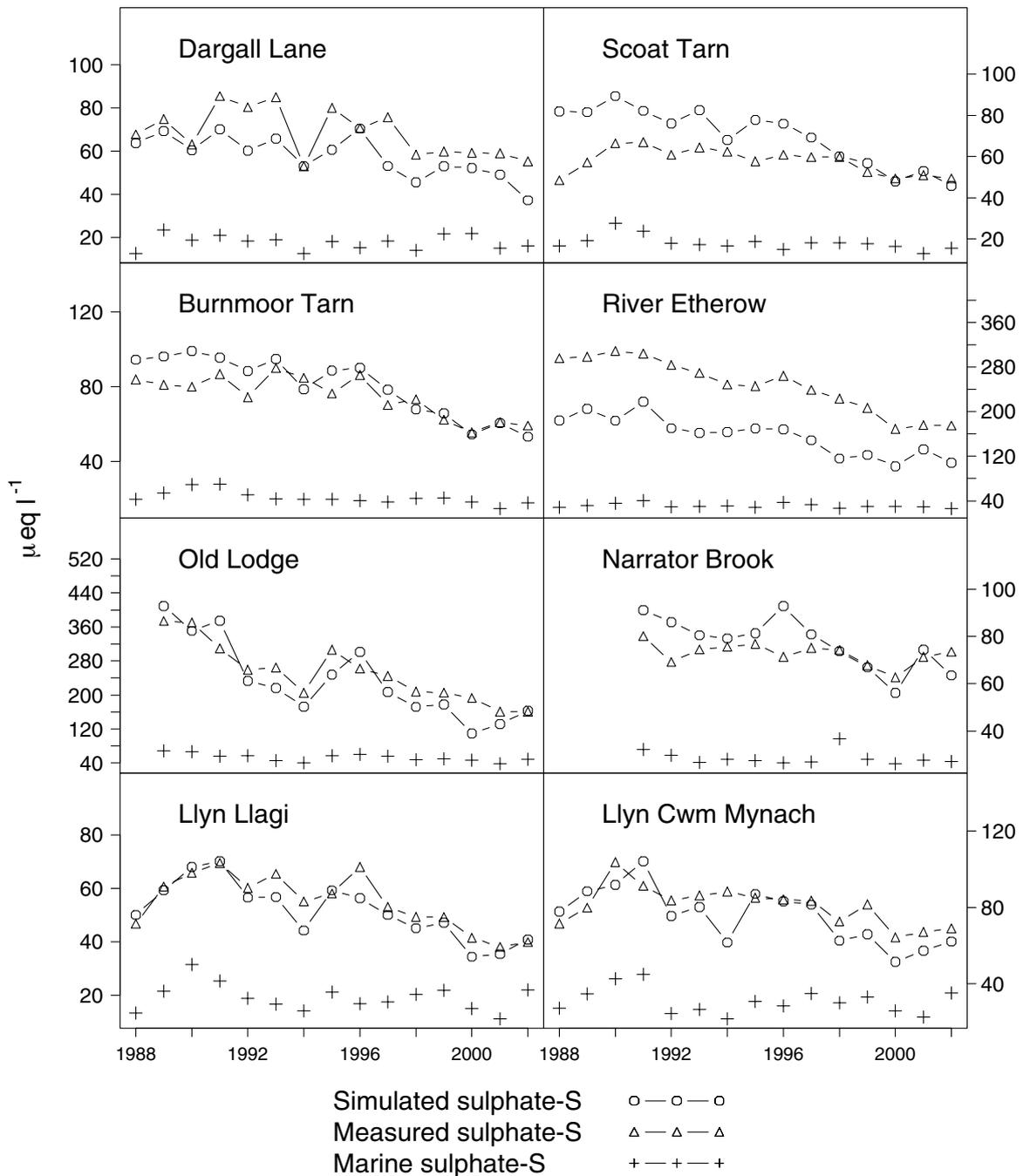


Figure 3.1b - AWMN sites sulphur budget 1988-2002

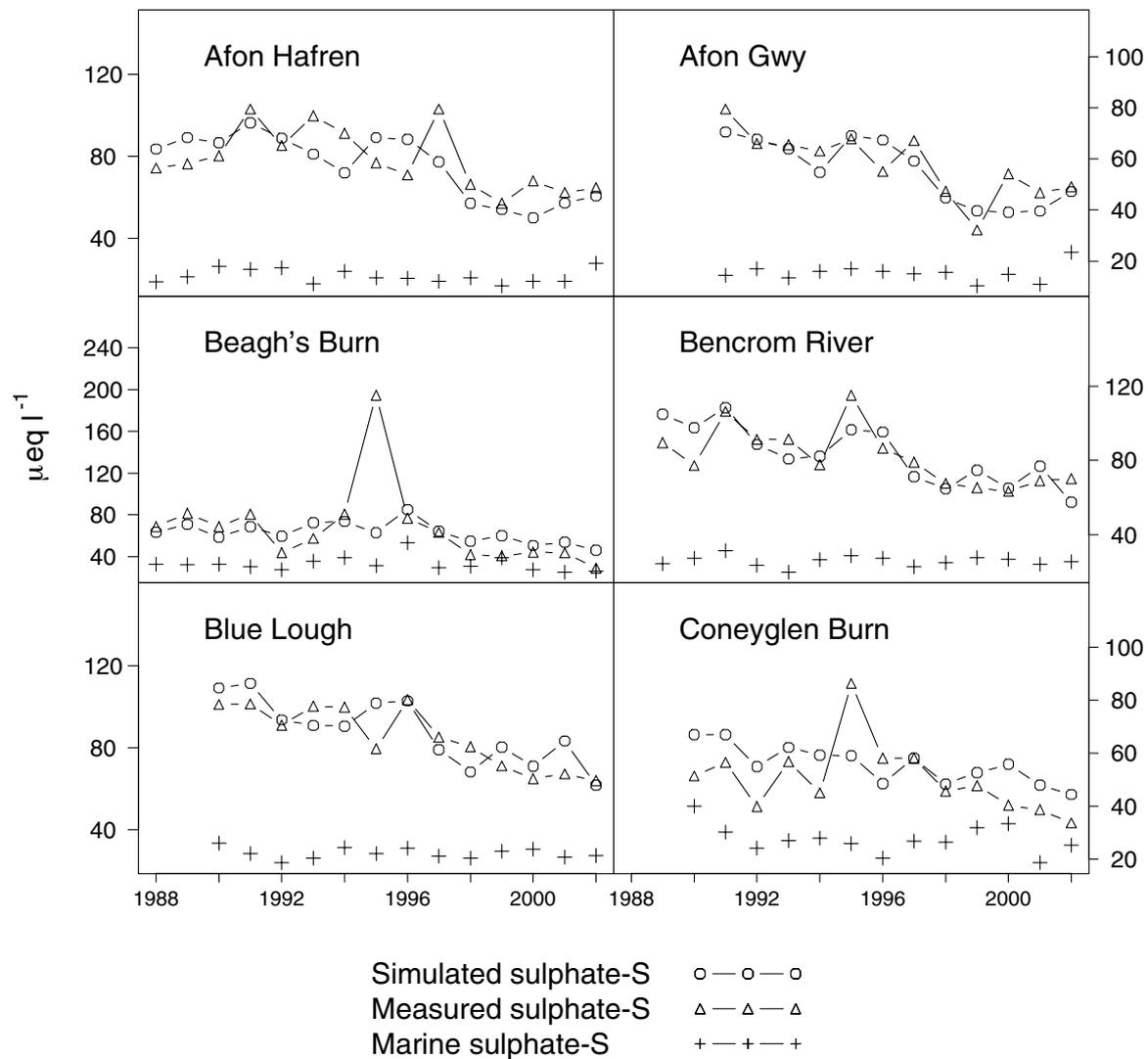


Figure 3.1c - AWMN sites sulphur budget 1988-2002

UK and wider European estimates over the monitoring period suggest a monotonic decline in S emissions (NEGTA, 2001). However, it is clear that this is not entirely reflected in the simulations based on the deposition record, which itself shows no significant decline for S up to 1995 at most sites. Emissions are deposited where the weather takes them, and this varies from day to day and from year to year. Monteith and Evans (2000) and Evans *et al.* (2001a) noted that from 1990 to 1995 the North Atlantic Oscillation (NAO) was in decline, implying a lower frequency of westerly winds, which include a lower xSO_4^{2-} component of both precipitation and deposition. An increasing frequency of easterly weather from 1990 to 1995 is a likely reason for S deposition being maintained despite reductions in emissions over the period. Early 1996 showed particularly high deposition at ADN sites, and this corresponded with a prolonged period of easterly weather, coupled with significant precipitation. After 1996 the NAO ceased to decline, and no longer masked the influence of declining emissions. For example, 1997-98 had no significant periods of easterly weather, and consequently lower deposition concentrations of S, reflected in a marked and general reduction in surface water concentrations of sulphate.

At many AWMN sites, not only is the simulated S concentration close in magnitude to the annual mean based on surface water measurements, but the pattern of variability between years is remarkably similar. This is particularly notable at, for example, Loch Chon. This provides strong evidence of a causal mechanism operating at an annual time scale, and suggests that no major S storage changes are occurring over the monitoring period.

The greatest discrepancy between simulated and measured values occurs at the River Etherow, where the measured concentrations in stream water are very much higher than simulated values. For this site the reduction in measured concentrations has exceeded the reduction in the simulated values, although both trajectories show a fairly uniform decline over the period. In view of its proximity to major local sources, to both east and west, it is likely that these dominate the inputs, and the influence of the NAO is less than at many other sites. This would explain the uniformity of the decline. The magnitude of the measured losses could be due to underestimation of deposition from NEG-TAP tables, or to release of S from storage. The simulated deposition for the years 1995-97 can be compared with 5 km square CEH estimates. These give an estimated deposition equivalent to a concentration of $170 \mu\text{eq l}^{-1}$ for grass and $230 \mu\text{eq l}^{-1}$ for *Sitka* spruce, the vegetation actually present being *Calluna*. Measured stream concentrations are some $250 \mu\text{eq l}^{-1}$, and simulated values based on NEG-TAP values around $150 \mu\text{eq l}^{-1}$. This suggests underestimation of deposition using ADN and NEG-TAP estimates, and possible underestimation by the CEH values. Alternatively, the catchment may be showing delayed recovery from even higher inputs.

At several sites simulations are higher than measurements during the early part of the monitoring period. These include Lochnagar, Scoat Tarn, Burnmoor Tarn and Narrator Brook. Although the greatest discrepancies are before 1995-97, a comparison of simulations for these years with estimates based on CEH 5 km grid data may give some insight. For Scoat Tarn in 1995-97, annual deposition estimated by CEH as 1.9 kg ha^{-1} deposition implies around $65 \mu\text{eq l}^{-1}$ simulated concentration in runoff. This compares with some $70 \mu\text{eq l}^{-1}$ simulated from ADN and NEG-TAP data. These two deposition estimates are quite close, as they prove to be at the remaining three sites. The additional information provided by the CEH data does not provide evidence that the deposition data are substantially incorrect. However, it may be more plausible that both deposition estimates are wrong, than to suggest there is some non-equilibrium over the monitoring period.

One feature of some of the Northern Irish sites is a large peak in concentrations in 1995, out of all proportion to any change in deposition. This has been interpreted (Evans and Monteith, 2001) as a flush response due to oxidation of sulphides following prolonged drought and high temperatures. This feature is largely absent from the time series for Blue Lough, possibly due to the extensive riparian margin surrounding this site which may buffer it from the effects of local drought conditions.

Other features of the data are poor estimation at Loch Grannoch during the middle years of the monitoring period, and mixed results at Loch Coire nan Arr, Allt Coire nan Con and Dargall Lane. For some sites and years estimates from surface waters are influenced by one or two extreme events. This is apparent in 1998 on the Afon Hafren, where the peak is due to a single extreme event.

Figure 3.1 shows a close correspondence between changes in concentration at an annual time scale. Separate weekly time series for the Afon Gwy, not presented here, show significant short-term fluctuations in SO_4^{2-} concentrations, and these can be identified with variation in the SO_4^{2-} concentration in immediately preceding rainfall. This implies an immediate throughput of much of the S in rainfall, lending further support to the hypothesis of approximate mass balance at an annual time scale. However, when there has been no significant recent rainfall, S may accumulate and a direct response to precipitation when it does arrive may not be apparent.

Since they are well-correlated with measured values, the simulated concentrations can be used to predict future change in sulphate concentrations at the AWMN sites under further reductions in S deposition. The advantage of prediction based on mass balance is that it does not extrapolate to unrealistic values, and maintains a causal link between input and output. It is also likely that the same model applies more widely than at the AWMN sites alone. Table 3.3 shows prediction

AWMN Site	Bias	Prediction s.e
1		3.2
2		5.7
3		5.8
4		4.2
5		3.8
6	3.8	1.5
7		4.5
8		6.6
9	-12.9	6.3
10		4.6
11		5.4
12	-76.4	22.4
13	-35.4	27.6
14		5.9
15	-3	2.6
16	-9.5	4.7
17	-10.8	9.1
18		7.6
19	11.2	6.8
20		8.7
21		10.6
22	7.2	5.7

Table 3.3 - Prediction bias and standard error in using simulations to predict annual mean sulphate concentration in surface waters ($\mu\text{eq l}^{-1}$). Based on post-1996 data.

errors based on using the mass balance simulation model. Values have been computed for post-1996 data, when simulations for several sites are greatly improved. Where there is significant prediction bias, this is indicated by a value in column 2. This bias should be subtracted from the simulation value to provide an approximately unbiased estimate of future annual mean sulphate concentrations in surface water. At some sites the bias, although statistically significant, is quite small. The final column gives the approximate standard error of prediction, after adjustment for bias if necessary.

The standard errors do not account for possible convergence of series, which is probably occurring at the River Etherow. It also does not account for events such as occurred in Northern

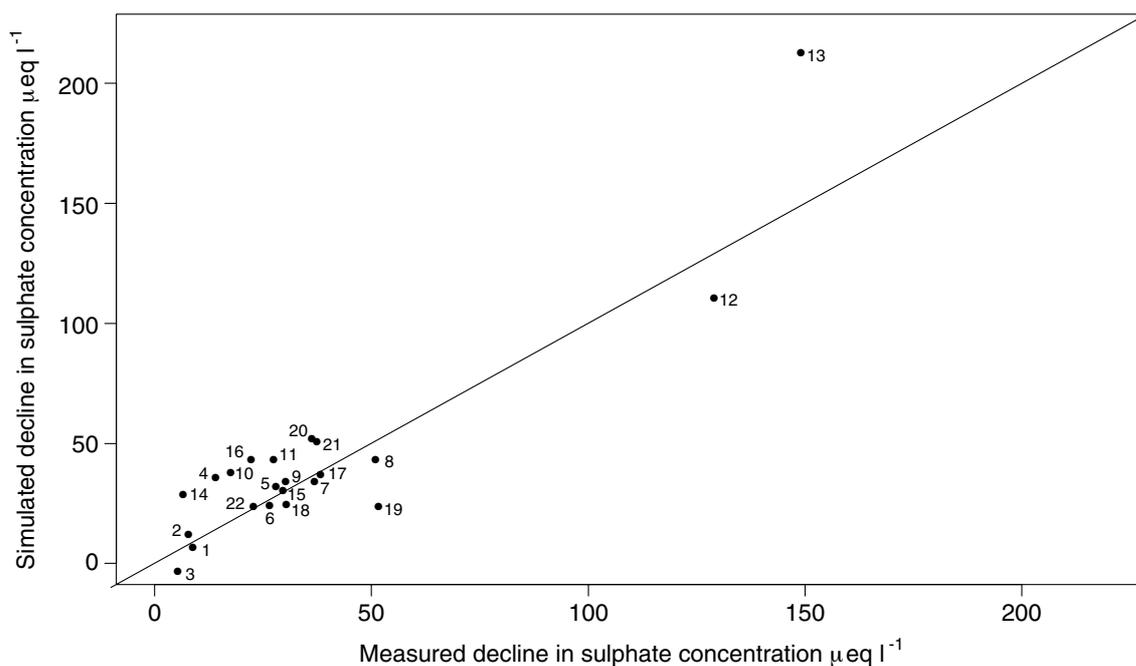


Figure 3.2 - Decline in sulphate at AWMN sites 1991-2002

Ireland in 1995. The table is intended to give an indication only of how closely the simple mass-balance simulation model is likely to predict in general.

As a further presentation of results, Figure 3.2 shows the change in simulated and measured annual mean concentration of sulphate at each site between 1991 and 2002, calculated from the difference in values for these individual years. 1991 is the first year for which there is a measured value for all sites

3.5.2 Nitrogen

Figure 3.3 shows simulated and estimated components of the N budget. Concentrations are quoted in $\mu\text{eq N l}^{-1}$ as NO_3^- , which can be read as $\mu\text{mol N l}^{-1}$. The simulated values are based on wet and dry inputs of NO_3^- and ammonia (NH_3), and are computed using equation (1.1). The

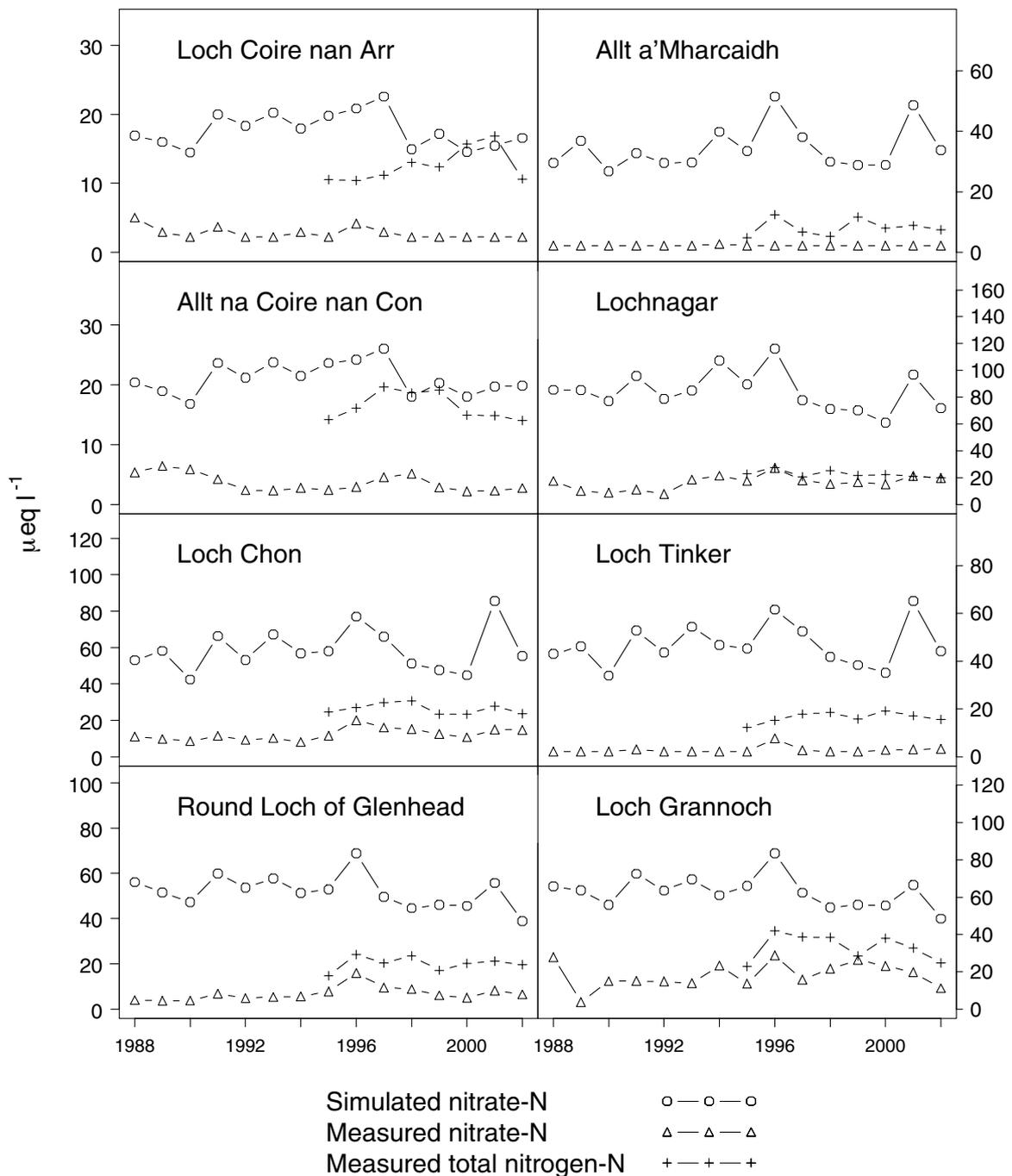


Figure 3.3a - AWMN sites nitrogen budget 1988-2002

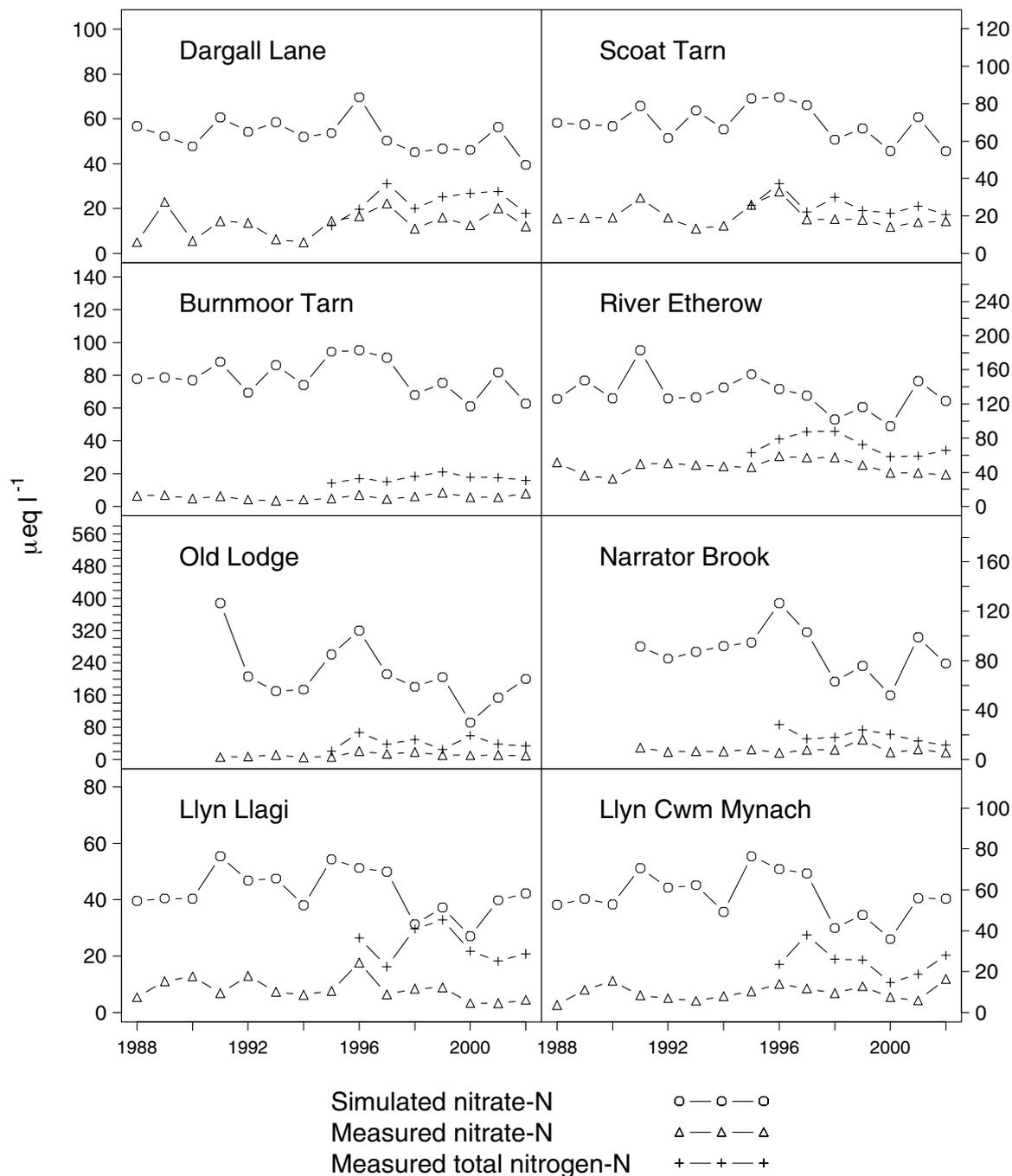


Figure 3.3b - AWMN sites nitrogen budget 1988-2002

total N concentration shown (values only since 1995) includes NO_3^- , which is also shown separately. Most of the difference is DON. The N budget does not include denitrification, but this is unlikely to be a major contributor to the budget of the AWMN catchments (Machefert *et al.*, 2002). The other major missing component is biological accumulation of organic N. Because of the significance of missing components, measured concentrations do not resemble the estimated inputs. Inference is also complicated by the presence of organic N, which is generally correlated with dissolved organic carbon (DOC), and is believed unrelated to short term atmospheric N deposition. At Coneyglen Burn, for example, the fact that estimated N inputs approximately match outputs as total N is almost certainly fortuitous. It would seem highly unlikely that the N deposited on the catchment is detected in run-off in the same year. Nor is there any necessary link between organic N and NO_3^- concentrations. Coneyglen Burn has very high DOC concentrations, and this explains the high total N, which is seen in conjunction with a virtual absence of NO_3^- .

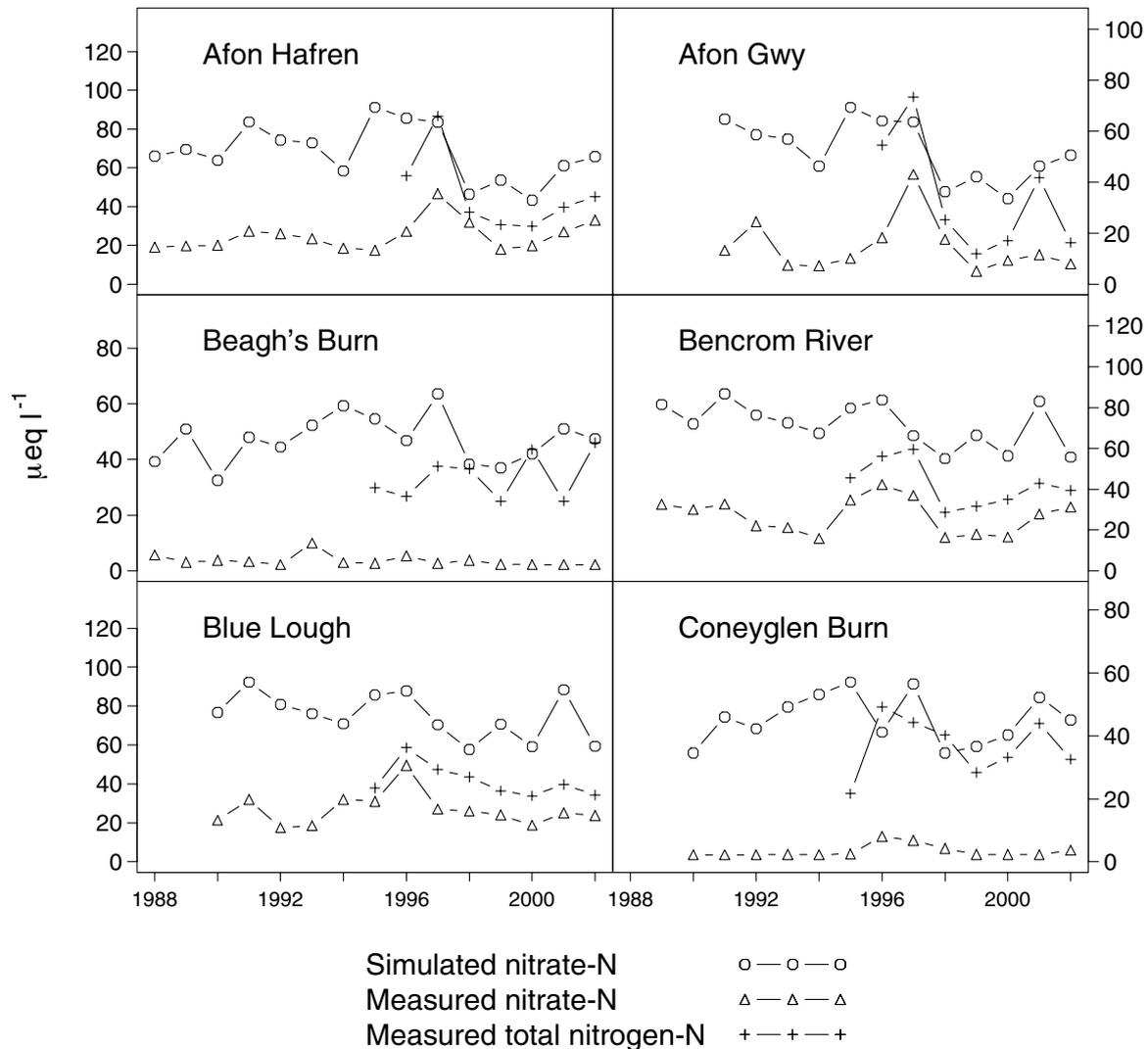


Figure 3.3c - AWMN sites nitrogen budget 1988-2002

3.6 Summary

- Although S emissions are estimated to have declined throughout the period, measured deposition at most sites did not decline significantly until 1996. This deposition pattern tends to be supported by measurements of sulphate in streams.
- The fairly constant deposition up to 1996 is thought due to differences in prevailing weather conditions between years. This is also reflected in changing chloride concentrations, which have in turn been linked to the NAO. Declining chloride concentrations from 1990 to 1995 reflect a declining low-sulphate Atlantic weather source, consistent with an increase in non-marine S deposition. A period in early 1996 combining significant precipitation with a lengthy period of easterly winds largely explains high stream and lake concentrations in 1996
- Although S retention and release processes operating at time scales longer than a year have been identified elsewhere, changes in SO_4^{2-} concentrations in AWMN streams and lakes over the monitoring period have generally coincided at an annual time scale with and been of similar magnitude to changes in estimated S deposition. This is particularly true of reductions since 1996.

Chapter 3

- The coincidence between measured stream and lake concentrations of SO_4^{2-} and estimates independently inferred from deposition, rainfall and evaporation data suggests a causal relationship. It implies limited long term retention or loss of S in catchments, in relation to short-term throughput.
- The greatest absolute reductions in SO_4^{2-} concentrations in streams have occurred at sites where there has been the greatest reduction in deposition, namely the River Etherow and the stream at Old Lodge.
- Some sites show SO_4^{2-} flushes in autumn, believed due to oxidation of sulphides. Although some recovery might be expected by greater immobilisation in succeeding years, this is not immediately apparent from measurements.
- NO_3^- and NH_4^+ deposition have not changed substantially over the period of AWMN monitoring at most sites. NO_3^- concentrations at AWMN sites are not closely related to input concentrations. The biological component of the N cycle is known to include major storage and release characteristics at time scales quite different from inputs. Sites with high DOC concentrations generally show high DON concentrations. This N is not thought to be associated with hydrological translation or short-term changes in N storage.

Chapter 4

How has the chemistry of acid sensitive surface waters responded to the decline in acid deposition?

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4.1 Introduction

Levels of acidic deposition over the UK have fallen substantially since the onset of monitoring by the UK Acid Waters Monitoring Network (AWMN) (Chapter 2). As S fluxes have declined concentrations of non-marine sulphate (i.e. anthropogenic sulphate or $x\text{SO}_4^{2-}$) have fallen accordingly at most AWMN sites (Cooper and Jenkins, 2003; Chapter 3). A reduction in $x\text{SO}_4^{2-}$ (the dominant acid anion) is expected to be accompanied by declines in base cations and increases in pH and alkalinity, while proportionally larger declines in hydrogen ions (H^+) and inorganic, labile aluminium ions (Al_{lab}) relative to base cations should result in an increase in acid neutralising capacity (ANC) (Evans *et al.*, 1998). This chapter examines trends in these determinands in order to assess the responses of AWMN sites to the changing deposition regime.

Trend analyses were initially applied to AWMN data by Patrick *et al.* (1995) using data from the first five years of monitoring. Few trends were found in the dataset at this early stage although several rising trends for sulphate (SO_4^{2-}) were observed. After ten years of monitoring, Monteith and Evans (2000) found that most rising trends in SO_4^{2-} had disappeared and three sites were showing evidence of significant declines in this ion. However, they found little evidence of anthropogenically driven recovery from acidification; increases in pH and alkalinity were observed at six and four sites respectively, but none of these showed concurrent declines in acid anions. Rather, these increases were put down to the effects of variations in sea-salt inputs and/or rainfall. The lack of evidence for recovery at this stage was attributed to several factors, including relatively small reductions in S deposition at AWMN sites; noise generated by short-term variability; decadal-scale climatic variations at coastal sites; and the release of stored S from soils.

In recent years, increasing evidence of long-term chemical recovery from acidification at AWMN sites has been presented by Evans and Monteith (2001; 2002). As the monitoring period lengthens and the influence of short or medium term variability weakens against a background of continued decline in the deposition of acid anions, it is likely that trends in surface water

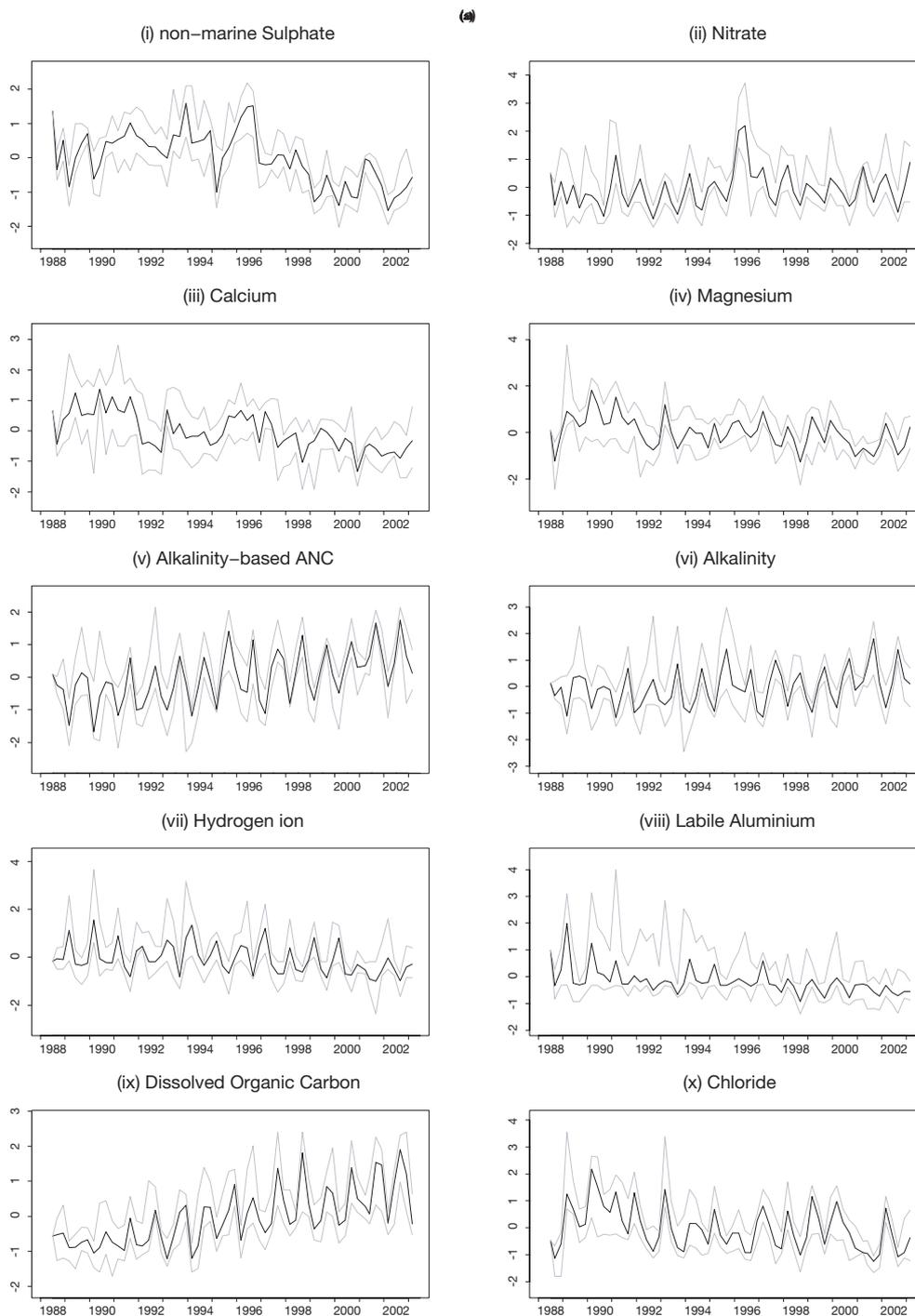


Figure 4.1a Median standardised time series for lakes (black lines). Grey lines represent the 2nd highest and 2nd lowest standardised concentration for each time step.

chemistry will become stronger and more effective assessments can be made of anthropogenically driven recovery. The current analysis of data from 15 years of monitoring identifies many additional and stronger trends than previously observed, although there are still clear differences in response between sites.

