UK Centre for Ecology & Hydrology

UK Upland Waters Monitoring Network data interpretation 1988-2019

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Cover photograph: The UWMN site Llyn Llagi, Snowdonia – by Ewan Shilland

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Background

This report is the latest in a series of occasional interpretive reports to Defra, extending back to 1993, that have documented trends in the chemistry and biota of UK Upland Waters Monitoring (UWMN) sites.

Due to the limited resources available on this occasion, we have focussed specifically on the analysis and interpretation of trends in water chemistry and communities of epilithic diatoms (siliceous algae growing on submerged stones) and macroinvertebrates (e.g. aquatic stages of insects, crustaceans, leeches etc.) across 23 UWMN sites and covering the period since the initiation of the network in 1988 to 2019, i.e. approximately the first three decades of monitoring.

The UK UWMN (formerly known as the Acid Waters Monitoring Network or AWMN) was established in 1988 by the UK's Department of the Environment (DoE) in order to assess the impact of national and international controls on the atmospheric emission of acidic pollutants (particularly sulphur (S) and nitrogen (N) based compounds) on the ecological health of the UK's acidified surface waters.

One major aim of internationally agreed atmospheric emission treaties, under the United Nations Economic Council for Europe Convention on Long Range Transboundary Air Pollution (UNECE LRTAP), and more recently the European Union's National Emissions Ceilings Directive (NECD), has been to reduce the emission of acid gasses to a level at which acid deposition, and consequently the acidity of acidified surface waters, is brought below ecologically acceptable levels wherever feasible.

The primary water chemical indicator of freshwater environmental damage, or policy success, is acid neutralising capacity (ANC) – commonly determined as the difference in the equivalent concentrations of base cations and acid anions in surface waters. On the basis of a Norwegian study of fish and macroinvertebrate populations, a critical level of ANC (ANC_{crit}) of 20 μeq L^{-1} has been used widely as water chemical target for acid-sensitive UK waters. Below this threshold, it has been argued, acidity becomes increasingly intolerable for a range of more acid-sensitive freshwater species.

The network

The AWMN initially comprised 22 lakes and streams, mostly draining catchments underlain by acid-sensitive geologies, and distributed across a large acid deposition gradient. The majority of the selected lakes had already been demonstrated to have acidified over the course of the previous two centuries as a direct consequence of anthropogenic acid deposition (more commonly referred to as "acid rain").

Some closely located pairs of forested and moorland catchments were included in the network design to allow investigations into the importance of coniferous forestry and forestry management in determining acidity status and acidification recovery prospects. Levels of ANC for the majority of UWMN sites at the onset of monitoring were substantially below the ANC_{crit} (i.e. 20 μeq L^{-1}) and were lower in forested catchments than in their moorland counterparts.

Chemical and biological monitoring has been maintained according to consistently applied protocols at nearly all of the originally selected sites up to the present day. While most monitoring and analysis over the first two decades was funded by Defra, reductions in central support in more recent years led to the need for a broader funding base, in-kind support from some organisations and considerable input from volunteers (particularly with respect to the collection of water samples) (see acknowledgements for further details).

Water samples are collected monthly and quarterly from UWMN streams and lakes respectively, and analysed for a range of chemical determinands. These include surrogates for atmospheric pollutant drivers of acidification (e.g. concentrations of non-marine sulphate (xSO_4^{2-} : i.e. sulphate not derived from sea salt) and nitrate (NO_3^-)) and geochemical responses (e.g. pH and labile aluminium (Al^{3+}) concentration).

Samples of epilithic diatoms and macroinvertebrates are collected each summer and spring respectively. They are analysed by taxonomic specialists to determine the abundance of each species, in the case of epilithic diatoms, or at mixed taxon level (i.e. species, genus or family) with respect to macroinvertebrates.

Due to a temporary analytical backlog resulting from a funding hiatus, biological data for most sites were available for analysis up to 2016 or 2017 only, while water chemistry were available up to the end of 2019. During the course of writing this report the biological data have now been brought up to date through additional support from Defra. This report also includes an analysis of trends in S and N deposition, estimated by UKCEH's CBED (Concentration Based Estimated Deposition) model for each UWMN catchment, over the period for which data were available (1990 to 2017).

Trends in acid deposition

Analysis of CBED data indicates that at the onset of monitoring the deposition of acidity contributed by non-marine S (xS) compounds and all species of N (or total N) compounds was highest in central England, while the lowest deposition rates occurred in the far north of Scotland and north-western Northern Ireland. Assumptions within the CBED model determine that deposition loads are enhanced in higher rainfall regions such as the English Lake District, and with respect to forested catchments relative to moorland catchments.

The CBED estimates also indicate that the catchments receiving the highest acid deposition loads at the onset of monitoring experienced the most rapid reductions in xS and oxidised N deposition over the last three decades - largely a consequence of the closure, or at least the desulphurisation, of most of the UK's coal and oil burning power stations.

By 2017, the last year for which CBED estimates were available at the time of data analysis, the CBED estimate for xS deposition to the most atmospherically polluted UWMN catchments had fallen beneath the 1990 estimates for the least impacted catchments in the far north and west of the UK.

While rates of oxidised N deposition have fallen substantially over the monitoring period, the deposition of reduced N species is estimated to have increased slightly, resulting in at most small reductions in total N deposition relative to the reductions in xS.

Trends in UWMN water chemistry

Over the first three decades of freshwater monitoring, annual fluxes of xSO_4^{2-}, from UWMN sites declined at similar rates to reductions in CBED estimated xS deposition fluxes, suggesting broadly conservative behaviour (i.e. relatively little retention of deposited S within catchments).

In general, xSO_4^{2-} concentrations across UWMN sites showed similar spatial variation to the CBED estimates of xS deposition fluxes. Despite receiving relatively little xS deposition, however, the streamwater of Old Lodge in south-east England exhibited extremely high xSO_4^{2-} concentrations in the early years of monitoring, largely as a consequence of relatively low precipitation and high evaporative loss in this part of the country. Consequently, Old Lodge's xSO_4^{2-} concentration has also declined at one of the fastest rates of all sites on the network, while xSO_4^{2-} concentrations have declined more rapidly in forested catchments than their moorland pairs as a consequence of historically enhanced rates of pollutant interception by forest canopies.

The deposition of hydrochloric acid (HCl) has often been overlooked as a contributor to acid deposition, but is estimated to have made a comparable contribution to xS historically. Chloride concentrations in UWMN sites also fell at a similar rate to xSO_4^{2-} concentrations, indicating this trend was driven by a reduction in HCl deposition, and that controls on common pollution sources (particularly coal burning power stations) were responsible.

Although trends in total N deposition mostly lacked clear direction (CBED data for reduced available from 1999 only), significant downward trends in nitrate (NO_3^-) concentration in UWMN waters were identified in around one third of the UWMN sites. As these are the more acidic and acidified sites on the network, their declining NO_3^- concentrations appear to reflect increased capacity of their catchment soils, as they recover from acidification, to retain, cycle and possibly denitrify deposited reactive N, more than to changes in N deposition per se.

Only one site, Llyn Cwm Mynach, that has recently been undergoing major catchment disturbance by forest management activities, experienced an increase in NO_3^- concentration. More generally, the changes in NO_3^- concentration provided no evidence to suggest that long-term accumulation of reactive N is leading to an increase in NO_3^- leaching (i.e. as predicted under the "N saturation" hypothesis).

The large reductions in acid anion (i.e. $xSO_4^{2-} + NO_3^- + Cl^-$) concentration across the UWMN have been partially balanced by reductions in base cation concentrations, but also by reductions in acid cations (i.e. Al^{3+} and H^+) in the most acidified waters, increases in organic acid anions (as indicated by dissolved organic carbon concentration (DOC)), and, in the least acid-sensitive waters, increases in bicarbonate anion concentrations. In general, the larger the reduction in acid anion concentration the more rapid the increase in pH, ANC, Gran alkalinity and DOC and decrease in Al^{3+}.

Pronounced increases in Gran alkalinity in several Scottish sites since around 2014, appear to be linked to a prolonged period of below-average water tables and consequent increased contributions from groundwater, but further years of data are required to verify this.

The more rapid reduction in acid anion concentrations experienced by forested catchments, relative to their paired moorland sites, has been accompanied by more rapid increases in pH and reductions in Al^{3+}, although in two of the three site pairings, water in the forested catchments has remained slightly more acidic in the most recent years of monitoring.

Concentrations of DOC have approximately doubled in the majority of sites across the network. This is largely due to an increase in the solubility of soil organic matter as soil water ionic strength has declined in response to a reduction in pollutant deposition. The resulting increase in organic acidity has partially offset the increase in water pH, once expected to be one of the main responses to acid emission controls.

In some of the UWMN lakes, the increase in water colour associated with the rise in DOC is estimated to have brought about a major reduction in the proportion of the lake bed that remains within the theoretical photic zone (i.e. the depth range within which aquatic photosynthesis is possible).

Acid Neutralising Capacity (ANC) has increased significantly in all but the least acidified sites, and at a number of sites has progressed from being negative in most samples to largely exceeding the ANC_{crit} threshold of 20 $\mu eq\ L^{-1}$. In a minority of sites, ANC remains predominantly, or always, below this limit. For the majority of sites that are deemed to have acidified, current ANC remains on average 27 $\mu eq\ L^{-1}$ below that estimated by the dynamic acidification model MAGIC.

Dissolved organic matter (measured as DOC) also makes a contribution to water acidity, and it has been shown that an ANC of 20 $\mu eq\ L^{-1}$ is unlikely to provide sufficient protection for some of the more acid-sensitive species in browner (i.e. higher DOC) waters such as Loch Grannoch. On the other hand, the 20 $\mu eq\ L^{-1}$ threshold may be unnecessarily high for waters with very low DOC concentrations such as Lochnagar. Consequently, the ANC level required to provide protection for more acid-sensitive biota will have risen as DOC concentrations have increased, and a dynamic, DOC-adjusted ANC_{crit} metric (i.e. $ANC_{crit\text{-}ORG}$) may therefore be more appropriate for assessing progress in hydrochemical health than a nationally fixed value. Application of a dynamic approach shows that the long-term rise in ANC is likely to have been either more or less ecologically beneficial for waters with low and high DOC concentrations respectively, than previously assumed.

The extent to which the ANC of UWMN waters has increased toward or beyond both ANC_{crit} and $ANC_{crit\text{-}ORG}$ levels, is dependent on the relationship between the acid deposition flux and the current estimated flux of base cations in runoff (a measure of current catchment buffering capacity). Over the period 2015-2019, the ANC of four UWMN sites, Scoat Tarn, Loch Grannoch, Round Loch of Glenhead and Blue Lough remained substantially below their site-specific $ANC_{crit\text{-}ORG}$ levels. These sites exhibit particularly low rates of base cation production and are experiencing some of the highest residual acid deposition loads on the network. The ANC of a further three sites, Lochnagar, Afon Hafren, and Afon Gwy has also continued to frequently fall below their current $ANC_{crit\text{-}ORG}$ thresholds. In most of these cases, further reduction of the acid deposition load, to levels closer to those now experienced in the lowest deposition regions of the UK, should enable ANC to increase to a more ecologically benign condition. In the longer term, a gradual increase in soil base saturation, as weathering rates start to outpace acid deposition rates, should also make these sites more resistant to the prevailing deposition load.

The acidity of streamwater during acid episodes, which occur during high discharge- and sea salt deposition-events, has declined substantially in all sites that have experienced significant reductions in acid deposition. This should be conducive to the gradual re-colonisation of the historically more acidified streams by acid-sensitive taxa.

The water chemistry of UWMN sites with more westerly locations has always been strongly influenced by sea salt deposition, and as pollutant levels continue to fall, the importance of major storm events that generate sea salt aerosol has increasingly come to dominate short term fluctuations in surface water ionic strength, acidity, DOC concentrations and fluxes, and associated water colour. There is no indication of any directional change in sea salt inputs that could, for example, be linked to long-term changes in climate, over the UWMN monitoring period.

Trends in aquatic biota

There have been major changes in the epilithic diatom and macroinvertebrate communities of the majority of UWMN sites. Fourteen and twelve sites respectively (out of 23) experienced a 50% or more turnover in species composition over the full monitoring period, while monotonic change in these assemblages (i.e. in a single direction), has been the dominant mode of interannual variation in sixteen and twelve sites respectively.

Biological indicators of water pH have been developed for both biological groups (DAM for epilithic diatoms and LAMM for lake macroinvertebrates and AWICsp for stream macroinvertebrates). There is strong agreement between the sites showing positive trends in these metrics and the sites that are undergoing the clearest chemical recovery from acidification. Either or both biological metrics have increased in nearly all of the UWMN sites that are undergoing significant increases in ANC, regardless of whether ANC remains below, has reached, or has exceeded ANC_{crit} and $ANC_{crit\text{-}ORG}$ levels.

Of the fourteen sites that show a significant increase in pH, all also exhibit significant trends in epilithic diatom communities that are broadly reflective of a transition to less acid tolerant taxa. At lake sites there is also a strong correlation between the magnitude of diatom species change over the period of monitoring and the magnitude of pH change. We did not find a significant relationship between the magnitude of diatom species change and pH change in the UWMN streams, but this could be due to the challenges of temporally linking chemistry and biology of these highly dynamic systems, e.g. having chemistry data of sufficient time resolution to explain the fine-scale temporal dynamics of the biofilm.

Differences in rates of change in the epilithic diatom communities between paired forested and moorland sites largely mirror differences in chemical recovery. In three out of four cases (Loch Chon vs Loch Tinker, Afon Hafren vs Afon Gwy and Loch Grannoch vs Round Loch of Glenhead) diatom turnover has been larger in the forested sites.

There are differences in temporal recovery patterns in epilithic diatom assemblages between recovering acidified sites. Some show relatively linear recovery throughout the record whereas others indicate that recovery was largely restricted to the early years of monitoring and appears to have levelled off more recently. There is no clear chemical explanation for this between-site variation in diatom recovery trajectories. At some sites, the increase in organic acidity (indicated by the rise in DOC) may have partially confounded the expected rise in pH, and at two of the least deposition impacted (and non-acidified) sites may account for slight reductions over time in the DAM index – indicative of very slight acidification.

Some UWMN sites show a remarkable degree of recovery in diatom assemblages. Loch Chon and the River Etherow, for example, have evolved from chronically acidified states with a flora dominated by acid tolerant taxa, to ones characterized by acidiphilous (acid loving) diatoms indicative of naturally-acid soft waters.

This transition raises the question of the extent to which the contemporary diatom communities are fully recovered from acidification. A comparison of the proportions of key acid tolerant and acid sensitive taxa in lake epilithic samples with the same taxa in pre-acidification lake sediments suggests that the current diatom floras of six out of ten lakes continue to be characterised by acidobiontic taxa (i.e. those common in waters below pH 5.5), indicative of acute acidification and lack the acid sensitive taxa that were present prior to acidification. A more robust comparison of contemporary and pre-acidification communities is provided by the comparison of pre-acidification lake sediments with modern sediment trap samples. This was last explored for UWMN lakes in the previous interpretive exercise and will be re-visited, subject to the availability of resources, once the UWMN sediment trap diatom record is fully updated.

The majority of sites that have been recovering from acidification have undergone change in their macroinvertebrate assemblages. For some (e.g. Blue Lough) the improvement has been modest, but for other sites (e.g. Loch Chon, Round Loch of Glenhead, and Dargall Lane) there has been a substantial change in the community, with acid-sensitive taxa becoming well-established.

The River Etherow has undergone a remarkable transformation in its macroinvertebrate fauna, from a species-poor macroinvertebrate community dominated by acid-tolerant taxa, to one supporting a much more diverse macroinvertebrate community, including an increasing number of acid-sensitive taxa. This is particularly interesting given that the River Etherow continues to experience occasional highly acidic episodes, normally associated with high discharge events, and provides a clear demonstration that such events do not pose a major barrier to the recolonization of acid-sensitive taxa.

It is not possible to confidently assert if and when a river or lake macroinvertebrate community has fully recovered from acidification. While the Water Framework Directive provides tentative reference values for LAMM scores, these are highly generalised, covering only two humic (i.e. DOC) site classes without any consideration for other critical aspects of the lake water chemistry, geography or underlying geology.

There are a number of possible barriers that might prevent biological recovery keeping pace with chemical recovery. These include the continued occurrence of acid episodes (although see above), limitations on the dispersal of acid-sensitive colonists from unimpacted source areas, hysteresis in the recovery trajectory due to biological interactions within the acid-tolerant assemblage, and climate change or other effects disrupting a straightforward recovery from acidification. Further monitoring and analysis will allow a more in depth testing of these hypotheses and a clearer understanding of the prospects for the community structures of the more acidified sites to ever fully return to those that may have characterised the sites prior to acidification.

Conclusions and forward look

Over the decade since the UWMN monitoring data were last formally assessed, the deposition of acid pollutants to acid-sensitive lake and stream catchments across the UK has continued to decline. This has stimulated further improvements in the chemical quality of lake and stream water, and the freshwater biological communities of an increasing number of UWMN sites are now demonstrating changes consistent with strong ecological recovery from acidification. Changes in biological communities has been occurring at most sites where water acidity has been declining and regardless of where sites lie on an ANC gradient. However, geochemical modelling suggests that the ANC of most recovering sites remains substantially below pre-acidification levels, and recent diatom assemblages of most acidified but recovering lakes appear to represent more acidic conditions than those in pre-acidification lake sediments.