While time series chemistry plots for individual sites are provided in the Appendix, here we present summary plots representing median standardised concentrations (or Z-scores) for groups representing all lakes and all streams in order to illustrate the extent of coherence in

chemical signals across the Network. Data for individual sites are standardised by subtracting the mean of the full sample set from individual concentrations and dividing by the standard deviation, so that the resulting time series have a mean of zero and a standard deviation of one. Median, 2nd lowest and 2nd highest values are determined and plotted for each sampling time to create dimensionless 'regional time series' for lakes or streams (Evans and Monteith, 2001), in order to give an indication of general trends across AWMN monitoring sites. In addition, trend analyses for determinands indicative of acidification and recovery are used to illustrate ionic responses to reductions in pollutant loadings at individual sites. Methods of trend analysis are similar to those of Evans and Monteith (2001, 2002) and include the use of the non-parametric Seasonal Kendall (SK) Test (Hirsch *et al.*, 1982; Hirsch and Slack, 1984), described in detail by Evans *et al.* (2001a), to determine statistically significant temporal trends in water chemistry. This is a non-parametric test for monotonic trend, so that the detection of a trend does not necessarily imply that it is linear, and quoted trend estimates similarly do not imply linearity over the period.

4.2. National trends

Standardised median time series for a range of relevant ions (Figure 4.1) demonstrate that trends across the AWMN are generally similar despite some local and regional variation; the ranges between the 2nd lowest and 2nd highest values are generally narrow and the extreme values exhibit similar behaviour to the median. Coherence between sites is more marked for AWMN lakes (Figure 4.1a) than for streams (Figure 4.1b). While this can be attributed largely to the smaller influence of short-term episodic variability on lake chemistry it should be noted that the AWMN lakes are more clustered geographically; most are located in northwestern areas while the streams are dispersed more widely (Figure 1.1). Despite this, the Z-score patterns for both site types are broadly comparable and this approach would appear to provide an effective method of assessing the response to reduction in acid anion emission at a national scale.

Figure 4.1a demonstrates a regionally coherent post-1995 decline in $x\text{SO}_4^{2-}$ concentrations in AWMN lakes accompanied by a decline in calcium (Ca^{2+}) and an increase in H^+ and ANC. The large increase in dissolved organic carbon (DOC) at most sites is also apparent in the combined trend, as is the regional decrease in Al_{lab} , while the plot for chloride (Cl^-) reflects elevated concentrations at the beginning of the record, which have declined and stabilised since 1993. Most median trends at lake sites are significant ($p < 0.05$), the exceptions being Cl^- ($p = 0.06$) and nitrate (NO_3^-) ($p = 0.27$). The absence of any trend in NO_3^- again supports observations at individual sites; the large pulse exhibited in 1996 may be related to a particularly cold winter in 1995-96 (see Section 4.3.1).

Concentrations of $x\text{SO}_4^{2-}$ show a slight regional increase during the first half of the record and only begin to decline from around 1996. This non-linear pattern has been attributed to a sea-salt deposition effect, whereby surface water $x\text{SO}_4^{2-}$ concentrations may have been suppressed by elevated sea-salt inputs in the early part of the record (Evans *et al.*, 2001a). However, the more recent analysis presented in Chapter 3 indicates that most variability can be directly related to the deposition flux which, in turn, can be loosely related to climatic variability (Chapter 2). By contrast trends in the "response" variables, Ca^{2+} and H^+ are relatively linear. Their concentrations in the early part of the record may have been coincidentally enhanced by sea-salts through displacement from the ion exchange complex in catchment soils (Evans and Monteith, 2001).

The higher temporal variability and episodicity experienced by AWMN streams result in weaker chemical trends (Figure 4.1b). Despite this, all median trends, with the exception of NO_3^-

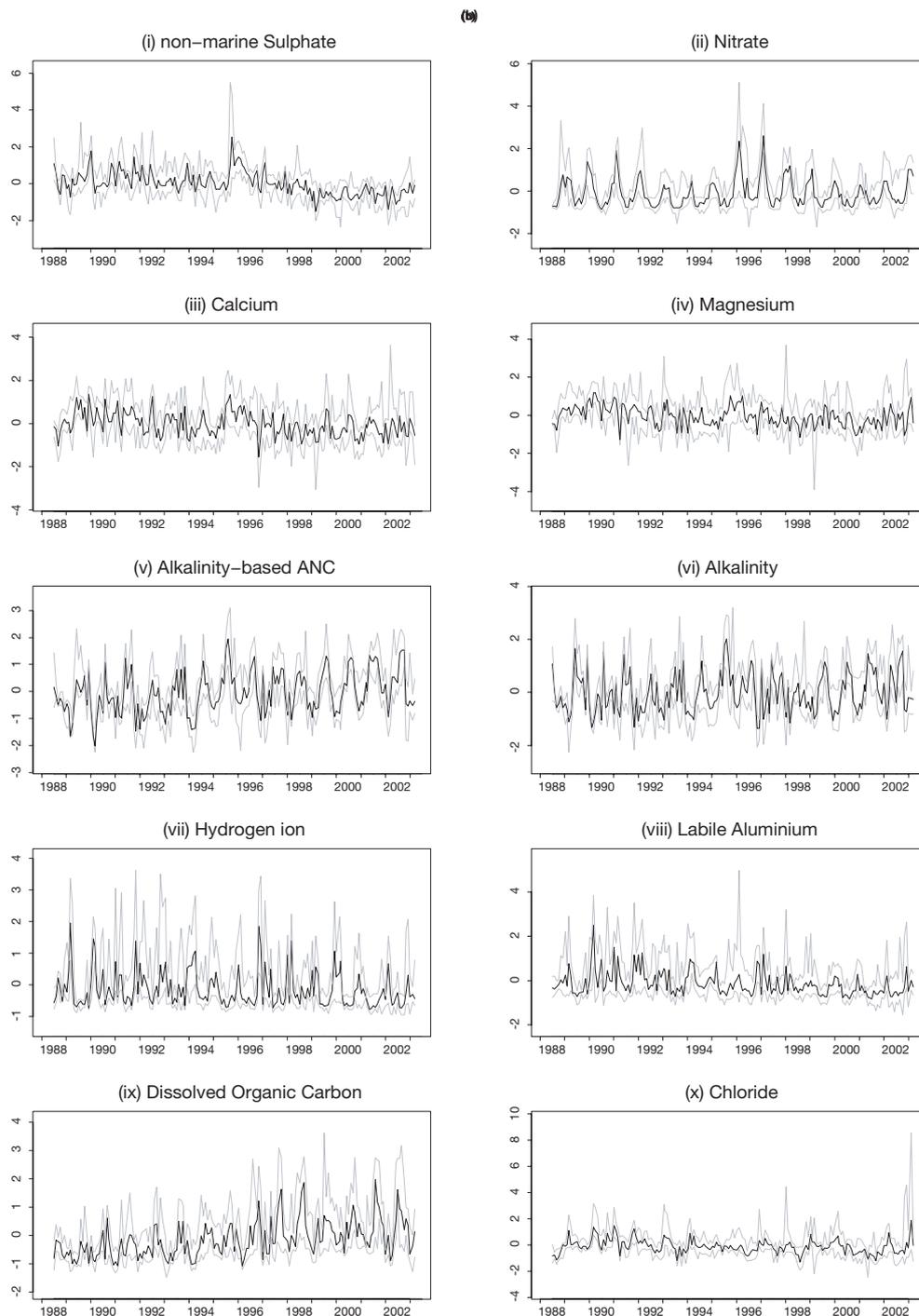


Figure 4.1b Standardised median time series for streams (black lines). Grey lines represent the 2nd highest and 2nd lowest standardised concentration for each time step.

($p=0.85$), are significant ($p<0.05$) and time series reveal very similar patterns to those for AWMN lakes. Variations in $x\text{SO}_4^{2-}$ concentrations are not as marked, with the exception of a pulse seen at many sites in 1996. This apparent anomaly has been reported elsewhere (e.g. Harriman *et al.*, 2001) and is argued to have resulted from effects of the summer drought in 1995, with subsequent flushing of oxidised S on re-wetting. However, it would appear to have been compounded by particularly high deposition during the winter of 1995-96 (Cooper and Jenkins, 2003; Chapter 3), and elevated S deposition throughout much of 1995 is also clear for several sites (see Figure 3.1). While the overall trend in H^+ at stream sites is weak there is evidence for a

general decline in extreme values over the course of the record and this is discussed further in Section 4.3.3a. Finally, it is interesting to note a large peak in median standardised Cl^- at the end of the record for streams which reflects elevated concentrations at several sites at this time, including Allt a'Mharcaidh, Allt na Coire nan Con, River Etherow (the particularly extreme concentration of over $2000 \mu\text{eq l}^{-1}$ at this site may reflect additional contamination by road salt), Afon Hafren and Afon Gwy. These are probably associated with winter storms in January and February 2003 although no effect is discernible in the March 2003 lake samples.

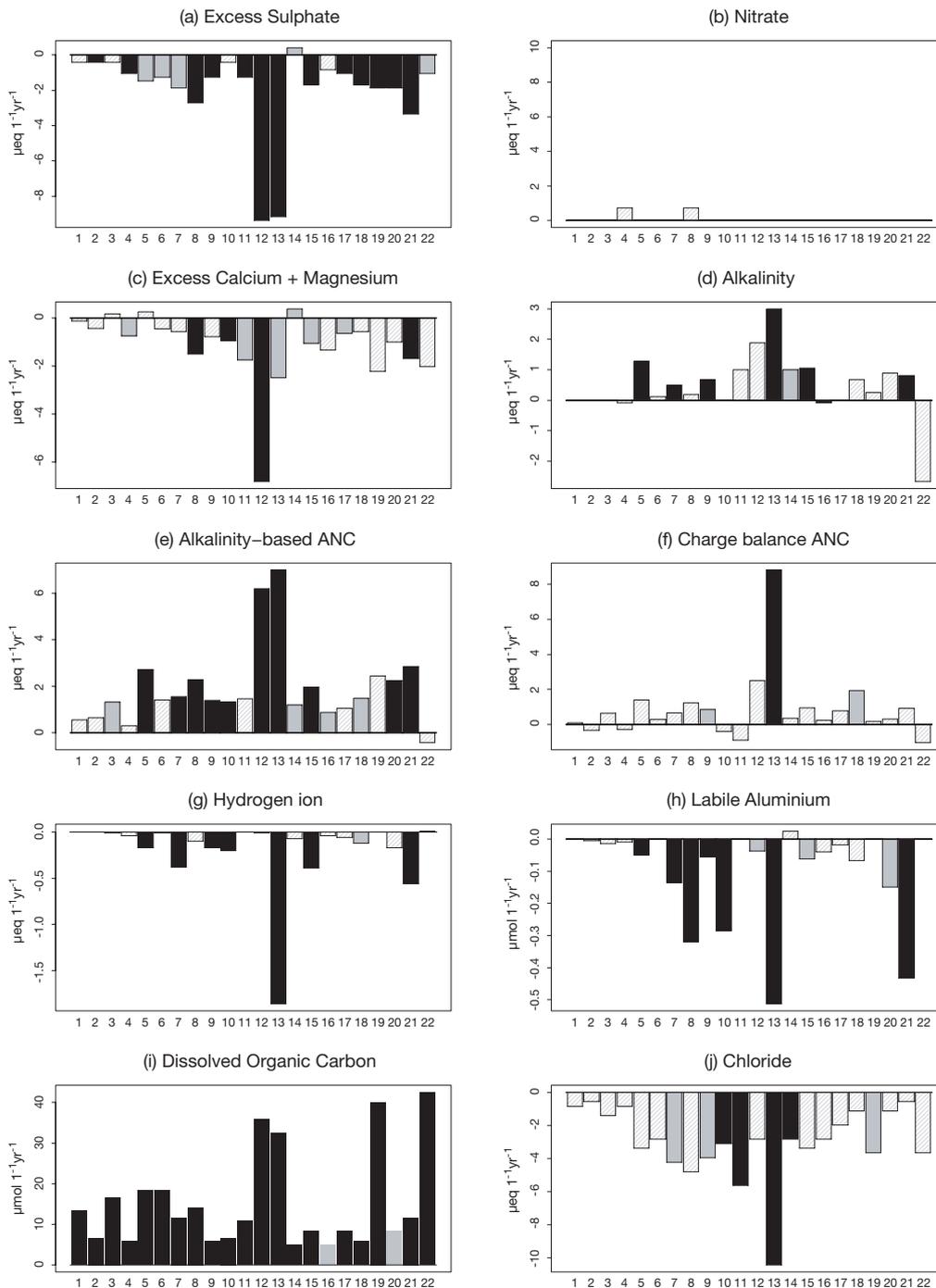


Figure 4.2 Trend slopes and significance levels for chemical determinands at AWMN sites resulting from Seasonal Kendall trend analyses. Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and hatched bars those which are insignificant.

4.3 Trends at individual sites

4.3.1 Acid anions

Most sites show significant downward trend in xSO_4^{2-} (Figure 4.2), in line with the significant decline in atmospheric S over the monitoring period as discussed in Chapter 3. Of the exceptions, Loch Coire nan Arr and the stream Allt na Coire nan Con have historically received relatively low levels of anthropogenic S deposition and are not expected to exhibit strong trends. Elsewhere Scoat Tarn and Llyn Cwm Mynach do exhibit recent declines in xSO_4^{2-} but the longer-term trend is less clear, possibly due to the effects of high sea salt inputs causing under-estimates of xSO_4^{2-} towards the beginning of the record (Section 4.5.2). The slight upward trend in xSO_4^{2-} at Narrator Brook in southwest England is consistent with observations of slight increases in deposition in this region (associated with an increase in sulphur from shipping – Chapter 2).

Trend strengths in xSO_4^{2-} (Figure 4.2a) reflect those in S deposition (Chapter 2). Sites which experienced the highest initial levels and largest declines in S deposition have undergone the largest decreases in surface water xSO_4^{2-} . The largest absolute declines are apparent for the River Etherow in north-central England and Old Lodge in southeast England (Table 4.1), conforming with their positions close to significant emissions sources of S. Loch Coire nan Arr and Allt na Coire nan Con in northwest Scotland show very small, and statistically insignificant, trends. Between these two extremes the slope of decline in concentrations decreases in a northwesterly direction. In Northern Ireland, Blue Lough in the south-east exhibits a relatively large, highly significant trend and Coneyglen Burn in the north-west one of the smallest of all the significant xSO_4^{2-} trends exhibited by the AWMN.

Site	xSO_4^{2-} $\mu\text{eq l}^{-1}\text{yr}^{-1}$	NO_3^- $\mu\text{eq l}^{-1}\text{yr}^{-1}$	$xCa+xMg$ $\mu\text{eq l}^{-1}\text{yr}^{-1}$	Alkalinity $\mu\text{eq l}^{-1}\text{yr}^{-1}$	AB-ANC $\mu\text{eq l}^{-1}\text{yr}^{-1}$	CB-ANC $\mu\text{eq l}^{-1}\text{yr}^{-1}$	H^+ $\mu\text{eq l}^{-1}\text{yr}^{-1}$	Al_{lab} $\mu\text{mol l}^{-1}\text{yr}^{-1}$	DOC $\mu\text{mol l}^{-1}\text{yr}^{-1}$	Cl^- $\mu\text{eq l}^{-1}\text{yr}^{-1}$
1 Loch Coire nan Arr									13.33**	
2 Allt a'Mharcaidh	-0.42**								6.67**	
3 Allt na Coire nan Con					1.32*				16.67**	
4 Lochnagar	-1.04**		-0.74*						5.83**	
5 Loch Chon	-1.46*			1.27**	2.70**		-0.17**	-0.49**	18.33**	
6 Loch Tinker	-1.25*								18.33**	
7 Round Loch of Glenhead	-1.88*			0.50**	1.54**		-0.38**	-1.35**	11.67**	-4.23*
8 Loch Grannoch	-2.71**		-1.50**		2.27**			-3.20**	14.17**	
9 Dargall Lane	-1.25**			0.67**	1.39**	0.86*	-0.17**	-0.56**	5.83**	-3.94*
10 Scoat Tarn			-0.95**		1.32**		-0.20**	-2.85**	6.67**	-3.10**
11 Burnmoor Tarn	-1.25**		-1.75*						10.83**	-5.63**
12 River Etherow	-9.38**		-6.82**		6.21**			-0.37*	35.83**	
13 Old Lodge	-9.17**		-2.48*	3.00**	7.01**	8.81**	-1.86**	-5.13**	32.50**	-10.42**
14 Narrator Brook	0.42*		0.38*	1.00*	1.19*				5.00**	-2.82**
15 Llyn Llagi	-1.67**		-1.05*	1.06**	1.95**		-0.39**	-0.62*	8.33**	
16 Llyn Cwm Mynach				-0.08**	0.87*				5.00*	
17 Afon Hafren	-1.04**		-0.65*						8.33**	
18 Afon Gwy	-1.67**				1.48*	1.95*	-0.12*		5.83**	
19 Beagh's Burn	-1.88**								40.00**	-3.66*
20 Bencrom River	-1.88**				2.25**			-1.50*	8.33*	
21 Blue Lough	-3.33**		-1.69**	0.81**	2.85**		-0.56**	-4.33**	11.67**	
22 Coneyglen Burn	-1.04*								42.50**	

Table 4.1 Seasonal Kendall trends in AWMN data (1988 – 2003) significant at $p < 0.05$ (*), $p < 0.01$ () and $p < 0.001$ (***)**

Nitrate concentrations have not declined at any site on the Network (Figure 4.2b). It has been theorised that as catchments become more saturated with N, increased 'breakthrough' will occur even at stable levels of deposition (Aber *et al.*, 1989, Stoddard, 1994), leading to increased surface water NO_3^- concentrations. Monteith and Evans (2000) tentatively linked AWMN sites to a four stage classification of N saturation proposed by Stoddard (1994), with year-round soil retention of N progressing to pronounced seasonality, and further to year-round leaching. There is little

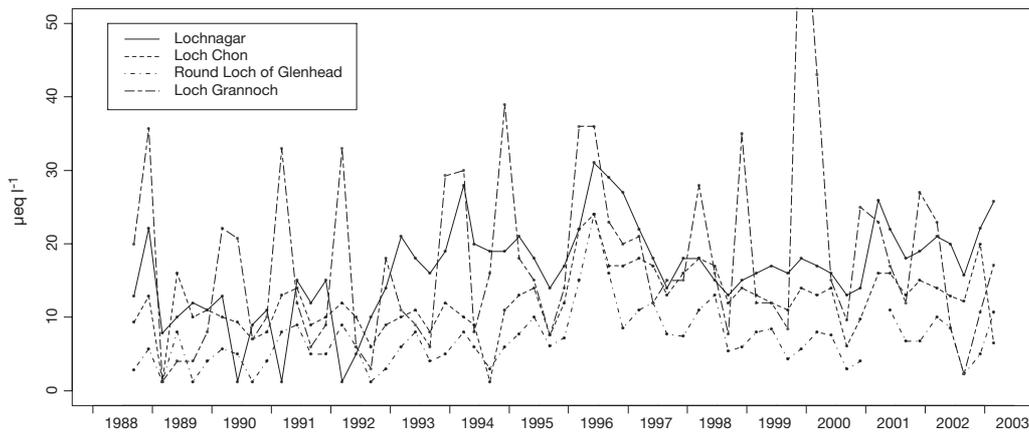


Figure 4.3 Nitrate time series for Lochnagar, Loch Chon, Round Loch of Glenhead and Loch Grannoch.

evidence of a temporal progression in saturation stage at AWMN sites or other long-term datasets (Wright *et al.*, 2001). Examination of time series, however, reveals evidence of step-change increases in NO_3^- at Lochnagar, Loch Chon, the Round Loch of Glenhead and Loch Grannoch (Figure 4.3) after the 1995 summer drought and the unusually cold winter of 1995-1996 (see below). These changes reflect a shift from some seasonality in the earlier years of monitoring to more elevated year-round leaching, but are unlikely to represent a breach of a saturation threshold, as the timing would be expected to be site-specific. Nevertheless, elevated or increasing levels of NO_3^- leaching have important implications for recovery from acidification as they will, to some extent, reduce or even nullify the impact of xSO_4^{2-} decline on acidity. This was suggested as the cause of the apparent slight increase in acidity observed at Lochnagar after

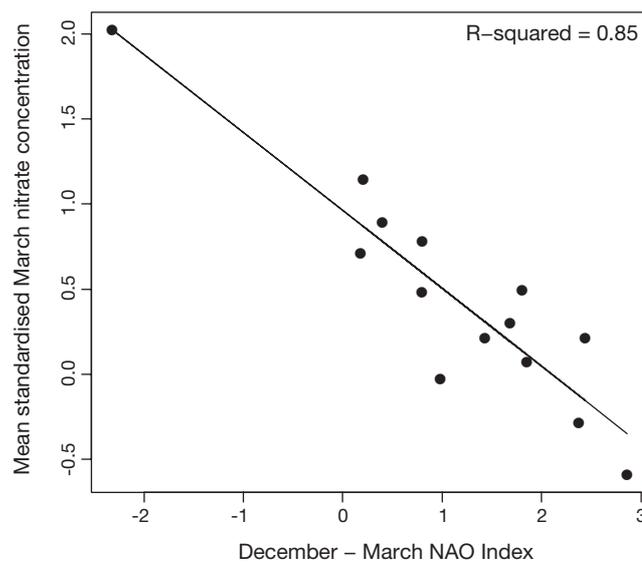


Figure 4.4 Relationship between AWMN median standardised nitrate concentration for all AWMN lakes and the North Atlantic Oscillation Index (December-March mean).

ten years of monitoring (Monteith and Evans, 2000), and even now this site shows no significant trend in either pH or ANC despite a significant decrease in $x\text{SO}_4^{2-}$.

Monteith *et al.* (2000) linked the relatively elevated peaks in NO_3^- observed in spring samples for most sites in 1991 and 1996 with variations in the winter North Atlantic Oscillation Index (NAOI). They noted that the years of highest spring concentrations with the most negative winter NAOI. A similar relationship between NO_3^- concentration and the NAOI has been described for Lake Windermere by George *et al.* (2000). It was argued that NO_3^- leaching is enhanced during cold (negative NAO) winters when a greater duration and intensity of soil freezing enhances biocidal effects, releasing more nitrogen for mineralization, while low soil temperatures may also retard assimilation of N by soil biota leading to a greater loss to the watershed. Differences between winters in the prevailing wind direction may also be important, with a potentially greater supply of pollutant N from the easterly direction associated with a negative NAOI.

With five more years of data than were available for the analysis of Monteith and Evans (2000) the NO_3^- – NAOI relationship still holds (Figure 4.4). Negative winter NAOI scores have been relatively rare over the past two decades. Unfortunately, the most recent, in the winter 2000-2001, coincided with foot and mouth access restrictions when water samples could not be taken from several sites. The consistent step-change patterns for the four lochs listed above may also be winter temperature related; since 1996 the average December to March NAOI has been less than 1.0 in every year but one, whereas between 1988 and 1995 the Index was greater than 1.4 in all but two years.

4.3.2 Base cations

The assessment of trends in the sum of base-cations is vulnerable to seasalt deposition effects, where cations are temporarily retained and then released, and is sensitive to the effects that the rarer ions, particularly K^+ , have on the total, especially when concentrations are close to detection limits. This assessment is therefore confined to excess Ca^{2+} and magnesium ($x\text{Ca}+x\text{Mg}$), which are the dominant non-marine base-cations at all AWMN sites and usually strongly correlated with the sum of all non-marine base cations, i.e. also including Na^+ and K^+ . Significant declines in $x\text{Ca}+x\text{Mg}$ (Figure 4.2c) are widespread. This is an expected consequence of the $x\text{SO}_4^{2-}$ decrease and is sometimes referred to as a “confounding factor” in the recovery of catchments from acidification, despite its inevitability at any site where the cation supply has not been completely exhausted. Well-buffered sites should show the largest proportional decreases in base cation concentrations and, consequently, the effects of $x\text{SO}_4^{2-}$ decline on ANC will be small at these sites (Evans *et al.*, 2001b). In poorly buffered catchments, where more run-off $x\text{SO}_4^{2-}$ is currently accompanied by H^+ and Al_{lab} , a larger decline in these ions is expected relative to base cations, leading to more pronounced effects on pH and ANC. This is exemplified by a comparison of trends at the neighbouring Lake District lakes which have experienced a similar reduction in $x\text{SO}_4^{2-}$ deposition; the $x\text{Ca}+x\text{Mg}$ trend slope at Scoat Tarn is smaller than at the better buffered Burnmoor Tarn, while pH and ANC trends are highly significant at the former and not significant at the latter.

4.3.3 Measures of acidity

The decline in $x\text{SO}_4^{2-}$ is expected to be accompanied by a decline in the acidity of acidified systems and this is clearly essential for their biological recovery. Aquatic biota may be directly sensitive to H^+ or Al_{lab} toxicity, or respond to variations in the availability and form of dissolved inorganic carbon (represented by alkalinity) or an excess of a toxic agent such as Al_{lab} over potential buffering from Ca^{2+} or DOC. Here we consider the trends in H^+ , alkalinity, Al_{lab} , DOC and ANC. Several AWMN sites now show significant positive trend in one or more of these

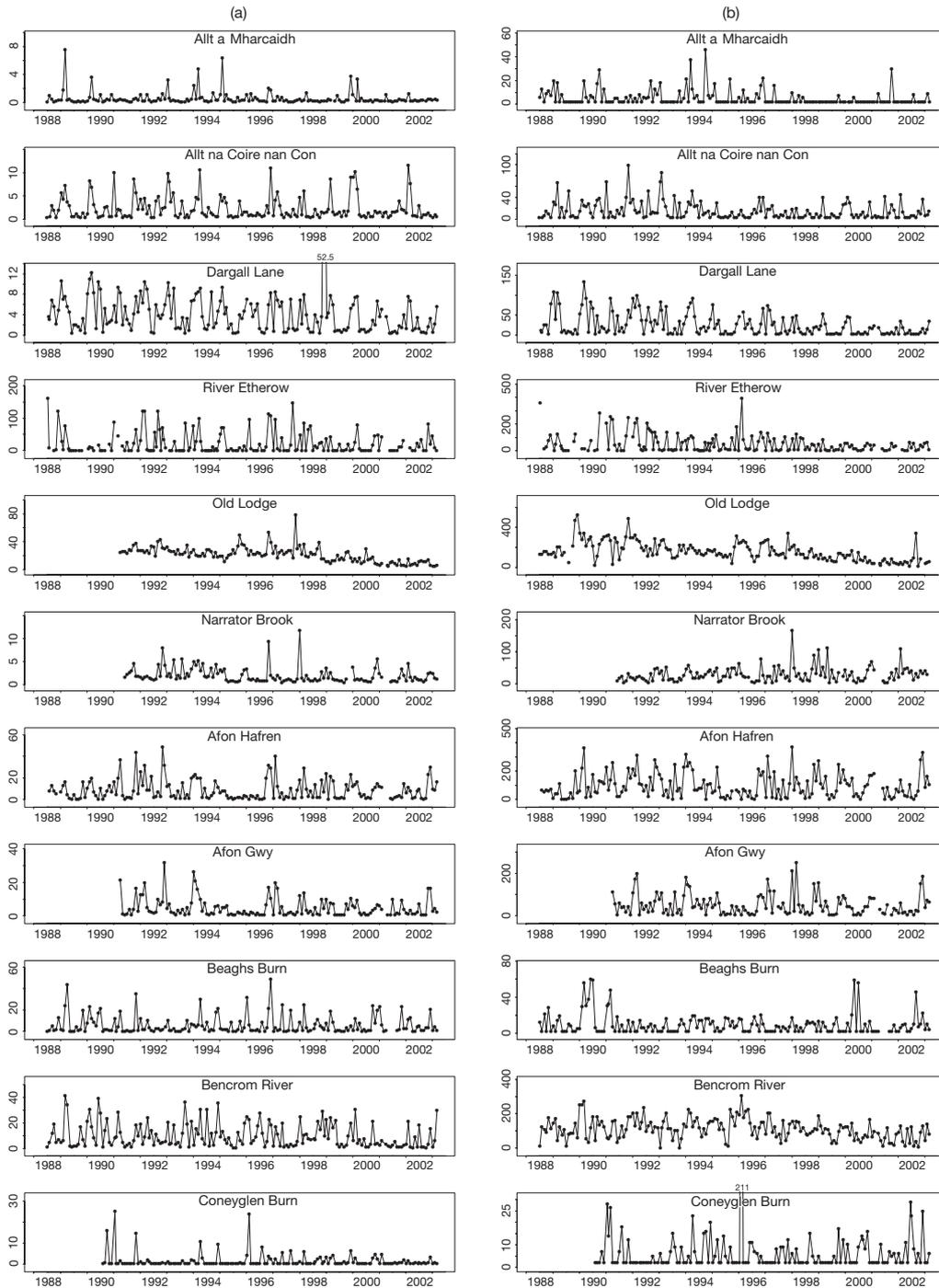


Figure 4.5 Time series for (a) H^+ ($\mu\text{eq l}^{-1}$) and (b) Al_{lab} ($\mu\text{mol l}^{-1}$) at AWMN streams.

indicators, the largest being at sites which show the largest decrease in xSO_4^{2-} , namely the River Etherow and Old Lodge.

(a) Hydrogen ion, alkalinity and labile aluminium

Eight sites show a significant decrease in H^+ (Figure 4.2g): Loch Con (Trossachs), Round Loch of Glenhead and Dargall Lane (Galloway), Scoat Tarn (Lake District), Llyn Llgi (Snowdonia), Afon Gwy (Plynlimon), Blue Lough (Mourne Mountains), and Old Lodge (Ashdown Forest). Of

these all but two, Scoat Tarn and Afon Gwy, also show a significant increase in alkalinity (Figure 4.2d), while two sites show an exclusive significant trend in alkalinity: Llyn Cwm Mynach (which actually shows a very slight decline of $0.07 \mu\text{eq l}^{-1}$) and Narrator Brook. With the exception of Old Lodge the recovering sites lie in an area of central western UK, some 300 km from north to south and less than 200 km from east to west where the strongest downward trends in xSO_4^{2-} have been recorded. This region also includes the relatively well buffered sites, Loch Tinker (Trossachs) and Burnmoor Tarn (Lake District), two lakes with afforested catchments, Loch Grannoch (Galloway) and Llyn Cwm Mynach (Rhinog Mountains) and three acidic and strongly episodic streams, the River Etherow (Pennines), Bencrom River (Mourne Mountains) and Beagh's Burn (Glens of Antrim). Despite the absence of overall trends the stream sites above show a tendency for declining hydrogen ion maxima (Figure 4.5a). There is, therefore, very good agreement between the rate of decline in xSO_4^{2-} concentrations and the clearest improvements in the pH and alkalinity of acidified sites, with the exception of two with afforested catchments. Ten sites show a significant decline in Al_{lab} (Figure 4.2h), again broadly mimicking patterns of decline in xSO_4^{2-} and H^+ , with time series for streams similarly showing a decline in maxima even at sites where no statistically significant trend is detected (Figure 4.5b). The observed decline in the intensity of episodically elevated H^+ and Al_{lab} may be of considerable biological significance and possibly more important than any shift in average levels of acidity in determining the biological species composition and diversity of these surface waters.

(b) Acid Neutralising Capacity

ANC is a calculated variable, and subject to a number of errors related to the accuracy of constituent data and the method of calculation. Charge-balance ANC (CB-ANC) is defined stoichiometrically on the basis of charge balance such that the sum of strong acid anions (SO_4^{2-} , NO_3^- , Cl^-) is subtracted from the sum of base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), with all determinands in $\mu\text{eq l}^{-1}$. This method of ANC calculation is widely used (e.g. Stoddard, 1999) and has been utilised in all previous analyses of AWMN data. It is also particularly suited for modelling purposes because charge balance is an underlying requisite in chemical equations. However, Evans *et al.* (2001c) have argued that CB-ANC is sensitive to small errors in individual ion determinations, the cumulative effect of which may lead to considerable inaccuracies in ANC calculations, especially where ion concentrations are high, such as in waters with a high marine ion input. They suggested that this sensitivity is particularly acute when examining temporal changes in ANC which may be only a few $\mu\text{eq l}^{-1} \text{yr}^{-1}$, and demonstrated that two sets of ANC estimates based on duplicate analysis of the same sample set for the Round Loch of Glenhead exhibited little correlation, and inconsistent long term trends.

An alternative method of ANC calculation, proposed initially by Harriman and Taylor (1999) and Neal *et al.* (1999) and adapted by Evans *et al.* (2001c), is based on titrated alkalinity (gran), Al_{lab} and DOC, according to the equation:

$$[\text{ANC}] = [\text{Alkalinity}] + (F * [\text{DOC}]) - (3 * [\text{Al}_{\text{lab}}]) \quad (1)$$

where ANC and alkalinity are in $\mu\text{eq l}^{-1}$, Al_{lab} in $\mu\text{mol l}^{-1}$ and DOC in mg C l^{-1} . This method reduces inaccuracies due to the cumulative error of individual constituents, but is subject to a number of generalisations which may not hold for all surface waters. Al_{lab} is assumed to be present entirely as Al^{3+} , and all organic Al is assumed to be undissociated. In addition, F, the charge density ($\mu\text{eq mg}^{-1}$) of DOC, is assumed to be 4.5 where pH is 4.5 – 5.5 and 5 where pH > 5.5, based on the work of Harriman and Taylor (1999). We will refer to this approach as “alkalinity-based” ANC or AB-ANC.

Trends based on the two methods of ANC calculation (Figure 4.2) exhibit quite different patterns of ANC increase. Few CB-ANC trends are identified with the exception of a large increase at Old Lodge, which is consistent with the large decrease in $x\text{SO}_4^{2-}$ at this site. At the other site showing a large negative slope in $x\text{SO}_4^{2-}$, the River Etherow, there is no significant CB-ANC trend, and of the remaining sites, only Dargall Lane and Afon Gwy show significant, but small, increases in CB-ANC. For many sites, the effects of $x\text{SO}_4^{2-}$ trends on CB-ANC have been offset by similarly negative trends in base cation concentrations. By contrast, AB-ANC time series reveal many large and significant positive trends, most notably at River Etherow and Old Lodge. These trends show a similar distribution to those in H^+ and alkalinity, but the influence of increasing DOC concentrations is clear. Where trends in alkalinity and H^+ are considerably weaker than those for AB-ANC (e.g. River Etherow), it would appear that there has been a shift from mineral to organic acidity (Evans *et al.*, 2001c). It is clearly essential, therefore, that the cause of the large and significant DOC increases observed at all sites is established before trends in AB-ANC can be categorically attributed to decreasing acid deposition.