Similar improvements are being reported for long-term monitoring sites in acid-sensitive regions over much of industrialised North America and north-western Europe (as for example represented by the ICP Waters network). They are a testament to the international cooperation developed to address one of the largest transboundary pollution issues ever to arise, and serve as a demonstration of what can be achieved where there is a common international resolve to mitigate an environmental problem.

Despite the improvements across much of the UWMN, the chemistry of waters draining some of the more poorly buffered catchments that are also receiving the largest residual acid deposition loads, remains potentially too acidic to allow the establishment of some of the UK's most acid-sensitive soft water taxa. The extent to which further chemical recovery is possible, and the timescale this might involve, will depend on the extent to which S and N deposition in these regions can be further controlled, the extent to which further reductions in NO_3^- leaching may occur (e.g. as a consequence of increased terrestrial retention of N), and the degree to which base cation generation via geological weathering is able to begin to outpace the local acid deposition rate. Further monitoring of these sites, alongside better buffered sites and those in lower deposition regions, will clearly be necessary to track further progress.

Historically, afforested UWMN sites acidified more than moorland equivalents. While they have been recovering faster over the monitoring period, mostly remain slightly more acidic. All of the UWMN afforested catchments are undergoing substantial changes, under UK Forestry Standard Guidelines, particularly with respect to a drive to replace coniferous monocultures with mixed coniferous/deciduous stands, and the long-term UWMN records will serve as invaluable baselines in assessing how these and other forested watersheds are influenced by such procedures in the coming years.

Additional constraints are likely to limit the extent of further biological improvements. While the biology of several of the UWMN lakes appears to remain in a more acidified state now than prior to acidification, it is also possible that some of these fresh waters have developed into phosphorus limited systems that have no pre-industrial precedent, as a consequence of the rise in availability of reactive nitrogen in the form of NO_3^- relative to pre-industrial times. It is encouraging, therefore, that NO_3^- concentrations appear to be falling in some of the most impacted systems, bucking the expectation of increased NO_3^- leaching as a consequence of progressive soil N saturation. There is a clear need, however, to continue to monitor biological trajectories and gain a clearer insight into the degree to which freshwater ecological structure, and biogeochemical and ecological functioning is being restored. Repeat assessments of trends in the UWMN sediment trap diatom data in the context of pre-industrial diatom community structure (not provided in this report) should be very informative in this respect.

More generally, fluctuations and directional change in the biogeochemistry of UWMN sites, including concentrations and fluxes of dissolved organic matter, are becoming increasingly dependent on temporal patterns in runoff and sea salt deposition. There has been little net warming of UWMN waters over the 1988-2019 monitoring period, but UKCP18 climate change projections suggest that annual mean air temperatures across much of the UK uplands may warm by an order of 1.5 to over 4.0 °C by 2080 relative to 1980. Warming is expected to accelerate the microbial decomposition of soil organic matter and bring about further increases in DOC, particularly in the waters of the more peat dominated UWMN catchments. The uplands make a substantial contribution to the UK's overall flux of organic carbon from the land to the sea, and development of a clearer understanding of the environmental factors influence its spatial and temporal variability is important in the development of the UK's Net Zero strategy.

Warming, "browning" (by increased DOC), and change in the timing, frequency and intensity of storms, may also change lake stratification behaviour that determines the extent to which lake water remains mixed and oxygenated, and influences redox processes that affect the mobility and biological availability of sediment-borne nutrients. Although not assessed in this report, the UWMN thermal profile measurements are the only detailed source of long-term temperature data for upland UK lakes, and will prove increasingly valuable in determining how these systems are responding to global warming over the coming decades.

Increased dissolved organic matter concentrations have consequences not only for the aquatic productivity of upland waters, through light limitation of photosynthesis, but also for the quality of upland drinking water resources. A large proportion of the UK's drinking water is derived from upland catchments, and water companies have been facing increasing treatment costs due to increases in DOC - up to now driven primarily by deposition-driven reductions in soil water ionic strength. Highly detailed long-term upland hydrochemical records such as those produced by UWMN are already proving vital sources of evidence for developing an understanding the key drivers of DOC change and what the future impacts of climate change may be for these vital UK assets.

In summary, the UK UWMN has proved, and is continuing to prove, a highly effective source of evidence for assessing the efficacy of emissions reduction policy in restoring damage upland freshwater ecosystems. But as acid deposition loads fall to levels possibly not experienced since the early stages of the industrial revolution, UWMN monitoring is also providing new insights into how these vitally important ecosystems, and drinking water resources, may remain compromised by the eutrophying influence of reactive N, may be responding to evolving forest management practices and may be influenced by projected changes in climate. The value of the network to science and policy therefore continues to address issues central to determining air quality impacts on ecosystems, and is also becoming increasingly pertinent in the fields of climate change, biodiversity loss and the development of Net Zero strategy.

1 Introduction

The environmental problems posed by acid deposition were first highlighted in the mid-nineteenth century by the Scottish chemist Robert Angus Smith. He was first to us the term “Acid Rain” to describe the phenomenon of unusually acidic rainfall over cities in the north of England and southern Scotland that he linked to coal combustion. It took a further century for national governments to recognise the extent to which the atmospheric deposition of anthropogenically-derived acidic compounds had harmed soils, terrestrial vegetation, surface waters and urban infrastructure. Action to control emissions was eventually coordinated under the auspices of the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP). A series of international atmospheric emission protocols, including the First Sulphur Protocol, Second Sulphur Protocol and the Multi-Pollutant Multi-effect Protocol, set governments increasingly stringent targets for emissions of acid gasses to the atmosphere (RoTAP, 2012). In addition, the EU National Emissions Ceilings Directive (NECD), most recently repealed in 2018, committed EU members to limiting emissions of five pollutants (sulphur dioxide, nitrogen oxides, volatile organic compounds, ammonia and fine particulate matter) responsible for acidification, eutrophication and ground-level ozone pollution (https://www.eea.europa.eu/themes/air/air-pollution-sources-1/national-emission-ceilings). Article 9 of the revised NECD requires member states to implement monitoring systems to identify negative impacts of air pollution on ecosystems (acidification, eutrophication and ozone damage) across sensitive habitats (see Section 1.2).

The UK Upland Waters Monitoring Network (UWMN) was originally established as the UK Acid Waters Monitoring Network (AWMN), specifically to assess the impact of air pollution emission controls on the chemical and biological status of acid-sensitive upland lakes and streams. The original network came into operation in 1988 and has since provided fundamental evidence to a number of international and national air quality impact assessments, including Defra’s Review of Transboundary Air Pollution (RoTAP, 2012). It provides UK data and expertise to the UNECE International Cooperative Programme for assessment and monitoring of the effects of air pollution on rivers and lakes (or ICP Waters), and is a central data resource for surface waters within Defra’s developing UKAPIENS project (see http://www.apis.ac.uk/).

1.1 Impacts of air pollution on upland waters

Acid deposition results from the emission of acid gasses to the atmosphere, particularly sulphur dioxide, oxides of nitrogen and hydrogen chloride. These are generated principally through the burning of fossil fuels by power stations, heavy industry, road transport and domestic heating systems. After further oxidation in the atmosphere, reactions with water, either in the air, or once deposited (as dry deposition) to surfaces on the ground, result in the formation of strong acids, including sulphuric acid, nitric acid and hydrochloric acid. Since the advent of the industrial revolution, acid emissions and deposition loads have varied substantially across the UK. Acid loads have tended to be largest in areas close to major urban and industrial emission sources, and in general decline along a gradient from central England to northern and western Scotland and Northern Ireland, although they are also enhanced in high rainfall upland regions as a consequence of increased scavenging of pollutants from the atmosphere.

The agricultural sector makes a further important contribution to nitrogen emissions, particularly through the release of ammonia from urea-based fertilisers, slurry and intensive pig and poultry units. Ammonia can be taken up directly by plants via their stomata, or may react in the atmosphere or on the ground with water to form ammonium (NH_4^+). Plant root uptake of NH_4^+ ions involves the release of H^+ ions, thereby also contributing to soil acidity.

The impact of acid deposition on water quality depends on the nature of catchment soils and the underlying geology. Chemical weathering of the latter generates alkalinity and base cations (such as calcium (Ca^{2+}) and magnesium (Mg^{2+})) that bind to negative ion exchange surfaces on soil particles. A proportion of the soil-bound base cations are subsequently leached in runoff – with their net charge balanced by accompanying anions, i.e. bicarbonate (HCO^{3-}), strong acid anions (i.e. sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-)) or weak organic acids. For as long as rates of base cation generation by weathering exceed the rate at which they are removed, runoff will remain at most only slightly acidic. However, when and where the rate of deposited acidity exceeds the weathering rate, soils become progressively more acidic as soil-bound base cations are replaced by hydrogen (H^+) and aluminium (Al^{3+}) ions, and soil base cation supply eventually becomes insufficient to continue to buffer the incoming acidity.

In the event of the latter, H^+ and Al^{3+} ions increasingly accompany the acid anions in runoff, resulting in progressively more acidic water. The difference in equivalent concentrations of base cations and strong acid anions (when all concentrations are determined in units of charge equivalence) provides one definition for Acid Neutralising Capacity (ANC). The occurrence of significant concentrations of Al^{3+} (or labile aluminium) and low or negative ANC levels, therefore, both provide some indication of acidification status. Lake-water or streamwater pH is less diagnostic in this respect, as the pH of non-acidified sites receiving high concentrations of naturally produced organic acids (as indicated by high concentrations of dissolved organic carbon (DOC), e.g. in waters draining peatland catchments) can be relatively low, e.g. < pH 5.4 without an accompanying increase in Al^{3+} concentrations (most aluminium being bound to organic complexes and therefore not in ionic form). The chemistry of such organic-rich acidic waters is generally considered relatively benign biologically, although low levels of water transparency associated with high DOC concentrations can also influence aquatic ecosystems by restricting the availability of light for aquatic photosynthesis.

Reductions in water pH (i.e. increases in H^+ concentration), increases in Al^{3+} concentration, and the loss of bicarbonate alkalinity, can affect aquatic ecosystems in various ways. These range from reductions in the rate of bacterial decomposition of organic matter (e.g. Leuven and Wolfs, 1988); to reduced availability of carbon dioxide in sediments to support aquatic photosynthesis of some aquatic plant species (Farmer, 1990) and large changes in algal assemblages (e.g. Birks et al., 1990); to direct toxicity effects on fish (Kroglund et al., 2008) and macroinvertebrates (Weatherley and Ormerod, 1987). In extreme circumstances entire groups of species can be lost; for example salmonids, including Atlantic salmon and brown trout, and various aquatic macroinvertebrate taxa, are highly sensitive to elevated concentrations of labile aluminium, and their populations were heavily affected in acidified waters at the height of the acid rain problem.

Chemical weathering of the siliceous rock types that characterise most upland regions of the UK tend to be slow relative, for example, to those more calcareous regions in the south and east. Consequently, UK upland surface waters tend to be particularly vulnerable to the effects of acid deposition.

The extent to which lakes across the UK have acidified since the onset of the industrial era has been demonstrated using diatom pH reconstructions (Battarbee et al., 2014a). Freshwater diatoms comprise a diverse group of species, many of which thrive over relatively species-specific restricted pH ranges. The relative abundance of diatom species in a water body therefore provides an indication of water acidity. Diatom cells are encased in siliceous frustules that are robust to decomposition and accumulate over time in lake sediments. Lake sediment cores therefore provide a chronological record of change in diatom communities (Renberg, 1990), and thus, by inference, change in water pH, while the age of the sediment can be determined using radiometric (^{201}Pb) dating (Appleby, 2001). Application of these approaches to UWMN lakes around the time the AWMN was initiated demonstrated that lake water acidity was broadly stable prior to the early 19th century, after which the majority of UWMN lakes became progressively more acidic (Patrick et al., 1993). The timing of the initial inflection in diatom-inferred pH (i.e. the onset of acidification) in these cores tended to coincide with the point at which heavy metal contaminants and spherical carbonaceous particles (Rose, 2015), both indicators of fossil fuel combustion, started to increase, and thus provided strong support for the hypothesis that the acidification of these systems was tightly linked with effects of atmospheric pollutants from fossil fuel burning sources. The declines in diatom-inferred pH continued until rates of acid deposition peaked in the mid-1970s to early-1980s. The only UWMN lake not to show clear signs of acidification over the industrial period are Burnmoor Tarn (situated in a polluted region but relatively well buffered by calcite in the catchment's glacial till), and Loch Coire nan Arr and Loch Coire Fionnaraich in the far northwest of Scotland, where acid deposition remained at low levels throughout the industrial period.

1.2 History of the network

As part of its commitments under the UNECE protocols, the UK Department of the Environment supported a range of scientific research and monitoring to assess acidification status of the UK's surface waters and the efficacy of acid emissions controls in improving their ecological condition. The UK Acid Waters Monitoring Network (AWMN) was established in 1988 for this purpose. It was designed and managed from the outset by UCL ENSIS Ltd, and for most of its duration has involved a scientific partnership comprising UCL, the Centre for Ecology & Hydrology (CEH - now UKCEH), Queen Mary University of London (QMUL) and Marine Scotland, amongst other organisations. As part of its national role, the AWMN has also contributed data and scientific expertise to the UNECE International Cooperative Programme (ICP) Assessment of Acidification of Rivers and Lakes, otherwise known as ICP Waters.

After approximately 20 years of operation, the name of the network was changed to the Upland Waters Monitoring Network (UWMN) to recognise its widening potential to address issues relating to climate change, nitrogen deposition and upland land use (Curtis et al., 2014). Defra ceased supporting the network in 2016, after which financial contributions from Natural Resources Wales (NRW), Scottish Natural Heritage (SNH – now NatureScot), Welsh Government (WG) and Forest Research (FR), coupled with in-kind contributions from UKCEH, UCL, Marine Scotland, and considerable volunteer effort, allowed the network to continue under ENSIS Ltd management, albeit in a significantly restricted state.

Following the closure of ENSIS Ltd in March 2018, management of the network passed to UKCEH. Over the financial years 2018-20, UKCEH focussed primarily on maintaining UWMN water sampling (much of which was provided by volunteers and in-kind support), water chemistry analysis (provided by NERC National Capability funding) and water chemistry data management. Complementing this activity, UKCEH established, and have since annually renewed, a UWMN funding partnership agreement with NRW, SNH, WG, FR. This supported wider data management, management/development of the UWMN website and oversight of the continued collection of biological samples (most of which has been underpinned by UCL-based funding sources and considerable volunteer effort). Separate support was provided to cover water chemistry analysis of samples from the UWMN site, the River Etherow, from the Moors for the Future under the Peak District National Park Authority (with funding provided by Yorkshire Water, United Utilities and Severn Trent Water).

The recent (2016) revision of the National Emissions Ceilings Directive (NECD) obliged member states to report on the impact of air pollutants on sensitive ecosystems ((2016/2284/EU). The UK drew up a list of sites and datasets to meet the reporting recommendations under the new Defra-funded UK APIENS project, and UWMN sites and records were identified as a principal resource for UK freshwater reporting. A list of UWMN sites was reported as part of the UK's first submission to the European Commission in July 2019. Since departure from the EU, UK air quality policy is now developed around the UK's own National Emissions Ceilings Regulations (NECR) which align closely with the NECD with respect to reporting obligations. Consequently there remains a need for UWMN data for national reporting of air pollutant impacts on freshwater systems, while the UWMN continues to provide data to the UNECE ICP Waters programme.

Following reductions in UWMN funding from 2014, ENSIS Ltd continued to maintain most biological sampling, but a significant backlog of unanalysed biological samples developed. Between 2019-2021, however, Defra has supported the taxonomic work necessary to bring the UWMN epilithic diatom and macroinvertebrate datasets largely up to date. Some of this work has only recently been completed, and the fully updated time series were not available in time for the data analysis reported here. Consequently, the time-spans of the datasets analysed and reported in this report are 1988-2019 for water chemistry, 1988-2018 for epilithic diatoms and 1988-2016 for aquatic macroinvertebrates. Resources have also now been secured to bring the sediment trap diatom data fully up to date. Aquatic macrophyte data have continued to be collated by Ewan Shilland as part of a PhD study, but electrofishing for salmonids has not been carried out since 2014.

1.3 Broad network description

A detailed description of the current network is provided on the project website (https://uwmn.uk). The UWMN currently conducts regular physical, chemical and biological analysis at around 25 sites, of which 22 have been monitored for over 20 years (most over 30 years). Biological measurements are targeted on groups with known sensitivity to water acidity, as well as other stressors, including eutrophication and climate change. The key biological groups monitored are 1) epilithic diatoms, unicellular siliceous algae that grow on rocky substrates in streams and around lake perimeters, 2) aquatic macroinvertebrates, that are most abundant in well aerated riffle stretches of streams, and shallow water locations in lakes, 3) aquatic macrophytes, higher aquatic plants, mosses and liverworts, and 4) sediment trap diatoms, diatoms that accumulate in deep water traps in lakes, the relative species abundance of which can be compared directly with historical diatom communities recorded in lake sediment cores. Some of the collected sediment has also been analysed for heavy metals and carbonaceous particles in unfunded work conducted at UCL. Salmonids (mostly brown trout, and at a minority of sites Atlantic salmon) were electrofished in streams and the outflows of lakes until 2014 when monitoring ceased due to reductions in funding.