(c) Dissolved organic carbon

Observed increases in DOC are large and highly significant at all sites (Figure 4.2i). The widespread existence of DOC trends was first noted for AWMN sites and reported in the journal *Nature* (Freeman *et al.*, 2001a). Previously, similar trends had been noted at individual sites in the UK (e.g. Robson and Neal, 1996; Reynolds *et al.*, 1997; Harriman *et al.*, 1995; Naden and McDonald, 1989) and subsequently rising DOC has also been noted in other parts of Europe, and in North America (Skjelkvåle *et al.*, 2003; Stoddard *et al.*, 2003). There is an ongoing debate regarding the causes of these increases (e.g. Freeman *et al.*, 2001a; Tranvik and Jansson, 2002; Evans *et al.*, 2002; Stoddard *et al.*, 2003; Worrall *et al.*, 2004) with a range of hypotheses suggested. Further analysis and discussion of DOC trends is given in Chapter 5.

Site	$x\text{SO}_4^{2-}$ $\mu\text{eq l}^{-1}\text{yr}^{-1}$	NO_3^- $\mu\text{eq l}^{-1}\text{yr}^{-1}$	$x\text{Ca}+x\text{Mg}$ $\mu\text{eq l}^{-1}\text{yr}^{-1}$	Alkalinity $\mu\text{eq l}^{-1}\text{yr}^{-1}$	AB-ANC $\mu\text{eq l}^{-1}\text{yr}^{-1}$	CB-ANC $\mu\text{eq l}^{-1}\text{yr}^{-1}$	H^+ $\mu\text{mol l}^{-1}\text{yr}^{-1}$	Al_{lab} $\mu\text{mol l}^{-1}\text{yr}^{-1}$	DOC $\mu\text{eq l}^{-1}\text{yr}^{-1}$	Cl^-
12 River Etherow	-10.00**		-8.06*		5.07*				45.83**	
13 Old Lodge	-8.33**			3.00**	7.15**	6.85*	-2.05**	-0.58**	42.50**	
8 Loch Grannoch	-5.21**		-2.51**		3.33**		-0.66*	-0.41**	21.67**	
21 Blue Lough	-4.38**		-2.06*	0.80*	2.43**		-0.69**	-0.42**	10.00*	
7 Round Loch of Glenhead	-3.54**			0.82**	2.07**		-0.53**	-0.13**	15.00**	
15 Llyn Llgi	-2.92**			1.14*	2.12**		-0.42**		9.17*	
16 Llyn Cwm Mynach	-2.92**				2.12*					
17 Afon Hafren	-2.71**								10.00**	
20 Bencrom River	-2.71*				3.09**		-0.51*	-0.33*		
11 Burnmoor Tarn	-2.50**								8.33**	-3.38*
19 Beagh's Burn	-2.50*									
9 Dargall Lane	-2.29**				1.22*		-0.15**	-0.06**	5.83*	
18 Afon Gwy	-2.29**									
6 Loch Tinker									23.33**	-5.63*
5 Loch Chon				1.42*	2.82**		-0.13*	-0.04*	22.50**	
10 Scoat Tarn	-1.46**				1.00**		-0.15*	-0.23**	4.17*	
3 Allt na Coire nan Con									16.67*	
4 Lochnagar	-1.25**		-0.84*				-0.26**	-0.09**	6.67*	-3.66**
22 Coneyglen Burn									39.17*	
1 Loch Coire nan Arr	-0.83**								8.33**	
2 Allt a'Mharcaidh									10.00**	-2.82*
14 Narrator Brook									6.67*	-1.69*

Table 4.2 Seasonal Kendall trends in AWMN data (1993 – 2003) significant at $p < 0.05$ (*), $p < 0.01$ (**) and $p < 0.001$ (***)

4.4 Ionic response to declining $x\text{SO}_4^{2-}$

In order to elucidate the chemical response to $x\text{SO}_4^{2-}$ decline, we have examined trends for the period 1993 – 2003 only, as the particularly high sea salt inputs observed at many sites between 1988 and 1993 may have led to short term variations in ionic concentrations (Section 5.2) which could partly obscure the relationships. In Table 4.2 the trends are presented for all sites in order of declining strength of trend in $x\text{SO}_4^{2-}$ and therefore have a roughly geographical structure. Relationships between trend slopes in $x\text{SO}_4^{2-}$ and $x\text{Ca}+x\text{Mg}$, H^+ , AB-ANC and CB-ANC are strongly linear for those sites exhibiting significant trends in these species (Figure 4.6). Furthermore, regression analyses reveal that the variability between sites in significant trendslopes for $x\text{SO}_4^{2-}$ can account for 93%, 89% and 78% respectively of the variation in those for $x\text{Ca}+x\text{Mg}$, H^+ and AB-ANC (only one site exhibits a significant trend for both CB-ANC and $x\text{SO}_4^{2-}$). This indicates that the pattern of catchment recovery from acidification in response to $x\text{SO}_4^{2-}$ decline is relatively consistent across these sites, but there is still considerable variability among sites exhibiting non-significant trends.

The degree of decline in $x\text{Ca}+x\text{Mg}$ at individual sites is a function of both $x\text{SO}_4^{2-}$ decline and the degree of base cation buffering, while there is also likely to be a positive influence from the rise

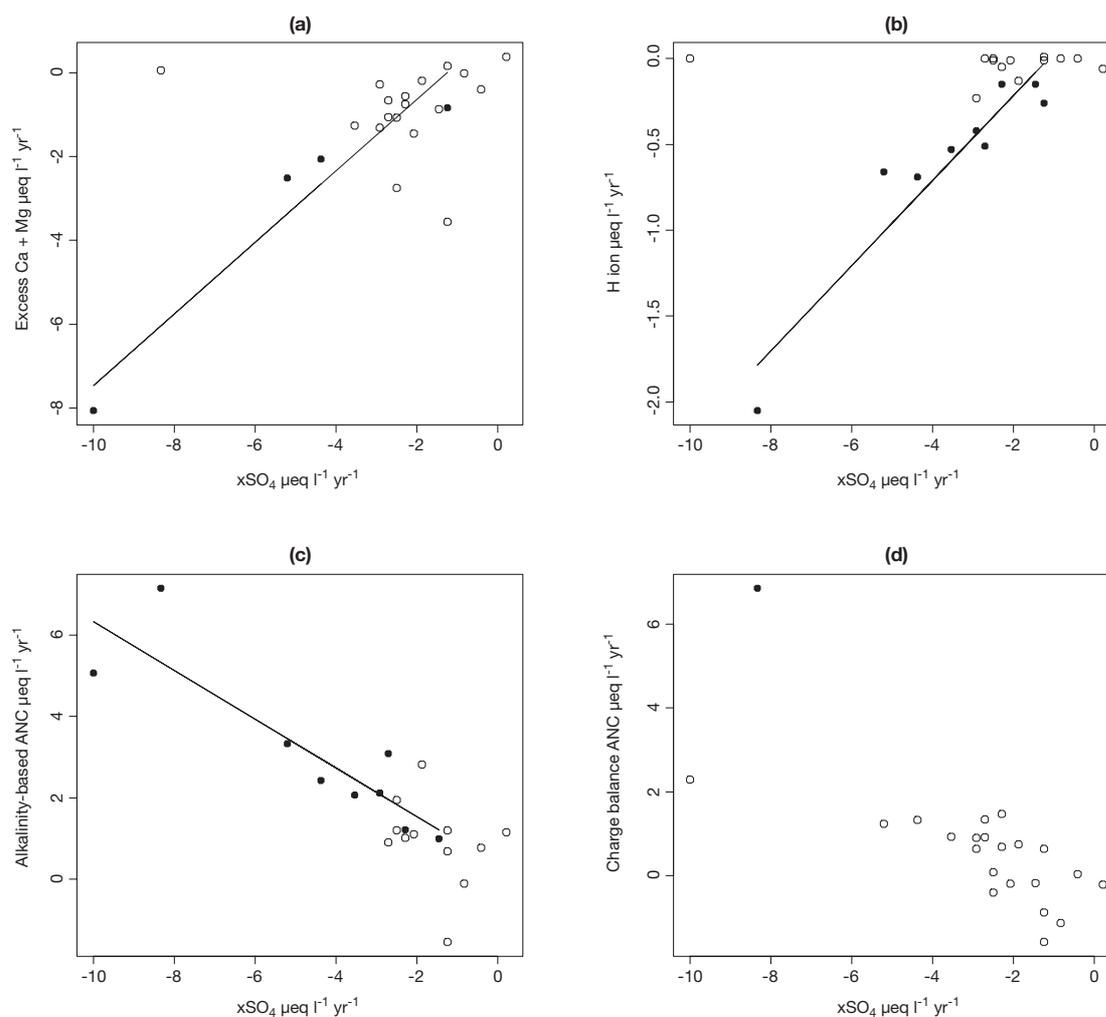


Figure 4.6 Relationships between trend slopes for $x\text{SO}_4^{2-}$ and the response variables $x\text{Ca}+x\text{Mg}$, H , CB-ANC and AB-ANC. Filled circles represent sites which are significant for both determinands, open circles those where either or both trends are insignificant. Trendlines apply to significant sites only.

in DOC. At the River Etherow, the large decline in $x\text{Ca}+x\text{Mg}$, amounting to 81% of the decrease in $x\text{SO}_4^{2-}$, is consistent with the relatively well-buffered nature of this site. Elsewhere, trends in $x\text{Ca}+x\text{Mg}$, although remaining significant, are more modest (47% -67% of the decline in $x\text{SO}_4^{2-}$), probably reflecting lower base cation buffering at these sites. Variation may also be related to base cation uptake at afforested sites.

The reduction in H^+ concentration, as a percentage of the decline in $x\text{SO}_4^{2-}$, ranges from 7% at Dargall Lane to 25% at Old Lodge. Most of the non-significant H^+ trends have a slope close to zero. Many of these sites are not acidic and exhibit weak trends in $x\text{SO}_4^{2-}$ (Allt a'Mharcaidh, Coneyglen Burn, Loch Coire nan Arr, Allt na Coire nan Con). At other sites confounding factors such as forestry (Afon Hafren), or strong levels of buffering (River Etherow, Coneyglen Burn, Beaghs Burn, Loch Tinker) may be important in minimising the impact on this parameter.

There is broad agreement between those sites showing an increase in AB-ANC and those showing a decline in H^+ . Declines in AB-ANC amount to between 51% (River Etherow) and 114% (Bencrom River) of declines in $x\text{SO}_4^{2-}$. For CB-ANC, only one site (Old Lodge) exhibits significant trends for both this species and $x\text{SO}_4^{2-}$. A weak negative linear relationship between trend slopes for $x\text{SO}_4^{2-}$ and non significant CB-ANC trend slopes can be identified (Figure 4.6), but there is considerable scatter in the plot, probably related to the variation in base cation response to declines in $x\text{SO}_4^{2-}$.

4.5 Drivers of short-term chemical variation

The regional pattern of decline in $x\text{SO}_4^{2-}$ concentration is indicative of a rapid catchment response to declines in S deposition. Moreover, observed changes in acidity are encouraging (Section 4), although there is some variability between sites in the nature and extent of change, even within particular regions of the UK. A number of local factors may affect catchment responses to inputs of acid anions, including: local variation in catchment geology and soils; variation in precipitation and sea-salt inputs; internal sources of SO_4^{2-} (at the River Etherow); high evaporative losses (particularly at Old Lodge); and catchment altitude. These factors may to some extent 'interfere' with the expected pattern of chemical recovery, and must be considered in any analysis of the recovery of acidified waters.

4.5.1 The role of hydrology

Hydrological variation may be particularly important in influencing the acidity of run-off. During dry periods, a relatively high proportion of water in the drainage network is likely to interact physically with the underlying geology, resulting in relatively well buffered run-off. Conversely, during periods of high precipitation or sudden snow-melt, water courses will receive a larger proportion of run-off as poorly buffered overland flow or through-flow, and this is likely to be enriched with organic acids. The net effect is, therefore, to vary the ionic balance, with more H^+ and Al_{lab} to base-cations accompanying $x\text{SO}_4^{2-}$ during wet or snow-melt periods. It will be important for hydrological effects on water chemistry to be better quantified if the influence of forecast changes in precipitation patterns (in response to global-scale climatic changes) is to be incorporated successfully within predictive models.

4.5.2 Sea-salt inputs

At some west coast sites (Round Loch of Glenhead, Dargall Lane, Scoat Tarn and Llyn Llagi), trends in $x\text{SO}_4^{2-}$ have been identified for the first time, despite the fact that trends in other indicators of recovery such as pH, alkalinity and Al_{lab} were identified as early as 2000 (Evans

and Monteith, 2001). The apparent discrepancy during the early years of monitoring may have resulted from the combination of an underestimate of $x\text{SO}_4^{2-}$ and an excessive supply of H^+ and Al_{lab} during and after sea-salt episodes. These events tend to occur during particularly energetic winter storms associated with the most positive phases of the NAO. Following significant sea-salt deposition short-term retention of SO_4^{2-} relative to chloride will have the effect of biasing the $x\text{SO}_4^{2-}$ estimate. Concurrently marine cations temporarily displace H^+ and Al_{lab} ions, thus raising levels of acidity in run-off (Evans *et al.*, 2001a). Since 1993 the winter NAOI has been generally less positive and this is reflected in lower Cl^- concentrations (at least for west-coast sites south of the Trossachs). This, in combination with the fact that the dataset encompasses a longer period of time, enables a clearer picture of $x\text{SO}_4^{2-}$ decline at most sites and the true response to this reduction in terms of acidity. Again, the possible consequences of global climate change on storminess, and the subsequent link with the intensity and frequency of sea-salt delivery to AWMN sites, need to be considered in future recovery predictions.

4.5.3 Forestry

Forested sites are likely to be more impacted by acidic pollutants than non-forested ones through 'scavenging' of air-borne pollutants by the forest canopy (Mayer and Ullrich, 1977), increased uptake of base cations (Miller, 1981), and reduced availability of soil water for dilution of pollutants (Neal *et al.*, 1986). This is supported by an examination of forested/non-forested 'pairs' of AWMN catchments which showed that forested sites have higher acid anion concentrations and are more acidic (Monteith and Evans, 2000) and may have implications for trend detection at AWMN sites. Of the five catchments which contain significant forest cover, three do not show significant trends in pH or alkalinity (Allt na Coire nan Con, Loch Grannoch and Afon Hafren) and one a small but significant decrease in alkalinity (Llyn Cwm Mynach), although most (except Afon Hafren) show a positive trend for AB-ANC. A study of ten forest stream monitoring sites in Wales reveals similar results, with few trends detected in the dataset after 10 years of monitoring (Forest Research, unpublished data). However, time series at forested AWMN sites do not reveal any major dissimilarity to those for other sites, and it is possible that trends at forested sites are simply obscured by variability caused by forest growth and felling. The felling and replanting expected at some forested sites in the next few years will reduce scavenging of atmospheric pollutants but may also increase base cation uptake, and the net effect is difficult to anticipate. Again, continued monitoring will be necessary to determine the longer term impact.

4.6 Summary and Conclusions

- Time series of standardised concentrations of surface water chemistry at AWMN sites for the 1988-2003 period reveal encouraging signs of surface water recovery from acidification at a regional scale.
- Significant declines in $x\text{SO}_4^{2-}$ and accompanying increases in pH, alkalinity and reductions in Al_{lab} concentrations provide clear evidence of chemical improvements at several sites and these can be related spatially to trends in SO_4^{2-} deposition. Generally, the more acidic sites, located in southern and central areas of the UK, also exhibit the strongest downward trends in $x\text{SO}_4^{2-}$ and acidity. The consistency of trends among sites suggests that this analysis should be representative of the wider population of acid deposition impacted catchments across the UK.
- Declining base cation concentrations also reflect a direct response to falling $x\text{SO}_4^{2-}$ inputs. The magnitude of change in base cation concentration relative to changes in acidity-related variables such as H^+ and Al_{lab} , can be linked to the acid sensitivity of the site. A reduction in base-cation

concentration is the dominant response at the least sensitive sites, while changes in H^+ and Al_{lab} are clearest at the most acidified sites.

- Cl^- concentrations have declined from, and have since remained lower than, the levels experienced in the early years of monitoring, a period dominated by strongly positive phase of the North Atlantic Oscillation.
- Concentrations of dissolved organic carbon have increased significantly at every AWMN site.
- No site has experienced a decline in NO_3^- concentration, but equally there is no evidence to suggest a detrimental shift in status as predicted by nitrogen “saturation” models. Interannual variability in NO_3^- can be closely linked to interannual variations in climate.
- Despite evidence for regional-scale reductions in acidity, specific chemical responses to declines in S deposition vary. Local factors such as forestry, catchment buffering capacity and catchment N saturation are likely to affect patterns of recovery in response to xSO_4^{2-} decline at individual sites. More work is required to quantify the influence of changes in hydrology and sea-salt inputs on acidity anticipated in the light of predicted regional-scale changes in climate.
- The response of ANC in particular remains unclear, with few sites demonstrating significant improvements in CB-ANC. However, the strength of widely observed increases in AB-ANC, which incorporates DOC concentration within its calculation, show reasonable linearity with changes in xSO_4^{2-} and is therefore consistent with a catchment response of a shift from strong mineral to weaker organic acidity. It is clearly vital that the drivers of change in DOC are better understood before this apparent improvement can be interpreted in ecological terms.
- Although there is strong evidence for the continuing recovery of AWMN sites from acidification, these key uncertainties provide a strong case for continued monitoring in order to confirm the long-term recovery of AWMN sites and improve understanding of the processes involved.

Chapter 5

What may be driving upward trends in dissolved organic carbon?

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5.1 Introduction

One of the most striking observations made in Chapter 4 concerns the near ubiquitous increase in dissolved organic carbon (DOC) concentration across the Network. While similar increases have been identified elsewhere, both within the UK and internationally, there is as yet no consensus regarding the underlying cause. Most hypotheses fall in one of two camps, representing either responses to changing climatic conditions (and possibly linked to long term “global-warming”) or responses to declining acid deposition. The former potentially represents unprecedented environmental change while the latter represents a “recovery” process. It is clearly important to resolve this issue if the wider AWMN dataset is to be correctly interpreted. The aims of this Chapter are to: (i) review the current understanding of the properties of DOC; (ii) investigate the nature of recent DOC trends; (iii) review the various hypotheses which have been proposed; and, finally, (iv) test statistically the most appropriate of these hypotheses using AWMN and meteorological data.

5.2 Characteristics of dissolved organic matter

Dissolved organic matter (DOM) is a ubiquitous component of natural waters, and is operationally defined as comprising any organic compound passing through a 0.45 μm filter. The number of such organic compounds is effectively limitless, and it is thus impossible to provide a general chemical description of DOM. However, in general it includes a small proportion of identifiable, low-molecular weight compounds such as carbohydrates and amino acids, and a larger proportion of complex, high-molecular weight compounds collectively termed humic substances. Humic substances have a medium to high molecular weight, and are a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, ketone and other functional groups (Leenheer and Croué, 2003). Humic substances absorb visible light, most strongly at the blue end of the spectrum, giving high-DOM water a characteristic brown colouration.

DOM is generated by the partial decomposition of, or exudation from, living organisms including plants, animals, and soil microorganisms. Much of the organic matter generated by these processes may be stored in the soil for a varying length of time (e.g. as peat) before decomposition processes render a part of this material soluble. The compounds comprising DOM in natural waters may therefore range in age from relatively recent to thousands of years (Raymond and Bauer, 2001). DOM directly affects the functioning of aquatic ecosystems through its influence on acidity (Eshleman and Hemond, 1985), trace metal transport (Lawlor and Tipping, 2003), light absorbance and photochemistry (Schindler, 1971; Zafiriou *et al.*, 1984), energy supply (Wetzel, 1992), and nutrient supply (Stewart and Wetzel, 1981). It also affects water treatment processes (Alarconherrera *et al.*, 1994) and, as a transfer of carbon from terrestrial to aquatic and ultimately marine ecosystems, forms a non-negligible component of the global carbon cycle (Hope *et al.*, 1994).

In the AWMN, the dissolved organic carbon (DOC) component of DOM is measured. Dissolved organic nitrogen (DON) has also been determined since 1995. Concentrations of DOC in natural waters vary widely, from < 1 to > 50 mg l⁻¹ (Thurman, 1985), with a generally positive spatial relationship between DOC and the extent of wetlands and peatlands in the catchment (e.g. Curtis, 1998, Xenopoulos *et al.*, 2003). In the UK, Hope *et al.* (1997) demonstrated a correlation between riverine DOC flux and the amount of organic matter (predominantly peat) in catchment soils. Controls on spatial DOC variations among freshwaters can therefore be considered reasonably well understood. However, the causes of temporal change in DOC at a particular site remain subject to considerable uncertainty. This chapter therefore examines the nature of observed changes in the AWMN; compares these trends to other observations in the UK, Europe and North America; attempts to identify the possible drivers of DOC change; and assesses the significance of these changes in terms of local biological impacts and larger-scale environmental change.

5.3 DOC Trends in the AWMN

DOC trends in the AWMN have been assessed using the Seasonal Kendall Test. After ten years of monitoring, significant ($p < 0.05$) trends were observed at 17 out of 22 sites (Monteith and Evans, 2000). At this time, very few sites showed decreases in non-marine sulphate (xSO_4^{2-}), or increases in alkalinity or pH, associated with recovery from acidification. After a further five years of monitoring, there is now evidence of recovery (decreasing xSO_4^{2-} , and increasing pH and ANC) at many sites (Chapter 4). Over the same period, the trends in DOC have been sustained, with all 22 sites now showing significant rising trends. The magnitude of trends ranges from 0.06 to 0.51 mg l⁻¹ yr⁻¹. With few exceptions, trend magnitudes over 15 years have remained similar to those observed after 10 years, and trend significances have increased or remained constant at 21 of the 22 sites. In percentage terms, DOC concentrations have increased on average by 91% relative to 1988-93 means.

Examination of individual time series (Figure 5.1) does show some evidence of variability in the pattern of temporal variation. At a number of sites (e.g. Loch Coire nan Arr, Allt na Coire nan Con, Loch Chon, Round Loch of Glenhead) increases appear approximately linear, and are apparent in both minimum and maximum concentrations. At others, notably the River Etherow and Old Lodge, increases are most apparent in episodic maxima. At Dargall Lane, Scoat Tarn and Burnmoor Tarn, initially linear increases appear to have levelled off from the mid-1990s, whilst at Lochnagar, the Afon Hafren, and three of the Northern Ireland sites, there are indications that increases occurred as a step change around 1996. The fourth Northern Ireland site, Bencrom River, is the only site in the network where the trend appears to have reversed in recent years, with trend significance having decreased relative to the 1988-97 estimate as a result.

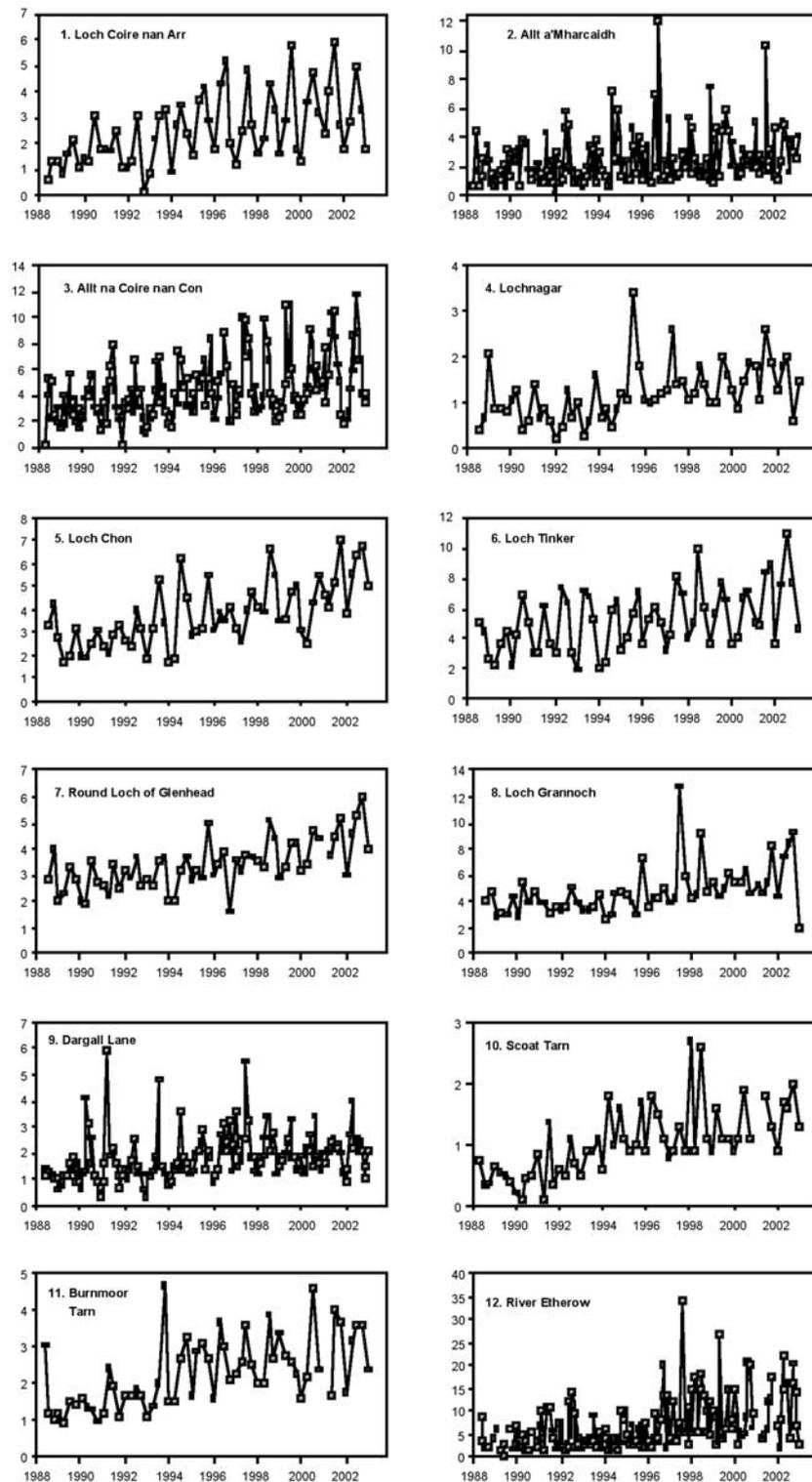


Figure 5.1a Trends in DOC at AWMN sites nos. 1-12.

These variations in temporal pattern suggest that, at least to some extent, local factors have contributed to observed DOC variations. Nevertheless, all 22 sites have shown a significant rising DOC trend, and the ubiquity of these increases suggests the presence of one of more underlying drivers of change, operating in a uniform and, over the timescale of monitoring, essentially unidirectional manner across the whole acid-sensitive area of the UK.

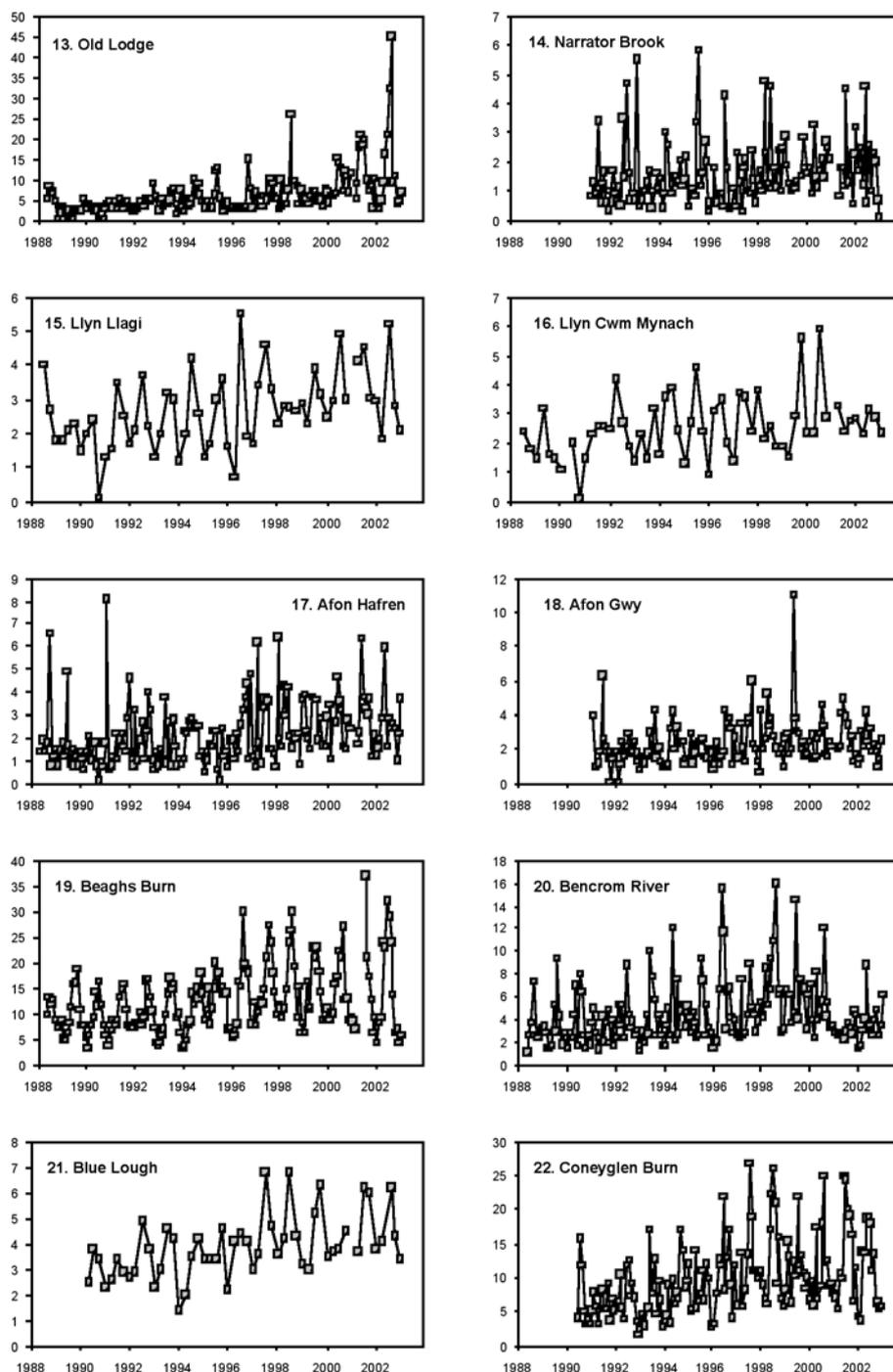


Figure 5.1b Trends in DOC at AWMN sites nos. 13-22.

5.4 Comparison with Trends in Other Datasets

5.4.1 Trends in other UK datasets

The possibility that water colour was increasing in the UK was first raised during the 1980s (e.g. McDonald *et al.*, 1989; Kay *et al.*, 1989), but prior to the initiation of the AWMN, systematic monitoring of DOC in upland waters was restricted to a small number of sites, notably the Plynlimon and Beddgelert catchments in North Wales (Reynolds *et al.*, 1997; Robson and Neal, 1996; Stevens *et al.*, 1995) and the Galloway Lochs and Loch Ard streams in Scotland (Harriman *et al.*, 2001). In almost every case, these datasets also show increasing DOC, and suggest that

these increases were occurring from at least the early 1980s. Longer-term data extending back into the 1960s and 1970s are limited to water colour records collected by water supply companies for peaty upland areas of northeast England (Watts *et al.*, 2001; Worrall *et al.*, 2003). Trends for these long-term datasets are variable, but several show significant increases, while none show decreases. All of these datasets, plus others including the AWMN sites, Forestry Commission monitoring sites in Wales (Forestry Commission, unpublished data), and a large set of Scottish Environmental Protection Agency monitoring sites in Northeast Scotland, were collated by Worrall *et al.* (2004). Of a total of 198 sites, 153 (77%) showed significant increases when analysed using the Seasonal Kendall Test, and none showed significant decreases. Overall, therefore, it appears that the AWMN sites are representative of the wider situation in UK upland waters; that DOC increases have been near-ubiquitous in these systems; and therefore that the driving mechanism for these increases must have operated across the whole country and over a prolonged period.

5.4.2 Trends in Europe and North America

The most extensive analysis of trends in acid-sensitive European surface waters available has been undertaken by the ICP Waters programme of the UN Economic Commission for Europe. A recent review of trends after 15 years of monitoring (Sjkelkvåle *et al.*, 2005) suggests that DOC concentrations have increased widely across the Nordic Countries and British Isles (these data include 6 AWMN sites), with no overall trends in Central Europe. Other studies have shown somewhat differing patterns; Hejzlar *et al.* (2003) report increasing DOC for a river in the Czech Republic since the mid-1980s, whereas Forsius *et al.* (2003) found few increasing DOC trends in the 1990s for a large Finnish lake dataset. However, more intensive monitoring data for Finnish streams do now show evidence of rising DOC (Finnish Environment Institute (SYKE), unpublished data).

In a large-scale study of trends in the northern and eastern US from 1990 to 2000, four out of five areas studied showed regionally significant increases in DOC (Stoddard *et al.*, 2003). On average, concentrations increased by 10% over the 10 years. The authors note that DOC increases have now been observed across nearly all regions of Europe and North America, and suggest that this must indicate a large-scale cause. Other data from the northeastern North America show similar trends, with DOC increases observed at 8 out of 17 lakes monitored since 1982 in the Adirondacks (Driscoll *et al.*, 2003), at 17 out of 51 lakes in Southern Quebec between 1985 and 1993 (Bouchard, 1997), although an assessment of lake DOC in Ontario and Quebec during the 1990s found few significant trends (Jeffries *et al.*, 2003). Schindler *et al.* (1997) reported a decrease in DOC for lakes in northwestern Ontario between 1970 and 1990, linked to changes in climate.

5.5 Potential Drivers of Change in DOC

5.5.1 Recovery from acidification

It has been suggested that, in response to increasing inputs of mineral acids, soils may release lower quantities of organic acids, thereby buffering the impact of acid deposition on runoff acidity (Rosenqvist, 1978; Krug and Frink, 1985). Surface water DOC concentrations would thus be depressed during periods of high acid anion concentrations, and would be expected to increase as concentrations of these ions are reduced. Palaeolimnological evidence has been used to support this hypothesis, with lake cores showing diatom assemblages characteristic of less coloured waters during the period of maximum acidification (Davis *et al.*, 1985; Dixit *et al.*, 2001). Laboratory experiments on organic soils suggest that organic matter dissolution release is positively related to pH (e.g. Tipping and Hurley, 1988; Kennedy *et al.*, 1996) although studies of

podzolic mineral horizons have shown inverse relationships (e.g. David *et al.*, 1989). With regard to the biological processes controlling DOM production, Cronan (1985) concluded that pH variations had a relatively minor impact.

Field-scale manipulation experiments provide equivocal evidence for the role of pH. Studies by Schindler *et al.* (1992, 1997) showed large DOC decreases due to enhanced in-lake removal at experimentally acidified lakes, and a temporary decline in bog pools within an acidified peatland. Catchment-scale acidification experiments at Lake Skjervetjem, Norway (Hessen *et al.*, 1997) and Bear Brook, Maine (David *et al.*, 1999) showed no clear evidence of changes in surface water DOC, although some evidence of decreasing organic anion concentrations was observed at Bear Brook. Similarly, a whole catchment acid-exclusion experiment at Risdalsheia, Norway (Wright *et al.*, 1993) showed no evidence of DOC change, but increased organic acid dissociation. Using long-term monitoring data, Stoddard *et al.* (2003) suggest an inverse correlation between DOC and $x\text{SO}_4^{2-}$ trends in US surface waters, consistent with an acidification control on DOC, although correlations were weak, and only observed when waters were subdivided into low- and high ($> 5 \text{ mg l}^{-1}$) DOC classes. Using the same approach, somewhat stronger relationships were noted for European surface waters in the ICP Waters network (Sjkelkvåle, 2003; J. Stoddard pers. comm.). Since emissions and deposition of acidifying compounds have decreased in the UK since 1988, changes in acidity may have contributed to observed DOC trends, and are considered in the analysis below.

Soil solution ionic strength has also been proposed as a control on DOC mobilisation. Laboratory studies show fairly consistent reductions in DOC release with increasing ionic strength in both organic and mineral soils (e.g. Tipping and Hurley, 1988; Evans *et al.*, 1988; Vance and David, 1989). Since acid deposition raises ionic strength, any ionic strength effects are difficult to distinguish from those of acidity in the field. In this respect, the absence of DOC response to pH change in many of the field manipulation experiments described above also implies a lack of response to ionic strength change. It is worth noting, however, that in almost all of the AWMN surface waters, the dominant ions are sodium (Na^+) and chloride (Cl^-), associated with high levels of sea salt deposition. Climatic fluctuations have been shown to cause large, cyclical variations in the concentration of sea salt ions in runoff (Evans *et al.*, 2001a), and consequently variations in ionic strength in these waters are, to some extent, decoupled from those in acid deposition. Since sea salt concentrations were higher during the early years of monitoring, this mechanism could also contribute to observed DOC trends.

5.5.2 Temperature change

In spatial terms, there is generally a negative relationship between DOC concentration and temperature, with the highest concentrations observed in waters draining peatlands characteristic of cold, northern latitudes (Meybeck, 1982). However, the influence of temperature on temporal variations at an individual site appears very different. Laboratory studies have consistently shown a positive influence of temperature on soil DOC production (e.g. Christ and David, 1996; Andersson *et al.*, 2000; Moore and Dalva, 2001; Fenner, 2002), and positive within-year correspondence between DOC and temperature have been observed in field studies of a range of soil waters (e.g. Cronan and Aiken, 1985; Liechty *et al.*, 1995; Chapman *et al.*, 1995; Michalzik and Matzner, 1999). A translocation study by Tipping *et al.* (1999) also showed increased DOC leaching from peaty soils moved to warmer, dryer locations. A 4°C catchment-scale warming experiment at Risdalsheia, Norway produced an apparent increase in runoff DOC concentrations (Wright and Jenkins, 2001).

It has been argued that the enzymatic hydrolysis of high molecular weight organic matter, into

smaller molecules utilisable by microorganisms, represents the rate-limiting step within organic matter decomposition (Hoppe *et al.*, 1988; Chróst, 1991). High levels of recalcitrant phenolic compounds in peaty soils can inhibit enzyme activity (Wetzel, 1992; Kang and Freeman, 1999) and the phenol oxidase enzyme, which degrades these compounds, has been shown to be highly sensitive to climatic conditions (Freeman *et al.*, 2001a; Freeman *et al.*, 2001b; Fenner, 2002). Peat warming experiments under laboratory conditions showed increased levels of phenol oxidase activity, DOC concentrations, and the proportion of phenolic compounds within this DOC (Freeman *et al.*, 2001b; Fenner, 2002), implying both a temperature effect on DOC production, and increased recalcitrance of that DOC, which would tend to limit further degradation of this DOC to CO₂. This mechanism was proposed as a cause of observed DOC increases in the AWMN by Freeman *et al.* (2001a). A further proposed influence on DOC production are enchytraeid worms (Oligochaeta), which form the dominant soil fauna in UK upland peat soils. Studies by Briones *et al.* (1998) and Cole *et al.* (2002) suggest that enchytraeids increase in abundance at higher temperatures and, through their influence on microbial activity, litter fragmentation and soil aeration, appear to significantly enhance DOC production.

Data from the Central England Temperature Record (CET) (Parker *et al.*, 1992), which are considered representative of temperature trends across the UK as a whole, show that temperatures during the 15 years following the initiation of monitoring (1988-2002) were on average 0.75°C higher than those for the period 1960-1987. Five of the six warmest years in the CET, which began in 1659, have occurred since 1989. Although temperature trends within the AWMN monitoring period are less apparent (Figure 5.2), given the potential delay between production of DOC within the soil and washout of this material to surface waters (e.g. Mitchell and McDonald, 1992), any DOC-temperature response is likely to be fairly lagged and damped.

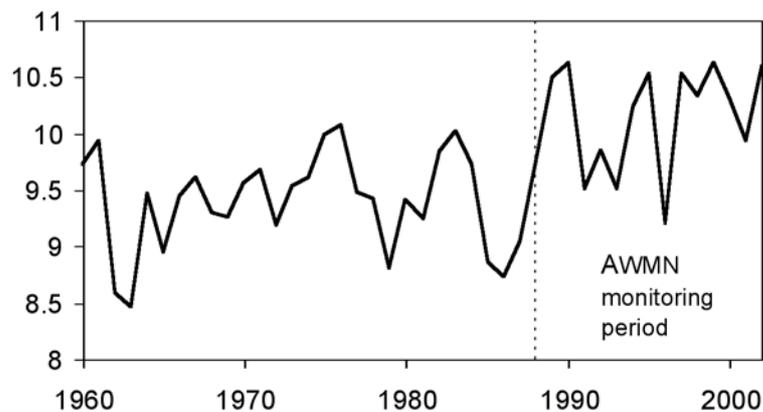


Figure 5.2 Annual mean central England temperatures, 1960-2002. Date provided by the Hadley Centre (www.met-office.gov/research/hadleycentre) (Parker *et al.*, 1992)

5.5.3 Hydrological change

Three possible mechanisms by which hydrological processes could affect the input of DOC to surface waters may be identified:

a) In the absence of any change in the DOC flux entering the stream network, a decrease in discharge should lead to increased DOC concentrations.

b) Conversely, increased flow may increase both DOC flux and concentration by altering water flowpath, with an increased proportion of runoff routed through shallow, organic-rich soil horizons, relative to deeper mineral horizons in which DOC adsorption is high (Cronan and Aiken, 1985; McDowell and Likens, 1988). Flowpath-related hydrological changes have been associated with long-term lake DOC variations in Sweden (Forsberg, 1992) and Ontario (Schindler *et al.*, 1997) whilst Clair *et al.* (1999) used a neural network model to show a positive relationship between runoff and DOC in Canadian surface waters, as a basis for predicting DOC response to climate change.

c) Changes in the distribution of rainfall and runoff within the year may affect both DOC production and transport processes. In particular, drought-rewetting cycles have been identified

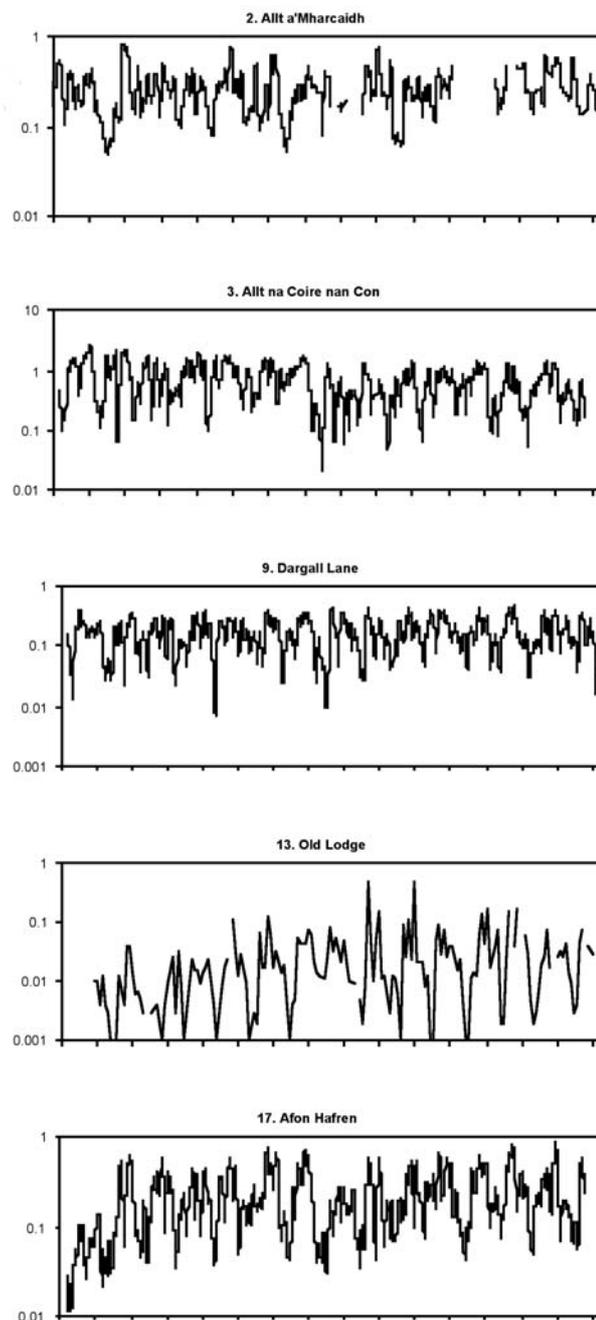


Figure 5.3 Daily mean discharge records for AWMN streams. (Old Lodge data represent monthly spot-sampled flow)

as a major influence on DOC production in the UK, characterised by a two stage process of i) enhanced organic matter decomposition due to aeration of normally saturated peaty soils; and ii) flushing of accumulated DOM into streamwaters upon rewetting (McDonald *et al.*, 1991). Freeman *et al.* (2001b) argue that, since activity of the key phenol oxidase enzyme is inhibited under anaerobic conditions, the link between peat decomposition and aeration may be highly sensitive. It is worth noting, however, that aerobic conditions tend to favour the production of CO₂ rather than DOC, and that the breakdown of DOC is itself moisture dependent (Kalbitz *et al.*, 2000). Therefore, the response of DOC to drought is not straightforward, and may depend on the initial moisture conditions of the soil. Nevertheless, field studies of the effects of dry-wet cycles have consistently shown a DOC increase following rewetting (Mitchell and McDonald, 1992; Hughes *et al.*, 1998; Tipping *et al.*, 1999; Lundquist *et al.*, 1999), often with DOC concentrations suppressed during the drought period itself (Mitchell and McDonald, 1992; Hughes *et al.*, 1998). A wetland manipulation experiment by Hughes *et al.* (1998) suggested that repeated droughts might generate a long-term increase in DOC losses, and Watts *et al.* (2001) noted that water colour data for a number of reservoirs in Northern England showed apparent step-change responses to a sequence of natural droughts in 1976, 1984 and 1995, with colour levels apparently not returning to pre-drought levels between each drought.

Over the AWMN monitoring period, available data do not show decreases in flow consistent with hypothesis a), and estimates of DOC fluxes at both the Afon Hafren (Cooper and Watts, 2002) and at two rivers in Northeast England (Worrall *et al.*, 2003) indicate that fluxes have increased in line with concentrations. There is some evidence of long-term increasing trends in river flows in Northwest Britain from 1961 to the early 1990s (Cannell *et al.*, 1999a; Werrity *et al.*, 2002), but these have not been sustained during the 1990s (DEFRA, 2003). Discharge monitoring data for a number of AWMN rivers (Figure 5.3) do not show clear or consistent trends. Overall, therefore, there is little evidence to suggest that the long-term runoff changes required to generate a change in DOC concentration have occurred.

With regard to the role of drought/re-wetting cycles, there is evidence of a recent trend towards wetter winters and drier summers in the UK (Burt *et al.*, 1998). Again this trend is not apparent within the AWMN monitoring period (e.g. Figure 5.4), but the majority of sites were affected by the severe drought of 1995. Although droughts form part of the natural hydrologic variation of these systems, the recent sequence of three severe droughts could potentially have affected long-term DOC trends. Apparent step change increases in DOC following the 1995 drought at a

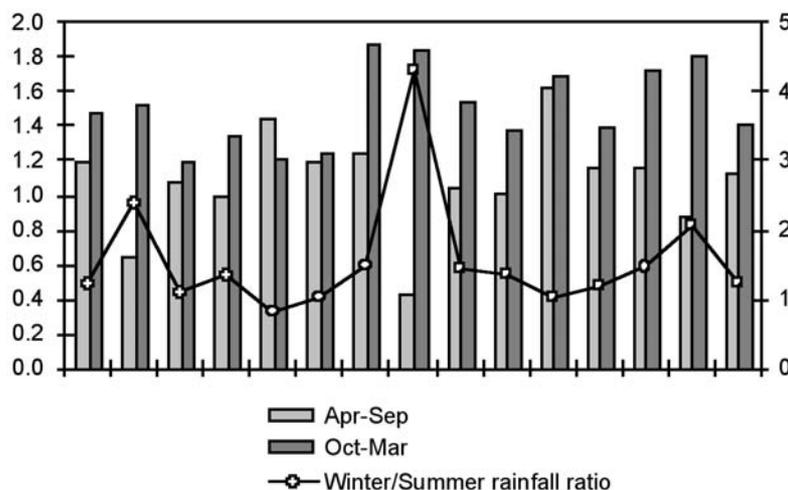


Figure 5.4 Six-monthly rainfall totals and winter/summer rainfall ratios from the England & Wales Precipitation Series, during the UK AWMN monitoring period. Data provided by the Hadley Centre (Alexander and Jones, 2000)

number of sites (e.g. sites 17-22, Figure 5.1) lend some support to this hypothesis.

5.5.4 Land-use change

The major land-use influence within the AWMN catchments is rough grazing, primarily by sheep, which influences vegetation cover, soil compaction and drainage patterns (Milne, 1996; Holman *et al.*, 2002). Census data show that overall stocking levels in upland areas of England have increased since 1980 (English Nature, 2001). Coniferous afforestation affects five sites, and there is some evidence that this influences DOC generation, particularly following felling (Hughes *et al.*, 1990; Neal *et al.*, 1998). Peatland drainage, which was widespread in some upland areas during the last century, has been identified as a possible contributor to DOC trends by Worrall *et al.* (2003), whilst heather burning for management of red grouse has been shown to have a profound impact on peatland soil carbon cycling (Garnett *et al.*, 2000).

Of the 17 moorland AWMN catchments, the nature and intensity of grazing vary widely, with several sites largely or entirely ungrazed. There are also no indications of extensive drainage or burning activities at the majority of sites. At the five afforested sites forest ages vary, with harvesting having taken place during monitoring at the Allt na Coire nan Con, Loch Chon and Afon Hafren. Despite the potential for forest-related factors to impact on DOC export, DOC trends for forested sites show no systematic deviation from those at nearby moorland sites

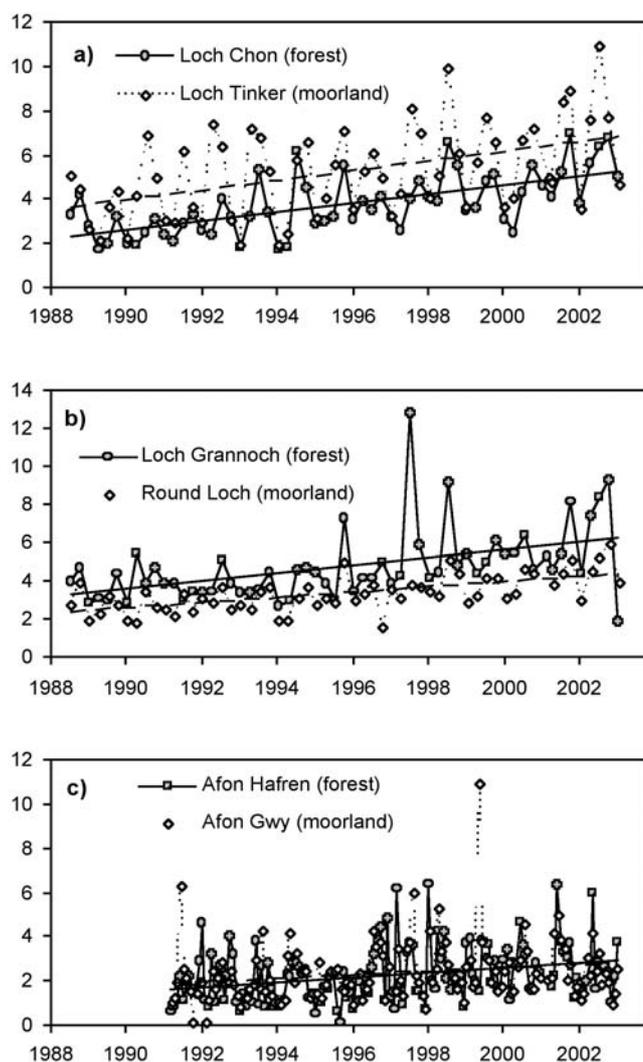


Figure 5.5 DOC trends at three paired moorland and forest catchments

(Figure 5.5). A larger set of 9 monitored Welsh forest catchments (Forestry Commission, unpublished data) also show similar DOC trends to the Welsh AWMN sites. In Scotland, although Grieve and Marsden (2001) found higher DOC concentrations in forest versus moorland soil solutions, Harriman *et al.* (2003) found similar DOC trends in waters draining forest and moorland catchments, and concluded that forest impacts on DOC export were relatively minor.

On the evidence available, there do not appear to have been any systematic trends in land-use affecting all of the AWMN sites. Although one or more of land-use factors could have contributed to DOC trends at individual sites, then, it appears improbable that any single land-use factor could explain trends across the network as a whole.

5.5.5 In-lake and in-stream removal

The influence of in-lake processes on DOC has received considerable attention in other regions, particularly in North America and Scandinavia, where microbial utilisation and photo-oxidation have been shown to cause significant reductions in DOC concentration (e.g. Hongve, 1994; Granéli *et al.*, 1996; Schindler *et al.*, 1997; Dillon and Molot, 1997). These authors have shown that both lake acidification and longer water residence times (associated with climatic changes) tend to decrease lake DOC. In-stream DOC removal, for example due to utilisation by biofilms, has also been demonstrated (e.g. Freeman *et al.*, 1990). However, the quantitative importance of these processes in UK waters is questionable, due to the relative recalcitrance of DOC generated from peaty soils, and short water residence times at most lakes due to a combination of typically high rainfall, and large catchment area:lake volume ratios. Although lake inflows are not monitored at AWMN sites, data collected over a two-year period for a set of similar lakes (Curtis *et al.*, 1998) show no consistent differences between lake main inflows and outflows for a range of DOC levels (Figure 5.6), suggesting that in-lake processing is minor. The short residence time of water in rivers, and the persistence of both high DOC levels and temporal patterns into the lower reaches of rivers draining peaty uplands (Eatherall *et al.* 1998; Worrall *et al.*, 2003) further indicate that in-stream removal processes are quantitatively minor.

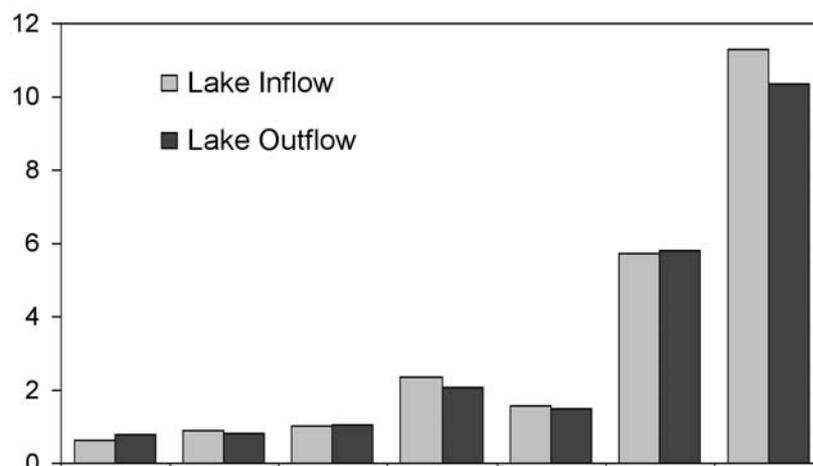


Figure 5.6 Two-year mean inflow and outflow DOC concentrations for a range of UK lakes (data from Curtis *et al.*, 1998)

5.5.6 Nitrogen Enrichment

Nitrogen enrichment has been proposed as a potential influence on DOC release through its role as a limiting nutrient in terrestrial ecosystems, and due to the role of labile organic matter in N immobilisation (Aber, 1992; Zech *et al.*, 1994). However, no evidence of increased DOC loss was observed in a number field N addition experiments (Gundersen *et al.*, 1998, McDowell *et al.*, 1998). Additionally, for the UK there is little evidence of nationally consistent changes in either N deposition (Chapter 2 & 3) or surface water NO_3^- (Chapter 3 & 4) that would be consistent with nitrogen as a driver of observed DOC trends.

5.6 Analysis of AWMN Data

From an assessment of previous work, and of environmental changes in the UK over the last 15 years, it appears that a limited number of drivers have the potential to explain observed DOC increases at the AWMN sites. These are i) decreasing soil acidity; ii) decreasing ionic strength of soil solutions; iii) increasing temperature; and iv) effects of dry-wet cycles. The relative role of these drivers is examined firstly through an assessment of spatial patterns in observed chemical trends. Secondly, a stepwise regression analysis of raw DOC data is undertaken for the lake sites, using a range of potential chemical and climatic predictor variables.

5.6.1 Spatial variations in chemical trends

When comparing DOC trends between sites, a striking feature is the strong correlation ($R^2 = 0.71$) between the rate of annual DOC increase, and the mean DOC concentration for the first five years of sampling (Figure 5.7). These observations are indicative of a relatively uniform increase in DOC release per unit organic carbon at a UK-wide scale, and imply that the proportional increase in DOC has been fairly similar between sites, on average 6.1% per annum, i.e. 91% over the 15 years of monitoring. This correlation has been replicated with a larger dataset by Worrall *et al.* (2004). Since mean DOC concentrations largely reflect the amount of organic carbon stored within catchment soils (Hope *et al.*, 1997), these observations suggest that there has been an increase in DOC release per unit of organic carbon, and that this increase has been fairly uniform at a UK-wide scale. This would seem to suggest the need for a driving mechanism which has

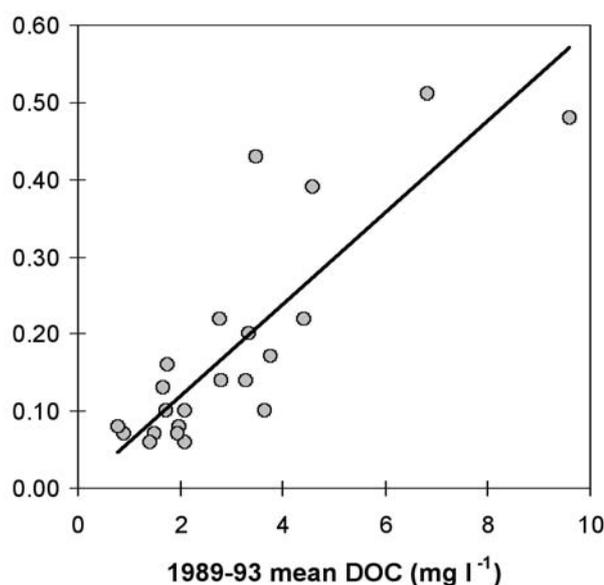


Figure 5.7 Relationship between the magnitude of trends in DOC and mean DOC during the first five years of monitoring.

operated consistently at the same scale.

If decreases in acid (primarily S) deposition were responsible for increasing DOC, a correlation might be expected between the magnitude of trends in $x\text{SO}_4^{2-}$ and DOC concentration, as suggested by Stoddard *et al.* (2003). The correlation for the AWMN sites is significant ($p = 0.01$) but relatively weak ($R^2 = 0.29$, Figure 5.8a), and reliant on two sites with large DOC increases and $x\text{SO}_4^{2-}$ decreases (the River Etherow and Old Lodge). The correlation is not improved by subdividing sites into low- (mean $< 5 \text{ mg l}^{-1}$) and high-DOC classes. It is worth noting that the two sites with the largest DOC increases, Coneyglen Burn and Beaghs Burn, are located in the low-deposition region of Northwest Northern Ireland, and exhibit relatively small $x\text{SO}_4^{2-}$ decreases. Similarly, the two sites in Northwestern Scotland, Loch Coire nan Arr and Allt na Coire nan Con, show some of the clearest DOC increases (Figure 5.1) but are located in a region of very low S deposition, with no significant $x\text{SO}_4^{2-}$ trends observed over the 15 years. Although apparently correlated with DOC trends, then, changes in acid deposition may provide only a partial explanation for observed DOC increases.

Finally, a similar assessment of the role of ionic strength was undertaken, using trends in the sum of mineral acid anions (SAA, calculated as $\text{SO}_4^{2-} + \text{Cl}^- + \text{NO}_3^-$) as indicative of ionic strength trends (based on the mobile anion concept, changes in overall ionic strength should be driven by changes in these ions). In addition to decreases in anthropogenic S inputs, SAA has also decreased at all sites due to a general reduction in sea salt deposition from the high levels observed in the early 1990s. Despite this, correlations between trend slopes for SAA and DOC remain weak ($p = 0.01$, $R^2 = 0.30$, Figure 5.8b). Again, therefore, it appears that changes in ionic

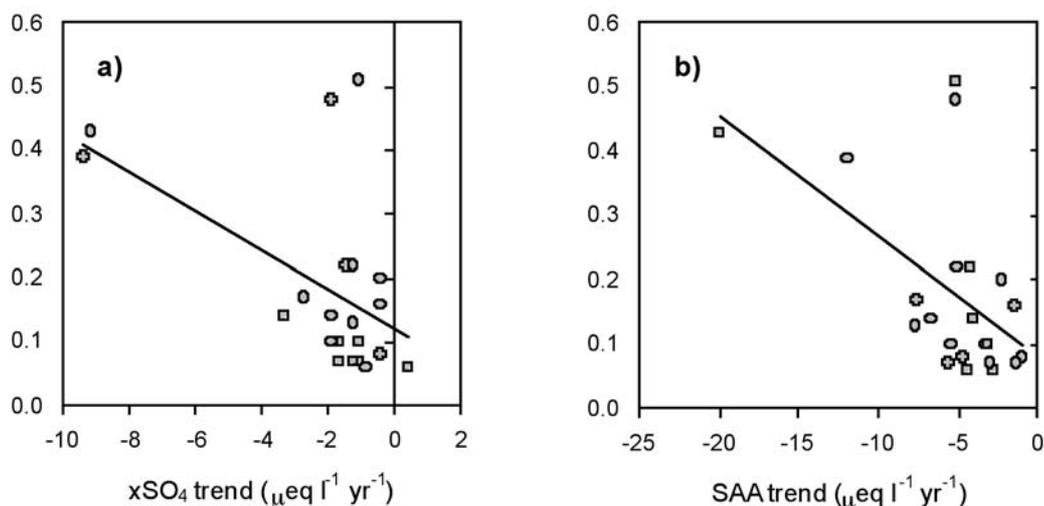


Figure 5.8 Relationship between the magnitude of trends in DOC and trends in (a) non-marine sulphate and (b) sum of acid anions.

strength alone may not account for the increases in DOC at all sites.

5.6.2 Stepwise regression analysis

As a first assessment of potential drivers of temporal DOC variations, time series of DOC concentrations were analysed using three simple statistical models, as follows:

- Model 1: A simple stepwise regression model, in which time series of DOC measurements were analysed against a range of chemical and climatic variables. Chemical predictor variables used were pH, $x\text{SO}_4^{2-}$, Cl^- and SAA. Climatic predictor variables were rainfall measurements from nearby meteorological stations (totals for 1, 2, 3, 6, 12 and 24 month antecedent periods) and

temperatures from the Central England Temperature record (averages for 3, 6, 12, 24 and 36 month antecedent periods). The CET was considered a suitable temperature variable for all sites, given that a strong seasonality controlled correlation between this and water temperature records at all lakes. Stepwise regressions were undertaken using a standard selection procedure (forward selection and backward elimination with a 0.15 significance threshold). Variable selection was constrained such that i) a maximum of one short-term (< 1 yr) and one long-term (1 year) variable was included for rainfall and temperature; ii) only the most significant of SAA and Cl^- were included (since Cl^- is the dominant acid anion at all sites). In practice, these constraints were not required in most of the analyses undertaken.

- Model 2: A baseline model, in which a linear trend and four-level seasonal component were fitted to the DOC concentrations based simply on year and time of year. The extent to which this model, which does not attempt to divine a causal mechanism, is able to represent the variability in the time series provides a basis for assessing the quality of fit of any proposed causal model. A causal model would be expected to be at least comparable in predictive power with this baseline model.
- Model 3: A strong stepwise elimination model using Model 2 trend and seasonal variables, plus all climatic and chemical variables included in Model 1. Variable selection constraints were as in Model 1. The stepwise elimination procedure was weighted in favour of low-dimensional models, so that a submodel with fewer parameters may be selected over one with a lower residual standard error (RSE).

The analysis was limited to the 11 lake sites, as these show greater chemical stability over the short term, whereas large episodic DOC variations at streams tend to obscure the long-term pattern.

The simple stepwise regression analysis, Model 1, gave R^2 values ranging from 0.21 to 0.72 among sites. Although the selected predictor variables varied (Table 5.1), a number of general observations may be made:

- At all sites except Scoat Tarn, at least one temperature variable was selected, with a long-term temperature variable selected at seven sites. In all cases, regression coefficients were positive.
- Rainfall and pH were selected less frequently, and regression coefficients showed both positive and negative values. Either SAA or Cl^- was selected at eight sites. In all cases, regression coefficients were negative. The three sites in which neither variable was selected were all in the relatively low deposition area of Northern/Central Scotland.
- xSO_4^{2-} was selected only at Loch Grannoch. However, changes in SO_4^{2-} were incorporated

Site	Seasonal climatic	Long-term climatic	Chemical
1	CET _{3month} (+), Rain _{1month} (-)	CET _{3year} (+), Rain _{1year} (-)	pH (-)
4	Rain _{1month} (+)	CET _{1year} (+), Rain _{2year} (+)	
5	Rain _{2month} (+)	CET _{2year} (+)	pH (+)
6	CET _{3month} (+)	CET _{2year} (+)	SAA (-)
7		CET _{2year} (+)	SAA (-)
8	CET _{3month} (+), Rain _{1month} (-)	CET _{1year} (+)	Cl (-), xSO_4 (-), pH (-)
10			SAA (-)
11	Rain _{6month} (-)	CET _{2year} (+)	Cl (-), pH (-)
15	CET _{3month} (+)		SAA (-)
16	CET _{3month} (+)		SAA (-)
21	CET _{6month} (+)		SAA (-)

Table 5.1 Variables selected in stepwise regression, Model 1.

within SAA at six other sites.

These observations appear to support both a positive association between DOC and temperature, and a negative association between DOC and ionic strength at a majority of the lakes. Any relationship to recovery from acidification is less clear, but may be incorporated within the ionic strength predictor. Association between DOC concentrations and variations in rainfall is also hard to detect. Modelled time series based on the regression equations (Figure 5.9) show that, at most sites, much of the observed rising trend in DOC is successfully reproduced, suggesting that correlations are not simply seasonal.

While these results therefore appear consistent with temperature and deposition (of seasalt and/or anthropogenic acids) as driving variables, this conclusion is subject to a number of major caveats. First, the simple linear predictor variables used are fairly crude, and may not adequately reflect the conditions affecting DOC production. For example, antecedent rainfall totals provide only a weak indicator of soil moisture status and drought occurrence. Additionally, surface water DOC is a function both of the DOC composition of source waters, and of the relative proportion of water from different sources. Thus, while dry conditions and high pH might increase DOC concentrations in soil waters, short-term variations in lake water chemistry might be more strongly related to the proportion of water from shallow (relatively acid, high-DOC) versus deep (less acid, lower DOC) soil horizons. Even though these flowpath variations may not explain long-term trends, they may be sufficient to confound correlations between DOC and either lake pH or rainfall.

Second, all lakes show some seasonal variation. DOC is typically highest in September samples, when temperatures are high, and lowest in March samples, when seasalt concentrations, and hence ionic strength, are typically highest. The observed correlations must therefore to some extent reflect seasonal, rather than long-term, correlations. This is particularly true for the sub-annual rainfall and temperature variables, which essentially account for seasonal variability, and may be quite independent of any mechanism influencing long-term trend.

Finally, there is a risk that any variable with a long-term trend will, to some extent, show a correlation with the trend in DOC; again, this does not necessarily demonstrate a causative relationship.

Model 2 demonstrates the extent to which observed DOC variations can be explained fitting simple seasonal and linear trend components. A comparison of RSE values (Table 5.2) shows that

Site	Model 1		Model 2		Model 3	
	RSE	R ²	RSE	R ²	RSE	R ²
1	0.71	0.74	0.71	0.74	0.71	0.74
4	0.51	0.36	0.55	0.25	0.56	0.18
5	0.83	0.60	0.79	0.70	0.70	0.76
6	1.30	0.62	1.18	0.69	1.05	0.72
7	0.65	0.55	0.59	0.63	0.61	0.60
8	0.95	0.71	1.10	0.53	0.85	0.55
10	0.50	0.22	0.43	0.46	0.44	0.41
11	0.60	0.61	0.73	0.46	0.61	0.58
15	0.76	0.55	0.71	0.62	0.69	0.64
16	0.95	0.24	0.93	0.28	0.81	0.52
21	0.74	0.66	0.72	0.67	0.59	0.78

The model with the lowest RSE for each site is highlighted in bold

Table 5.2 Residual standard error (RSE) and R² values for each statistical model.

in only three cases does the stepwise regression Model 1 provide a better fit than Model 2. While this does not invalidate the relationships observed in Model 1, it suggests that the variables selected provide at best only a first approximation of a causal mechanism.

Model 3 condenses the contributions from a very comprehensive candidate causal model and Model 2. The selected variables in this model (Table 5.3) in general include 3 components: a descriptor of seasonality, a descriptor of trend, and one or more chemical variables (which may incorporate both seasonal and long-term variation). Note that all the variables contribute to reducing the residual variance, by virtue of remaining after stepwise elimination. This model provided the lowest RSE values of the three models applied at 7 of the 11 sites. General observations that may be made are:

- Sub-annual temperature and rainfall variables appear more successful in describing within-year variability than a seasonal factor, which was not selected at any site. However, since a seasonal factor effectively uses 3 parameters in contrast to the single parameter used by a single seasonal variable, it tends to be excluded in stepwise regression.
- The descriptor of DOC trend selected was generally the simple linear trend, rather than longer-term climate variables
- An acid anion (Cl^- , SO_4^{2-}) was selected at 6 sites. This may be explaining in part both trend and seasonality. Selection of Cl^- suggests a possible ionic strength effect, selection of SO_4^{2-} either an ionic strength or acidity effect.

From this exploratory data analysis, it is not possible to identify any single simple linear predictor of DOC concentration increase in the AWMN lakes. The results provide some support to the hypotheses that DOC concentrations are affected positively by temperature and negatively by soil solution ionic strength and non-marine SO_4^{2-} concentration, but variability between sites, and the failure of any long-term variable to perform significantly better than a simple linear trend, suggest that other or more complex (e.g. non-linear) mechanisms may be required. Nonetheless, the consistent pattern of rising DOC at all sites does suggest one or more common drivers.