1.4 Key observations prior to this report

Over its history, the AWMN, under UCL/ENSIS Ltd management, has carried out a series of interpretations of the amassing datasets on behalf of Defra. These have been published in a sequence of reports (i.e. (Monteith and Evans, 2005, 2000; Monteith and Shilland, 2007; Patrick et al., 1993), available to download from the UWMN website (https://uwmn.uk), and have been expanded upon in a series of scientific publications, some of which are cited below. The most recent interpretive report (Kernan et al., 2010) covered data collected up to 2007 only, so there is clearly a need to take stock of the considerable amount of data that has accumulated since. The key points to emerge from the reports and UWMN-papers published to date are as follows.

1) Between 1988 and 2007 there had been a very large reduction in the deposition of acidic pollutants, and particularly sulphur, across much of the UK (Monteith et al., 2014). This was directly attributable to reductions in acid emissions both nationally and internationally. The largest reductions in deposition occurred in the south and east of the UK with rates of reduction declining further north and west;

2) While deposition reductions had been substantial, by 2007 there remained a significant spatial pattern in residual acid deposition rates, with the largest acid loads remaining in parts of the country that had historically been the most polluted, i.e. central and northern England and southwest Scotland;

3) There was mounting evidence for widespread, but spatially variable, improvements in the water chemistry and aquatic biological assemblages of the more acid-sensitive and chronically acidified lakes and streams. This evidence began to emerge after about 15 years of monitoring and had become clearer as further time had elapsed;

4) The more acid-sensitive lakes and streams, as indicated by low base cation concentrations, had generally shown the largest acidity responses, in terms of reductions in labile aluminium concentrations, and increases in pH and alkalinity;

5) Acid Neutralising Capacity (ANC) had risen over time at all sites experiencing significant reductions in non-marine SO_4^{2-} concentrations. By 2007, ANC at some historically acidified sites had risen above the widely applied “critical level” of 20 µeq L^{-1}. However, ten sites continued to exhibit a mean annual ANC of <20 µeq L^{-1}, and hydrochemical modelling using the MAGIC model indicated that the ANC of all but two UWMN sites was still significantly below pre-acidification levels;

6) With respect to future chemical recovery, much would depend on whether theoretical “nitrogen saturation”, i.e. the accumulation of deposited reactive nitrogen to a point of first seasonal, and ultimately year round, leaching of nitrogen in the form of nitrate, would be realised. Some UWMN sites in more nitrogen-polluted parts of the UK had shown evidence of nitrogen saturation at the outset of monitoring, but by 2007 there was little indication of rising nitrate concentrations across the network;

7) The UWMN data had demonstrated that part of the long term reduction in acid inputs was attributable to reductions in HCl deposition (see also Evans et al., (2011)) . This had been largely

ignored as a contributory factor in the early phases of the UWMN and analyses of comparable datasets from other countries;

8) A significant element of the chemical response to a reduction in the deposition of "mineral" acidity (i.e. inorganic contributions from xSO_4^{2-}, NO_3^- and Cl^-) had been a cross-network increase in the concentration of organic acids (as indicated by the concentration of DOC), mostly derived from catchment soils (see also Monteith et al., (2014)). This had resulted in weaker pH increases in most UWMN sites than had originally been predicted using geochemical models such as MAGIC. The UWMN was the first network internationally to identify a regional increase in DOC concentration (Freeman et al., 2001), and this has since led to research demonstrating a strong link between the rate of reduction in indicators of acid deposition, e.g. SO_4^{2-} concentration and the rate of increase in DOC (Monteith et al., 2007). The increase in DOC must therefore be considered an integral part of the wider acidification recovery process.

9) Water acidity had also been shown to be vulnerable to oscillations in climate and extreme events, particularly with respect to sea salt deposition episodes, periods of high rainfall and variations in the severity of winter temperatures. Several of these features can be linked to regional-scale variations in climate teleconnection metrics such as the North Atlantic Oscillation Index (NAOI) (Evans et al., 2001), that determines both the degree of winter storminess (a precursor for major sea salt deposition events), winter precipitation (a key control on runoff acidity) and winter temperature (linked to nitrate release).

10) Clear signals were emerging in epilithic diatom, macroinvertebrate and aquatic macrophyte data (Monteith et al., 2005; Murphy et al., 2014) that were broadly consistent with the degree of change in water acidity. There have also been significant increases in brown trout densities in some of the most acidic UWMN sites (Malcolm et al., 2014), although fish monitoring ceased in 2014 due to funding cuts.

11) In general, by the time of the 2010 report, biological changes have not been as substantial as had been expected given the size of recent improvements in water chemistry. It has remained unclear to what extent this may be due to water quality remaining in a partially acidified condition, hysteresis (i.e. lagged biological responses) or over-estimation of appropriate biological recovery targets (Monteith et al., 2005). However, comparisons of diatom assemblages in recently collected UWMN lake sediment trap samples (i.e. modern sediment) with those in pre-acidification sediments demonstrated considerable and continuing differences between pre-acidification and modern biological communities (Battarbee et al., 2014a).

In summary, UWMN data gathered up to 2007 had provided clear evidence of widespread, and ecologically positive, responses to the reductions in acid emissions that had been achieved over recent decades. However some chemical changes had been more muted than originally predicted, and most of the biological changes had been surprisingly subtle for the degree of chemical change. Considerable further change was expected with respect to continuing declines in acid deposition, lagged effects on water chemistry resulting from gradual improvements in soil base status, and possibly lagged biological responses to improving water chemistry. It was also acknowledged that societal interest in the chemical and ecological health of the UK's upland waters extends well beyond the surface water acidification story alone (Curtis et al., 2014). These intensively monitored sites are broadly representative of a much wider range of upland water resources that are vital sources of drinking water, have a major role in the processing of organic matter and thus in the terrestrial-aquatic carbon cycle, and serve as important refuges for a range of aquatic species, some of which are particularly vulnerable to changes in climate. It was recognised, therefore, that as acid deposition began to level out, the UWMN would continue to provide important insights into how these critically important water resources are being affected by the eutrophying effects of nitrogen, climate change and changes in the use and management of the uplands.

1.5 Focus of this report

Due to the resources available, it was agreed with Defra to restrict the focus of the current interpretative analysis to the currently funded and most up to date time series available, i.e. water chemistry, epilithic diatoms and macroinvertebrates. We concentrated particularly on addressing the following key questions.

1) What are the general patterns of change and variation in the UWMN water chemistry, epilithic diatom and macroinvertebrate datasets?
2) To what extent can changes in water chemistry be linked to changes in the deposition of atmospheric pollutants, and to the geographical, biogeochemical and land-use characteristics of sites?
3) Are the acidity, and wider chemical, characteristics of UWMN lakes and streams continuing to respond to long-term reductions in atmospheric deposition? Is there evidence that chemical change is tailing off as acid deposition loads approach those probably not experienced since close to the onset of the industrial revolution?
4) How do current water chemical acidification metrics compare with modelled chemical reference conditions?
5) Are the biological communities of UWMN lakes and streams continuing to respond to recovery from acidification?
6) What are the prospects for further chemical and biological recovery from acidification?
7) What other factors are influencing recent chemical and biological trends and what implications could these have for future biogeochemical and ecological trajectories of UK Upland Waters.

2 UWMN Sites

The lakes and streams of the UK Upland Waters Monitoring Network (UWMN) (Figure 2.1) cover wide ranges of altitude, acid-sensitive geology and organic-rich soil types. Further details on site characteristics are provided on the UWMN website (https//uwmn.uk) and in the site-specific section of this report's Appendix. Palaeoecological analysis of sediment cores demonstrated that most UWMN lakes acidified over periods of between 100 – 200 years prior to the 1980s (Juggins et al., 1996). The chemical characteristics of most of the stream sites at the outset of monitoring were also indicative of an acidified condition, in that they showed unnaturally high concentrations of acid anions, relative to base cations (i.e. a low Acid Neutralising Capacity), and high concentrations of labile aluminium.

Chemical and biological monitoring of most sites commenced in 1988. Blue Lough and Coneyglen Burn were included in the network 1-2 years later, while Afon Gwy replaced a neighbouring stream site in 1991 following access problems with the latter. The water chemical monitoring of Narrator Brook was moved approximately 1 km upstream in 1991 to remove any influence from conifer forestry. Monitoring of Loch Coire nan Arr, an acid-sensitive, low deposition control site in the far north west of Scotland ceased following the installation of a dam on the outflow to serve a local fish farm in 2002. It was replaced by the nearby Loch Coire Fionnaraich, a more exposed and less vegetated site, but with similarly sensitive (i.e. poorly buffered) water chemistry. In recent years, additional sites and measurements have been introduced to the network in order to broaden the range of acid sensitivity, increase the potential to identify potentially eutrophying influences of atmospherically deposited nitrogen, and begin to document the longer term impacts of climate change on UK upland waters. The chemical and biological time series available from these sites are currently short and have not been examined as part of this report which has a focus on assessing multi-decadal trends.

A key requirement for initial site selection was that the catchments should be subject to minimal anthropogenic activity. Partially afforested catchments were the one exception to this rule. Forested catchments have been shown to be more vulnerable to acidification as a consequence of the increased amount of interception of acid pollutants by forest canopies relative to grassland and heathland equivalents (Kreiser et al., 1990). The five partially forested UWMN sites are Allt na Coire nan Con, Loch Chon, Loch Grannoch, Llyn Cwm Mynach, and the Afon Hafren. Some of these can be paired with neighbouring moorland sites to allow testing of forestry-related hypotheses concerning recovery. Loch Chon is thereby linked with Loch Tinker, Loch Grannoch with the Round Loch of Glenhead, and the Afon Hafren with the Afon Gwy. In addition, Llyn Cwm Mynach has at times been paired with Llyn Llagi, but the relatively large distance and differences in underlying geology between these two sites limit the scientific value of the comparison. Significant felling, and to some extent replanting has taken place within all forested catchments during the monitoring period. The processes associated with felling and re-planting (detailed in the site-specific sections of the Appendix) are anticipated stages in the evolution of these catchments and thus an integral part of the experimental design.

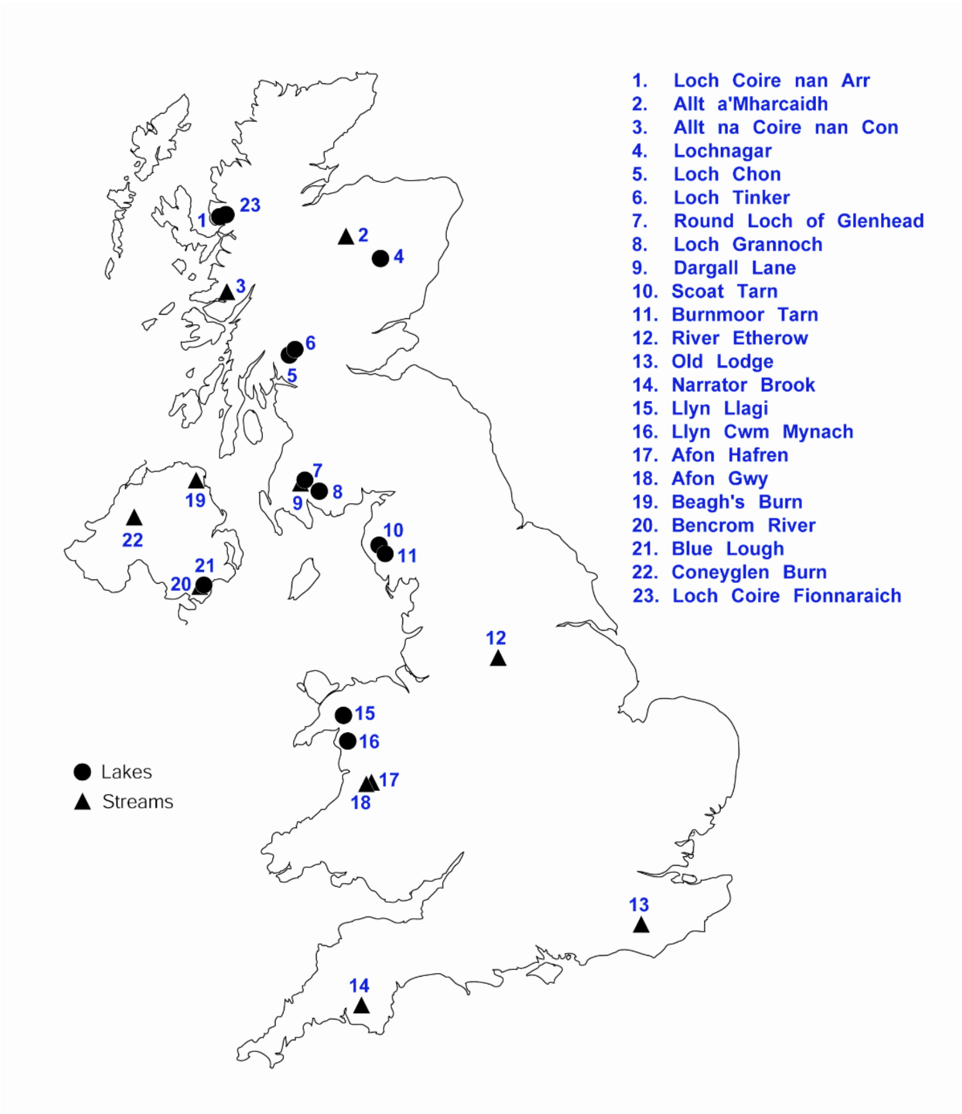

Figure 2.1 Location of UK Upland Waters Monitoring Network lakes and streams

3 Water chemistry trends

Authors: Don Monteith, David Norris, Sam Tomlinson & Chris Evans

3.1 Introduction

In this chapter we report changes in water chemistry in the context of modelled change in pollutant deposition over the same period. We describe spatial patterns relating to geography and (in the case of forested vs non-forested paired sites) contrasting land-use, and consider the evidence for cause-effect relationships.

3.2 Methods

3.2.1 Atmospheric deposition

Modelled estimates of annual total non-marine oxidised sulphur (S) deposition, total oxidised nitrogen (N) deposition, and total reduced N deposition, generated by the CBED model (Concentration Based Estimated Deposition; Levy et al. (2020); Levy et al. (2021)), were obtained for the 5 km grid squares appropriate for each UWMN catchment for the period 1990-2017. The CBED model estimates the sum of wet, dry, cloud droplet and aerosol deposition, most of which is deposited as rain (wet deposition) or gases (dry deposition), on the basis of national mapping of extrapolated wet and dry concentration measurements. Estimates of wet deposition use Met Office precipitation data modified to account for the orographic enhancement of both rainfall volume and rain ion concentration. Estimates of dry deposition are based on a modified "big leaf" model (Monteith and Unsworth, 2013; Smith et al., 2000). This determines rates of transfer of pollutants from the atmosphere to the canopy surface, and uptake via various routes and mechanisms within the plant canopy.

Modelled CBED estimates are available for both moorland and forest surfaces. We used deposition estimates for moorland for the majority of UWMN catchments, but included 50% contributions to forested surfaces at Allt na Coire nan Con, Loch Chon, Llyn Cwm Mynach and the Afon Hafren, a 70% contribution to forest at Loch Grannoch, and a 30% contribution to forest at Old Lodge - proportions roughly commensurate with the proportion of tree cover in these catchments.

Modelled annual CBED estimates of S and nitrogen deposition, expressed in units of kg ha^{-1} yr^{-1}, were converted to units of keq ha^{-1} yr^{-1} (by dividing by 16 and 14 respectively), in order to provide theoretical (potential) contributions of acidity via deposition.

3.2.2 Water chemistry analytical methods

Water samples for water chemistry have been collected monthly from UWMN streams and quarterly from UWMN lakes since monitoring began under the UK Acid Waters Monitoring Network in 1988. Samples are kept dark and cool and sent as soon as possible for laboratory analysis. For the majority of the duration of UWMN, most analysis has been conducted either at CEH (now UKCEH) or the Marine Scotland Freshwater Laboratory, Pitlochry, using methods calibrated specifically for low ionic strength waters. The UKCEH laboratory became the sole UWMN analytical facility in 2015.

Water samples are analysed for indicators of the key drivers of: acidification, i.e. concentrations of the acid anions, (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and chemical responses of catchments to changes in acid deposition (e.g. pH, labile aluminium (i.e. inorganic monomeric aluminium or Al^{3+}) and Gran alkalinity, concentrations of the base cations calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K+); and dissolved organic carbon (DOC). All chemical analyses, other than pH, Gran alkalinity and electrical conductivity (EC), are performed on 0.45 µm Whatman cellulose nitrate filtered samples. Acid anions are analysed by ion chromatography, and base cations using an Inductively Coupled Plasma Mass Spectrometer or Optical Emission Spectrometer (i.e. ICP-MS or ICP-OES). Up until 2016, labile aluminium was determined by the Marine Scotland laboratory by subtracting the concentration of total dissolved monomeric aluminium (catechol violet method) that passed through an ion-exchange column (i.e. organic monomeric aluminium (non-labile)) from that of an unfractionated sample. Dissolved Organic Carbon (DOC) is analysed using a TOC analyser by first acidifying samples to purge all inorganic carbon, followed by high temperature combustion and spectrometric analysis of the resulting CO_2. Analyses follow strict protocols, ensuring intra- and inter-site comparability (Patrick et al, 1991) and have been subjected to rigorous analytical quality control comparisons (Gardner, 2008).

3.2.3 Statistical methods

The presence of statistically significant monotonic change in UWMN chemistry variables was determined by applying the Seasonal Kendall test (Hirsch et al., 1982) under the R package “Trend”. Rates of change over the period 1990 – 2019 in UWMN variables, and 1990 – 2017 for CBED estimates, were determined using the Sen slope estimator in the R package, “Kendall”.

3.3 Water chemistry results

3.3.1 Trends in acid deposition to UWMN catchments (1990 – 2019)

Trends in CBED estimates for non-marine oxidised S, oxidised N and reduced N deposition for the 5 km square covering the centroid of each UWMN catchment are presented in Figures 3.1 and 3.2. Sites are arranged in approximate geographical order – i.e. generally the most northerly at the top and more westerly to the left. The two plots illustrate the same data, but the axes of Figure 3.2 have been truncated to provide a clearer view of recent changes. They demonstrate that rates of oxidised S and N deposition have declined substantially over the first three decades of UWMN monitoring, with trends apparent across all sites. While the most marked declines at many sites occurred in the late 1990s, trends have persisted at the majority up to the end of these modelled sequences (2017). Estimates of the deposition of reduced N species are currently available from 1998 onwards only. These provide less evidence of long-term (i.e. from 1999–2017) directional change, and indeed slight increases to catchments in North Wales, northern England and southwest Scotland over more recent years.

The finer recent detail provided in Figure 3.2 indicates that the decline in the deposition of both oxidised S and N has continued in more recent years, particularly in Galloway (Loch Grannoch, Round Loch of Glenhead and Dargall Lane Burn) the Mourne mountains (Blue Lough and Bencrom River) and the southern Pennines (River Etherow). This plot also demonstrates that while S deposition comprised a significantly larger proportion of the total reduction in oxidised S+N acid deposition in the first half of UWMN operation, because S deposition has fallen more sharply, the deposition of oxidised N has come to increasingly dominate.

Historically, the northern sites, Loch Coire nan Arr (see Loch Coire Fionnaraich), Coneyglen Burn and Allt a'Mharcaidh, were considered the low deposition "control" catchments for the network (Patrick et al., 1993). The CBED model suggests that the combined theoretical contributions to acidity from oxidised S and N fluxes at these sites in 1990 amounted to approximately 1 keq ha^{-1} yr^{-1} (Figure 3.3). By 2017, this had fallen below 0.5 keq ha^{-1} yr^{-1} at these sites and below 0.75 keq ha^{-1} yr^{-1} at the majority of sites across the network (Figure 3.4). Hence, falling deposition rates across the UK have converged substantially over time, but by 2017 significant differences in deposition loads remained between the "cleanest" sites in the north and the more atmospherically polluted sites further south. By 2017, estimated contributions to acidity from all S and N species ranged from around 3 keq ha^{-1} yr^{-1} (Scoat Tarn and the Afon Hafren) to around 1 keq ha^{-1} yr^{-1} for the least impacted sites in the far north and west. Figure 3.1 demonstrates that CBED estimates of reduced N deposition are considerably higher than for oxidised N at the majority of sites. In a region ranging from southern Scotland to North Wales, CBED reduced N deposition estimates have been rising at similar rates to the decline in oxidised N. Thus, for the majority of sites, total N deposition has remained relatively constant throughout much of the UWMN monitoring period.

The total reduction in acidifying pollutant species will have been significantly greater than that represented by S and N species alone, as HCl deposition has also been shown to have declined substantially across the UK over this time period, to what are considered to now be negligible levels (Evans et al., 2011).

Rates of change in the deposition of oxides of S and N over the 1990-2017 period, estimated as Sen slopes, are provided in Table 3.1. Sites are arranged in order of strength of trend in S. Trend estimates for the two species are correlated (R^2 = 0.46), indicating some shared sources (i.e. fossil fuel combustion), and the largest reductions in acid load are estimated to have occurred to the River Etherow catchment (southern Pennines), where peak deposition levels in the 1970s-1980s were some of the highest in the entire UK. Relatively large reductions in S deposition are also estimated at the catchments of Afon Hafren and Afon Gwy (mid Wales), Scoat and Burnmoor Tarn (English Lake District), and Loch Grannoch, Round Loch of Glenhead and Dargall Lane Burn (Galloway). The most gradual reductions in both species are for sites in northern Scotland, north-west Northern Ireland, and south-east England. The main sources of reduced N (i.e. NH_4^+ and NH_3) are agricultural, i.e. from intensive livestock rearing and slurry applications.

As a consequence of CBED's enhanced estimates for deposition to forest relative to moorland, deposition to the UWMN forested sites is inevitably determined to be greater than to neighbouring moorland sites. Providing the enhanced pollutant interception efficiency of forest canopies has remained relatively constant over time, we would expect rates of decline in oxidised S and N at the forested sites to have also have been more rapid, and this is reflected in these estimates (Table 3.1). Differences in rates of change are least apparent for the forested Llyn Cwm Mynach in comparison to moorland Llyn Llagi, but the "pairing" of these sites is a little tenuous as they are some 25 km apart and subject to different precipitation regimes, and the Llyn Cym Mynach catchment has been subject to substantial disturbance in recent years (see Appendix Section 16.1).

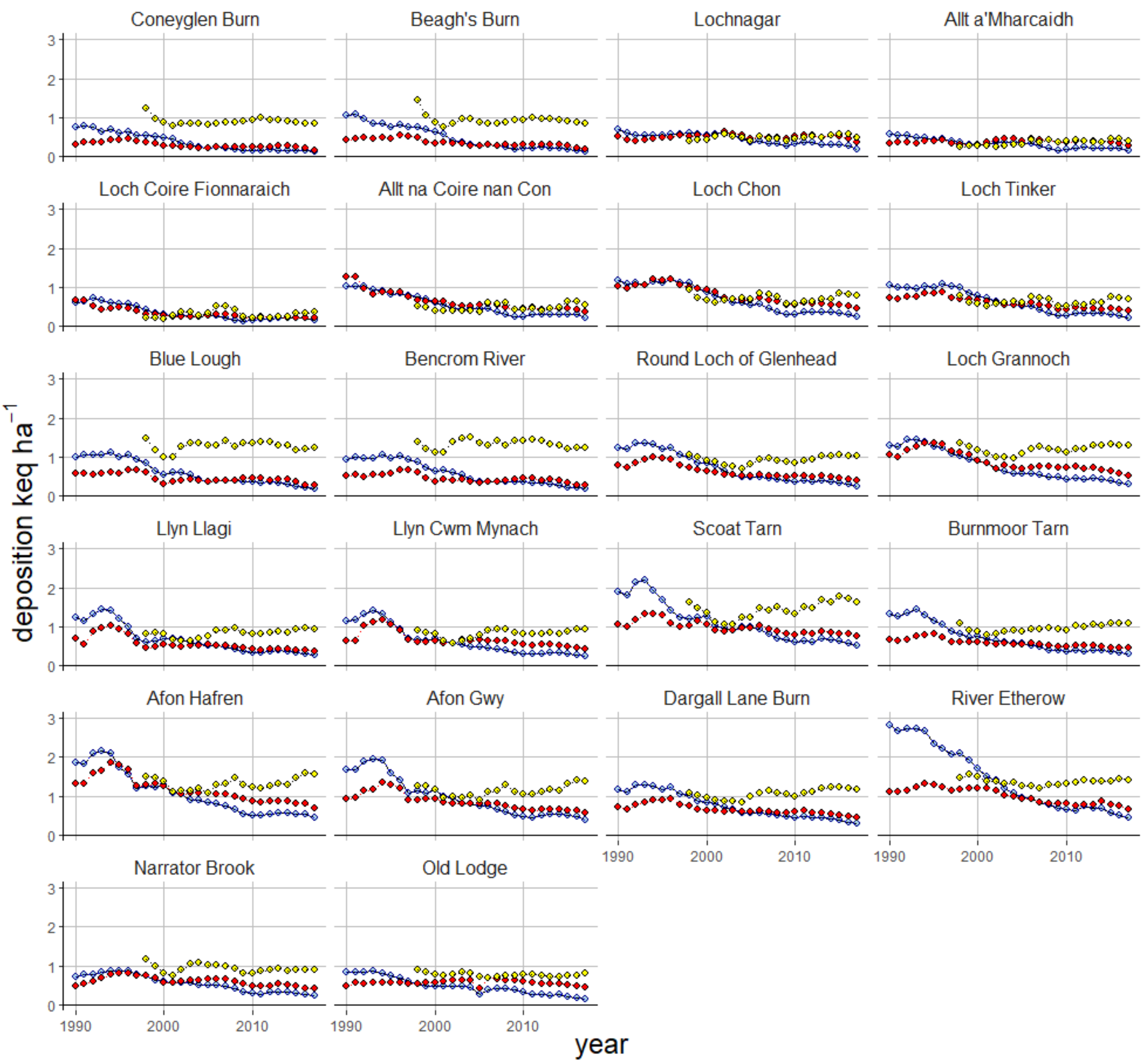

Figure 3.1. CBED estimates of trends (1990 – 2017) in total non-marine oxidised sulphur (blue), total oxidised nitrogen (red), and reduced nitrogen (yellow) to UWMN catchments, accounting for enhanced deposition to forested surfaces (Section 3.2.1). Deposition is calculated in terms of the theoretical contribution to acidity, i.e. assumes that all deposited S and N will ultimately be exported from catchments in the form of strong acids. Given the degree of retention, cycling and atmospheric release of N, acidity estimates for nitrogen species represent the most extreme case only. Note: CBED reduced nitrogen estimates only available from 1998.

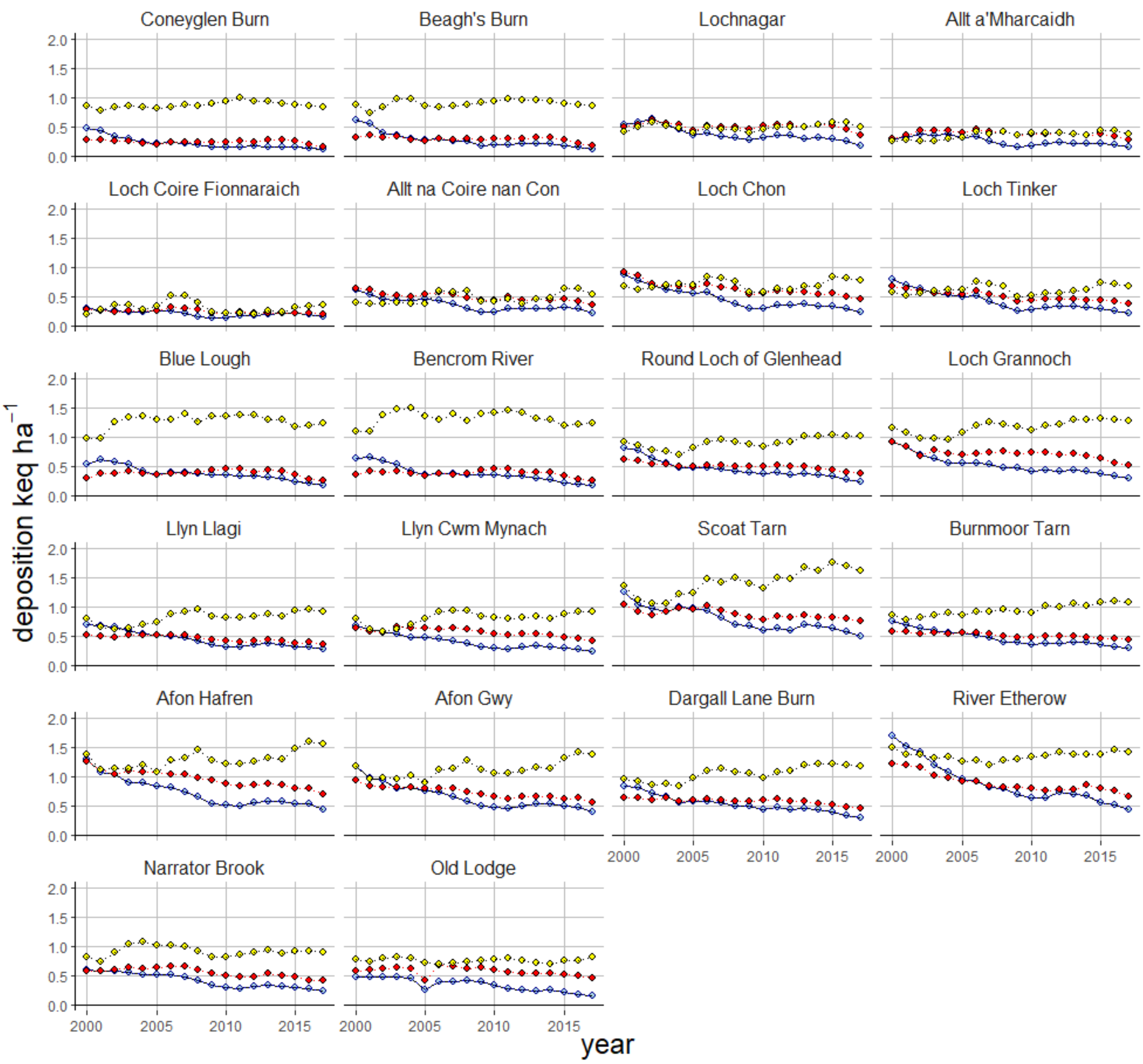

Figure 3.2. Repeat of Figure 3.1, but with axes truncated to highlight recent changes. CBED estimates of trends (2000 – 2017) in total non-marine oxidised sulphur (blue), total oxidised nitrogen (red), and reduced nitrogen (yellow) to UWMN catchments, accounting for enhanced deposition to forested surfaces (Section 3.2.1).

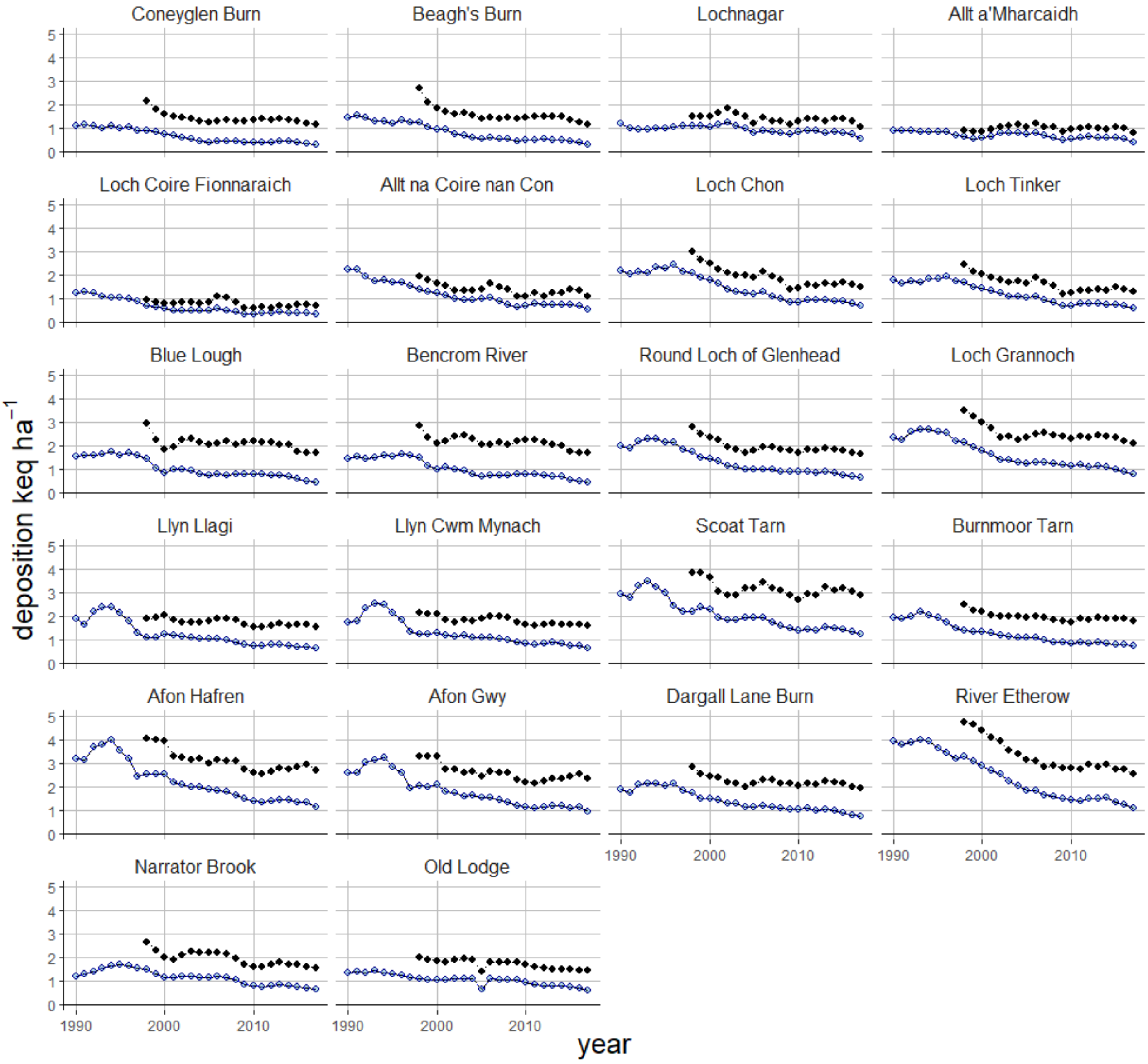

Figure 3.3. CBED estimates of trends in total oxidised sulphur and nitrogen deposition (blue) (1990 – 2017) and total oxidised sulphur, oxidised nitrogen and reduced nitrogen deposition (black) (1998 – 2017), accounting for enhanced deposition to forested surfaces (Section 3.2.1). Deposition is calculated in terms of the theoretical contribution to acidity, i.e. assumes that all deposited S and N will ultimately be exported from catchments in the form of strong acids. Given the degree of retention, cycling and atmospheric release of N, acidity estimates for N deposition represent the most extreme case only.