5.7 Environmental Impacts of Rising DOC

The lakes and streams of the AWMN have clearly undergone major chemical change during the last 15 years, and increased concentrations of DOC are likely to have had a significant impact on other chemical variables. In particular, metal transport may have increased due to the increased complexation by organic compounds. This is apparent for Al, which has shown generally increasing concentrations of the organic form (significant at 8 sites) at the same time as

Site	Seasonal	Long-term	Chemical
1	CET _{3month} (+), Rain _{6month} (-)	Trend	
4		Trend	
5	CET _{6month} (+)	Trend	Cl (-)
6	CET _{3month} (+)	Trend, Rain _{1year} (+)	Cl (-)
7	CET _{6month} (+)	Trend	
8	CET _{6month} (+), Rain _{2month} (-)		SO ₄ (-), pH (-)
10		Trend	
11	Rain _{6month} (-)	Trend	Cl (-)
15	CET _{3month} (+)	Trend, CET _{2year} (-)	
16	CET _{3month} (+), Rain _{2month} (-)	Trend	SO ₄ (-), pH (-)
21	CET _{6month} (+)	Trend	Cl (-)

Table 5.3 Variables selected in stepwise regression, Model 3.

concentrations of toxic inorganic Al have decreased (significant at 10 sites). Total iron concentrations have also increased significantly at 13 sites, consistent with the importance of organic complexes for iron transport. Other, unmonitored, trace metals forming organic complexes may also have increased along with DOC. Monitoring of DON only began in 1995, so trends are not yet apparent, but again a correlation with DOC would be expected. Additionally, the increase in organic acidity has clearly, to some extent, offset the decrease in mineral acid anions over the monitoring period, resulting in pH and alkalinity increases that are generally weaker than those in ANC (Chapter 4). However, the impact of DOC changes on runoff may be complicated by changes in soil solution DOC; a modelling study for the Afon Gwy (Evans, 2005) suggested that the suppression of soil water pH by increasing organic acids could lead to displacement of soil base cations, thereby reducing the impact of DOC increases on runoff pH (but leading to a reduction in soil base saturation).

Given the influence of DOC on light regime, energy and nutrient supply, and metal toxicity, the large increase observed might be expected to have generated observable biologic responses. These include transparency effects, for example on the maximum depth of macrophyte growth within lakes, and indirect effects on the toxicity of Al to fish and other biota (Roy and Campbell, 1997; McCartney *et al.*, 2003). While the former have not yet been observed, a link has been identified between sites showing trends in ANC and those showing biological change (Chapter 6). Although this may simply represent an acidity response, it would also be consistent with a process of exchange of mineral for organic acidity at these sites and the effect this would have on Al complexation. Given the complexity of factors influencing aquatic biota, clear identification of biological responses to changing DOC may require further monitoring.

The downstream effects of DOM increases may also be significant. Waters containing high levels of humic substances, although not directly harmful, are generally removed from drinking water for aesthetic reasons. In addition, it has been suggested that the presence of humic substances in water during the chlorination process may i) reduce residual chlorine levels leading to increased risk of bacterial contamination; and ii) produce carcinogenic organo-chlorine compounds (Alarconherrera *et al.*, 1994). Since humic substances are generally considered fairly unreactive on the timescale of most river (and small lake) residence times in the UK, much of the DOM released from upland regions is transported to estuaries, and into the oceans. The significant input of terrestrially-derived DOM to coastal waters has been noted by Raymond and Bauer (2001), and may significantly affect their functioning as a source of energy and nutrients, and through its influence on light regime.

Regardless of the direct consequences of changing DOC in the short term, however, the fundamental significance of the increases observed depends on the mechanism driving this increase. Because pre-industrial, reference conditions for UK surface waters are essentially unknown, and levels of natural variability not well quantified, it remains unclear whether recently observed changes are i) a return to reference conditions following anthropogenic perturbation; ii) fluctuations within a natural range, or iii) an increase towards levels that have not previously occurred. If DOC increases are driven by declining acid deposition, then any biologic changes resulting can be considered part of a return towards the pre-industrial state of the system. If increases are related to natural climate variability, then they can in turn be considered natural. However, given projected climate changes for the UK based on current greenhouse gas emission forecasts, most notably increases in temperature and in the ratio of winter to summer rainfall (Hulme *et al.*, 2002), even 'natural' changes observed to date may be indicative of future trends in response to climate change. Furthermore, the recent succession of warm years in the UK since 1988 have been attributed to the effects of human perturbation of the climate system (Hulme *et al.*, 2002), and it is therefore possible that observed DOC trends already

represent a response to this climate change.

If DOC increases in surface waters can be attributed to warming, or to other meteorological factors associated with climate change, the potential consequences in terms of carbon cycling may be significant. DOC fluxes from UK rivers were estimated at 0.69 Mt yr^{-1} in 1995 (Hope *et al.*, 1997), comparable in magnitude to the UK C sink associated with peat accumulation (Cannell *et al.*, 1999b). Based on the monitoring dataset compiled by Worrall *et al.* (2004) the UK DOC flux was recalculated for 2000 at 0.86 Mt/yr . This represents a significant transfer of organic C from terrestrial stores to the more active dissolved form, and ultimately to the atmosphere as CO_2 .

5.8 Summary

- There is now overwhelming evidence that concentrations of dissolved organic carbon have increased during the last two decades in the UK. There is also evidence of similar changes at many other monitored sites across Europe and North America.
- These observations clearly suggest a systematic response to one or more external drivers across a large spatial scale.
- The increases at the AWMN sites represent a near-doubling in concentrations over 15 years, and it seems highly likely that changes of this magnitude will have significant long-term impacts on lake and stream biota.
- At a larger scale, these increases may also impact on drinking water treatment, on the functioning of coastal marine ecosystems, and on the carbon balance of UK uplands.
- Several hypotheses have been proposed to explain these trends but as yet there is no consensus on the most likely drivers. A better understanding of mechanisms is clearly necessary for the wider interpretation of AWMN data.
- Although some potential drivers, such as land-use change, can probably be excluded at a UK scale it has, to date, been difficult to determine the relative importance of deposition-related and climate-related factors.
- The tentative conclusion of this analysis is that both deposition and climate-related factors may be significant; it seems probable that recovery from acidification has been a significant driver of DOC trends in those regions where sulphur deposition has decreased, but comparable trends at essentially unimpacted sites in the northwest suggest an additional role for climate-related factors, for example associated with changes in sea-salt deposition or temperature.
- Although the AWMN dataset has been fundamental to the identification of long-term increases in DOC in the UK, a full understanding of the drivers of these trends will require additional research, including: further studies of DOM generation processes within terrestrial systems; manipulation experiments incorporating a range of potential climatic and chemical drivers; and studies of DOM transfer between soils and drainage waters. Improved palaeo reconstruction techniques are also needed to establish baseline conditions, and the trajectory of past changes in DOC concentration relative to known historic variations in climate and deposition.
- Ultimately, process-based models are required in order to predict future response of terrestrial carbon stores to changes in climatic and/or deposition drivers, and to simulate the chemical

Chapter 6

Is the decline in acidity prompting improvements in freshwater flora and fauna?

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6.1 Introduction

After 15 years of integrated monitoring, clear chemical responses to reductions in acid deposition are now detectable across much of the Network (see Chapter 4). Several sites show chemical improvement, as indicated by increases in pH, alkalinity and Acid Neutralising Capacity (ANC) and declines in labile aluminium (Al_{lab}) concentration. Falling acidity is expected to promote the re-establishment of species and communities which have been lost to AWMN sites during acidification, reduce physiological stress on more resistant organisms and bring about changes in trophic structure. This biological recovery represents a major aim of emissions reduction policy.

In this chapter we have adopted similar statistical approaches to those applied in the 10 Year Interpretative Report (Monteith and Evans, 2000) in order to test the null hypothesis that there has been “no overall change” in the biological parameters measured. Biological change may of course occur for reasons other than those directly associated with acid deposition decline, such as changes in climatic conditions. It is important, therefore, that evidence for biological improvement is supported, wherever possible, by evidence for a concomitant improvement in water chemistry.

6.2 AWMN Biological Data

The AWMN monitors several biological parameters, providing a range of perspectives on the biological composition and functioning of these ecosystems. These are summarised in Table 6.1. Wider descriptions and sampling methodologies are available from the AWMN web page www.ukawmn.ucl.ac.uk in the Sites and Methodologies Report.

Biological Group	Annual Measurement	Season
Epilithic diatoms	% abundance of taxa in samples from 3-4 locations (stone scrapes)	summer
Sediment trap diatoms Lakes only	% abundance of taxa in sediment trap sample (trap sub-sample)	summer
Aquatic macrophytes – lakes	0-5 classification of abundance, based on several methods (see below)	summer
Aquatic macrophytes – streams	% cover of species in 10 consecutive 5 m stretches	summer
Macroinvertebrates	Absolute abundance of taxa in samples from 5 littoral locations (kick sampling)	spring
Salmonids (brown trout & Atlantic salmon)	Numbers of fish, and their length and weight, from each age class per unit area of stream (or lake outflow), (electro-fishing)	autumn

Table 6.1 A summary of AWMN biological measurements.

The assessment of aquatic macrophyte populations in lakes is complicated by the spatial heterogeneity within sites. The aquatic macrophyte survey methods for lakes are therefore designed to detect change using a variety of techniques, including:

- 1) Mapping distributions of dominant taxa and precise locations of rare taxa during a shoreline walk;

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

6.3 Data analysis

Analysis of biological data in the following sections was designed to answer the following questions:

- (i) *Is significant change occurring in species composition over time?*
- (ii) *Is the nature of species change consistent with our prior knowledge of the acid sensitivity of taxa?*
- (iii) *Is there a spatial link between sites showing biological change and chemical improvement?*
- (iv) *Is there a direct temporal link between species composition and acidity in chemically recovering sites?*

To answer question (i) we used multivariate and univariate statistical approaches to test for significance of changes with time. For (ii) we referred to existing datasets to determine the indicator value of individual taxa. We compared the occurrence of trends in biota and various acidity parameters to answer question (iii), while (iv) was assessed using multivariate methods and simple graphical comparisons of biological and chemical metrics

6.3.1 Data formats and transformations

Table 6.2 summarises the data formats and transformations used in the following analyses. Data were first screened for erroneous values, and in the case of macroinvertebrates some species were combined at a lower taxonomic level according to approaches outlined in Monteith and Evans (2000).

Duplicate analyses were conducted on two forms of the macroinvertebrate data. The first incorporated all individual animals, including those identified only to family level, e.g., Chironomidae, Simuliidae, etc.. Since individuals from the family level groups sometimes dominate the assemblage numerically, the second data set was based almost solely on organisms classified at least to Genus level (with the exception of the family group Leptophlebiidae, which was also included).

Biological Group	Data format
Epilithic diatoms	Log % frequency of all taxa in each of 3 or 4 samples for each year
Sediment trap diatoms	Log % frequency of all taxa in each annual sample
Aquatic macrophytes – lakes	1-5 measure of relative abundance of each taxon for each year
Aquatic macrophytes – streams	% cover of 50 m survey stretch for each year
Macroinvertebrates	Log % frequency of all taxa in each of 3 or 4 samples for each year
Salmonid fish	Density of each Salmonid age class for a 150 m survey stretch for each year. Fork length of each fish from each year class and sampling year Weight of each fish from each year class and sampling year

Table 6.2 AWMN biological data formats

6.3.2 Analysis of time trends in biological data

Time trend assessments of epilithic diatom, aquatic macrophyte and macroinvertebrate data were based on multivariate methods, while trends in brown trout (*Salmo trutta*) density were assessed by linear regression. Atlantic salmon (*Salmo salar*) occur in two AWMN sites only and were not included in this analysis.

All multi-variate statistical analysis were performed using the programme CANOCO 4.5 (ter Braak, 1998). Epilithic diatom and macroinvertebrate data were first subjected to Detrended Canonical Correspondence Analysis (DCCA), with “sample year” used as a single explanatory variable, in order to determine the time-constrained species gradient lengths. This method provides a measure of species “turnover”, in units of standard deviation; a gradient length of 4.0 or more would imply a complete change in species representation over the monitoring period. The results indicate whether subsequent time-trend analysis should be based on a linear model (where species show monotonic change) or a unimodal model (where species abundances rise and then fall over the duration of monitoring). In all cases, gradients lengths were less than 3.0 and the linear methods of Principal Components Analysis (PCA) and Redundancy Analysis (RDA) (ter Braak, 1994) were therefore selected.

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

Second, the year of sampling was used as the single explanatory variable. Here, the first, and only, constrained axis of RDA ($\lambda_1 RDA_{\text{year}}$) represents the proportion of the total between-sample variance which can be explained by a linear change over time. This was the only application of RDA to the aquatic macrophyte data which has no within-year replicate component. Monte-Carlo permutations (999 permutations) were used to determine the statistical significance of a time trend in the species data. PCA was applied to determine the maximum variance which can be explained by a single constraining variable ($\lambda_1 PCA$). The ratio of $\lambda_1 RDA_{\text{year}}$ to $\lambda_1 PCA$ therefore provides an indication of the strength of linear change (i.e., a time trend) relative to the dominant mode of between-sample variation in the species assemblage, while the ratio of $\lambda_1 RDA_{\text{year}}$ to $\sum RDA_{\text{years}}$ demonstrates the importance of linear temporal change relative to the total variation in composition between years.

Preliminary analysis of the aquatic macrophyte data suggested that multivariate approaches were insensitive to some types of biological change, i.e., the occurrence of small numbers of new species at low abundances. As an alternative approach we identified sites where species have only been recorded in the second half of the monitoring record, (i.e., those detected since 1994 only). Aquatic macrophytes are, by definition, relatively large plants which are easily identified and often form significant stands. It is reasonable to assume, therefore, that “post-1994 only” records will often indicate recent colonization, and/or expansion, and may reflect biological recovery.

Linear regression of brown trout density with time also revealed little evidence of positive unimodal trends in either age group. However, recruitment, i.e., the detection of 0+ fish (or those less than one year old), was observed for the first time at a minority of sites during the monitoring period, and this was taken as evidence of a potentially significant change in population structure.

Epilithic diatoms and macroinvertebrate species which showed the strongest change at individual sites (i.e., over 20% of between-sample variance could be explained by sample year) were considered to be driving species. In this context the key aquatic macrophytes were those recorded at individual sites since 1994 only.

6.3.3 Analysis of temporal links between acidity and biology at individual sites

To determine whether changes in the assemblages of epilithic diatoms and macroinvertebrates could be linked to acidity at an inter-annual scale a range of acidity parameters, pH, alkalinity, ANC (represented by AB-ANC, see Chapter 4), Al_{lab} , DOC and Ca^{2+} concentrations were applied both singly and jointly as explanatory variables in RDA.

Recent work by Hirst *et al.* (2004) suggests that epilithic diatom communities respond rapidly, i.e., on a time scale of days to weeks, to changes in water chemistry. As these communities are sampled in mid-Summer we focussed our analysis on water chemistry measurements made in June for most lakes and July for most streams, to represent conditions immediately prior to sampling. Sampling in Northern Ireland is carried out later in the summer than at other sites and September measurements were therefore deemed most appropriate for the lake (Blue Lough), and August measurements for the three streams, in this region. The extent to which macroinvertebrate communities, sampled between April and May, might “integrate” any chemical signal is less clear but we assumed that responses might be more delayed than for epilithic diatoms, reflecting longer generation times. Therefore, the average of March-June measurements for lakes and March-April-May averages for streams were selected to represent conditions over the whole Spring period.

Chemical data are not available for all the determinands of interest for the entire period covered by the biological datasets. This results from i) chemical monitoring at most sites only commencing in the Autumn of 1988, ii) foot and mouth related site access problems in 2001 and iii) occasional problems revealed by quality control procedures which led to the rejection of samples. The analyses therefore covered fewer years of data ($n = 11 - 14$) than used in the full time-trend analysis. While, “sample-year” was also used as a variable in the biology-chemistry analysis, the results from the two analyses are therefore not directly comparable.

The same analytical procedures used in the time-trend analysis were followed i.e., inter-species correlations, log-transformed data for species and chemistry (with the exception of pH), and centred and standardised sample scores. “Sample year” and the six chemical variables were first applied individually as the single explanatory variable and a significance threshold of $p < 0.05$ was used as the acceptance criteria following a restricted Monte-Carlo permutation test. In this case the size of the first (and only) constrained Eigenvalue represented the maximum variance in the species data which can be explained by each variable, regardless of possible interactive effects. All significant chemical variables were then applied together (joint chemistry) in RDA and the total amount of variance explained was determined from the “sum of all constrained Eigenvalues”.

We adopted the approach of Halvorsen *et al.* (2003) to calculate the amount of variance in the species data which can be attributed to an interaction between each chemical variable and

“time”. This was determined by subtracting the amount of variance explained by “sample year” and each chemical variable when applied together in RDA, from the total variance explained by the two variables when applied separately. A similar method was used to determine the total variance shared between “time” and all the chemical variables deemed significant in the earlier analysis combined. All results were presented as a percentage of the total variance that can be explained by “time”. In effect this represents the maximum amount of the linear trend in the species data which can be explained by changes in chemistry.

Finally, to control for the possibility that significant correlations with chemical variables might reflect lagged responses, or simply result from effects of temporal covariance, RDA was repeated on chemical variables, identified earlier as significant, after “sample year” was first selected in a Forward Selection procedure. This equates to a partial RDA, with “time” held as covariable, in which case the residuals are linearly detrended for time. The occurrence of significant residual relationships increases the likelihood that these variables have an influence on species composition at an inter-annual scale.

Dissolved inorganic carbon (DIC) availability is considered to be a limiting factor for many aquatic macrophytes species in acid-sensitive systems (e.g. Brandrud, 2002; Arts, 2002; Maberly and Madsen, 2002). We therefore plotted presence-absence data for recently recorded aquatic macrophyte species against time-series of alkalinity, to investigate, qualitatively, whether these new occurrences might relate to an alkalinity threshold. Similarly, comparisons were made between brown trout density and ANC for the three sites where the 0+ group were detected for the first time after several years of absence. ANC is frequently applied as the chemical predictor of presence-absence of salmonids in acid-sensitive waters, particularly with respect to modelling studies (e.g. Lien *et al.*, 1996).

6.4 Results

6.4.1 Epilithic diatoms

6.4.1.1 Sites showing change in epilithic diatom species composition over time

The results of the multivariate time-trend analysis are provided in Table 6.3. Time constrained gradient lengths are short, indicating that there has been little “species turnover” at any site. There is no evidence for a relationship between the amount of turnover and the amount of chemical change experienced over the period (based on trend strengths reported in Chapter 4) or the acidity status of the site.

Although turnover is relatively small, significant linear changes in diatom assemblages are apparent at 12 sites ($p < 0.05$). For several sites showing time trends the ratio of the Eigenvalues of the first axes of RDA and PCA is high, suggesting that unimodal change with time is the dominant mode of between-sample variation.

The 12 sites showing trends are largely confined to a geographic region encompassing north Wales, the Lake District, Galloway and the Trossachs, where the largest reductions in sulphur and acidity have been observed. However, they also include the three sites in northern Scotland, where few chemical trends have been detected. Change is often characterised by small proportional increases or decreases in a minority of taxa as can be seen from the time-series plots in Appendix 2.

Site	a	b	c	d	e	f	g	h
	λ_1 PCA	DCCA time- constrained gradient length	Σ RDA _{years} Between- year variance	Within- year variance	λ_1 RDA _{year}	P restricted test	λ_1 RDA _{year} λ_1 PCA	λ_1 RDA Σ RDA _{years}
Allt a' Mharcaidh	17.7	1.18	66.5	33.5	10.9	.016	0.62	0.16
Allt na Coire nan Con	32.0	1.03	76.3	23.7	10.7	.011	0.33	0.14
Lochnagar	19.3	1.12	44.9	55.1	4.2	.210	0.22	0.09
Loch Chon	28.1	1.33	56.3	43.7	18.9	.016	0.67	0.34
Loch Tinker	17.3	1.06	47.5	52.5	6.3	.139	0.36	0.13
Round Loch Glenhead	22.2	0.79	49.7	50.3	9.1	.057	0.41	0.18
Loch Grannoch	36.4	1.67	57.4	42.6	29.3	.018	0.80	0.51
Dargall Lane Burn	32.8	0.89	60.7	39.3	15.2	.047	0.46	0.25
Scoat Tarn	18.2	1.24	47.7	52.3	6.7	.022	0.37	0.14
Burnmoor Tarn	17.5	1.27	57.8	42.2	12.3	.011	0.70	0.21
River Etherow	37.6	1.19	81.5	18.5	6.6	.286	0.18	0.08
Old Lodge	28.2	1.21	60.9	39.1	6.0	.302	0.21	0.10
Narrator Brook	19.4	1.15	54.9	45.1	6.0	.360	0.31	0.11
Llyn Llagi	28.4	1.27	61.1	38.9	24.6	.011	0.87	0.40
Llyn Cwm Mynach	20.6	1.06	44.6	55.4	9.7	.031	0.47	0.22
Afon Hafren	30.2	1.18	66.0	34.0	19.4	.016	0.64	0.29
Afon Gwy	24.5	1.17	60.0	40.0	9.1	.036	0.37	0.15
Beagh's Burn	25.0	1.12	74.6	25.4	8.3	.314	0.33	0.11
Bencrom River	19.5	0.63	55.5	44.5	6.9	.079	0.35	0.12
Blue Lough	25.0	1.01	48.1	51.9	5.7	.224	0.23	0.12
Coneyglen Burn	21.6	1.29	68.3	31.7	7.0	.254	0.32	0.10

Table 6.3 Epilithic diatom multivariate analysis results. Eigenvalues as percentages of total between-sample variance based on inter-species correlations: a) Maximum variance explained by an unknown "latent variable" in Principal Components Analysis; b) Time constrained gradient length according to Detrended Canonical Correspondence Analysis; c) Between-sample variance explained by differences between years d) Between-sample variance explained by differences within years; e) Between-sample variance explained by a linear time trend f) significance of linear time trend based on 999 Monte Carlo permutations (restricted test). Sites shaded grey are those showing statistically linear time trends ($p < 0.05$).

6.4.1.2 Species changes

Table 6.4 lists those species which are increasing or decreasing in relative abundance most strongly and their associated pH optima (derived from the Surface Waters Acidification Project training set, (Stevenson *et al.*, 1991)) at the 12 sites showing time trends. Seven sites (Loch Chon, Loch Grannoch, Dargall Lane, Burnmoor Tarn, Llyn Llagi, Llyn Cwm Mynach and the Afon Gwy) show a shift from species with lower to higher pH optima. The two sites with the clearest linear change both show strong trends in *Tabellaria quadrisepitata*, although while this acid-indicator has declined in Llyn Llagi (with the five year average falling from 18.9 -1.0%) it has increased in Loch Grannoch (1.2 - 58.2%) over the same period. As it has a low pH optimum (pH 4.9) it is difficult to reconcile change at the latter site with recovery and it may be that its recent expansion in Loch Grannoch represents a gradual return to more oligotrophic conditions following disturbance from forestry fertiliser application in the mid-1980s (Flower *et al.*, 1990).

Site	Taxa showing temporal change	mean % per sample		SWAP pH optima mean (1 sd)		difference in mean pH optima between increasing and decreasing groups
		1988-1992	1998-2002	increasing taxa	decreasing taxa	
Loch Coire nan Arr	<i>Achnanthes marginulata</i>	0.15	0.94	5.65	5.63	+0.02
	<i>Achnanthes minutissima</i>	12.45	29.42	(0.55)	(0.59)	
	<i>Achnanthes pusilla</i>	0.00	0.95			
	<i>Cymbella perpusilla</i>	0.27	1.01			
	<i>Eunotia exigua</i>	0.35	2.07			
	<i>Nitzschia gracilis</i>	0.04	0.96			
	<i>Cymbella microcephala</i>	3.51	0.53			
	<i>Frustulia rhomboides</i> var. <i>saxonica</i>	6.35	3.31			
	<i>Tabellaria flocculosa</i>	20.91	8.76			
Allt a' Mharcaidh	<i>Eunotia incisa</i>	0.20	1.40	5.10	6.15	-1.05
	<i>Fragilaria vaucheriae</i>	18.35	10.11		(0.21)	
	<i>Hannaea arcus</i>	8.43	0.00			
Allt an Coire nan Con	<i>Eunotia incisa</i>	2.16	10.97	5.10	5.70	-0.60
	<i>Achnanthes saxonica</i>	58.01	25.41			
Loch Chon	<i>Brachysira brebissonii</i>	2.67	12.36	5.70	5.0	+0.70
	<i>Brachysira vitrea</i>	6.63	24.67	(0.25)	(0.19)	
	<i>Cymbella lunata</i>	0.05	1.33			
	<i>Nitzschia gracilis</i>	0.00	0.66			
	<i>Nitzschia perminuta</i>	0.02	0.30			
	<i>Achnanthes marginulata</i>	10.21	1.62			
	<i>Eunotia denticulata</i>	0.64	0.04			
	<i>Eunotia incisa</i>	7.81	3.22			
	<i>Fragilaria</i> [cf. <i>oldenburgiana</i>]	3.19	0.26			
<i>Navicula leptostriata</i>	20.37	9.46				
Loch Grannoch	<i>Brachysira brebissonii</i>	0.17	2.43	5.20	5.08	+0.12
	<i>Eunotia vanheurckii</i> var. <i>intermedia</i>	0.16	1.11	(0.26)	(0.19)	
	<i>Tabellaria quadrisepata</i>	1.24	58.17			
	<i>Achnanthes altaica</i> var. <i>minor</i>	8.10	0.47			
	<i>Asterionella ralfsii</i>	6.85	0.00			
	<i>Eunotia rhomboidea</i>	5.98	1.14			
	<i>Frustulia rhomboides</i> var. <i>saxonica</i>	11.72	1.54			
	<i>Pinnularia irrorata</i>	1.17	0.10			
	<i>Pinnularia subcapitata</i> var. <i>hilseana</i>	9.06	0.33			
	<i>Peronia fibula</i>	26.19	52.88	5.3	5.05	+0.25
Dargall Lane Burn	<i>Eunotia incisa</i>	16.29	7.23		(0.07)	
	<i>Eunotia naegelii</i>	16.16	4.27			
	<i>Navicula subtilissima</i>	0.15	2.26	5.2	5.2	no change
Scoat Tarn	<i>Eunotia tenella</i>	0.51	0.00			
	<i>Cymbella cesatii</i>	0.38	3.75	6.03	5.70	+0.33
Burnmoor Tarn	<i>Denticula tenuis</i>	0.96	6.20	(1.00)	(0.00)	

Table 6.4 continued overleaf.

	<i>Navicula cumbriensis</i>	0.00	1.56			
	<i>Cymbella lunata</i>	2.28	0.63			
Llyn Llagi	<i>Nitzschia perminuta</i>	3.70	1.41			
	<i>Brachysira vitrea</i>	0.97	6.45	5.70	4.90	+0.80
	<i>Cymbella lunata</i>	0.18	1.69	(0.25)		
	<i>Nitzschia gracilis</i>	0.00	0.82			
	<i>Nitzschia perminuta</i>	0.89	18.60			
	<i>Peronia fibula</i>	0.94	4.28			
Llyn Cwm Mynach	<i>Tabellaria quadrisepata</i>	18.91	1.03			
	<i>Navicula madumensis</i>	0.00	1.24	5.10	4.95	+0.15
	<i>Navicula tenuicephala</i>	1.83	7.53	(0.28)	(0.17)	
	<i>Eunotia [vanheurckii var. 1]</i>	4.27	0.17			
Afon Hafren	<i>Fragilaria [cf. oldenburgiana]</i>	1.42	0.00			
	<i>Eunotia [sp. 13 (minutissima)]</i>	0.00	0.14	5.25	5.25	no change
	<i>Eunotia exigua</i>	63.82	83.46	(0.21)	(0.21)	
	<i>Tabellaria flocculosa</i>	0.08	2.79			
	<i>Achnanthes helvetica var. minor</i>	18.20	1.65			
	<i>Eunotia vanheurckii var. intermedia</i>	9.11	2.59			
Afon Gwy	<i>Navicula mediocris</i>	0.00	0.12	5.40	5.25	+0.15
	<i>Eunotia [vanheurckii var. 1]</i>	1.81	0.19		(0.07)	
	<i>Peronia fibula</i>	1.12	0.23			

Table 6.4 For sites showing time trends only: species with the strongest relationships with RDA Axis 1. i.e., those species for which over 20% of total variance is explained by a linear change with time. pH optima (in parentheses) according to Surface Waters Acidification Project Training Set (Stevenson, 1991) and based on surface sediment assemblages.

Despite this there is a very slight upward shift in the average pH optima of the driving taxa. There are no clear differences in the pH optima of increasing and declining species in Loch Coire nan Arr, Scoat Tarn and the Afon Hafren. Negative trends in average pH optima are apparent only at two stream sites from northern Scotland, Allt a'Mharcaidh and Allt na Coire nan Con, neither of which have been strongly impacted by acidification.

6.4.1.3 Spatial links between sites showing trends in epilithic diatom communities and water acidity

Table 6.5 provides a comparison of the spatial occurrence of significant trends in species composition and significant trends in acidity parameters according to the analysis presented in Chapter 4.

This assessment shows reasonably good agreement between biological and chemical trends and can be summarised as follows:

- Nine of the twelve sites showing trends in epilithic diatom communities have undergone improvements in one or more of pH, alkalinity and Al_{lab} . These are, Loch Chon, Dargall Lane, Burnmoor Tarn, Llyn Llagi and Llyn Cwm Mynach, Afon Gwy, Scoat Tarn, Bencrom River and Loch Grannoch.

site	LINEAR TREND	CHEMICAL TREND SLOPES			
		pH	alkalinity	labile aluminium	ANC
Loch Chon	Δ	0.04	1.27	-1.33	2.7
Dargall Lane	Δ	0.03	0.67	-1.5	1.39
Burnmoor Tarn	Δ		*+		*+
Llyn Llagi	Δ	0.05	1.06	-1.67	1.95
Llyn Cwm Mynach	Δ		-0.08		0.87
Afon Gwy	Δ	0.03			1.48
Scoat Tarn	Δ	0.01		-7.69	1.32
Bencrom River	Δ			-4.04	2.25
Loch Grannoch	Δ			-8.63	2.27
Loch Coire nan Arr	Δ				
Allt a'Mharcaidh	Δ				
Allt nan Coire nan Con	Δ				1.32
Round Loch Glenhead		0.01	0.5	-3.65	1.54
River Etherow				-1	6.21
Old Lodge		0.05	3	-13.85	7.01
Narrator Brook			1		1.19
Blue Lough		0.01	0.81	-11.68	2.85
Lochnagar					
Loch Tinker					
Beagh's Burn					
Coneyglen Burn					

Table 6.5 Occurrence of trends in epilithic diatom assemblages and trends in various measures of acidity. Slopes of chemical trends only provided for statistically significant trends according to Seasonal Kendall Analysis ($p < 0.05$). (Δ = significant trend in assemblage, \uparrow or \downarrow = significant increase/decrease in average annual DI-pH ($p < 0.05$), *+ = positive trends identified in a modified dataset after the removal of outliers – see text)

- Of the remaining three sites to show species trends, Loch Coire nan Arr, Allt a'Mharcaidh and Allt na Coire nan Con, there is no indication of trends in pH, alkalinity or Al_{lab} .
- There is no detectable trend in diatom species at five sites showing trends in either pH, alkalinity or Al_{lab} . These are the Round Loch of Glenhead, the River Etherow, Old Lodge, Narrator Brook and Blue Lough. With the exception of Narrator Brook these sites rank among the most acidic on the AWMN.
- Four sites, Lochnagar, Loch Tinker, Beagh's Burn and Coneyglen Burn show no trends in either diatom species or any measures of acidity.

6.4.1.4 Temporal links between epilithic diatom assemblages and water chemistry

Table 6.6 provides a summary of the results of the RDA relating epilithic diatom relative abundance to summer water chemistry parameters. While the number of years of data included in this analysis is shorter than that used for the trend analysis described earlier, the distribution of sites showing significant species trends is broadly similar. One or more water chemistry variable explained a significant proportion of variance in assemblages at twelve of the sixteen sites to show species trends and at two of the six sites which did not show trends. DOC was the most frequently occurring significant variable overall ($n=9$), while DOC and Ca^{2+} were most

site	Δ_1 RDA - % variance in species composition explained by chemistry						% variance explained by time trend shared with chemistry						% variance explained when time covariable									
	TIME	pH	Alk	Al	Ca	ANC	DOC	allchem	pH	Alk	Al	Ca	ANC	DOC	all_chem	pH	Alk	Al	Ca	ANC	DOC	
1	12.1																					
2	10.6						10.1	10.1						40.6	40.6							5.8
3	9.0	5.9					7.8	11.8	21.1					11.1	16.7							6.8
4	3.8																					
5	16.5	8.5	10.1	8.6		12.8	12.4	24.4	45.5	48.5	44.2		67.9	62.4	64.8							
6	6.9																					
7	9.1	7.4	7.6	6.7	5.6	8.4	8.1	22.6	50.5	52.7	50.5	23.1	74.7	67.0	76.9							
8	29.9			11.9	26.0	9.5	30.5		33.8	70.9	28.1				71.9				4.7			
9	18.2																					
10	6.0						5.4	5.4														
11	10.4																					
12	10.8																					
13	5.4																					
14	15.1		8.1			9.2	11.8		29.1				29.1	31.8								
15	19.5		5.6		15.2	8.0	23.2		-2.1			67.7	21.0	61.5					6.0			3.9
16	8.7				3.8		8.2					1.1		31.0								3.8
17	19.1				10.5	9.0	20.7					28.8	25.7	40.3								
18	9.4			9.2	6.6		21.3				20.2	29.8		71.3								5.8
19	10.7	9.6			12.0	7.5	34.3		-0.9			-5.6	5.6	86.9					9.7		12.6	6.9
20	6.7	8.4	8.8	5.2	6.0		28.3		4.5	6.0	7.5	1.5		28.4				8.1	8.4	4.7	5.9	5.8
21	6.2	7.7					13.1							50.0								
22	6.1																					

Table 6.6 Epilithic diatom - water chemistry relationships based on RDA. With the exception of "TIME" all regressions significant at p<0.05. Significant relationships with "TIME" (p<0.05) in bold. Percentage between-sample variance explained by "sample year" and six water chemistry parameters when applied as single explanatory variables. "all chem" represents the net effect of all individually significant chemistry parameters. Variance shared with time determined according to the approach of Halvorsen et al., (2003).

frequently significant at sites showing species trends. DOC and Ca^{2+} also most frequently explained the highest proportion of variance in the raw data when compared with other chemical variables. pH and alkalinity were significant at six sites each but were rarely the strongest predictor. The combined significant chemical parameters explained between 0-87 % of the total variance associated with the significant time trends, an average of 31 % per site. Of the individual parameters, Ca^{2+} and DOC most frequently explained the highest proportion of linear change.

After temporal detrending of the data, substantially fewer parameters remained significant when applied separately as explanatory variables (Table 6.6: column headed “% variance explained when time covariable”). However, significant relationships were found for eight sites, all of which showed species trends. While a total of sixteen significant regressions were obtained, no more than six would be expected by chance given a p value of 0.05. DOC was most frequently significant ($n = 5$) followed by Ca^{2+} ($n = 4$). pH and/or alkalinity remained significant at two sites each. The majority of the significant relationships in the detrended data were observed for AWMN streams (12 out of 16), possibly reflecting the stronger between-year variation in the sites as opposed to the lakes. Overall, these results are indicative of biological responses both to long term change and to short term variability in chemistry. It is not possible to separate the relative effects of the various chemical parameters given their strong co-variability. However, the repeated observation of relationships with increasing DOC and declining Ca^{2+} concentration, both likely to be part of the chemical recovery process, is striking. Clear links with changing pH and alkalinity, in contrast, are apparent at only a few sites.

6.4.1.5 Epilithic diatom summary

Species composition has changed over the past 15 years at 12 sites. The majority of these sites are in the region which has experienced the strongest chemical improvement over the same period. There is generally good agreement between those sites showing trends in species composition and those showing trends in chemistry. While there is consistency in terms of the direction of change in pH and/or alkalinity and the nature of the biological response according to our understanding of the species-acidity relationships, the dominant response would appear to be related to increasing DOC and declining Ca^{2+} concentration, both of which may be linked to the recent declines in acid deposition (see Chapter 4).

Species changes for the three sites in northern Scotland are indicative of a slight deterioration which may reflect wetter, and hence more acidic, summer conditions.

The main exceptions to the overall evidence for biological sensitivity to changing chemistry are:

- a) the most acidic sites, Round Loch of Glenhead, Old Lodge and Blue Lough, which show declines in summer acidity but no significant diatom response;
- b) Scoat Tarn, where the trend in the diatom assemblage is indicative of a decline in pH whereas pH has increased; and,
- c) Llyn Cwm Mynach, where a decline in summer acidity cannot be linked statistically to the trend in the diatom assemblage although this is indicative of a response to an increase in pH.

The discrepancies for Scoat Tarn and the other more acidic lakes and streams might reflect their relatively elevated aluminium concentrations which may be limiting the availability of phosphorus. If this is the case we may expect to see a threshold response to improving water chemistry as aluminium concentrations continue to fall. At Llyn Cym Mynach there is clear physical separation between the epilithic diatom sampling points and the outflow where water chemistry is sampled. Water chemistry data for this site may, therefore, not provide a reliable indication of the environment in which the diatoms are growing.

6.4.2 Macroinvertebrates

6.4.2.1 Sites showing change in macroinvertebrate species composition over time

Routine multivariate analyses were conducted on two macroinvertebrate datasets as described in Section 6.3.1. The results were very similar for the two datasets and only those for the full assemblage are presented in Table 6.7. In common with results from the epilithic diatom analysis, time constrained gradient lengths were short, suggesting that there has been little species turnover. Again, there was no relationship between the amount of turnover and the amount of chemical change at a site or its acidity status.

Site	a	b	c	d	e	f	g	h
	λ_1 PCA	DCCA time- constrained gradient length	Σ RDA _{years} Between- year variance	Within- year variance	λ_1 RDA _{year}	P restricted test	λ_1 RDA _{year} λ_1 PCA	λ_1 RDA Σ RDA _{years}
Loch Coire nan arr	32.2	1.53	63.0	37.0	18.1	0.052	0.56	0.29
Allt a' Mharcaidh	31.2	0.60	56.7	43.3	4.9	0.182	0.16	0.09
Allt an Coire nan Con	23.4	1.09	50.0	50.0	9.7	0.006	0.41	0.19
Lochnagar	25.7	1.21	51.3	48.7	6.5	0.416	0.25	0.13
Loch Chon	17.6	1.61	59.0	41.0	10.0	0.040	0.57	0.17
Loch Tinker	20.1	1.20	41.7	58.3	8.2	0.138	0.41	0.20
Round Loch Glenhead	24.3	0.87	35.0	65.0	2.9	0.434	0.12	0.08
Loch Grannoch	22.9	1.59	54.3	45.7	11.3	0.024	0.49	0.21
Dargall Lane Burn	27.6	0.89	54.2	45.8	9.2	0.198	0.33	0.17
Scoat Tarn	23.6	1.40	26.4	73.6	8.2	0.018	0.35	0.31
Burnmoor Tarn	23.2	1.62	52.5	47.5	14.2	0.014	0.61	0.27
River Etherow	28.7	0.99	73.6	26.4	10.7	0.020	0.37	0.15
Old Lodge	32.7	0.83	66.6	33.4	10.6	0.020	0.32	0.16
Narrator Brook	21.2	0.85	50.5	49.5	6.0	0.114	0.28	0.12
Llyn Llagi	25.9	1.27	58.3	41.7	14.6	0.038	0.56	0.25
Llyn Cwm Mynach	22.5	1.42	49.4	50.6	14.1	0.004	0.63	0.29
Afon Hafren	29.6	0.73	53.2	46.8	3.8	0.530	0.13	0.07
Afon Gwy	24.8	0.87	48.2	51.8	5.3	0.016	0.21	0.11
Beagh's Burn	32.6	0.86	72.5	27.5	9.6	0.224	0.29	0.13
Bencrom River	18.4	0.77	42.3	57.7	6.6	0.012	0.36	0.16
Blue Lough	34.7	1.58	58.7	41.3	22.0	0.018	0.63	0.37
Coneyglen Burn	26.3	0.10	57.5	42.5	9.8	0.172	0.37	0.17

Table 6.7 Macroinvertebrate multivariate analysis results. Eigenvalues as percentages of total between-sample variance based on inter-species correlations: a) Maximum variance explained by an unknown "latent variable" in Principal Components Analysis; b) Time constrained gradient length according to Detrended Canonical Correspondence Analysis; c) Between-sample variance explained by differences between years d) Between-sample variance explained by differences within years; e) Between-sample variance explained by a linear time trend f) significance of linear time trend based on 999 Monte Carlo permutations (restricted test). Sites shaded grey are those identified as showing statistically linear time trends ($p < 0.05$).

Monte Carlo permutation tests revealed statistically significant trends ($p < 0.05$) at 12 sites. At several lakes λ_1 RDA: λ_1 PCA was over 0.5 indicating strong temporal change relative to overall between sample variance. For streams this ratio was almost invariably smaller. Generally, the proportion of total variance distributed between and within years is similar for lakes and streams, but for lakes more of the between-year variance tends to be associated with a long term trend. This suggests that, for sites with significant trends, the lake fauna are undergoing smoother transitions with time, perhaps as a result of the more stable physical and chemical lentic environment.

The geographical distribution of sites showing trends is similar to that for epilithic diatoms, with the majority of trends observed in the region where trends in acidity are occurring.

Site	Increasing Taxa	Declining Taxa
Allt an Coire nan Con	<i>Heptagenia lateralis</i> (M) <i>Siphonoperla torrentium</i> (S) <i>Oreodytes sanmarkii</i> (B)	<i>Brachyptera risi</i> (S) <i>Protonemura</i> sp. (S) (<i>Isoperla grammatica</i> (S))
Loch Chon	<i>Leuctra nigra</i> (S) <i>Enallagma cyathigerum</i> (D) <i>Oulimnius tuberculatus</i> (B) <i>Cyrnus</i> sp. (C)	<i>Ischnura elegans</i> (D) <i>Hesperocorixa sahlbergi</i> (CX) (<i>Callicorixa praeusta</i> (CX))
Loch Grannoch	<i>Cyrnus</i> sp. (C) Chironomidae Empididae	<i>Oulimnius tuberculatus</i> (B)
Scoat Tarn	<i>Polycentropus</i> sp. (C) <i>Cyrnus</i> sp. (C) Limnephilidae (C) <i>Halesus</i> sp. (C)	
Burnmoor Tarn	Leptophlebiidae (M) <i>Caenis horaria</i> (M) <i>Caenis luctuosa</i> (M)	Oligochaeta
River Etherow	<i>Brachyptera risi</i> (S) <i>Elmis aenea</i> (B)	
Old Lodge		Simuliidae
Llyn Llgi	<i>Oulimnius tuberculatus</i> (B) <i>Mystacides</i> sp. (C)	<i>Nemoura</i> spp. (S)
Llyn Cwm Mynach	<i>Pisidium</i> sp. (M) Chironomidae (<i>Sigara scotti</i> (CX))	Leptophlebiidae (M) <i>Polycentropus</i> sp. (C) (<i>Anabolia nervosa</i>) (C)
Afon Gwy	<i>Isoperla grammatica</i> (S)	
Bencrom River	<i>Siphonoperla torrentium</i> (S)	
Blue Lough	Leptophlebiidae (M) <i>Polycentropus</i> sp. (C) (<i>Glaenocorisa propinqua</i> (CX))	Oligochaeta Chironomidae (<i>Potamonectes griseostriatus</i>) (B))

Table 6.8 For sites showing time trends only: macroinvertebrate species with the strongest relationships with RDA Axis 1, i.e those species for which over 20% of total variance is explained by a linear change with time. Species in parentheses only significant when family level groups (e.g. Chironomidae) are excluded from the dataset prior to analysis. (B = Beetle, C = Caddisfly, CX = Corixid, D = Damselfly, M = Mayfly, S = Stonefly).

6.4.2.2 Species changes

Those species showing the strongest linear changes at sites with significant trends in the whole assemblage are listed in Table 6.8. These can be considered to be driving the trends in the assemblages. All species at Genus level and below which are changing proportionally in the full dataset also show significant change when family level data are excluded from the analysis. A few additional species (identified by parentheses) show trends in relative proportion in the latter analysis. The following discussion is based on the analysis of the full dataset only.

Several more taxa show strong increases in relative abundance than show decreases. This may seem counter-intuitive for these “closed” data sets, but it would appear that the species which are increasing in relative abundance were rare or even absent at the beginning of the record. In many cases their expansion does not appear to have led to the competitive displacement of other species, but, rather, has had a random influence on the relative abundance of the more persistent species and often abundant species.

There are some common characteristics in these faunal changes:

- Caddisfly species are increasing in proportional abundance at five of the lakes to show community change, Loch Chon, Loch Grannoch, Scoat Tarn, Llyn Llagi and Blue Lough.
- Predatory, net-spinning Caddis (either *Cyrtus* sp., or *Polycentropus* sp.) are increasing proportionally at Loch Chon, Loch Grannoch, Scoat Tarn and Blue Lough. The Caddis species increasing in Llyn Llagi (*Mystacides* sp.) is a detrital feeder.
- The abundance of other predatory species has also increased including the Stoneflies, *Siphonoperla torrentium* in the streams Allt nan Coire nan Con and Bencrom River, and *Isoperla grammatica* in the Afon Gwy; and, the Damselfly *Enallagma cyathigerum* in Loch Chon.

In total therefore, the representation of one or more predatory species has increased in seven out of the twelve sites to show time trends. In Burnmoor Tarn, the River Etherow, Llyn Llagi and Llyn Cwm Mynach, the increasing taxa are largely collector gatherers which feed principally on organic detritus. Of the species to show declines in relative abundance, the majority are detritivorous, with the main exception of Loch Chon where there has been a reduction in the abundance of the predatory Damselfly *Ischnura elegans* and the Corixid Water Boatman *Hesperocorixa sahlbergi*. A decline in Caddis abundance is only apparent at one site, Llyn Cwm Mynach. Our interpretation of the significance of these species changes for biological recovery is restricted by our limited understanding of macroinvertebrate species-acidity relationships over the relatively small acidity gradients represented by AWMN sites. There is a clear need for a high quality macroinvertebrate spatial dataset for acid-sensitive lakes to allow a more detailed interpretation of the changes we are observing.

The reference data available for streams is much better developed. A species-chemistry dataset was compiled for acidic streams as part of the DEFRA funded CLAM project (Critical Loads for Acidity and Metals). Species-ANC relationships have been modelled using generalised linear models and reported by Juggins (2001). He showed significant ($p < 0.01$) positive relationships between ANC and abundance of the Beetles *Oreodytes sanmarkii*, *Elmis aenea*, the Mayfly *Heptagenia lateralis* and the Stoneflies *Brachyptera risi* and *Isoperla grammatica*, with particularly strong slopes to the relationships around zero ANC. These species dominate the macroinvertebrate trends identified at Allt na Coire nan Con, the River Etherow and the Afon Gwy and the increase in their relative abundance can therefore be directly linked to chemical improvement. The only stream site where a significant trend cannot be attributed to chemical improvement in

this way is Bencrom River. The most strongly increasing species here, the Stonefly *Siphonoperla torrentium*, is distributed across a relatively wide acidity gradient.

6.4.2.3 Community-level changes

Principal component of assemblage variation

In section 6.4.2.1 it was shown that for many sites showing linear trends, and particularly lakes, the ratio of variance in the assemblage which can be explained by time was high relative to that explained by the first axis of Principal Components Analysis (PCA1). In most cases the variable “sample year” is strongly correlated with this component and the list of species which show strong relationships with the first axes of RDA and PCA are very similar. PCA Axis 1 sample scores therefore provide a convenient metric for the component of the species assemblage which is changing most strongly with time and by assessing as time series may provide clues as to the drivers of biological change.

Figure 6.1 reveals similarities in the pattern of change in mean PCA1 scores for the majority of sites which show linear change in their macroinvertebrate assemblages and this is particularly apparent for the subset of lakes presented in Figure 6.2. This regional coherence was previously described by Monteith and Evans (2000) after the first 10 years of monitoring, and, while there was no indication at the time of changes in water chemistry, was tentatively linked to variation in the North Atlantic Oscillation (NAO). Many sites exhibited a relatively rapid transition in their assemblage composition between 1994 and 1996 and the step change coincided with a switch in the January NAO Index from positive to negative values. Since this time, however, the January NAO Index has become progressively more positive, but has not been accompanied by a reversal in species composition. Comparisons of Figure 6.2 with the standardised water chemistry plots presented in Chapter 4 now reveal some similarities with the regional change in non-marine sulphate concentration (a surrogate for the amount of acid deposition – see Chapter 3). The period 1994-1996 represents a period of transition from higher to lower deposition and this is also reflected in the standardised ANC plots (Figure 4.1a). The regional pattern of change in invertebrate communities (although representing a variety of species responses at different sites) may therefore be linked to the regional pattern of changes in water chemistry in these sites. Further monitoring is, however, necessary to verify that these ecological shifts are indeed permanent rather than part of some longer term cyclicity.

Species richness

Acidity exerts a negative impact on aquatic biodiversity at many trophic levels in acid-sensitive systems (Petchey *et al.*, 2004), and this has previously been exemplified with AWMN data (Monteith and Evans, 2000). Time series of several biodiversity parameters have been examined with respect to AWMN macroinvertebrate data, including Hill's N1 (an estimate of the number of abundant species), Hill's N2 (an estimate of very abundant species) and Hill's E5 (the N1:N2 ratio – an “evenness” index). These show little evidence of linear change at most sites. Here we have used rarefaction approaches where species richness is estimated according to the shape of the curve which relates the cumulative number of taxa encountered to increasing sample size. Time series for several species richness estimates were generated using WS2M software (Turner *et al.*, 2003) for all sites. Temporal variation for specific sites in most of these is tightly inter-correlated and closely related to the total number of species observed (TNS). Most approaches provide occasional extreme results, particularly when the sample size is small, and we have therefore selected only one of the most consistently reliable, the Burnham Overton Index (or BO) (Burnham and Overton, 1978), as the representative estimate of actual species richness.

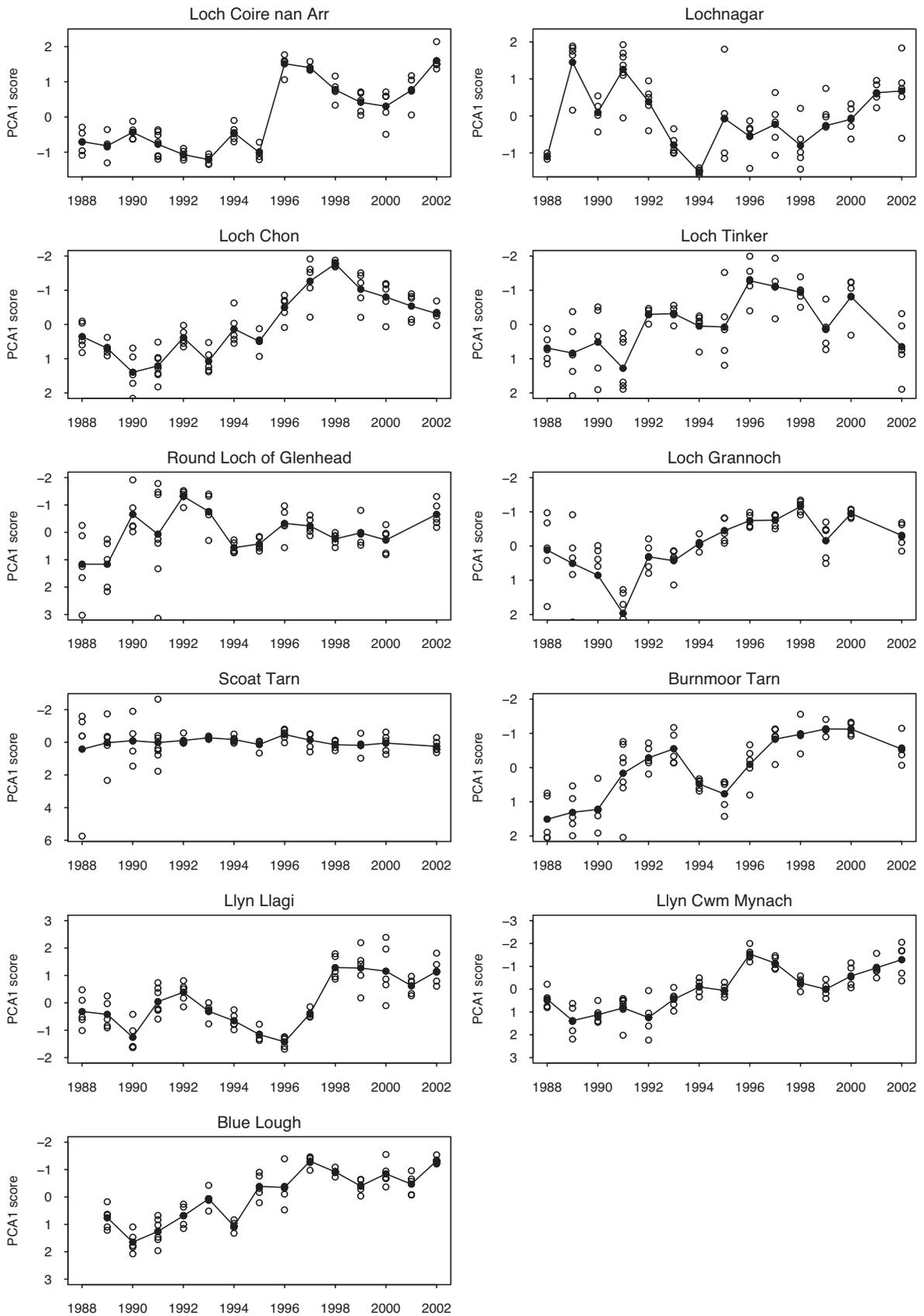


Figure 6.1a Time series of PCA Axis 1 sample scores for AWMN lake macroinvertebrate data (family level groups omitted). Filled circles linked by line represent annual means.

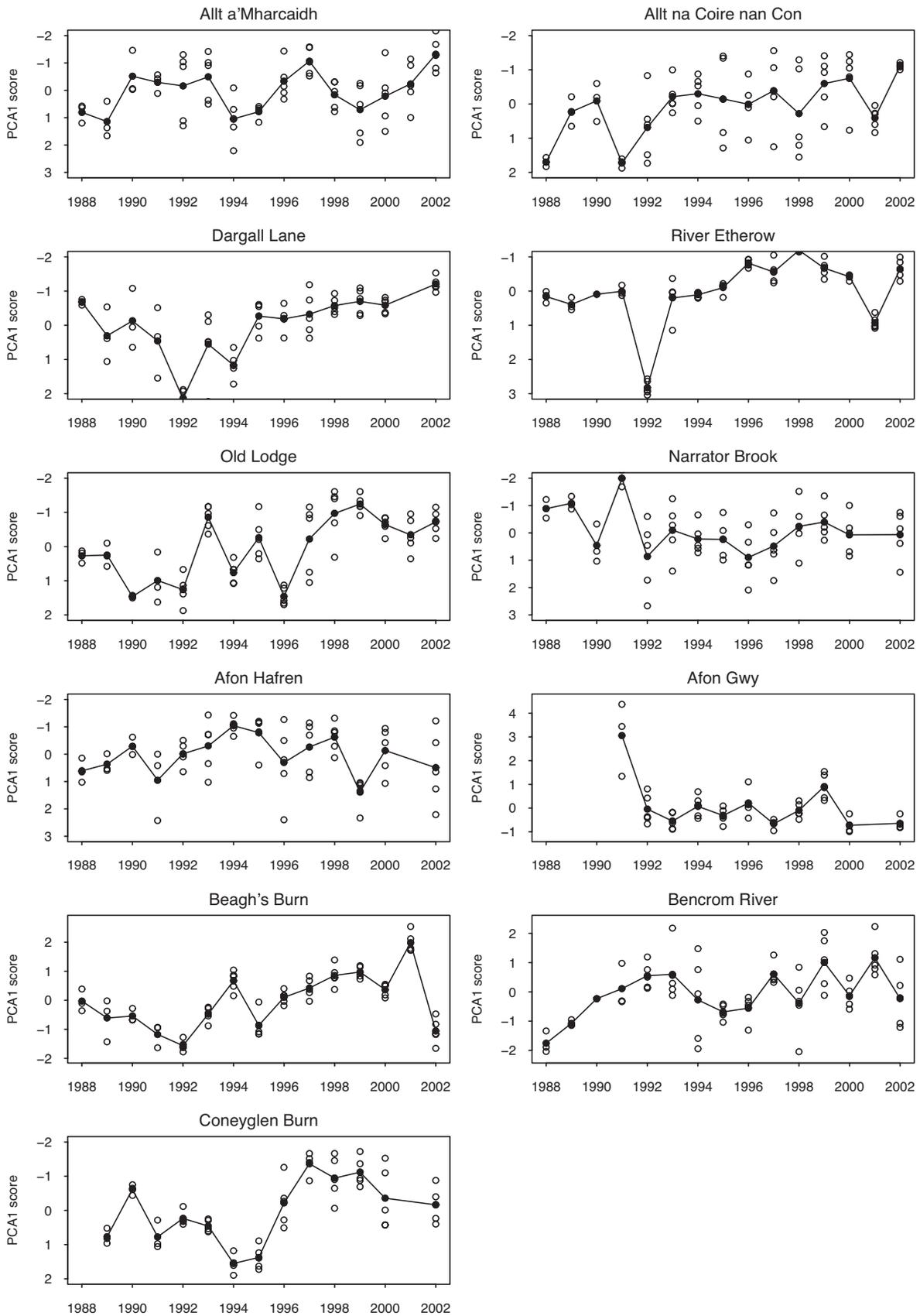


Figure 6.1b Time series of PCA Axis 1 sample scores for AWMN stream macroinvertebrate data (family level groups omitted). Filled circles linked by line represent annual means.

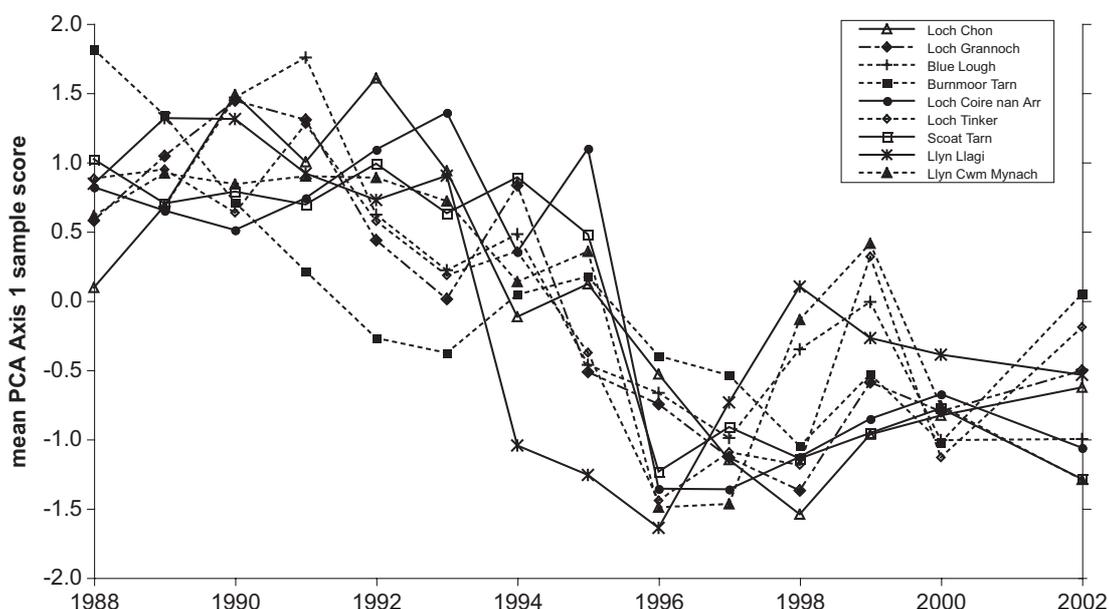


Figure 6.2 Composite plot of trends in mean PCA axis 1 macroinvertebrate sample scores for nine selected AWMN sites.

Figure 6.3 provides time series of TNS, BO and the average number of taxa recorded in individual samples each year. The former two provide little indication of linear change at most lakes (except for declines in Loch Grannoch and Llyn Cwm Mynach), but clear evidence of change at many stream sites. For some streams the increase in the number of species detected is particularly striking. For instance, numbers in the River Etherow have approximately doubled over the past 15 years.

In the 10 year report it was noted that changes in TNS at most stream sites were strongly correlated and this still applies with five additional years of data. There is no indication that these trends might result from changes in sampling or analytical procedures which have been minimal over the full duration of monitoring. When TNS or BO time series for all stream sites are assessed using Principal Components Analysis, the resulting site scores for the first two axes effectively represent a geographical map of the UK, the first component representing longitude and the second latitude. Between-year variation in species richness is therefore most strongly correlated between sites which are closest geographically. However, there is no obvious relationship between the degree of similarity of trends in species richness and trends in acidity.

The geographic nature of the correlations in species richness data is indicative of a climatic control, and, given the dominant east-west gradient, could reflect changing stream flow patterns over time. There is, indeed, evidence for an overall decline in the amount of precipitation during Spring at many sites as TNS and BO have increased. Importantly, neither TNS or BO is significant when applied as the single explanatory variable to the species assemblage data in RDA. These results are therefore consistent with a hydrological control on the population size which does not discriminate strongly between species.

6.4.2.4 Spatial links between sites showing trends in macroinvertebrate communities and water acidity

The analysis presented so far demonstrates that the structure of macroinvertebrate communities

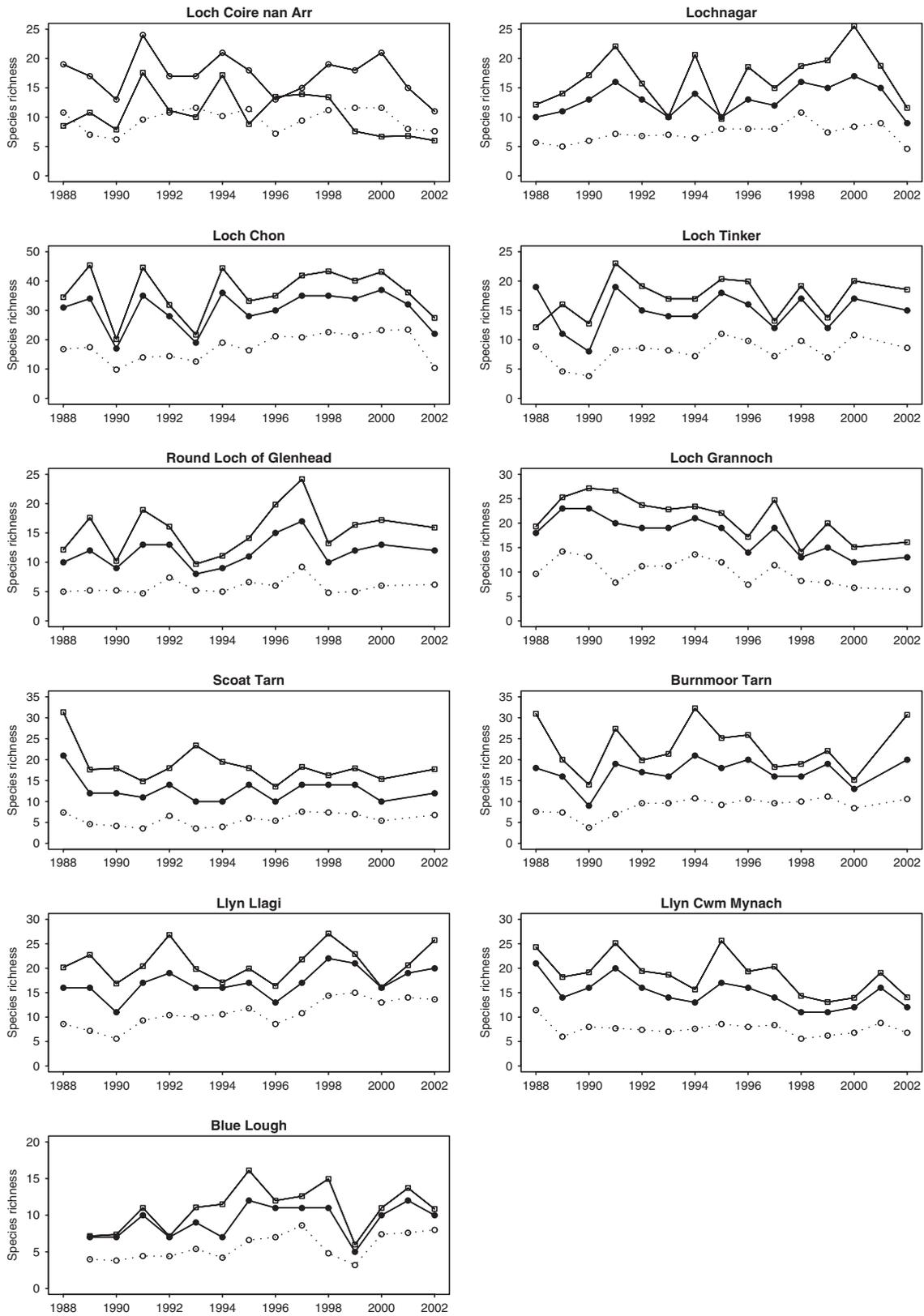


Figure 6.3a Time series of estimates of species richness for AWMN lake macroinvertebrate samples. Data represent the total number of species recorded (TNS) (filled circles), the Burnham Overton Index (BO) (open squares) and the average number of taxa per sample (open circles).

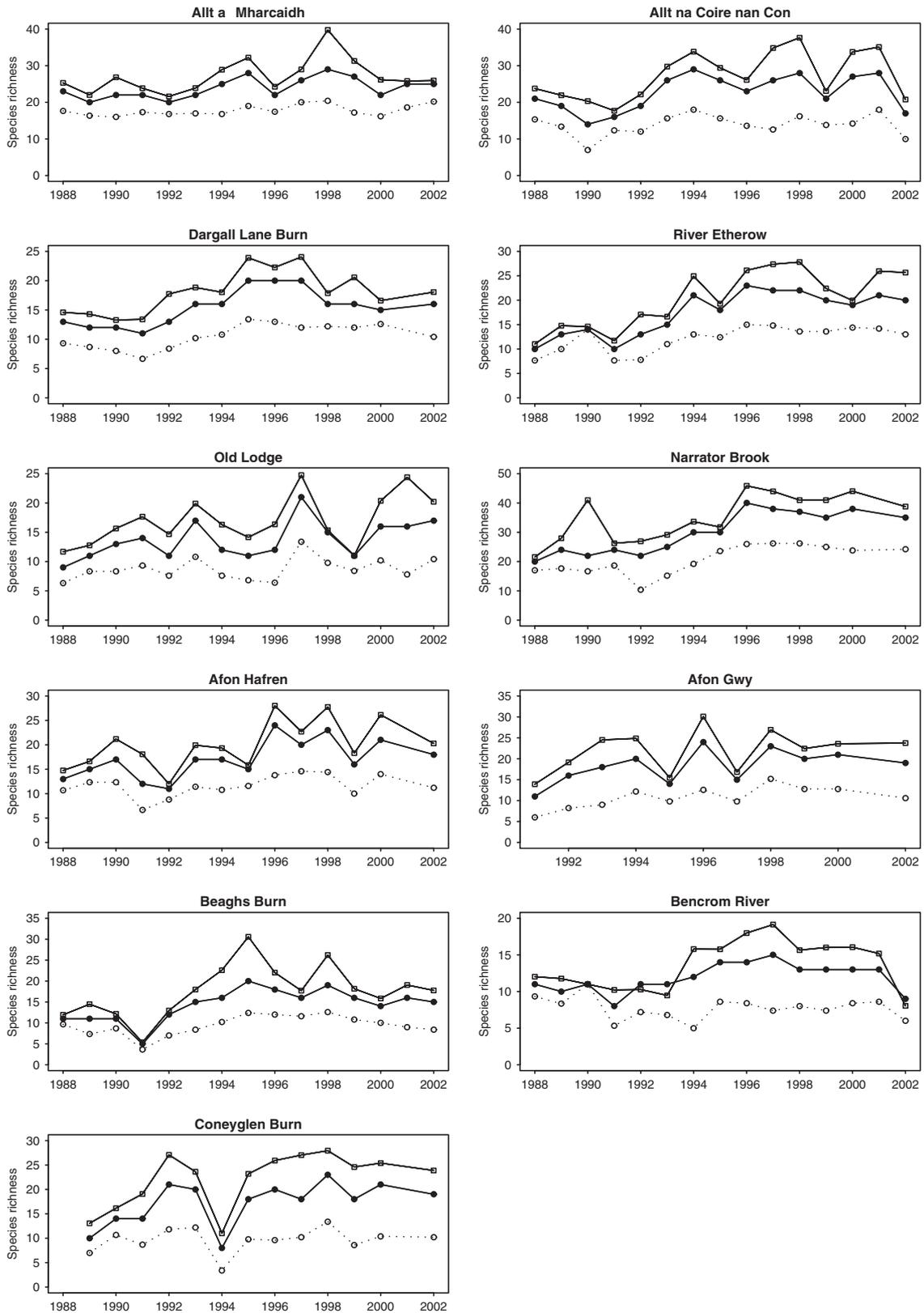


Figure 6.3b Time series of estimates of species richness for AWMN stream macroinvertebrate samples. Data represent the total number of species recorded (TNS) (filled circles), the Burnham Overton Index (BO) (open squares) and the average number of taxa per sample (open circles).

has changed over the past 15 years at more than half of AWMN sites, and, with the exception of changes observed in species richness, is broadly indicative of a response to chemical improvement. Here we consider the relationship between macroinvertebrate species change and chemical change between sites.

The relationship between those sites showing trends in macroinvertebrate assemblages and trends in various measures of acidity is presented in Table 6.9. Chemical trends for Burnmoor Tarn have been re-assessed following the removal of four particularly acidic outliers which represent extreme events when its outflow is contaminated by the overspilling Hardrigg Beck after periods of exceptionally heavy rain. Contamination tends to be largely confined to an area close to the outflow and chemistry samples at these times are therefore not applicable to the performance of the biota in the bulk of the lake.

Table 6.9 reveals a striking spatial relationship between sites showing biological trends and chemical trends which can be summarised as follows:

- Three sites, Loch Chon, Llyn Llagi and Blue Lough show trends in assemblage composition and improvements in all four measures of acidity, ANC, pH, alkalinity and Al_{lab} concentration.
- Nine further sites, Allt na Coire nan Con, Loch Grannoch, Scoat Tarn, Burnmoor Tarn, the River Etherow, Old Lodge, Llyn Cym Mynach, the Afon Gwy, Bencrom River show trends in assemblage composition and improvements in ANC and (with the exception of Allt nan Coire nan Con) one or more of pH, alkalinity or Al_{lab} concentration.
- The macroinvertebrate assemblage has not changed at two sites where ANC has changed – Round Loch of Glenhead and Dargall Lane.
- The macroinvertebrate assemblage has not changed at any of the eight sites where ANC has not changed.

6.4.2.5 *Temporal links between macroinvertebrate assemblages and water chemistry*

The above results demonstrate a clear spatial link between those sites showing chemical improvement, particularly increases in ANC, and those showing changes in their macroinvertebrate fauna. In this section we examine evidence for temporal links between macroinvertebrate assemblages and water chemistry within sites. This is summarized in Table 6.10.

One or more chemical variable was found to be significant in ten of thirteen sites to show species trends. Acid neutralising capacity was the most frequently significant variable in the analysis of the raw data ($n = 9$). The combined significant chemical parameters explained between 0-85 % of the total variance associated with the significant time trends, amounting to an average of 36% per site.