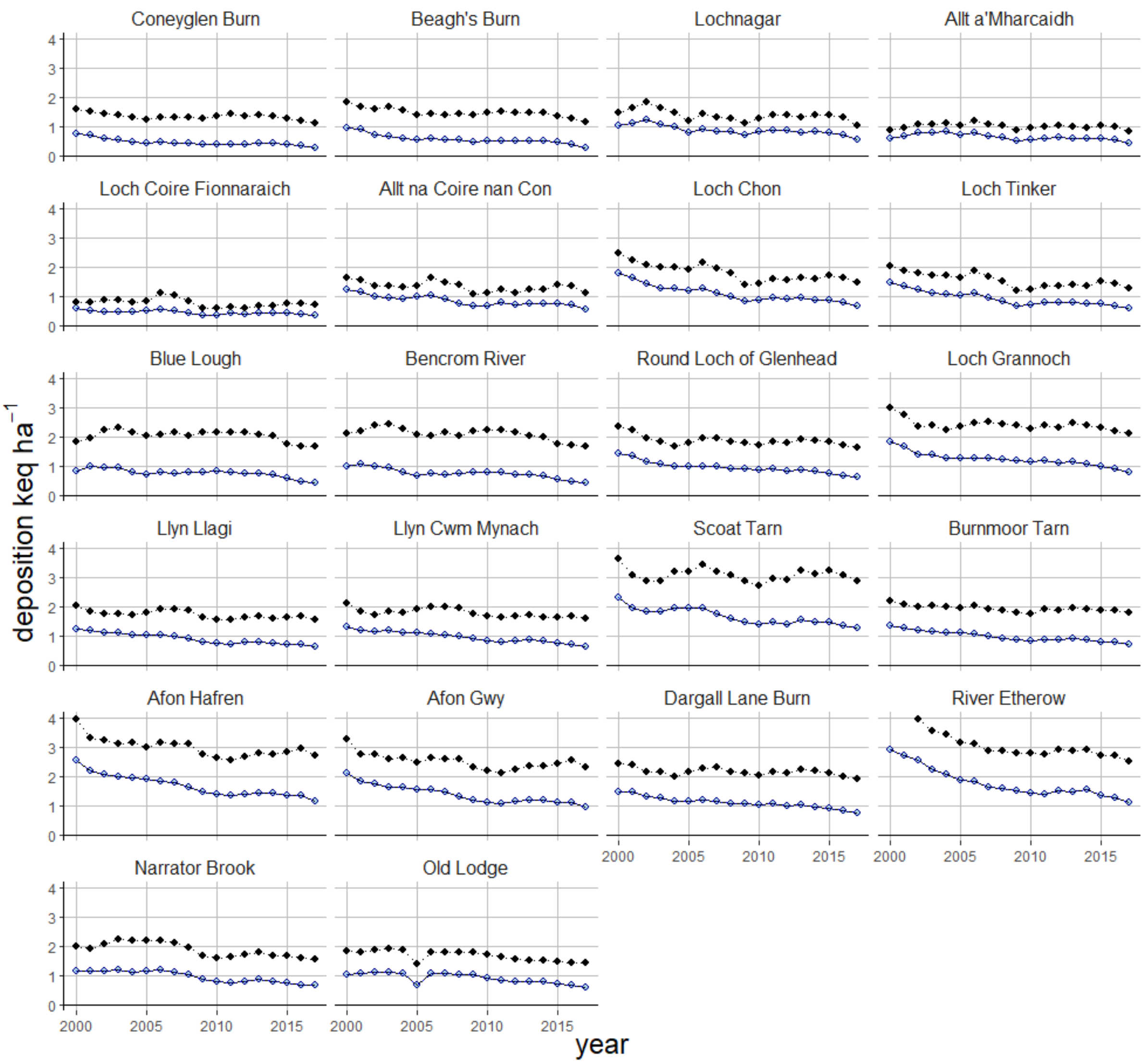

Figure 3.4. Repeat of Figure 3.1, but with axes truncated to highlight recent changes. CBED estimates of trends in total oxidised sulphur and nitrogen deposition (blue) and total oxidised sulphur, oxidised nitrogen and reduced nitrogen deposition (black), accounting for enhanced deposition to forested surfaces (Section 3.2.1).

Table 3.1. Rates of change in CBED estimated deposition fluxes of oxides of non-marine sulphur and nitrogen determined using the method of Sen, and sorted by rates of change in sulphur. Values in bold font indicate the trend is significant at p<0.05. Green shaded rows indicate partially forested sites, while arrows indicate forested vs moorland pairings. CBED generates separate deposition estimates for moorland and forested surfaces. Annual estimates for UWMN catchments are weighted by the relative cover of the two broad vegetation types (Section 3.2.1).

	CBED annual deposition sen slope (keq ha^{-1} yr^{-1})		
site	nitrogen	non-marine sulphur	sum
River Etherow	**-0.023**	**-0.097**	**-0.120**
Afon Hafren	**-0.030**	**-0.060**	**-0.090**
Afon Gwy	**-0.020**	**-0.054**	**-0.074**
Loch Grannoch	**-0.025**	**-0.044**	**-0.069**
Scoat Tarn	**-0.015**	**-0.052**	**-0.067**
Loch Chon	**-0.025**	**-0.039**	**-0.064**
Round Loch of Glenhead	**-0.016**	**-0.044**	**-0.060**
Allt na Coire nan Con	**-0.022**	**-0.033**	**-0.055**
Loch Tinker	**-0.016**	**-0.035**	**-0.051**
Dargall Lane	**-0.011**	**-0.038**	**-0.049**
Llyn Cwm Mynach	**-0.014**	**-0.034**	**-0.048**
Burnmoor Tarn	**-0.008**	**-0.039**	**-0.047**
Llyn Llagi	**-0.012**	**-0.035**	**-0.047**
Beagh's Burn	**-0.009**	**-0.035**	**-0.044**
Blue Lough	**-0.009**	**-0.034**	**-0.043**
Bencrom River	**-0.009**	**-0.033**	**-0.042**
Narrator Brook	**-0.012**	**-0.023**	**-0.035**
Coneyglen Burn	**-0.007**	**-0.026**	**-0.033**
Loch Coire Fionnaraich	**-0.011**	**-0.019**	**-0.030**
Old Lodge	0.000	**-0.025**	**-0.025**
Allt a'Mharcaidh	0.000	**-0.014**	**-0.014**
Lochnagar	0.001	**-0.015**	**-0.014**

3.3.2 Trends in UWMN water chemistry

3.3.2.1 Trends in acid anion concentrations

Sulphate and chloride

Detailed site-specific descriptions of changes in the water chemistry are provided in the Appendix of this report. Table 3.2 summarises trends in acid anion concentrations over the 1988-2019 period, with sites ordered by rates of change in the equivalent sum of sulphate (SO_4^{2-}), nitrate (NO_3^-) and chloride (Cl^-).

Rates of change in SO_4^{2-} and Cl^- concentrations are broadly similar and roughly correlated (R^2 = 0.32). In contrast, de-trended variation in Cl^- concentration (i.e. variation in Cl^- once a linear change component has been removed) in most UWMN waters is at most only weakly correlated with de-trended SO_4^{2-} concentration, and more associated with variation in sodium concentrations, demonstrating the influence of sea salt deposition on the inter-annual variability of Cl^- deposition loads. There is little indication for a directional change in sea salt deposition (see Section 3.3.2.5) and the long-term downward trend in Cl^- is likely to be almost entirely due to a reduction in the deposition of HCl (Evans et al., 2011).

Table 3.2. Rates of change in acid anion concentrations in UWMN sites (1988 – 2019) in units of μeq L^{-1} yr^{-1}. Sites are ordered on the basis of the rate of change in the sum of acid anions. Colour shading represents the relative intensity of trends, with the most rapid declines in red and slowest declines in dull green. Names of sites with partially forested catchments are shaded lime green and linked to their non-forested pairs with the double arrows. Trends significant at p<0.05 are indicated by a bold font. Values under "sum acid anions" are for the sum of the trends in the individual ions.

	Annual change in anion concentrations (μeq L^{-1} yr^{-1})			
site	SO_4^{2-}	Cl^-	NO_3^-	sum acid anions
River Etherow	**-5.41**	**-3.48**	**-0.79**	-9.68
Old Lodge	**-4.49**	**-1.24**	0.00	-5.73
Loch Grannoch	**-2.29**	**-1.56**	**-0.21**	-4.05
Beagh's Burn	**-1.19**	**-2.67**	0.00	-3.86
Blue Lough	**-1.85**	**-1.70**	0.00	-3.55
Bencrom River	**-1.69**	**-1.70**	**-0.04**	-3.43
Burnmoor Tarn	**-1.24**	**-1.69**	0.00	-2.94
Dargall Lane Burn	**-1.23**	**-1.69**	0.00	-2.92
Afon Hafren	**-1.04**	**-1.49**	**-0.36**	-2.89
Loch Chon	**-1.38**	**-1.29**	**-0.18**	-2.86
Allt na Coire nan Con	**-0.88**	**-1.71**	0.00	-2.59
Scoat Tarn	**-1.04**	**-1.15**	**-0.21**	-2.40
Round Loch Glenhead	**-1.50**	**-0.82**	0.06	-2.26
Coneyglen Burn	**-0.74**	**-1.31**	0.00	-2.05
Lochnagar	**-1.19**	**-0.59**	**-0.22**	-2.00
Llyn Llagi	**-1.13**	-0.78	0.00	-1.91
Loch Tinker	**-1.10**	-0.49	0.00	-1.59
Afon Gwy	**-0.79**	**-0.78**	0.00	-1.57
Narrator Brook	**-0.23**	**-1.30**	0.07	-1.47
Loch Coire Fionnaraich	-0.14	-1.16	0.00	-1.30
Llyn Cwm Mynach	**-0.98**	0.03	**0.06**	-0.88
Allt a'Mharcaidh	**-0.54**	**-0.24**	0.00	-0.77
Loch Coire nan Arr	**-0.19**	**-0.29**	0.00	-0.48

Similarities in the spatial distribution and magnitude of trends in SO_4^{2-} and Cl^-, demonstrated by Table 3.2, therefore indicate shared sources, of which coal-fired power stations are likely to have dominated over the majority of the monitoring period. The use of coal of relatively high chlorine content was largely phased out by the onset of the current century, so this component of the acid deposition flux is assumed to have reached negligible levels in recent years.

The relationship between the estimated reduction in acidity from S deposition (taking into account average annual runoff), and the equivalent change in SO_4^{2-} concentration in UWMN surface waters, is shown in Figure 3.5. Overall, declines in surface water SO_4^{2-} flux are around 60% of the estimated rate of reduction in S deposition. This is suggestive of some additional contribution to the surface water sulphate flux from desorbed S that may have accumulated in mineral soil layers when they were more acidified, but substantial scatter in the relationship and considerable uncertainties around catchment-specific pollutant and water fluxes prevents firm conclusions being drawn in this respect.

Again, the River Etherow, historically the most S-impacted site, shows the greatest fall in surface water SO_4^{2-} concentration, while sites in northern Scotland and southwest England show relatively low rates of change. The sites situated in the English Lake District, Galloway, the Trossachs and Northern Ireland show very similar rates of SO_4^{2-} concentration decline.

Importantly, while Old Lodge, in southeast England, has experienced relatively low levels of S deposition historically, and has undergone one of most gradual declines in S deposition of any UWMN site, Old Lodge streamwater has shown similar absolute SO_4^{2-} concentrations, and rates of reduction in SO_4^{2-} concentration over time, to the River Etherow. This is because the amount of run-off at Old Lodge is almost an order of magnitude lower than for the River Etherow, resulting in a far higher concentration of the pollutant, and thereby emphasises the crucial role of the local water balance in determining the hydrochemical response to change in the deposition load.

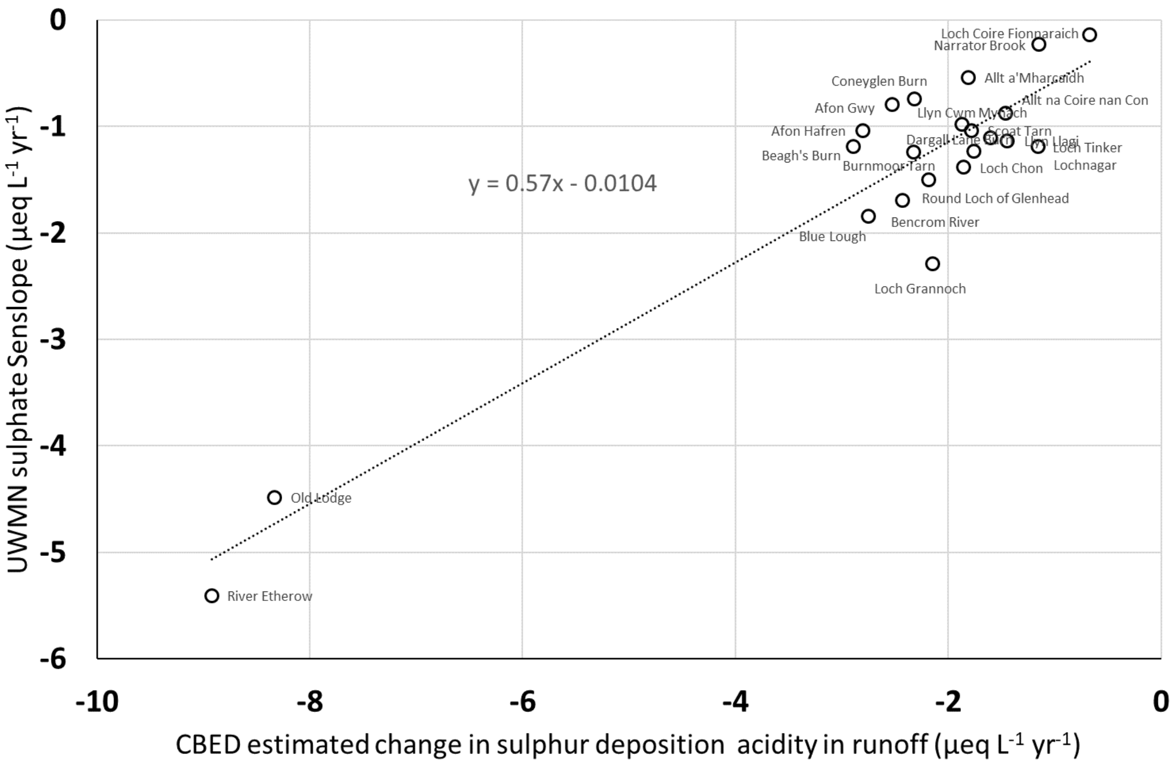

Figure 3.5. Rates of change in SO_4^{2-} concentration in UWMN surface waters (expressed in units of equivalence) in relation to estimated changes in the contribution of sulphur deposition to runoff acidity. The latter is calculated by dividing the CBED sulphur deposition estimate by the Standard Average Annual Rainfall (SAAR) minus annual evaporative loss.

The changing relationship between the estimated non-marine oxidised S deposition flux and the estimated non-marine sulphate deposition flux in run-off is provided in Figure 3.6. Here, runoff fluxes are approximated using mean concentrations multiplied by long-term run-off estimates over four five-year periods (1990-1994, 1998-2002, 2008-2012 and 2015-2017 for deposition and 1990-1994, 1998-2002, 2008-2012 and 2015-2019 for UWMN run-off chemistry).