Acid neutralising capacity was also the most frequently significant chemical variable at sites showing linear trends, while ANC and DOC most frequently showed the strongest relationships. Following temporal detrending, eight sites still showed significant relationships with chemical variables. pH, alkalinity, Al_{lab} , Ca^{2+} and ANC were all significant at between three and four sites. In contrast, DOC was not significant at any site. Although a similar number of significant relationships was found, these are more clustered than for the epilithic diatom data; of the seventeen significant relationships in the detrended data, eleven are for just three lake sites (Loch

site	LINEAR TREND	CHEMICAL TREND SLOPES			
		ANC $\mu\text{eq l}^{-1} \text{ yr}^{-1}$	pH yr^{-1}	alk $\mu\text{eq l}^{-1} \text{ yr}^{-1}$	labile Al $\mu\text{g l}^{-1} \text{ yr}^{-1}$
Loch Chon	Δ	2.7	0.04	1.27	-1.33
Llyn Llagi	Δ	1.95	0.05	1.06	-1.67
Blue Lough	Δ	2.85	0.01	0.81	-11.68
Burnmoor Tarn	Δ	*+		*+	
Afon Gwy	Δ	1.48	0.03		
River Etherow	Δ	6.21			-1.00
Old Lodge	Δ	7.01	0.05	3.00	-13.85
Loch Grannoch	Δ	2.27			-8.63
Scoat Tarn	Δ	1.32	0.01		-7.69
Llyn Cwm Mynach	Δ	0.87		-0.08	
Bencrom River	Δ	2.25			-4.04
Allt na Coire nan Con	Δ	1.32			
Dargall Lane		1.39	0.03	0.67	-1.50
Round Loch Glenhead		1.54	0.01	0.50	-3.65
Narrator Brook					
Allt a'Mharcaidh					
Coire nan Arr					
Lochnagar					
Loch Tinker					
Afon Hafren					
Beagh's Burn					
Coneyglen Burn					

Table 6.9 Occurrence of trends in macroinvertebrate assemblages and trends in acidity related parameters. Slopes of chemical trends provided for statistically significant trends only according to Seasonal Kendall Analysis ($p < 0.05$). (alk = alkalinity, labile Al = labile aluminium, Δ = significant trend in assemblage according to RDA ($p < 0.05$), *+ = positive trends identified in a modified dataset after the removal of outliers – see text)

Chon, Burnmoor Tarn and Blue Lough). Only five of the significant relationships were obtained for stream sites. In summary, relationships between chemical variables and the macroinvertebrate species data were widespread. Although not confined to temporal change, there is less evidence for the inter-annual sensitivity to chemistry apparent from the epilithic diatom analysis, although this appears marked for a minority of lakes. It is again impossible to separate chemical “effects” but ANC repeatedly appeared to be a particularly powerful explanatory variable.

6.4.2.6 Macroinvertebrates - summary

Trends in the relative abundance of macroinvertebrate species have been observed at 12 AWMN sites. There is very good agreement between sites showing macroinvertebrate trends and those showing trends in acidity, and particularly ANC, and ANC is repeatedly found to be the best predictor of between year variability at individual sites. Physiological reasons for the strength of this relationship are currently unclear but may primarily reflect aluminium and/or hydrogen ion toxicity. Indeed Al_{lab} is often almost as strong a predictor as ANC. Observations of apparent recovery responses in a number of streams are particularly encouraging given concerns that “acid-episodes” in flowing waters might retard biological improvement (Lepori *et al.*, 2003). However, over the past 15 years there has been a clear decline in the severity of acidity maxima (Chapter 4) and this must be biologically advantageous.

site	A ₁ RDA % variance in species composition explained by chemistry						% variance explained by time trend shared with chemistry						% variance explained when time covariable									
	TIME	pH	Alk	Al	Ca	ANC	DOC	allchem	pH	Alk	Al	Ca	ANC	DOC	allchem	pH	Alk	Al	Ca	ANC	DOC	
1	16.9																					
2	5.0	6.3					6.3									6.9						
3	10.7		5.9	6.1	6.3		14.0		26.2		22.4	29.0			55.1							
4	7.5																					
5	16.3	9.9	7.4	9.1	7.7	9.8	12.6	38.9	30.7	18.4	31.9	0.6	35.6	62.6	81.0	4.9	4.4		5.8			
6	13.9		3.7				5.1	9.1	8.6					12.2	27.3							
7	2.8																					
8	16.1			4.3	10.5	10.1		22.6			9.9	37.3	10.6		44.1					8.4		
9	11.0				6.4	9.0		16.4			-0.9	55.5			71.8				6.4			
10	12.8			9.8	11.5	8.5		16.0			65.6	83.6	43.0		74.2							
11	11.7	9.3	6.2	8.6	11.0		7.5	27.8	18.8	1.7	17.1	38.5		37.6	76.1	7.1	5.9	6.5	6.5			
12	25.1						19.0	19.0						58.2								
13	9.7																					
14	8.1		8.5			7.9		13.5	12.3			19.8		48.1					7.5			6.2
15	13.6	10.4						10.4	56.6					56.6								
16	9.7		7.5			7.5		9.5	44.3			37.1		44.3								
17	4.5																					
18	5.9																					
19	4.5																					
20	6.1			6.7		4.3		8.3			70.5		52.5	68.9					2.4			
21	20.6	11.1	12.6	13.1	12.7	10.6	10.0	44.9	20.4	30.6	37.9	34.0	24.8	36.4	85.4	6.9	6.3	5.4	5.4			5.5
22	13.1																					

Table 6.10 Macroinvertebrate - water chemistry relationships based on RDA. With the exception of "TIME" all regressions significant at $p < 0.05$. Percentage between-sample variance explained by "sample year" and six water chemistry parameters when applied as single explanatory variables. "all chem" represents the net effect of all individually significant chemistry parameters Variance shared with time determined according to the approach of Halvorsen et al., (2003). Alk = alkalinity (Gran or dual endpoint); Al = soluble labile aluminium; ANC = Acid Neutralising Capacity (method according to Evans, 2000); DOC = dissolved organic carbon.

Significantly, trends in the entire assemblage are often driven by an expansion of predatory taxa. Woodward and Hildrew (2001) similarly linked the invasion of Golden Ringed Dragonfly (*Cordulegaster boltonii*), in a stream neighbouring Old Lodge, to recovery from acidification. They proposed that an increase in the representation of predators may reflect a general expansion of the food web of these systems as they recover chemically and the diversity of potential prey species increases. In AWMN lakes, an increase in the representation of net-spinning Caddis species might relate to an increased availability of prey. The high proportion of Caddis species in the list of those showing positive trends might also relate to the strong dispersive ability of this winged group of insects. Studies using stable isotopes and molecular genetic techniques are suggesting that inter-catchment dispersal is much more prominent than previously appreciated (e.g. Wilcock *et al.*, 2001).

6.4.3 Aquatic macrophytes:

6.4.3.1 Sites showing change in aquatic macrophytes species composition over time

The results of multivariate analysis are provided in Table 6.11. Without exception time constrained gradient lengths are very short and “species turnover” has therefore been at most very slight. Analysis was not conducted on the dataset for Loch Coire nan Arr as the recent inundation of the shoreline following the installation of a dam has severely affected the littoral communities.

Site	λ_1 RDA year	p restricted test	$\frac{\lambda_1 \text{ RDA}}{\lambda_1 \text{ PCA}}$	$\frac{\lambda_1 \text{ RDA}}{\lambda_2 \text{ RDA}}$
Loch Coire nan Arr	data not analysed due to effects of damming			
Allt a' Mharcaidh	33.9	0.060	0.78	0.80
Allt na Coire nan Con	35.4	0.052	0.61	1.05
Lochnagar	22.8	0.166	0.49	0.50
Loch Chon	23.4	0.142	0.72	0.76
Loch Tinker	19.5	0.330	0.45	0.57
Round Loch Glenhead	6.7	0.476	0.13	0.08
Loch Grannoch	21.2	0.426	0.53	0.55
Dargall Lane Burn	27.3	0.095	0.46	0.71
Scoat Tarn	23.9	0.290	0.61	0.79
Burnmoor Tarn	19.7	0.174	0.48	0.63
River Etherow	35.6	0.076	0.40	0.64
Old Lodge	41.2	0.034	0.44	0.76
Narrator Brook	8.4	0.936	0.16	0.16
Llyn Llagi	28.1	0.102	0.84	1.16
Llyn Cwm Mynach	49.8	0.060	0.93	2.41
Afon Hafren	2.4	0.666	0.03	0.03
Afon Gwy	11.9	0.168	0.13	0.15
Beagh's Burn	20.6	0.492	0.29	0.29
Bencrom River	23.3	0.140	0.33	0.38
Blue Lough	4.7	0.806	0.08	0.05
Coneyglen Burn	9.2	0.350	0.11	0.12

Table 6.11 Aquatic macrophyte multivariate analysis results. Eigenvalues for Redundancy Analysis λ_1 RDA represent percentage of year variance in species data explained by a linear trend. P value = significance of linear time trend based on 999 Monte Carlo permutations.

6.4.3.2 Species changes

Time trend assessment

Time trend analysis of the aquatic macrophyte data provides little evidence of linear change in species abundance and change is only significant at the $p < 0.05$ level at one site, Old Lodge. However, the relationship with time is significant at the $P < 0.10$ level at six sites. These trends will occur by chance at a frequency of less than one analysis in ten and it is therefore likely that some of these represent real change with time. Given their relative ubiquity and the absence of evidence for clearer change, each is considered in further detail below:

At the **Allt a'Mharcaidh**, the weak trend is driven by an increase in the cover of the acid tolerant liverwort *Scapania undulata* and the moss *Fontinalis antipyretica*. These species have also increased proportionally relative to the acid sensitive moss, *Hygrohypnum ochraceum*, although the latter still forms a significant proportion of absolute cover. The major changes occurred after 1997 when overall bryophyte cover was substantially reduced following a major spate in the early summer. *S. undulata* appears to have responded most rapidly to the exposure of the rocky substrate following this event. More recently, new *H. ochraceum* plants have established within the stands of *S. undulata*, possibly benefiting from the physical protection these offer against effects of turbulence. These results are, therefore, consistent with a successional change following a major physical perturbation. Barring another event of similar magnitude it would seem likely that *H. ochraceum* will gradually regain dominance at the expense of *S. undulata*.

The trend detected at **Allt na Coire nan Con** reflects a substantial reduction in overall cover over the monitoring period. The most obvious effect has been a large decline in the cover of the acid sensitive moss, *Hygrohypnum ochraceum*, from over 15% over the first three years, to trace amounts from 1994 to the present. One explanation for the decline is the scouring effect from an increased amount of woody debris (ranging from small branches to sizeable tree trunks) which enters the stream channel as a result of forestry activity upstream. Felling immediately adjacent to the sampling stretch occurred during 1991 and brushwood has been deposited within the stream channel over the past few years.

Change at **Dargall Lane** results from a progressive decline in the cover of one liverwort species, *Nardia compressa*, relative to another, *Marsupella emarginata*. We have little information on their relative environmental preferences, but it is interesting to note that in a study of the macroflora of 88 Welsh stream sites, spanning a considerably wider acidity gradient than experienced on the AWMN, Ormerod *et al.*, (1987) grouped *N. compressa* with *Scapania undulata* as representing the more acidic sites (mean pH 5.2-5.8). They also demonstrated that *S. undulata* was better distributed across pH classes than *N. compressa* which was largely restricted to most acidic streams and this is supported by observations on the AWMN; *S. undulata* is ubiquitous whereas *N. compressa* is only found in the more acidic streams and is the dominant macrophyte only in Bencrom River, one of the most persistently acidic stream on the AWMN. A decline in the cover of this species, possibly as a result of competitive displacement, is therefore consistent with a biological recovery process.

At the **River Etherow** the trend is driven by a progressive decline in the cover of *S. undulata*, the only truly aquatic species at this site for most of the monitoring period. *S. undulata* was almost completely lost from the sample stretch following a major spate in the early summer of 2002. Given the tolerance of this species to a wide range of water acidity it seems likely that its decline is unrelated to the recent chemical improvement and could reflect physical disturbance from storm events.

The trend at **Old Lodge** results from a decline in filamentous algae and an apparent slight, but progressive reduction in *S. undulata*. The trend in *S. undulata* represents a shift from around 2% to 1% which is well within the error of the annual cover estimate and is not possible to confirm as a real change.

At **Llyn Cwm Mynach**, the most striking feature of change has been the progressive increase in the cover of the blue-green alga *Plectonema* sp. (possibly *P. gracillimum*, or *P. notatum*) which forms a thick mat over a substantial area of the littoral of the main basin. This has coincided with a slight decline of *J. bulbosus* var *fluitans*, over which it grows. *J. bulbosus* var *fluitans* was the dominant macrophyte at the onset of monitoring, with an abundance unmatched by any other AWMN lake. Vigorous growth of this species requires high concentrations of CO₂ and NH₄⁺ (Schuurkes *et al.*, 1987) and can be encouraged by the re-acidification of limed waters (Brandrud, 2002). Although no liming has been carried out it is possible that the lake sediments may have been enriched as a result of erosion during the planting of larch and pine in the catchment in the early 1970s. Continued acidification might then have resulted in anoxic conditions in the sediment and the mobilisation of CO₂, NH₄⁺, and possibly phosphorus. Prolific growth of *J. bulbosus* var *fluitans* tends to decline after exhaustion of any bicarbonate/carbonate pool in the sediments (Roelofs, 1983).

Increased availability of phosphorus following the afforestation process, or from the partial die-back of *J. bulbosus* var *fluitans*, may have encouraged the spread of *Plectonema* sp. The occurrence of cyanobacterial mats in acidified waters has been reported elsewhere (Farmer, 1990, Arts, 2002). Anecdotal reports suggest that growths of similar forms of this Genus over submerged aquatic plants are widespread in shallow, slightly acidic lakes but published reports are few. This particular species has also been associated with mine drainage waters containing excessive concentrations of zinc (Whitton pers. comm.). Perhaps significantly, old manganese mine workings extend into the catchment and were in operation until c. 1918. Over the first five years of monitoring, this site exhibited higher mean zinc concentrations than any other lake in the AWMN (Patrick, *et al.*, 1995).

Other observations of change: "new species" records.

While there is little evidence for change in aquatic macrophyte communities according to the analysis of DAFOR scores and stream bed cover, some species have been detected relatively recently at some sites for the first time. Records of "new" species have been made at Loch Chon, the Round Loch of Glenhead, the River Etherow, Llyn Llgi, Llyn Cwm Mynach, Afon Hafren and Beagh's Burn.

At **Loch Chon** *Subularia aquatica* was first recorded in 1995 and small numbers of plants have been recorded in various parts of the shoreline in every survey since. *Potamogeton berchtoldii* and *Elatine hexandra* have been found occasionally since 1993 in the north end of the lake, in a littoral area adjacent to cattle grazed grassland. Although it is possible that agricultural activity at this end of the loch may have caused slight local enrichment over the last decade, the appearance of these species is consistent with a response to rising alkalinity levels (based on our understanding of species distributions, Monteith (unpublished data)). Alkalinity has increased progressively since the onset of monitoring and has been positive in all samples since 1997 (see Figure 6.4). In addition to the above, small patches of the charophyte *Chara virgata* were first identified in shallow water close to the loch outflow in 1999 and have been recorded in every survey since.

The **River Etherow** survey stretch has been almost exclusively dominated by the acid tolerant liverwort species, *Scapania undulata* since monitoring began. However, a small patch of the acid

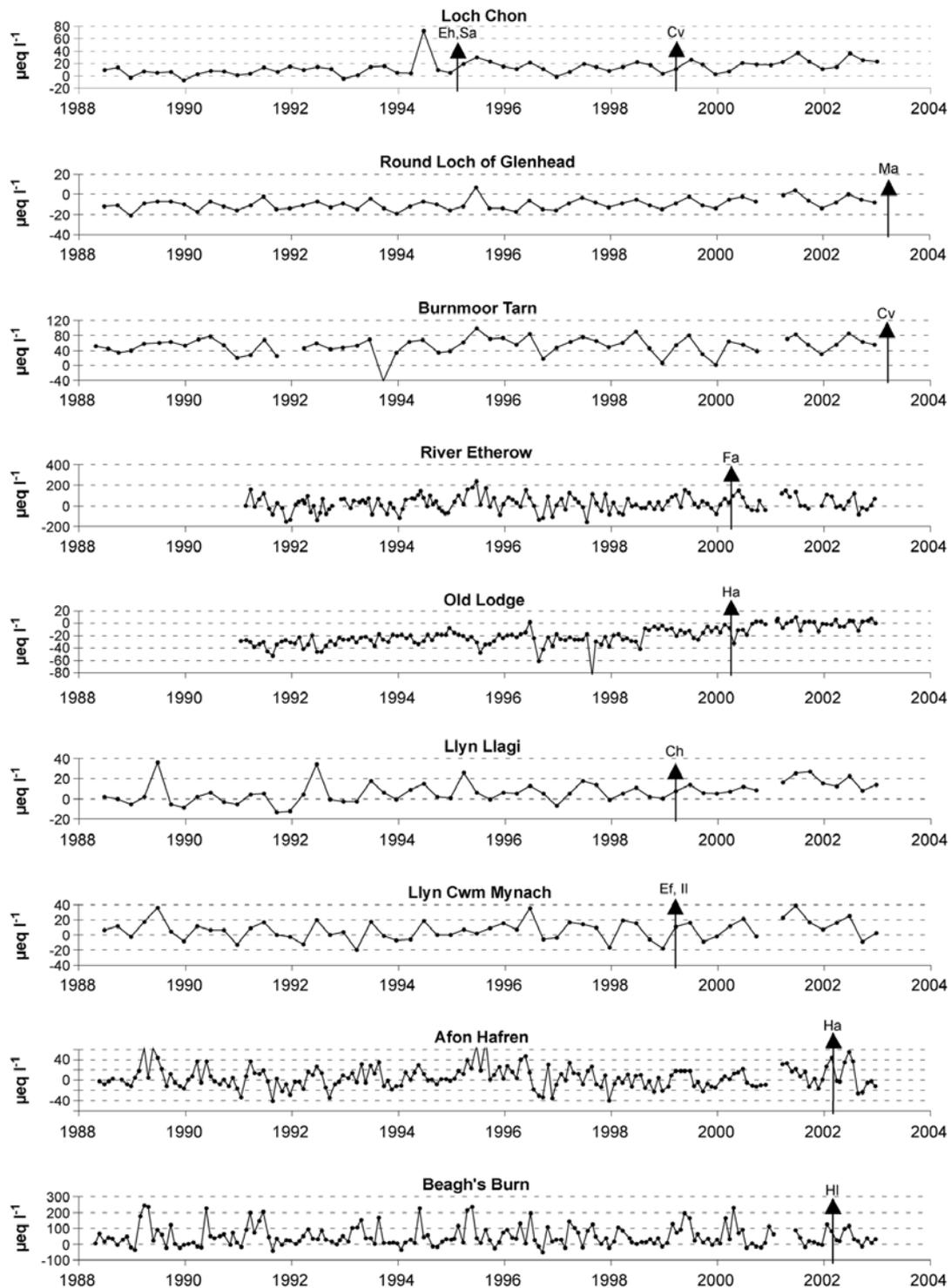


Figure 6.4: Temporal comparison of the first occurrence of “post-1994 only” aquatic macrophyte species (denoted by vertical arrows) and alkalinity (time series trace): Ch = *Callitriche hamulata*; Cv = *Chara virgata*; Eh = *Elatine hexandra*; Ef = *Eleogiton fluitans*; Fa = *Fontinalis antipyretica*; Ha = *Hycomium armoricum*; Hl = *Hygrohypnum luridum*; Il = *Isoetes lacustris*; Ma = *Myriophyllum alterniflorum*.

sensitive moss *Fontinalis antipyretica* was found in 2000 and detected again in 2001. A major spate in early summer resulted in the almost complete loss of bryophyte cover and this moss has not been detected since. Since early 1999 there has been a notable fall in Al_{lab} concentration and rise in pH and alkalinity, and there has been a particularly marked fall in the maximum levels of acidity experienced during episodes (Chapter 4). It is possible, therefore, that chemical conditions have recently become suitable for the temporary colonisation of *F. antipyretica*. Clearly, however, more permanent establishment will be dependent on the intensity and frequency of storm events in future.

The acid sensitive elodeid species *Callitriche hamulata* was found by Wade in his survey of **Llyn Llagi** in 1980 (Wade, 1980) but was not recorded on a Network survey until 1999 on a grapnel transect. It has since become abundant on this transect, and is now visible from the shoreline. Occurrence of this species appears to be largely confined to sites with positive alkalinity (Monteith, unpublished data). Its appearance in Llyn Llagi coincides with a shift to consistently positive alkalinity values in 1999 (Figure 6.4) and is therefore consistent with a threshold response to chemical recovery.

Despite the unusual macrophyte ecology of **Llyn Cwm Mynach** (see above) and the development of a blue green algal mat, two “new” species were recorded in 1999 and were found again in 2001. On both surveys the elodeid rush *Eleogiton fluitans* was listed as “occasional” in open-water locations while a few isolated *Isoetes lacustris* plants were detected around the shallow littoral. Spatial datasets are indicative of a positive alkalinity threshold for the former and there is evidence for a slight post-1998 increase in alkalinity. Its recent appearance is therefore consistent with chemical recovery. *I. lacustris*, however, does not show any obvious relationship with acidity and its recent detection is more likely due to recent changes in the availability of light as a result of localised changes in the cover of *J. bulbosus* var *fluitans*. The vegetational composition of Llyn Cwm Mynach, and its apparent change over the last fifteen years, may therefore reflect a complex interplay of factors resulting from elevated metal concentration, afforestation and recent recovery from acidification.

Although the **Afon Hafren** survey stretch has been almost exclusively dominated by the acid tolerant liverwort *Scapania undulata* since the onset of monitoring, a small patch of the moss *Hyocomium armoricum* was recorded in 2002 and 2003. Aquatic moss species tend to be particularly sensitive to acidic conditions (Ormerod *et al*, 1987), and, as the site was previously occupied only by liverworts its recent appearance is consistent with a recovery response. However, this is not corroborated by the water chemistry data which provide no indication of any recent improvement.

Like the Afon Hafren, **Beagh's Burn** was also almost exclusively dominated by *S. undulata* until relatively recently. In 2002 the moss *Hygrohypnum luridum* was recorded in several locations below normal water level and its cover had expanded still further by the 2003 survey. Although this is consistent with a recovery response it is again difficult to identify strong improvements in pH, alkalinity or Al_{lab} concentrations over time. There is, however, some indication of an improvement in ANC from the end of 1996, since when no negative values have been recorded. There is also evidence for a consistent increase in the pH of the most acidic samples (representing episodic events). This floristic change may therefore be linked to a reduction in the severity of acidic episodes of this site which is well buffered during base-flow conditions.

6.4.3.3 Aquatic macrophyte - summary

While there is less evidence of linear species change, in comparison with other multi-species groups monitored, the recent detection of sensitive aquatic macrophytes taxa at several sites can

be linked to improving chemical conditions, and particularly rising alkalinity.

An adequate supply of dissolved inorganic carbon (DIC) is a pre-requisite for aquatic photosynthesis and aquatic plants exhibit a variety of strategies to facilitate its sequestration. DIC occurs as carbon-dioxide (CO₂), bicarbonate or carbonate which exist in a pH dependent equilibrium. Below a pH of approximately 5.4 DIC is only present as CO₂ and concentrations tend to be so low in lakes that the macroflora is often restricted to isoetid species such as *Isoetes lacustris* and *Lobelia dortmanna* which can access CO₂ from sediments via internal lacunae, and *Juncus bulbosus* var. *fluitans*, which is able to fix much of the carbon necessary for growth in the early Spring (Svedäng, 1990). Some isoetids can also fix carbon at night using a process known as Crassulacean Acid Metabolism or CAM. For lakes, most elodeid species occur in less acidic systems only where DIC concentration in the water column is sufficient to allow uptake via submerged leaves. It is possible that a transition from negative to positive alkalinity is an important threshold for aquatic plants, representing the point at which bicarbonate generation can begin to buffer CO₂ concentration.

There is some indication that the recent detection of sensitive taxa is linked to this threshold (see Figure 6.4), although there is no common pattern which links all sites. The most striking changes concern those lakes where elodeid species have been detected at sites previously dominated by isoetid taxa (i.e. Llyn Llgi and most recently the Round Loch of Glenhead where *Myriophyllum alterniflorum* was recorded for the first time in the summer of 2003), and where aquatic moss species have recently been observed in streams which were previously exclusively occupied by liverworts (e.g. the River Etherow). "New" species records have been made at five of the eight AWMN sites which have undergone an upward trend in alkalinity over the monitoring period.

6.4.4 Salmonids

6.4.4.1 Density changes

Linear regression of brown trout density data provided produced little evidence of change at the majority of sites in the populations of either newly recruited (0+) or older (>0+) fish. Significant positive trends were observed for Old Lodge (both age groups) and Blue Lough (>0+ group only). However approximately one trend would be expected to occur by chance for each age group (with a $p < 0.05$ threshold) and we therefore attach little importance to these observations in this context. Other population parameters, i.e., weight and fish length also provide little evidence of significant change at any site.

The most striking observations relate to the appearance, at low densities, of 0+ fish at three sites where they were unrecorded during the first few years of monitoring (Figure 6.5). These might represent significant change in the viability of recently hatched brown trout within the locality of the survey stretches.

At **Old Lodge** small numbers of >0+ brown trout have been caught in every year of monitoring (i.e., since 1989) but there has been an increase in the density of this group from less than 1 fish 100 m⁻² prior to 1994, to over 5 fish 100 m⁻² after 1994. 0+ fish were not recorded until 1992 but have been detected every year since, with the exception of 1996.

Similarly, older fish have been recorded in the outflow of **Scoat Tarn** in every year of monitoring, although in contrast to Old Lodge there is no obvious trend in density which has remained very low. 0+ fish were recorded for the first time in 1998 and in three of the four subsequent years.

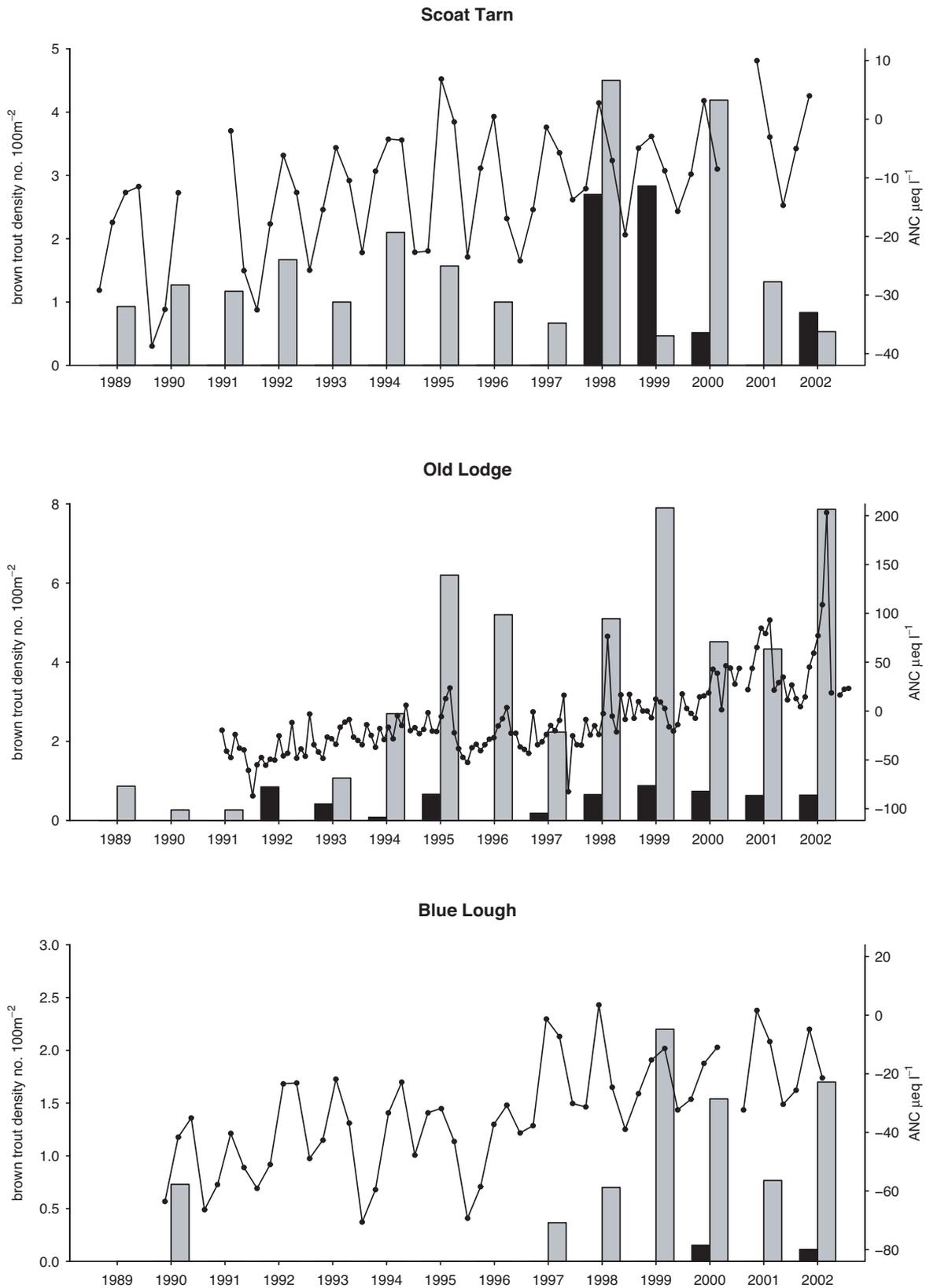


Figure 6.5: Relationship between annual mean pH (a), Al_{lab} concentration (b), and ANC concentration (c), and the density of 0+ group brown trout for all AWMN sites (with the exception of the fishless River Etherow) and all years of sampling

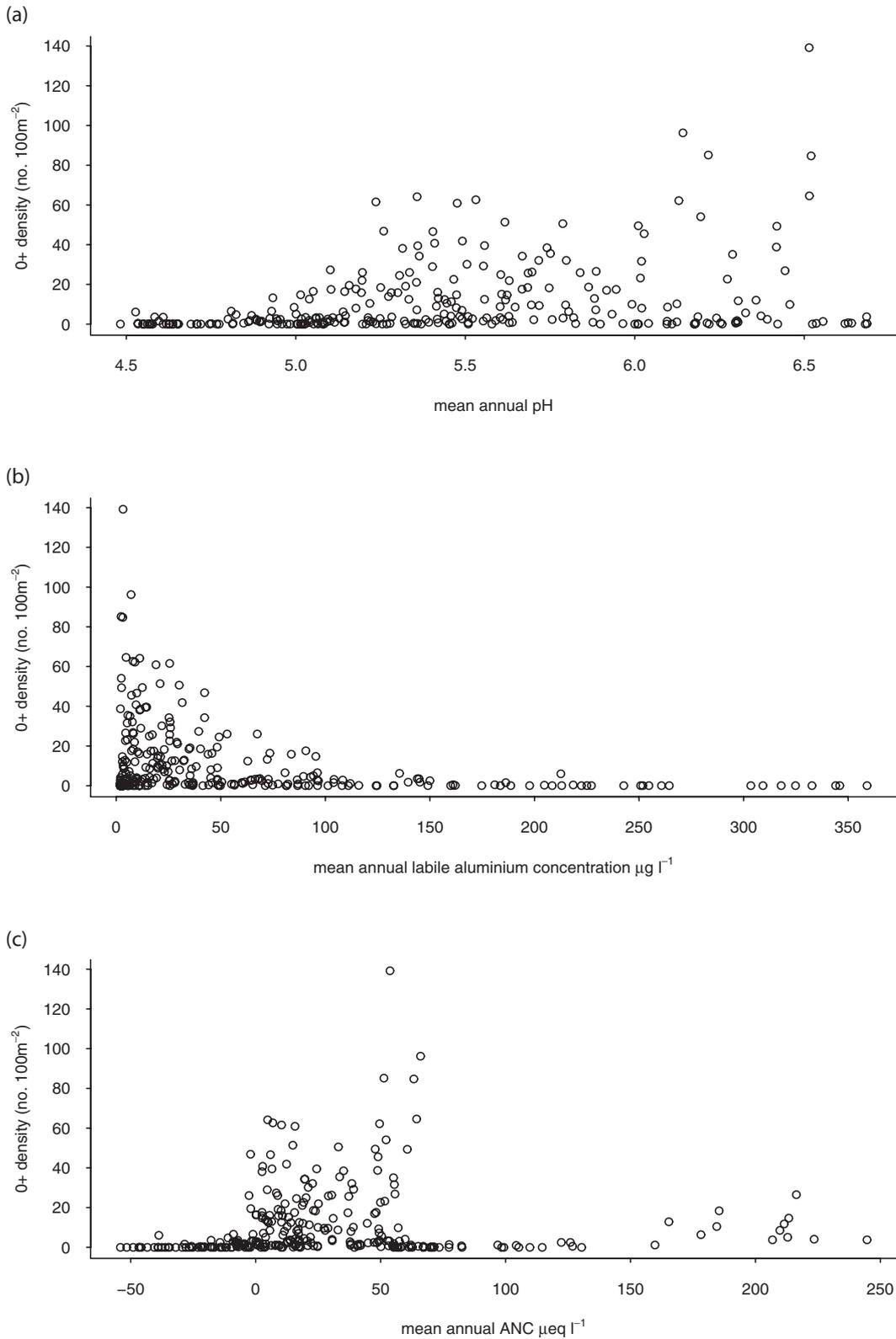


Figure 6.6: Temporal comparison of juvenile brown trout densities (0+) (black bars) and those over a year old (>0+) (grey bars) and Acid Neutralising Capacity (ANC) (time series trace) for the three sites where the 0+ group were detected after three or more initial years of absence. Electrofishing not conducted for Blue Lough in 1989.

In the outflow of **Blue Lough** no fish were recorded between 1991 and 1996. Since this time low densities of >0+ fish have been observed every year. 0+ fish were caught for the first time in 2000 and again in 2002.

6.4.2.4 Spatial and temporal links between brown trout populations and water chemistry

The significance of these changes with regard to recovery responses may be considered in the context of the wider relationship between 0+ brown trout density and acidity for all sites and all years. There are clear relationships between density and pH, Al_{lab} concentration and ANC (figure 6.6). Higher densities are only found in the least acidic waters, while fish are generally absent or at very low densities in the most acidic sites. Higher densities (i.e., >10 fish 100 m⁻²) are largely restricted to water with a pH >5.2 and Al_{lab} concentration <50 $\mu\text{eq l}^{-1}$. Perhaps the most striking relationship is apparent between density and ANC, with an apparent threshold for the likelihood of occurrence at around 0 $\mu\text{eq l}^{-1}$ (Figure 6.5c).

The three sites identified above are among the most acidic on the AWMN. In all cases ANC has been increasing over the monitoring period and has exceeded 0 $\mu\text{eq l}^{-1}$ ANC in at least one season in recent years (Figure 6.6b). The only other sites which are as acidic and have also crossed this chemical threshold in the last 15 years are:

- i) the River Etherow, for which the recovery of fish is precluded by a dam on the fishless reservoir it feeds; and,
- ii) the Round Loch of Glenhead outflow where ANC was fractionally negative at the outset of monitoring and which has always supported small numbers of these fish.