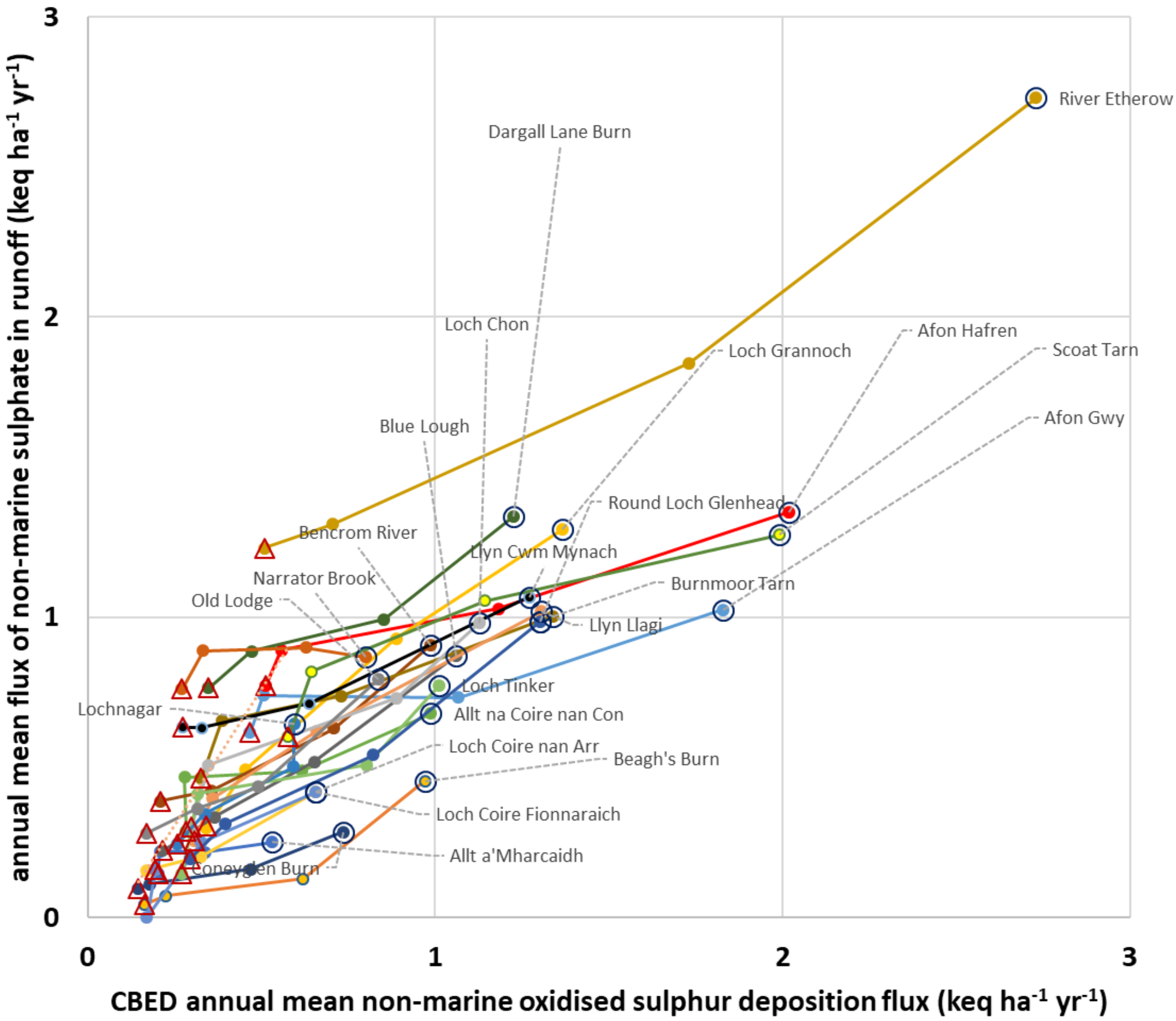

Figure 3.6. Trends in five-yearly estimates of rates of non-marine sulphur deposition and non-marine sulphur export in run-off, expressed as keq S ha^{-1} yr^{-1}, across all UWMN sites. Blue circles indicate first 5 year period (1990-1994) and red triangles the most recent period (2015-2017 for deposition and 2015-2019 for runoff). The intermediate periods represented by coloured points are 1998-2002 and 2008-2012. Note run-off estimates are based on a fixed mean annual SAAR estimate for the 1961-1990 period, as contemporary runoff estimates were not available at the time of analysis.

Nitrate

In contrast to the strongly directional changes in SO_4^{2-} and Cl^-, long-term trends in NO_3^- concentration have generally been much weaker or absent (see also Section 3.3.2.6). Eight sites showed statistically significant changes in NO_3^-, seven of which were reductions, and of these, three have partially forested catchments. Llyn Cwm Mynach, also forested, was the only site on the network to show a significant increase in NO_3^- concentration – possibly a reflection of recent catchment disturbances (see Appendix: Section 16). None of the moorland sites linked to forested pairs showed significant change in NO_3^-.

Waters draining the forested sites have exhibited higher concentrations of NO_3^- historically, so one possible explanation for the prevalence of downward NO_3^- trends in these catchments is that they will have undergone much larger reductions in the interception of nitrogenous pollutants, as suggested by CBED estimates (Table 3.1). However, four of the seven catchments to show reductions in NO_3^- are essentially treeless.

Figure 3.7 reveals a more complex relationship between trends in the runoff of NO_3^- and total N deposition than seen for S (Figure 3.6). In Figure 3.7, time series start in 1999 (reduced N deposition estimates not available for previous years). It shows a very clear between-site relationship between total N deposition and nitrate N in runoff, i.e., the greater the N deposition the greater loss of nitrate N in runoff. However, within-site temporal relationships are generally much weaker than for S.

The between-site structure of Figure 3.7 is consistent with the observations of Dise and Wright (1995) who analysed the relationship between N deposition and NO_3^- leaching across a wide range of European forested plots three decades ago. They identified an N deposition threshold of circa 10 kg ha^{-1} yr^{-1} (equivalent to 0.7 keq ha^{-1} yr^{-1}) below which NO_3^- leaching was negligible. The threshold is very similar to the modelled N deposition rate corresponding with NO_3^- concentrations occurring at almost undetectable levels at UWMN sites, ever since the late 1990s (Figure 3.7). Above this "threshold" the annual NO_3^- flux from UWMN sites increases at approximately 0.1 keq N ha^{-1} yr^{-1} for every 0.5 keq N ha^{-1} yr^{-1} in total N deposition. The reduction in nitrate N flux from a number of higher N deposition sites over a period when N deposition was relatively stable, has resulted in a reduction in the overall nitrate vs N deposition slope over time, but there is little evidence of a shift in the NO_3^- leaching threshold value. This is interesting, since a progressive accumulation of reactive N over time might have been expected to result in NO_3^- "breaking through" at progressively lower N deposition rates. Rather, the data are more indicative of the N deposition vs nitrate leaching relationship being in longer- term steady state.

Whereas the time tracks for individual sites for S (Figure 3.6) are broadly consistent with the wider between-site deposition vs run-off relationship, there is little comparable evidence for N. This is perhaps not surprising given that modelled total N deposition fluxes have changed so little as a consequence of reductions in oxidised N deposition flux being largely offset by an increasing flux of reduced N. In addition there are substantial uncertainties involved in both the CBED modelling of the total N deposition flux and the determination of the nitrate runoff flux on the basis of fixed long-term water run-off values. The relationship for the River Etherow is unusual, since both total N deposition and the estimated nitrate N flux are estimated to have fallen over time. The forested Loch Chon, and montane Lochnagar also demonstrate some linearity. The Lochnagar catchment has always been considered to have very limited capacity to retain deposited reactive N because of its sparse soil cover and low ambient temperature (due to its high altitude), both of which are likely to restrict soil microbial activity.

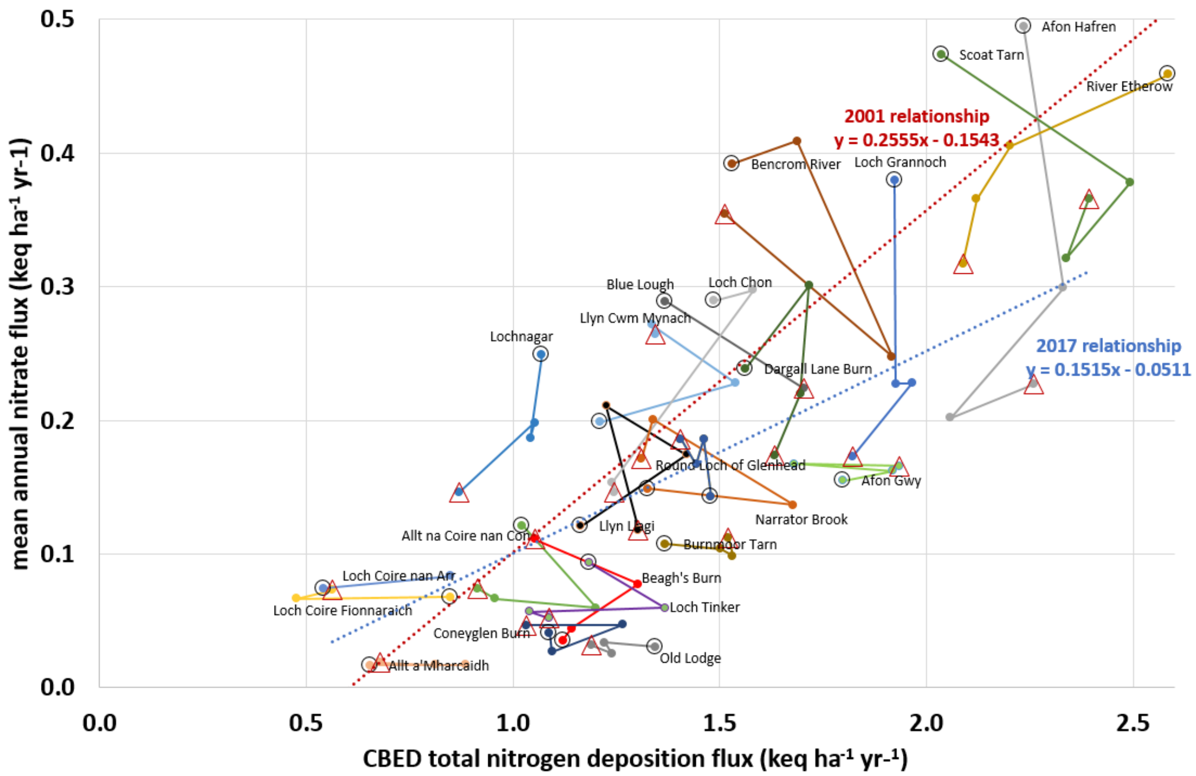

Figure 3.7. Trends in five-yearly estimates of rates of total nitrogen deposition and nitrate leaching in run-off, expressed as keq N ha^{-1} yr^{-1}, across all UWMN sites. Blue circles indicate first 5 year period (1999-2003) and red triangles the most recent period (2015-2017) for deposition and 2015-2019 for runoff). Other periods represented are 2004-2008 and 2009-2013. Note run-off estimates are based on a fixed mean annual SAAR estimates for the 1961-1990 period as contemporary runoff estimates were not available at the time of analysis.

Most of the sites that have undergone substantial reductions in NO_3^- leaching in recent years, i.e. Afon Hafren, Scoat Tarn and Loch Grannoch, have not experienced clear reductions in total N deposition according to CBED estimates. They are, however, some of the most acidified on the network. This suggests that recovery of catchment soils from acidification may be an important driver of negative NO_3^- trends. Similar behaviour was reported by Oulehle et al. (2011) for a highly acidified spruce catchment in the Czech Republic. They observed large (circa 50%) reductions in the carbon and N content of the soil organic (Oa) horizon, and a coincident reduction in NO_3^- leaching from substantial to negligible, over a period when S deposition was reduced by 80% but bulk N deposition did not change. Thus, the capacity of the soil microbial community to consume and either retain or denitrify reactive N at these sites may be increasing as they recover from severe acidification - a process driven primarily by reductions in non-marine S and HCl deposition. More marked reductions in N deposition to the catchments of the River Etherow, Lochnagar and Loch Chon, however, may also be contributing to NO_3^- decreases at these sites.

3.3.2.2 Trends in base cation concentrations

The reduction in the net negative charge of acid anion species must be balanced either by reductions in hydrogen (H^+), labile aluminium (Al^{3+}) or base cation species (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and/or by an increases in bicarbonate alkalinity (HCO_3^-) and organic acids (represented by DOC). Table 3.3 demonstrates that much of the balancing has been provided by a reduction in base cation concentrations. The rate of change in the concentration of the more dominant base cations (i.e. Na^+, Ca^{2+} and Mg^{2+}) is strongly correlated with reductions in acid anion concentrations. Trends in the concentration of K^+ are more variable and less clearly linked to the acid anion decline. The forested sites, Loch Grannoch, Afon Hafren and Llyn Cym Mynach, and the partly wooded Old Lodge, all show significant, albeit very slight, increases in K^+ concentrations, possibly indicative of recent catchment disturbances caused by forest management practices (Tripler et al., 2006).

Table 3.3. Rates of change in the sum of acid anion concentrations (Sen slopes) and individual base cation concentrations in UWMN sites (1988 – 2019) in units of µeq L^{-1} yr^{-1}. Trends significant at p<0.05 are indicated by a bold font. Sites are listed in order of the rate of decline in strong acid anions (see Table 3.2). Colour shading indicates relative rate of change with most rapid declines in red and slowest declines in dull green. Sites shaded lime green are forested– arrows represent forested – moorland pairings.

site	sum acid anions	Na^+	Ca^{2+}	Mg^{2+}	K^+	sum base cations
River Etherow	-9.68	**-2.33**	**-1.62**	**-1.73**	**-0.15**	-5.84
Old Lodge	-5.73	-0.72	0.33	**-0.73**	**0.18**	-0.94
Loch Grannoch	-4.05	**-1.19**	**-0.33**	**-0.22**	**0.10**	-1.63
Beagh's Burn	-3.86	**-2.09**	**-0.44**	**-0.73**	**-0.09**	-3.35
Blue Lough	-3.55	**-1.59**	**-0.31**	**-0.40**	**-0.06**	-2.37
Bencrom River	-3.43	**-1.24**	**-0.25**	**-0.46**	**-0.04**	-2.00
Burnmoor Tarn	-2.94	**-1.22**	**-0.55**	**-0.28**	-0.04	-2.08
Dargall Lane Burn	-2.92	**-1.31**	**-0.36**	**-0.33**	**-0.04**	-2.02
Afon Hafren	-2.89	**-0.97**	**-0.40**	**-0.27**	**0.04**	-1.61
Loch Chon	-2.86	**-1.02**	**-0.25**	**-0.19**	0.00	-1.46
Allt na Coire nan Con	-2.59	**-1.08**	**-0.48**	**-0.34**	-0.02	-1.92
Scoat Tarn	-2.40	**-1.09**	**-0.40**	**-0.36**	-0.04	-1.89
Round Loch of Glenhead	-2.26	**-0.96**	**-0.29**	**-0.26**	-0.03	-1.54
Coneyglen Burn	-2.05	**-0.71**	-0.30	-0.36	-0.04	-1.39
Lochnagar	-2.00	**-0.56**	**-0.37**	**-0.40**	-0.03	-1.36
Llyn Llagi	-1.91	-0.60	**-0.33**	-0.19	0.03	-1.09
Loch Tinker	-1.59	-0.64	**-0.50**	**-0.32**	0.00	-1.45
Afon Gwy	-1.57	**-0.39**	-0.07	-0.12	0.00	-0.58
Narrator Brook	-1.47	**-0.68**	-0.03	**0.00**	**0.06**	-0.65
Loch Coire Fionnaraich	-1.30	-0.02	0.01	-0.13	0.04	-0.10
Llyn Cwm Mynach	-0.88	0.19	-0.14	0.10	**0.08**	0.23
Allt a'Mharcaidh	-0.77	**-0.20**	-0.08	**-0.06**	0.01	-0.33
Loch Coire nan Arr	-0.48	-0.26	0.00	0.00	-0.02	-0.29

Figure 3.8 shows that, with the exception of Llyn Cwm Mynach, Ca^{2+} concentrations in the forested sites have fallen more rapidly than Mg^{2+} concentrations, suggesting a greater arboreal demand for Ca^{2+}. Similar behaviour is seen for some of the better buffered non-forested sites, i.e. Loch Tinker, Burnmoor Tarn and Llyn Llagi. At the remaining sites, which are less well buffered and mostly more acidified, Ca^{2+} and Mg^{2+} concentrations have either been falling at a similar rate, or the latter show larger declines.

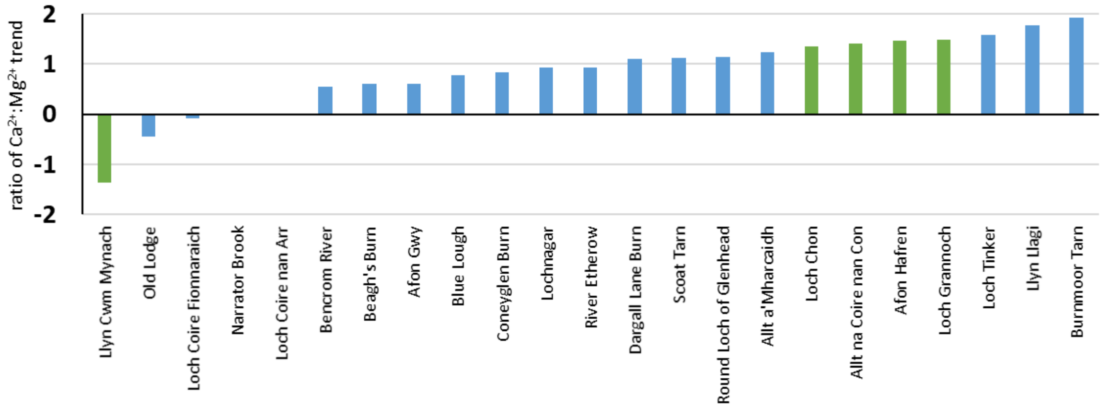

Figure 3.8. Ratios of rates of decline in calcium to magnesium concentration. Most forested sites (shaded green), together with some other sites with higher acid buffering capacity, show particularly strong reductions in calcium relative to magnesium concentration.

Figure 3.9 summarises the relationship between rates of change in all acid anions and base cations. This shows that at most sites, acid anion concentrations have been falling more rapidly than base cations, and that the difference can be explained largely by increases in calculated Acid Neutralising Capacity (ANC) (estimated in this report as the sum of base cations minus the sum of acid anions when all are expressed in terms of equivalence). An increase in ANC is a pre-requisite for chemical recovery from acidification, and can reflect various types of chemical response (see next section).

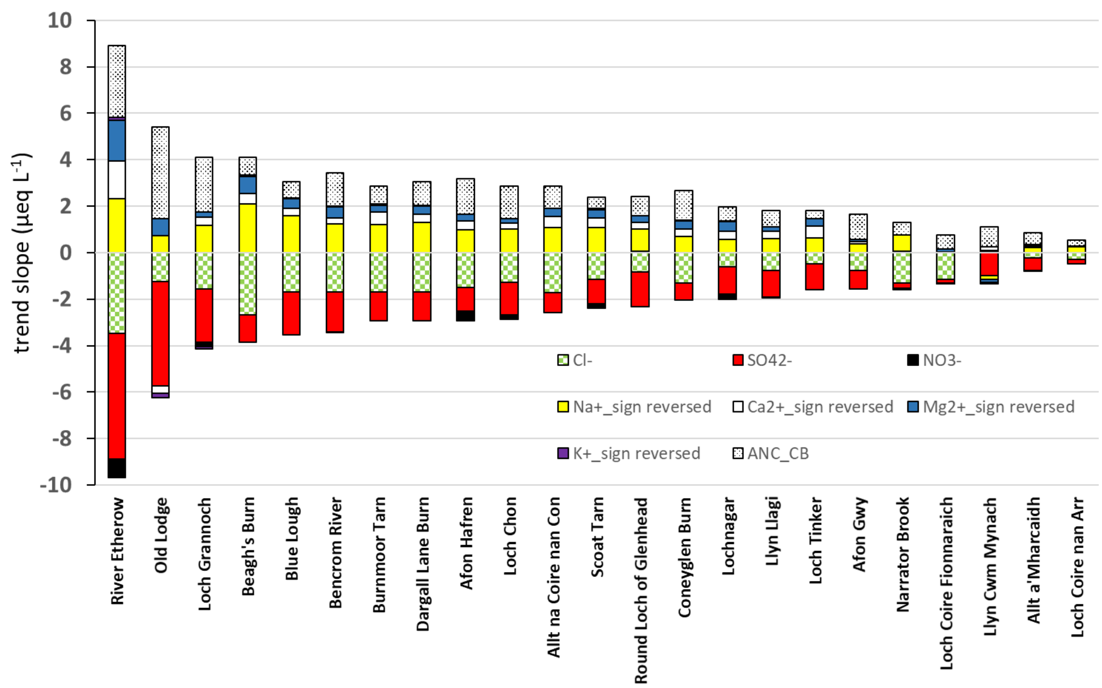

Figure 3.9. Comparisons of rates of change in individual acid anion concentrations and base cation concentrations (with the sign of the trend in the latter reversed to convey the balance between the two). Sites are arranged from left to right in order of the rate of decline in the sum of all acid anion species. ANC_CB refers to Acid Neutralising Capacity determined by charge balance (i.e. difference between the sum of base cations and acid anions).

3.3.2.3 Trends in inorganic and organic acidity

Table 3.4 shows that trends in Acid Neutralising Capacity (ANC) correlate broadly with rates of reduction in acid anions, and together with earlier observations demonstrates the following links: reductions in acid deposition → reductions in surface water acid anion concentration → chemical recovery. Changes in ANC reflect a range of processes and chemical responses that depend on the initial acidity of the system, which in turn is governed by site characteristics, such as the geology and soil type, as well as its acid deposition history. These changes may include a reduction in Al^{3+}, a reduction in H^+ (i.e. increasing pH) and an increase in HCO_3^- concentration (i.e. an increase in Gran Alkalinity above a baseline of 0 μeq L^{-1}).

Previous analysis of UWMN chemistry data has also identified links between rates of decline in acid anion concentration and rates of increase in Dissolved Organic Carbon (DOC) concentration (Evans et al. 2006), a relationship thought to reflect the effect of a reduction in acid pollutants on the solubility of catchment soil organic matter solubility (Monteith et al., 2007). This again contributes to the anion vs cation balance, as dissolved organic matter (DOM) is comprised partly of strong organic acids that contribute a net negative charge. Since DOC concentrations have been increasing at almost all sites over the monitoring period, the increase in acidity provided by organic acids will have partially offset the reduction in contributions to acidity by the strong acid anions (see also Section 6.2.2), resulting in less rapid reductions in H^+ concentration (i.e. slower increases in pH) than were predicted by biogeochemical dynamic models at the onset of monitoring.

The ubiquitous and sizeable increase in DOC concentration is important ecologically, not only from an acidity perspective, but also because it is driven by an increase in strongly light-adsorbing organic compounds (i.e. humic - soil derived molecules that include chromophoric structures). This is likely to have resulted in substantial reductions in the penetration of photosynthetically active radiation (PAR) and hence the depth of the photic zone of UWMN lakes (i.e. the depth beyond which photosynthesis is prevented). Light penetration declines exponentially per unit increase in dissolved coloured organic matter, so some of the largest changes in the photic depth are likely to have occurred in lakes with lower initial DOC concentrations, although the effect on lake benthic habitat insolation will also be dependent on lake-specific bathymetric structure.

Relationships between rates of change in acid anion concentrations and key indicators of acidity are presented in Table 3.4 and Figure 3.10. Trends in Gran alkalinity (Figure 3.10a) represent shifts in the chemical buffering capacity of the UWMN waters over time. Increases in Gran alkalinity in what were the more acidified sites mostly reflect reductions in the concentration of H^+ and Al^{3+} ions, whereas at un-acidified, and more strongly buffered, sites such as Burnmooor Tarn and Coneyglen Burn, increases are likely to mostly reflect a rise in HCO_3^- concentration.

There is a clear relationship between rates of reduction in both H^+ and Al^{3+} concentrations and strong acid anion concentrations (Figure 3.10b-c), reflecting the role of soil pH in determining inorganic aluminium mobility. The most rapid reductions in these acidity metrics are observed in Old Lodge, Loch Grannoch and Blue Lough, historically some of the most acidic, and most acidified, sites on the network. The sites that have experienced the smallest reductions in these species mostly fall into two groups: 1) those like Loch Coire nan Arr, Loch Coire Fionnaraich, Allt a'Mharcaidh and Coneyglen Burn, that have experienced the lowest rates of acid deposition historically and the smallest reductions in acid deposition over the monitoring period, and 2) sites that are relatively well buffered, and (according to palaeoecological analyses) show little indication of having been acidified, such as Loch Tinker and Burnmoor Tarn.

The one major outlier in the relationships presented in Figure 3.10b is the River Etherow, where the relatively slight Sen slopes for H^+ and Al^{3+} concentration contrast with the particularly rapid rates of reduction in acid deposition and acid anion concentrations. This is because during periods of low flow the streamwater is dominated by strongly buffered groundwater and is thus insensitive to acid inputs – resulting in a tempering of the long-term trend in acid species. Large reductions in H^+ and Al^{3+} concentrations are nevertheless evident during high flow conditions (see Section 3.3.2.7). It would seem likely that it is the chemistry of these extreme episodes that places most constraints on acid-sensitive aquatic organisms, so the large reduction in acidity during high flows could be of major significance ecologically despite the relatively subtle overall change indicated by the Sen slopes (see for example River Etherow macroinvertebrate trend results in Section 5.3).

Table 3.4 Rates of change in acidity indicators in UWMN sites (1988 – 2019) ordered by rates of change in acid anions. Trends in the sum of acid anions, Gran alkalinity (Gran Alk), hydrogen ion concentration (H^+), labile aluminium concentration (Al^{3+}) and Acid Neuturalising Capacity (ANC) in units of μeq L^{-1} yr^{-1}. Trends in Dissolved Organic Carbon concentration in units of mg L^{-1} yr^{-1}. Colour shading indicates relative rates of change. Sites shaded lime green are forested – arrows represent forested – moorland pairings.

site	site number	sum acid anions	Gran Alk	H^+	Al^{3+}	ANC	DOC
River Etherow	12	-9.68	2.33	-0.01	-0.04	3.06	0.16
Old Lodge	13	-5.73	2.15	-0.76	-0.82	3.94	0.20
Loch Grannoch	8	-4.05	0.81	-0.44	-0.66	2.36	0.16
Beagh's Burn	19	-3.86	0.22	0.00	0.00	0.75	0.15
Blue Lough	21	-3.55	0.61	-0.30	-0.65	0.70	0.02
Bencrom River	20	-3.43	0.99	-0.12	-0.28	1.43	0.01
Burnmoor Tarn	11	-2.94	0.47	0.00	0.00	0.77	0.03
Dargall Lane Burn	9	-2.92	0.67	-0.07	-0.04	1.02	0.04
Afon Hafren	17	-2.89	0.62	-0.06	-0.24	1.52	0.05
Loch Chon	5	-2.86	0.86	-0.04	-0.02	1.39	0.08
Allt na Coire nan Con	3	-2.59	0.17	0.00	0.00	0.94	0.11
Scoat Tarn	10	-2.40	0.46	-0.20	-0.35	0.48	0.02
Round Loch of Glenhead	7	-2.26	0.52	-0.21	-0.23	0.81	0.05
Coneyglen Burn	22	-2.05	0.58	0.00	0.00	1.28	0.05
Lochnagar	4	-2.00	0.30	-0.09	-0.04	0.61	0.03
Llyn Llagi	15	-1.91	0.54	-0.07	-0.10	0.70	0.03
Loch Tinker	6	-1.59	0.12	0.00	0.00	0.36	0.04
Afon Gwy	18	-1.57	0.64	-0.04	-0.11	1.07	0.03
Narrator Brook	14	-1.47	0.56	-0.01	-0.10	0.54	0.01
Loch Coire Fionnaraich	26	-1.30	0.29	-0.01	0.00	0.62	-0.02
Llyn Cwm Mynach	16	-0.88	0.16	-0.02	-0.10	0.86	0.02
Allt a'Mharcaidh	2	-0.77	0.55	0.00	0.00	0.52	0.04
Loch Coire nan Arr	1	-0.48	0.00	0.00	0.00	0.24	0.04

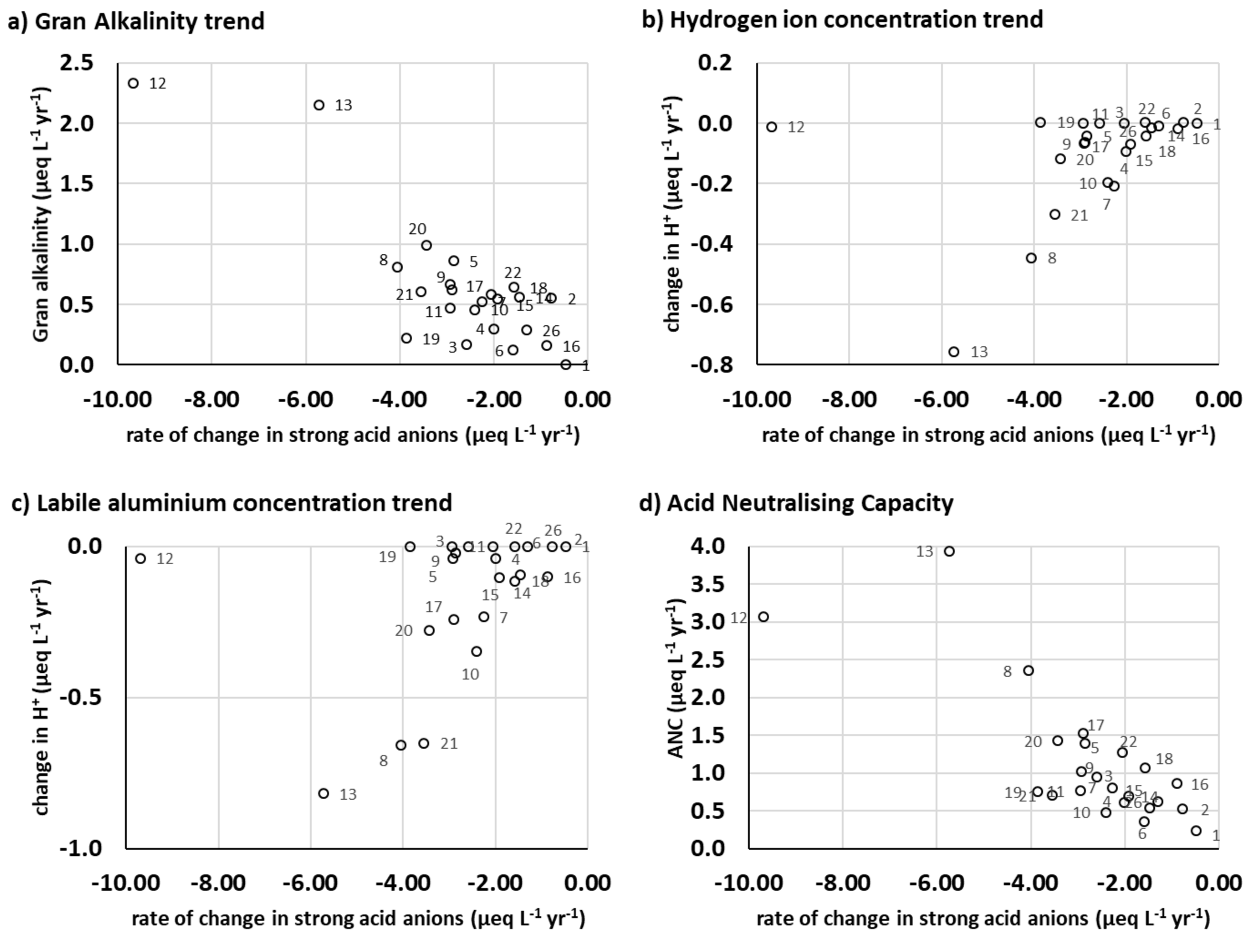

Figure 3.10. Relationships between rates of change in acidity indicators and the sum of rates of change in strong acid anion concentrations. Rates of change determined as Sen slopes. Sites are coded as site numbers, as provided in Table 3.4.

3.3.2.4 Influence of forestry on surface water acidity

In earlier sections we highlighted the tendency for larger reductions in acid anion concentrations in runoff from the forested sites relative to their moorland pairs (Table 3.3) which was consistent with the enhanced interception of atmospheric pollutants predicted by CBED for the forest canopies. We also showed that rates of reduction in H^+ and Al^{3+} concentration, and rates of increase in ANC, all responses to changing deposition, had also been more rapid (Table 3.4). These changes are illustrated as time series of mean annual values for the three most comparable pairs of forested and moorland sites in Figure 3.11.

In all three cases, Al^{3+} concentrations were much higher in the forested lakes and streams than the moorland pairs at the onset of monitoring, reflecting greater acidification. Over time, and up to 2016 when Al^{3+} measurements ceased, concentrations declined in both forested and moorland waters in the Plynlimon and Galloway pairs, but also steadily converged. Al^{3+} concentrations also declined in Loch Chon (forested catchment), but have mostly been below limits of detection in the less acid-sensitive Loch Tinker throughout the three decades. Despite the convergence, by 2016 Al^{3+} concentrations remained higher in all three forested sites relative to their moorland pairs. In recent years the differences were arguably negligible for the Plynlimon and Trossachs pairings, but the mean Al^{3+} concentration in Loch Grannoch in 2016 was approximately four times that of the Round Loch of Glenhead, and potentially still at a high enough level to limit the probability of observing brown trout in the outflow at least. In their assessment of UWMN brown trout data, Malcolm et al. (2014) determined that the Al^{3+} threshold for an 80% probability of observing brown trout in two out of three fishing reaches of UWMN streams was 26 µg L^{-1}; the mean concentration in Loch Grannoch in 2016 was 55 µg L^{-1}. Labile aluminium measurements have recently resumed, but it will require a further year or two before determining whether further gap closure has occurred.

Increasing surface water pH trends in the forested-moorland pairings have also converged over time. By 2019, pH levels were very similar in Afon Hafren and Afon Gwy, and more generally in recent years in Loch Chon relative to Loch Tinker. In common with Al^{3+}, however, there remains more of an offset for pH in the Galloway pair.

In all three forested sites, mean annual ANC has climbed over time from below to above the UK ANC critical limit of 20 µeq L^{-1} (see Section 6.2 for further consideration of the limitations of this metric). In the case of the Plynlimon and Trossach pairs, ANC levels have been very similar over the last decade, while in Loch Grannoch, mean annual ANC has, surprisingly, exceeded that for the Round Loch of Glenhead in four of the last seven years, partly as a consequence of the large increase in DOC (see Section 6.2.2).

With only three robust forest-moorland pairs, conclusions regarding differential responses to deposition should be treated cautiously. However, the evidence for more rapid reductions in acid anion concentrations in the forested UWMN sites is entirely consistent with prior understanding of the importance of canopy interception in enhancing the deposition load, and it follows that this will have led to more pronounced rates of recovery in acidity metrics. In all three cases between-site differences in acidity have narrowed rapidly as acid deposition has declined, but further years of monitoring will be required to determine whether secondary effects of afforestation, such as disturbances relating to felling, timber removal, re-planting and base cation uptake by the canopy, will leave a longer term legacy.