Acidification is widely recognised as a major threat to the health of salmonids and this is often considered to be a primary motivation for remedial action. Unsurprisingly, therefore, there is a large literature on the physiological effects of acid water on these species. The availability of Al_{lab} and its relationship with Ca^{2+} concentration is thought to be crucial for embryo and alevin gill membrane permeability (e.g. Leivestad *et al.*, 1980; Morris and Reader, 1990) and has been related to fish kills in acid sensitive waters (Howells *et al.*, 1990; Rosseland *et al.*, 1990) and changes in fish behaviour (Allin and Wilson, 1999). pH and DOC concentration have also been shown to be key factors for survival (e.g. McCartney *et al.*, 2003). ANC has been found to provide a convenient summary predictor of chemical conditions, particularly with respect to Critical Loads modelling (e.g. Wright and Cosby, 2004) and the relationship between brown trout status and ANC for Norwegian lakes has underpinned this approach. Lien *et al.* (1996) demonstrated that lakes with an ANC >20 and < 0 $\mu\text{eq l}^{-1}$ had a 95% probability of healthy and extinct populations respectively. AWMN data are not directly comparable with the Lien study as these are for flowing waters only but Figure 6.5 would seem to suggest a similar relationship.

While Spring chemistry is likely to be particularly important for the survival of newly hatched salmonids in these systems it is important to note that mean annual ANC, and Spring ANC in particular, in the outflows of Scoat Tarn and Blue Lough remain considerably below 0 $\mu\text{eq l}^{-1}$. Positive values at these sites have only been recorded in the Autumn. While we have no direct evidence, this observation points to some seasonal movement of fish into these headwater reaches from more buffered reaches further downstream. While the new records are encouraging, these populations remain at very low density relative to those populations in the majority of less acid lakes.

6.5 Summary

- Analysis of time series of biological data provides widespread evidence of subtle ecological improvement among AWMN lakes and streams which is consistent with the chemical recovery of these sites.
- Epilithic diatom and macroinvertebrate community composition has changed significantly at approximately half of all sites. Generally, the geographical distribution of these sites corresponds to the distribution of sites which have experienced the strongest declines in acid deposition and the clearest improvements in ANC, pH, alkalinity and Al_{lab} concentration.
- The majority of sites showing trends in epilithic diatom composition show a small shift towards less acidic species. However, trends in the north of Scotland are indicative of slight increase in acidity.
- Trends in macroinvertebrates are often characterised by an increase in the representation of predatory species which is indicative of wider changes in the food chain at these sites. There is a particularly strong spatial correlation between sites showing significant trends in ANC and those with trends in macroinvertebrates.
- Inter-annual variation in community composition of these two groups can often be linked to variation in acidity related variables. ANC and Al_{lab} provide the strongest predictors for macroinvertebrates, while epilithic diatom species composition shows the strongest relationships with DOC and Ca^{2+} concentration.
- Certain aquatic macrophytes have been detected for the first time at several sites since 1995, when xSO_4^{2-} concentrations first began to decline. The majority of these species are acid sensitive elodeids (which derive their inorganic carbon for photosynthesis directly from the water column) or acid sensitive mosses. At some sites the first detection of species roughly coincides with alkalinity approaching or exceeding $0 \mu eq l^{-1}$ for the first time.
- While there is little indication of significant change in salmonid densities, length and weight parameters or population structures at the majority of sites, newly recruited brown trout have been recorded in three of the most acidic sites on the AWMN for the first time after initial years of absence. These changes can be linked to declines in acidity of these systems over the monitoring period.

Chapter 7

Summary and Discussion

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7.1 Significance of this report in the context of previous AWMN interpretive exercises

While this report represents the third five-year interpretation of AWMN data, it provides the first opportunity to examine effects of significant emission induced declines in the acidity of deposition on sensitive waters across the whole of the UK.

In the first interpretative exercise (Patrick *et al.*, 1995) the five years of collated data were of insufficient length for many conclusions to be drawn on the occurrence and size of temporal trends. The report therefore focussed on chemical and biological characteristics of sites and monitoring methodologies, but also allowed the development and testing of appropriate statistical techniques, many of which have proved to be robust tools in subsequent assessments.

Analysis of the first ten years of data provided relatively little evidence of regional improvements in $x\text{SO}_4^{2-}$ concentration or acidity although striking improvements were observed at a minority of sites close to emission sources (Monteith and Evans, 2000). The inertia in $x\text{SO}_4^{2-}$ concentrations at the majority of sites over this period now appears to have resulted from relatively stable emissions over the first few years of monitoring and shifting weather patterns with a progressive decline in “westerlyness” from around 1990 to 1996. While it was, therefore, not possible to detect the effects of emissions decline at the majority of sites, the period provided a “baseline” against which the extent of natural variability in water chemistry and biology could be identified and quantified. Over this time, for example, we were able to demonstrate strong links between regional-scale climatic variation, represented by the North Atlantic Oscillation Index, and interannual variability in acidifying sea-salt episodes (Evans *et al.*, 2001a) and nitrate concentrations (Monteith *et al.*, 2000).

Since 1996 the UK has experienced a sharp downturn in S deposition as westerlyness has again increased and further emission reduction measures, such as the fitting of Flue Gas Desulphurisation (FGD) technology at two of the largest coal burning power stations in the UK,

have been implemented. In contrast there is little indication of any change in the flux of deposited nitrogen species (i.e. NO_3^- and NH_4^+) over the same period. In Chapter 2 of this report we show (with data provided by the Acid Deposition Network) that the concentration of xSO_4^{2-} and hydrogen ion (H^+) in deposition has declined by circa 50% over most of the UK since 1986. The absolute declines in acidity are geographically biased, with the strongest trends in southern and central England reflecting proximity to sources. Nevertheless, declines in the xSO_4^{2-} concentration of deposition are detectable even for sites in the least impacted regions of the UK, i.e., northwest Scotland and Northern Ireland. However, the magnitude of decline in some high rainfall areas is very small, possibly in part due to an increased delivery of S from shipping. This factor could offset significantly the expected improvements in water chemistry in more remote regions where declines in the deposition of terrestrially emitted S are small.

Observations in Chapter 2 of regional improvements in deposition chemistry, coupled with the analysis in Chapter 3 which demonstrates an immediate impact (at least within a yearly time-step) on the xSO_4^{2-} concentration of runoff from AWMN sites, raise expectations of regional scale improvements in the acidity of surface waters and consequent improvements in biological quality. The fundamental objective of the AWMN is to test for the occurrence and magnitude of these responses.

7.2 Summary of findings from the current (1988-2003) assessment

7.2.1 Chemistry

The water chemistry trend assessments (Chapters 3 and 4) demonstrate that xSO_4^{2-} concentrations of run-off from AWMN sites have been falling in line with declines in deposition and, in absolute terms, are broadly reflective of a gradient from Central and Southern England (maximum reduction observed at the River Etherow) to the far northwest of Scotland (where very slight reductions are deemed statistically insignificant) (see Figure 7.1). As there is no indication of a trend in NO_3^- concentration, any long term reductions in acidity (i.e., increases in pH, alkalinity or Acid Neutralising Capacity (ANC), or declines in Al_{lab} concentration), are likely to be driven primarily by changes in S deposition.

Figure 7.2 illustrates that the dominant effect of the decline in xSO_4^{2-} at the more acid sites has been a reduction in Al_{lab} and base cation concentrations. Some of the largest changes in Al_{lab} have been observed at particularly acid-sensitive sites underlain by granitic lithologies, such as those in Galloway and the Mourne Mountains, despite only moderate reductions in xSO_4^{2-} concentration in these regions. Thus, the rate of change in this particularly toxic agent is dependent both on the rate of change in xSO_4^{2-} and the longer term acidity status of the system. These observations are consistent with acidification recovery experiments such as at the heavily acidified Gårdsjön (Moldan *et al.*, 1995) where declining inorganic aluminium was the dominant response in the early stages of xSO_4^{2-} decline.

Temporal patterns in Acid Neutralising Capacity (ANC) depend on the method of determination. Only the AB-ANC method (Chapter 4) provides an indication of widespread improvement, but the high correlation between its trend strength and that for xSO_4^{2-} concentration (Figure 4.6c) is persuasive evidence of a regional improvement in water quality in response to falling S deposition. It is interesting to note that one or more of pH, alkalinity and Al_{lab} concentration show a significant trend of improvement at all sites showing significant change in AB-ANC and change in the latter may therefore be considered to provide a generic proxy for changing acidity. The fact that the large and ubiquitous trends in dissolved organic carbon (DOC) contribute to the size of slope of trends in AB-ANC suggests that, at least in part,

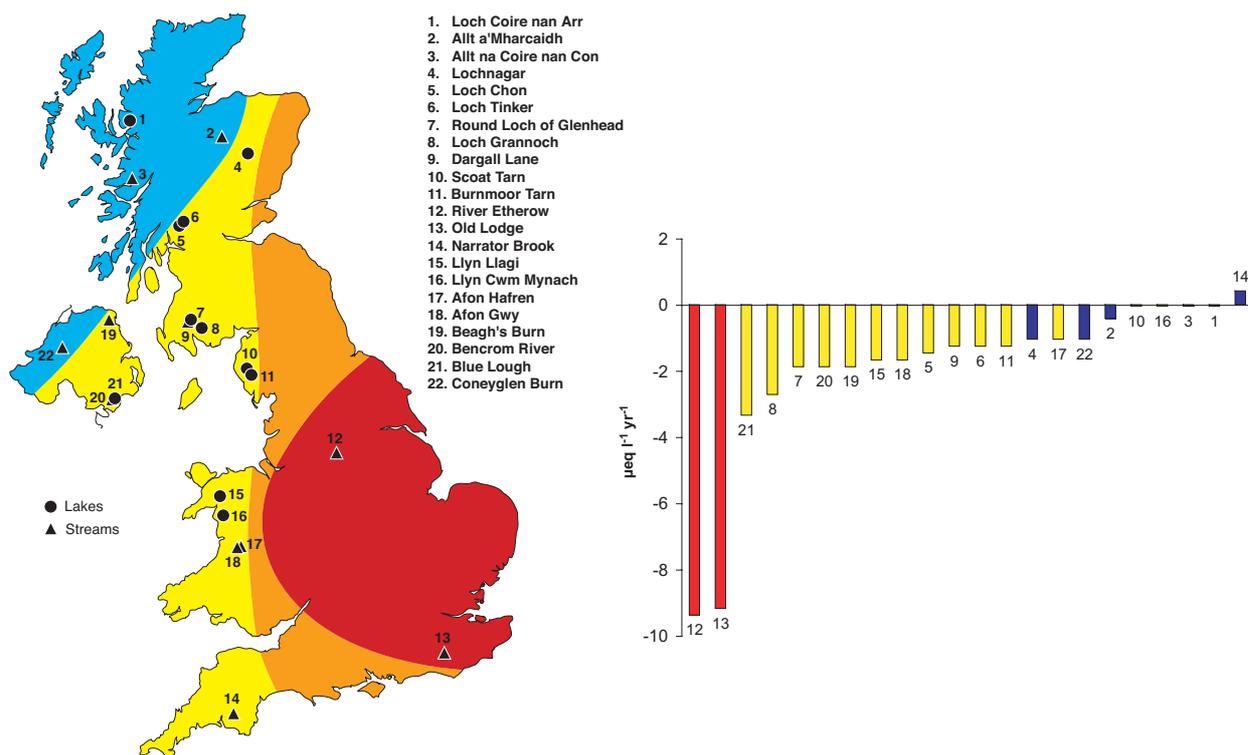


Figure 7.1 UK map of non-marine sulphur deposition trend banding according to Fowler *et al.* (Chapter 2), and trends in non-marine sulphate as determined by Davies *et al.* (Chapter 3).

rising DOC concentrations are integral to the larger chemical recovery story. This is consistent with the findings presented in Chapter 5, although the relative contributions of changes in deposition chemistry and climatic variation on DOC are still unclear. The absence of clear trends in CB-ANC may result from the additional “noise” in the data stemming from the compound errors associated with the seven constituent determinands (Evans *et al.*, 2001c).

In addition to illustrating the overall downward trends in acidity (the slope estimator is representative of change in annual median values), Chapter 3 also highlights clear reductions in the intensity of the acidity of acid episodes in several AWMN streams (i.e., short term maxima in H^+ and Al_{lab} concentration, normally associated with periods of high precipitation or seasalt deposition events) (Figure 4.5). Thus, for example, while the overall decline in Al_{lab} concentration in the Dargall Lane Burn approximates to $0.56 \mu\text{mol l}^{-1} \text{yr}^{-1}$ (Table 4.1), peak recorded values have fallen from over $100 \mu\text{mol l}^{-1}$ in 1989 to less than $40 \mu\text{mol l}^{-1}$ by 2002 (Figure 4.5b), a more rapid reduction by an order of magnitude. While difficult to quantify, the ecological significance of these changes may be considerable, given that the chemistry of episodic extremes may well impose the limiting factor for many acid sensitive organisms (see for example Lepori *et al.*, 2003).

7.2.2 Biology

The analyses presented in Chapter 6 provide the first indication of national-scale, if often rather subtle, biological responses to improvements in water chemistry. Most of the biological change has occurred within the region showing the strongest reduction in xSO_4^{2-} concentration and statistically significant increases in AB-ANC. While responses vary, some common patterns have emerged. The abundance of some acid-tolerant epilithic diatoms is declining relative to more sensitive species; acid-sensitive mosses and elodeid (leafy) aquatic macrophytes have recently

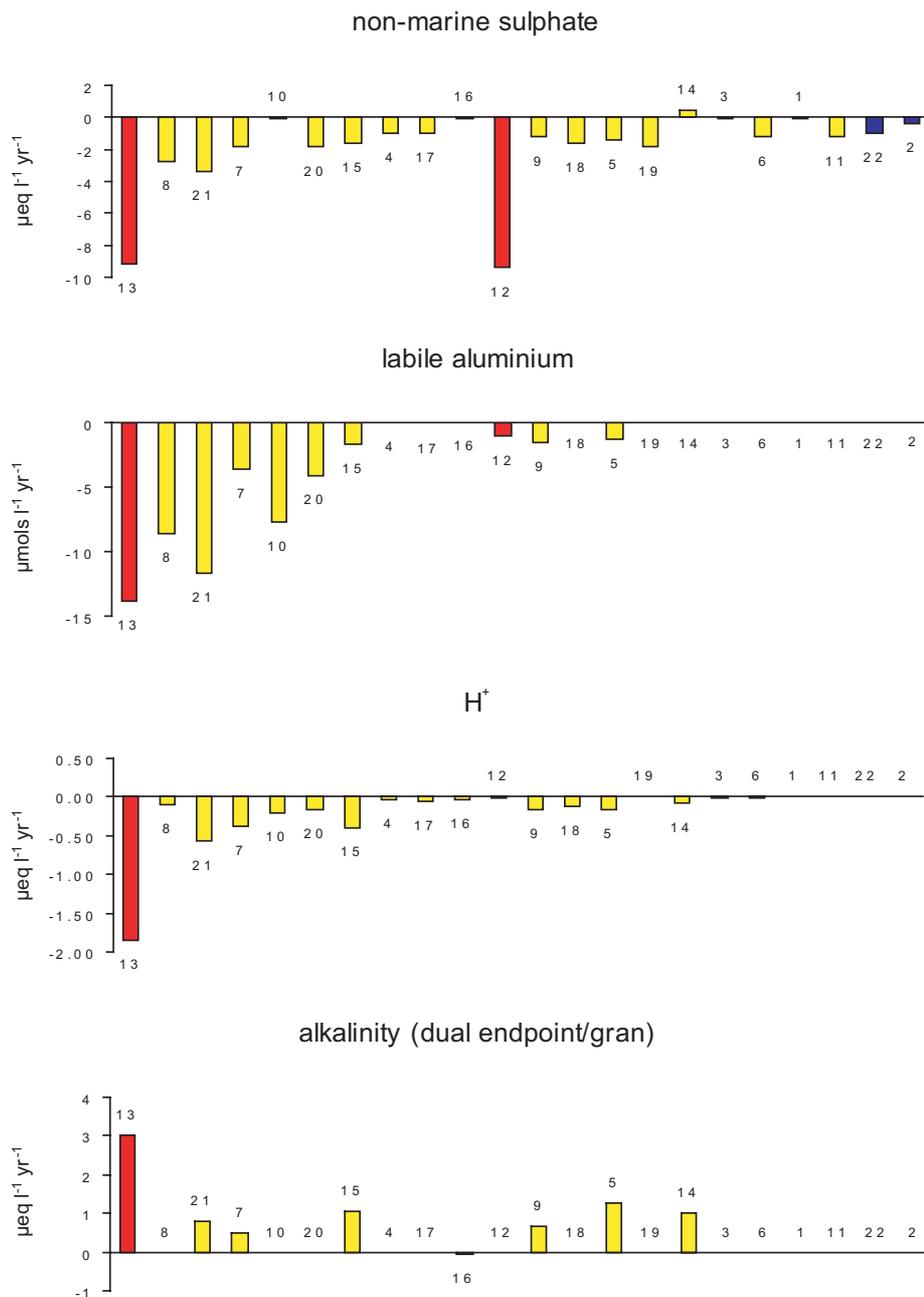


Figure 7.2 Trends in non-marine sulphate, Al_{lab} and hydrogen ion concentration, and alkalinity (according to Davies *et al.* Chapter 3). Sites sorted by increasing mean pH; AWMN sites colour coded according to deposition region indicated by map in Figure 7.1.

been detected for the first time at several sites; macroinvertebrate communities show indications of a shift in food web structure with an increased representation of predatory species, some of which are also noted for their acid-sensitivity; and, juvenile brown trout have been detected at three of the most acidic sites on the network after initial years of absence.

The varying nature of biological responses across the network may reflect differences between sites in chemical response to declining S deposition. Significant trends in epilithic diatom species composition have occurred at the majority of sites where ANC has increased significantly (Figure 7.3). However, there is inertia in the three most acid sites, despite all showing chemical

improvement. One potential explanation is that inorganic aluminium concentrations in soil are limiting the availability of phosphorus. If this is the case we might expect to see a biological threshold crossed in the near future, as aluminium levels continue to decline. While diatom species change at sites where ANC has increased is mostly reflected in a shift to species with slightly higher pH optima (i.e. more acid-sensitive taxa), change at sites in northern Scotland, where ANC has changed little if at all, appears if anything to show the opposite. While this might result from an increase in organic acidity at these sites further years monitoring are required to determine the underlying cause.

Aquatic macrophyte monitoring was incorporated within the AWMN primarily as a supporting element. Often occurring over broad environmental gradients, aquatic macrophytes are generally considered to be less sensitive to anthropogenic pressure in comparison with the other biological groups. However, they have an important role in the structuring of these ecosystems, particularly as sources of nutrients and habitat for other organisms, and by moderating the physico-chemistry of the substrates on which they grow. It is necessary, therefore, to maintain a record of the macrophyte assemblage if only so the cause of trends in other biological groups is to be comprehensively assessed. While conventional forms of community assessment (applied

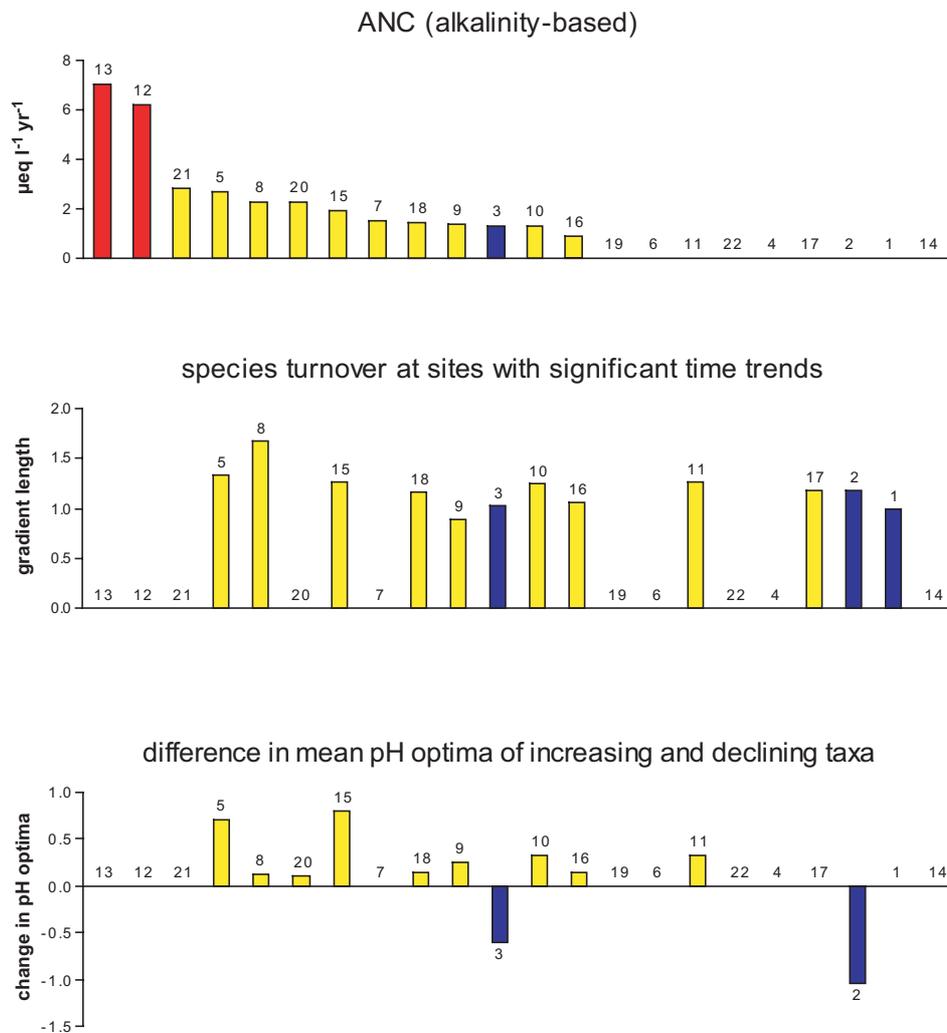


Figure 7.3 Trends in Acid Neutralising Capacity (AB-ANC) (according to Davies *et al.* Chapter 3), species turnover of epilithic diatom communities and differences in mean pH optima of expanding and declining taxa (Chapter 6). Sites sorted by AB-ANC trend strength; AWMN sites colour coded according to deposition region indicated by map in Figure 7.1.

successfully to the other groups) provided little indication of major structural change, the data have revealed a surprising number of records of “new” taxa over the monitoring period, most of which are consistent with acidification recovery responses in a group of less acidic sites. These observations may reflect a combination of an increase in the availability of dissolved inorganic carbon and, possibly, phosphorus, for the reason given above. The importance of these changes for their wider ecosystems should not be underestimated. At the Round Loch of Glenhead and Llyn Llazi the development of stands of elodeid species (which have an erect and branching growth form) represents a threshold with regard to the aquatic “architecture” of these lakes, dominated until recently by prostrate (i.e. low growing) isoetid growth forms. This should result in new habitats for a variety of invertebrate and epiphytic algal species, and provide some protection to zooplankton from predation. The recent establishment of mosses in AWMN streams is also likely to have wider ecological repercussions, particularly as these may provide a source of food for macroinvertebrate species which are unable to assimilate the dominant liverworts.

Chapter 6 also shows that the presence/absence of trends in ANC appears to be a particularly good predictor of the occurrence of trends in macroinvertebrate communities (Figure 7.4). Unlike the aquatic plant groups, macroinvertebrate communities have changed even in the most acid sites, perhaps hinting here at direct responses to declining Al_{lab} levels. The shift toward predatory species is particularly significant as it is indicative of wider ecological change, i.e., an expansion of aquatic food webs. It is highly likely that there will be a degree of hysteresis between chemical improvement and the recolonisation of many sensitive species for several reasons, not least because of the relative geographic isolation of many sites and the restricted dispersive ability of many taxa. However the much discussed issue of the limiting effect of continued acid episodes may not be as restrictive as has sometimes been argued, given the observations of sharply declining H^+ and Al_{lab} maxima in some stream sites. Clearly however, the magnitude of these events, although in decline, may continue to impose a ceiling on faunal

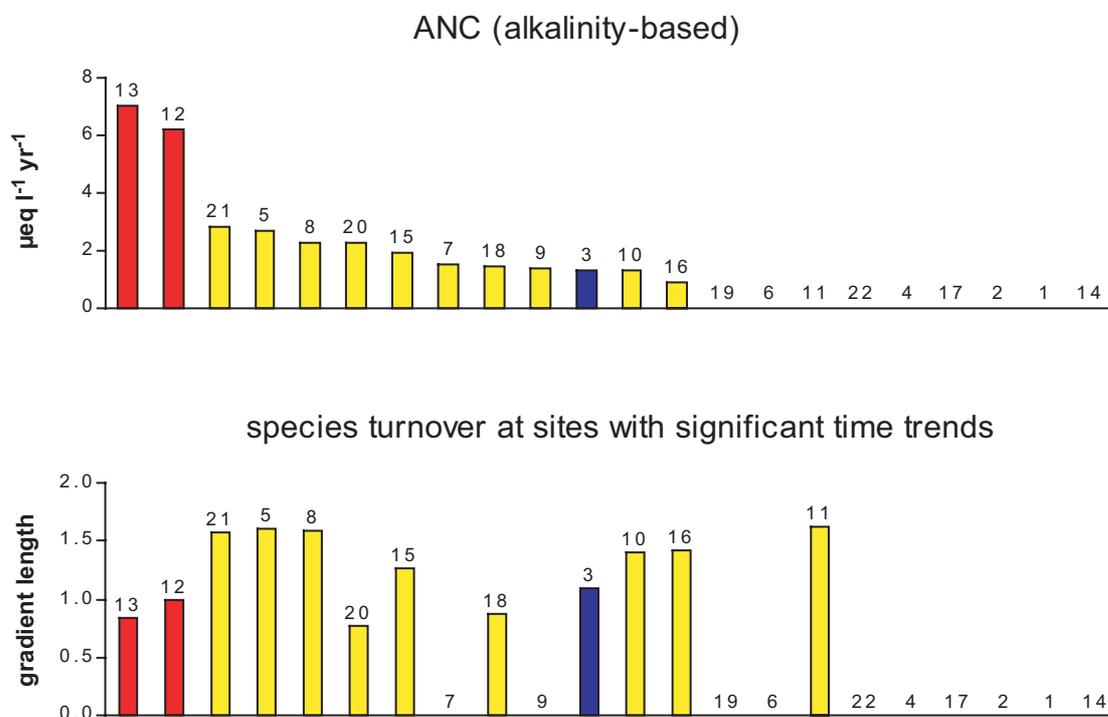


Figure 7.4 Trends in Acid Neutralising Capacity (AB-ANC) (according to Davies *et al.* Chapter 3) and species turnover of macroinvertebrates (Chapter 6). Sites sorted by AB-ANC trend strength; AWMN sites colour coded according to deposition region indicated by map in Figure 7.1.

recovery in these running waters. It is also possible that acid-tolerant “generalist” species which have filled niches vacated by acid-sensitive “specialists” (and particularly that of algal grazing) may be difficult to displace once chemical conditions are once again favourable to the latter (Ledger and Hildrew, 2005). Once again, only further monitoring will determine the extent and rate at which these macroinvertebrate communities are able to take advantage of the improving chemical environment.

In comparison with the other biological groups there are fewer indications of significant positive responses in salmonid taxa. This is perhaps not surprising, since we have focussed on the density of a single species, rather than the relative abundance of species, or at least presence/absence of a multi-species group (i.e aquatic macrophytes). Further analyses are necessary to investigate more subtle changes in fish health, but work to date provides little indication of change in relative growth rate or condition factor. Nevertheless, evidence for the recent arrival of juvenile (< 1 year old trout) at the three of the most acidic sites on the Network is clearly consistent with declining acidity in these systems. In addition to their symbolic role as “target” organisms for emissions abatement strategy, shifts in the populations of these higher predators have clear implications for the functioning of the wider ecosystem. Whether these changes are again primarily driven by declining Al_{lab} concentration is unclear, the clearest relationships would appear to be with ANC, but the data are again indicative of a biological response to improving chemistry for a subset of sites within the wider AWMN acidity spectrum.

To conclude, the current analyses demonstrate a rapid chemical response of AWMN sites to emission induced reductions in the acidity of deposition. This is characterised by significant declines both in the average acidity of acid-sensitive upland lakes and streams and in the magnitude of episodic extremes in flowing waters. Many sites have undergone biological change, often involving the recent appearance or increased abundance of acid-sensitive species, which is consistent with observed chemical change.

While the examples of apparent biological response to chemical improvement are encouraging, in the majority of cases the degree of change has been slight. In part this may reflect biological inertia, lags being expected in many cases before sensitive species are able to recolonise and develop viable populations. However, our interpretation of the significance of the degree of recent change is restricted by our limited understanding of appropriate ecological recovery targets. Palaeoecological work, and particularly the development of the Modern Analogues Technique (MAT, Simpson *et al.*, 2005), offers one approach to this problem. MAT identifies lakes with fossil-based contemporary biological characteristics (e.g. fossil diatoms and cladocerans) which are most similar to those found in pre-acidification sediments of damaged lakes. The wider biological characteristics of these “Modern Analogues” may therefore be used as a reference condition for damaged sites of interest. No comparable technique is of course available for AWMN flowing waters.

Ultimately, our assessment of the current degree of biological “gap-closure” requires further development of high quality spatial biological-chemical datasets. This would assist both in the development of the MAT approach and more widely in the interpretation of the likely drivers of species changes. Most importantly, however, biological monitoring must continue if we are to ascertain that recent apparent improvements are sustained and further enhanced into the future as emissions continue to fall. This is by no means inevitable, particularly given the potential future threat of nitrogen saturation at several sites, and concerns that future changes in climate (for example wetter and more hydrologically variable winter and spring conditions) may have a deleterious influence on the acidity of run-off and the frequency and intensity of acid episodes at these biologically sensitive times of year.

7.3 Network performance

It is a testament to the quality of the original design, in terms of the choice of sites and chemical and biological methodologies, that the AWMN has remained largely unchanged since the onset of monitoring in 1988. Most monitoring records, therefore, are already over 15 years in length although four are slightly shorter. Biological monitoring of Blue Lough and Coneyglen Burn began in 1989 with chemical monitoring commencing in the following year. In 1991 the Afon Gwy replaced a nearby site following access problems and chemical monitoring at Narrator Brook was moved 1 km upstream to remove any influence of coniferous forestry. Data quality has been underpinned by AQC procedures, most notably the annual chemical laboratory check conducted by WRC Medmenham (see the AWMN web page), and by minimal turnover of laboratories and analysts.

The most serious development with regard to sites has occurred relatively recently at Loch Coire nan Arr in northwest Scotland, initially considered a “negligible deposition” control for the Network on the grounds of its geographic position. Throughout the monitoring period the site has been used as a water supply to a local fish farm, but recent upgrading of a dam on the outflow and subsequent water level management has resulted in considerable physical disturbance to the littoral zone, and the occasional loss of the outflow (in which electrofishing was conducted). The site has a short residence time - in-lake processes are probably insignificant for much of the year - and to date there is no indication that water chemistry has been affected. However, the loss of the littoral macrophyte community and disruption to the outflow has rendered the continued monitoring of aquatic macrophytes and salmonid populations impractical and both have recently been discontinued. To compensate we adopted a replacement loch in 2002, Loch Coire Fionnaraich, within a few km of Loch Coire nan Arr and with similar physical and geological characteristics. The first data for this site are now being reported in the AWMN annual reports (see the AWMN web site) and the site will be included in the next full data assessment exercise.

While there have been very few breaks in records since monitoring began, the outbreak of foot-and-mouth disease across the country, and subsequent land access restrictions in the spring of 2001, resulted in the loss of data at several sites. This was a particular problem for the sites in the Lake District, for which access was prevented between March and August, and more widely for macroinvertebrate sampling, which was not possible at approximately half of the sites in that year. The disease, and recent reforms to the Common Agricultural Policy also have potential longer-term implications due to their impact on upland farming practices. While sheep have been the dominant grazers in the majority of AWMN catchments to date, this will not necessarily remain the case. Up until 2003, however, there is no evidence of major changes in grazing practices.

7.4 Developments and future requirements

The evidence for chemical and biological improvement at AWMN sites suggests that positive ecological responses to emissions reductions are occurring at a national scale. The recovery story is clearly complex, however, and a number of processes which could delay or even negate future improvements are still poorly understood. In particular, the threat of possible future N saturation, the mechanisms behind the large increase in organic acid concentrations, and the implications of forecast climate change for further chemical recovery need more thorough investigation. Furthermore, it is as yet unclear whether the tentative early stages of biological recovery will be sustained, and to what extent the rate of biological change is being inhibited by chemical and/or other biotic and physical factors. These uncertainties will only be addressed

through a continuation of the current monitoring programme, ideally in association with experimental work within AWMN catchments. Beyond the immediate acidification problem there is also a clear role for the AWMN in providing the data necessary to develop a better understanding of the wider linkages between the atmosphere and terrestrial and aquatic upland systems. This is particularly important with respect to the likely consequences of future climate change and land use for the quality of the water draining upland areas, associated fluxes of carbon, heavy metals and other elements, and impacts on aquatic biodiversity.

While fundamental chemical and biological measurements continue, the range of work conducted within AWMN catchments has expanded in recent years. For example, monitoring of deposition chemistry within the catchments of a sub-set of sites was initiated by the Acid Deposition Network in 1999 (Hayman *et al.*, 2001) to allow a closer assessment of the relationship between deposition and run-off chemistry. Metal concentrations in catchment mosses have been monitored since 2001, and surveys of soil carbon:nitrogen ratios and moss cover are scheduled at some sites to explore the factors which determine the extent of N leaching. Continuous monitoring of AWMN lake water temperature and thermal stratification has been ongoing since 1999, while particularly intensive meteorological and water column measurements have been made at Lochnagar (a key site in several other monitoring programmes) over the same period (Rose *et al.*, 2004).

There remains a need for further catchment characterisation, particularly with relation to soils and catchment vegetation, while an expansion of the currently restricted programme of continuous monitoring of conductivity, temperature, pH and discharge would benefit the assessment of the relative roles of hydrology, seasalt episodes and rising air temperature in influencing run-off chemistry. Further work is also required to allow a better understanding of the seasonal dynamics of the monitored biota, particularly with respect to phenology/climate interactions which may be important in influencing the composition of annually sampled assemblages. Finally, an expansion of the range of biological fossil groups in sediment trap and sediment cores would shed more light on appropriate reference conditions while placing current recovery rates in a longer-term context.

7.5 The AWMN and the wider research community

The use of AWMN data, findings and expertise extends considerably beyond assessments such as this and associated scientific publications. The information it generates is vital, both with regard to quantifying the success of emissions reduction strategy, and for the refinement of models with which the likely outcome of future policy decisions can be predicted. The ever-developing database is unique for upland freshwater systems in the UK, and is providing new insights into processes which are difficult to simulate experimentally. The AWMN is integral to other government funded air-quality related research, such as the UK freshwater acidification research programme (e.g. Curtis and Simpson, 2001; NEG-TAP 2001) and the development of dynamic acidification models (e.g. Jenkins and Cullen, 2001). AWMN data also feed into other national and international monitoring programmes, including the UK Environmental Change Network and the UNECE International Cooperative Programme Task Force on the Acidification of Rivers and Lakes (ICP Waters), and large EU Research Framework projects including EURO-LIMPACS (<http://www.eurolimpacs.ucl.ac.uk>) and REBECCA (<http://www.environment.fi/syke/rebecca>).

7.6 Conclusion

This report demonstrates the value, to science and policy, of a continuing commitment to long-term monitoring. While the previous interpretative report provided little indication of sustained trends (Monteith and Evans, 2000), a further five years of monitoring has now revealed clear evidence for a consistent pattern of chemical and biological recovery in acid-sensitive waters across much of the UK. While this is encouraging, considerable uncertainty remains, particularly regarding short-term and longer-term influences of climate variability on the future behaviour of nitrogen and organic acids, and the continued importance of acid episodes and other physical and biotic factors for continued biological recovery. Further monitoring is clearly crucial if the effect of continued emission reductions on freshwater ecosystems is to be revealed.

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