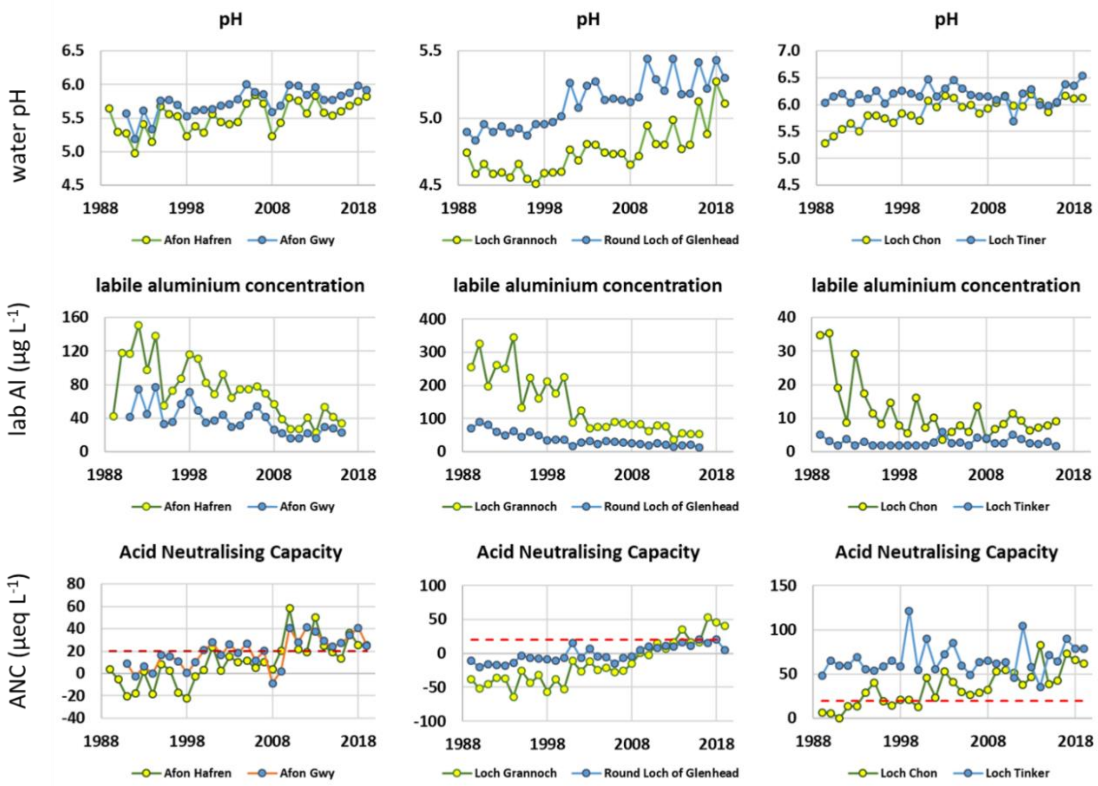

Figure 3.11. Trends in mean annual pH, labile aluminium (Al^{3+}) concentration and Acid Neutralising Capacity (ANC) in three geographically paired UWMN surface waters with either forested (green/yellow) or moorland (blue) catchments. Red dotted line in the ANC plots represents the UK ANC critical limit for ANC of 20 µeq L^{-1}.

3.3.2.5 Influence of sea salt and climatic variation on UWMN chemistry

The maritime geography of the UK has a major bearing on the water chemistry of upland lakes and streams, particularly in the west. This is partly because the elevated terrain of much of the west of Great Britain and Northern Ireland intercepts the prevailing moisture laden air masses originating from the Atlantic, resulting in some of the highest rates of precipitation in northern Europe. It is also because during stormy westerly weather, and particularly during winter, large wave heights and strong winds combine to generate an aerosol rich in sea salt that can travel several tens of kilometres inland. In previous analyses of UWMN data it was shown that concentrations of some major ions, and particularly sodium and chloride, vary substantially from year to year as a consequence of this variation in the generation and transport of sea salt aerosol (Evans et al., 2001), while temporal patterns can be linked to the North Atlantic Oscillation (NAO) – an indicator of regional scale weather systems (Hurrell, 1995; Hurrell and Van Loon, 1997).

The slow geological weathering rates of UWMN catchments restricts ion fluxes to the surface waters. Consequently, and in comparison with UK surface waters more generally, all UWMN waters were of low ionic strength at the onset of monitoring, and, as air pollutant loads have declined, ionic strength has been falling further across the network. The atmospheric deposition of sea salt has therefore always made a significant contribution to the ionic strength of these waters and its relative importance has been increasing over time, with respect not only to Cl^- and Na^+ ions, but other cations, including Ca^{2+} and Mg^{2+}. A range of biological functions could theoretically be limited by Ca^{2+} in low ionic strength waters. Calcium concentrations can be critical in determining the development of structural components of aquatic invertebrates and vertebrates, ion regulation, and muscular and neural functioning (Hessen et al., 2017), and it has been speculated that one side-effect of recovery from acidification will be potentially deleterious reductions in calcium levels in already highly dilute systems (Jeziorski and Smol, 2017; Weyhenmeyer et al., 2019).

Sea salt deposition to acid-sensitive catchments is also important with respect to its effects on water acidity and water colour. During sea salt deposition events, displacement of H^+ and Al^{3+} ions from acidified soil exchange sites by marine-derived base cations can cause potentially biologically harmful, bursts of acidity in runoff (Evans et al., 2001). As recently as January 2014, a major storm centred around the North Wales coast resulted in a sea salt deposition event detectable across the Welsh UWMN catchments that led to large depressions in pH and concentrations of labile aluminium rising above 100 µg L^{-1} in the Afon Hafren and Afon Gwy, i.e. well beyond levels deemed toxic for salmonids and a range of invertebrate species (see Appendix: Figure 17.2 & Figure 18.2). While fish monitoring of UWMN sites had discontinued by this time, the UWMN received reports of fish mortality in some other upland Welsh headwater streams. Formerly acidified catchments, such as those represented across the UWMN, are particularly vulnerable to this effect since exchangeable base cation levels remain very low, and are likely to take many decades under a low S deposition regime to begin to recover.

Analysis of UWMN and ICP Waters data has also emphasised the importance of sea salt deposition for concentrations of dissolved organic matter (Evans et al., 2006; Monteith et al., 2007; Wit et al., 2021). Recent work (Monteith et al., in press) provides evidence for a direct control of soil water ionic strength on DOC concentrations. It shows that at several UWMN sites, periods of relatively high sea salt inputs have a suppressive effect on the solubility of soil organic matter, and result, therefore in temporary reductions in DOC and water colour, and hence increased water transparency.

As the contribution of marine salts is so fundamental to UWMN water chemistry, and has become increasingly dominant, it is important to identify any evidence for directional changes in sea salt inputs that might be related to regional climate change effects. One immediate challenge, however, is disentangling the contribution of ions from marine and other sources. This is an issue for Cl^- concentrations particularly, since historically they have been dependent on atmospheric deposition of both (natural) sea salt and (pollutant) (HCl) (see Section 3.3.2.1).

In this section we have attempted to model the sea salt-derived component of the measured Cl^- concentration in UWMN waters by assuming that over the last 3 decades the decline in the non-marine component has been linearly correlated with the decline in SO_4^{2-} concentration (a consequence of both being derived from fossil fuel sources). We therefore first reduced the Cl^- and SO_4^{2-} concentrations of each site to annual means before running site-specific linear models to explain Cl^- as a function of SO_4^{2-}. We then took the residuals from these models, i.e. the component of the annual mean Cl^- concentration that could not be explained by the long-term decline in annual mean SO_4^{2-}, to represent the annual marine Cl^- trend. The effect of our attempt to remove the anthropogenic Cl^- contribution from the Cl^- trends for UWMN sites in westerly locations is illustrated in Figure 3.12a-b. In these plots the annual mean data have been standardised (by subtracting the mean and dividing by the standard deviation) in order to reveal any general similarities in temporal patterns across UWMN sites. Figure 3.12a provides the trends in the standardised means of the raw Cl^- data, and emphasises the long term downward trend which is broadly consistent across all of these sites. Figure 3.12b provides the trend in the residuals of the long-term Cl^- vs SO_4^{2-} relationship, i.e. our estimate of the trend in marine Cl^- concentration only. This suggests that although there has been significant inter-annual variation in sea salt inputs over time, there is no evidence of a monotonic trend that cannot be explained by a reduction in fossil fuel-based contaminants. Sea salt inputs were particularly high in 1990, 2008 and 2014-15 in the majority of sites.

a)
b)

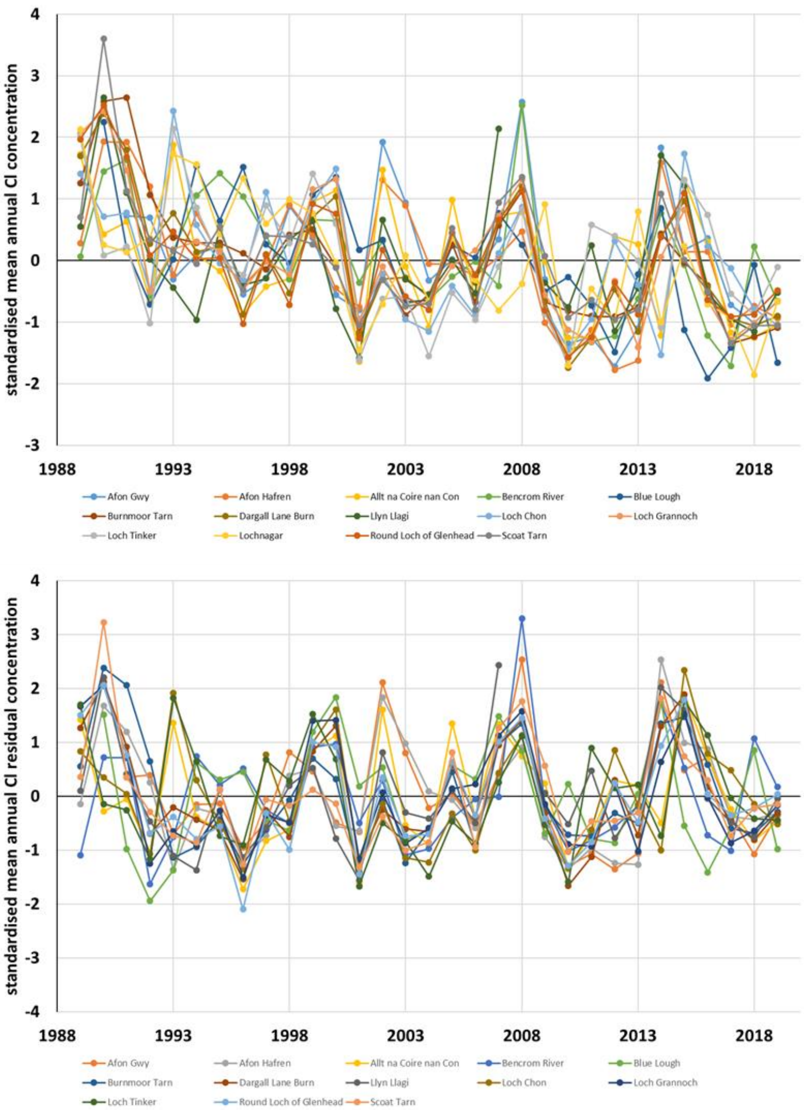

Figure 3.12. (a) Trends in site-standardised annual mean chloride concentration at UWMN sites with westerly locations, and (b) sulphate-adjusted chloride trends, i.e. after the "effect" of annual mean sulphate (assumed to be predominantly from anthropogenic sources) has been removed using site-specific linear models to provide an estimate of marine chloride contributions only

Support for the approach described above in representing the marine Cl^- contribution is provided in Figure 3.13 – a repeat of the earlier figure, but with the annual December to February NAO Index (NAOI) superimposed. The NAOI represents the mean atmospheric pressure difference between two stations in the Azores and Iceland. Winters when the mean December to February NAOI is positive are characterised by relatively warm, stormy and wet conditions caused by Atlantic storm tracks moving directly across the UK. In contrast, negative NAOI winters are characterised by a blocking high pressure system in the arctic that deflects storm tracks south of the UK, and results in relatively cold, calm and dry winters. Figure 3.13 demonstrates quite clearly that years with higher "marine" Cl^- concentrations are more likely to be associated with stormier positive NAO winters. As is the case for the marine Cl^- estimates, there is no evidence for a directional trend in the December to February NAO Index over the last three decades.

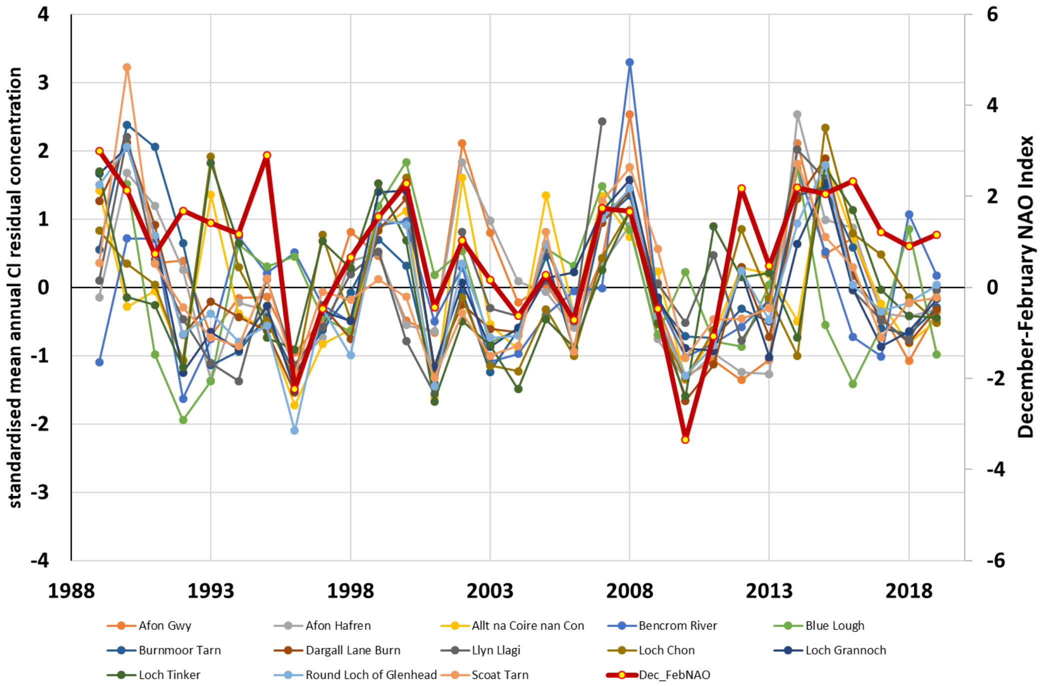

Figure 3.13. Repeat of Figure 3.12b, portraying inter-annual variation in standardised sulphate-adjusted chloride trends (to represent variation in chloride from sea salt) at a range of westerly UWMN sites, but with the mean December to February North Atlantic Oscillation (NAO) Index superimposed (red line).

Note that while the "marine" Cl^- and NAOI data in Figure 3.13 are presented on opposing y axes, the central zero values of the time series are aligned, so that negative NAOI values are associated with lower than average annual mean "marine" Cl^- concentrations, while positive NAOI values are often associated with higher than average annual mean concentrations. This is also demonstrated in Figure 3.14.

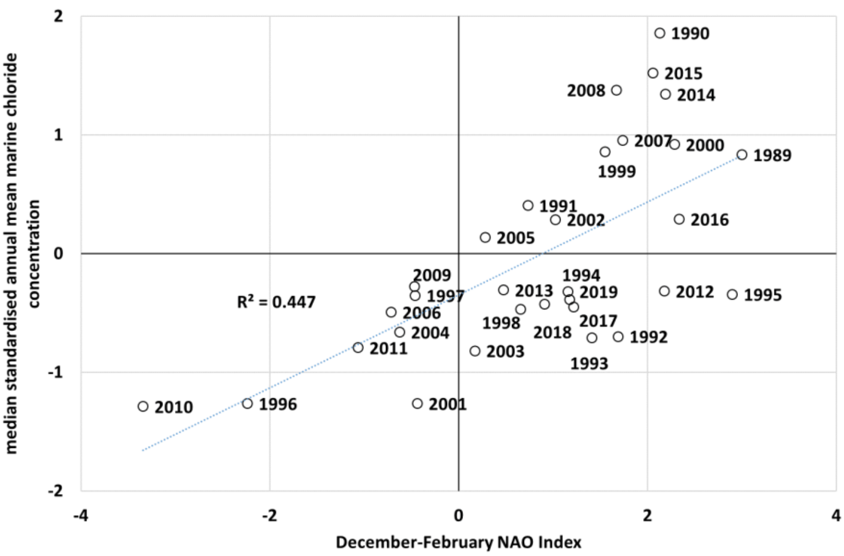

Figure 3.14. The median of annual mean marine chloride estimates for the 13 UWMN sites presented in Figure 3.13 with most exposure to sea salt from westerly directions.

While there is reasonable coherence in temporal patterns across the sites presented in Figure 3.13, it is also clear from this and the wider set of sites that there is some grouping of temporal patterns. It is likely that much of the between-site differences reflect the relative proximity of sites to the major sea salt sources and vulnerability to storms with different trajectories. We therefore applied a Euclidian Distance clustering approach to classify the main temporal patterns. This resulted in the identification of three coherent groups (Figure 3.15), and a further small set of sites that were distinct from each other.

The sites within the “east of the Irish Sea” group, , from mid Wales to Galloway in southern Scotland, are all situated within 25 km of the coast and show particularly tight coherence in inter-annual patterns. The marine Cl^- concentrations in this group provide some evidence for regular cyclicity, with the most prominent peaks in 1989, 1999-2000, 2007-2008 and 2014-15. This is broadly consistent with recognised patterns of NAO periodicity of between 6-9 years (Hurrell, 1995; Hurrell et al., 2003; Zhang et al., 2011). The degree of coherence within this group, relative to the more noisy signatures of other sites, is perhaps best explained by the physical protection offered by the Irish mainland and eastern parts of the British Isles to this part of mainland Britain from most dominant wind directions - with the exception of southwesterlies. Other groups of sites, and particularly those in the central-north Scotland group, are more prone to receiving significant sea salt inputs from westerly, northerly and easterly directions, resulting in considerably greater inter-annual variability in Cl^- concentrations and weaker correspondence with NAO periodicities. Now that inputs of anthropogenic pollutants are reaching relatively low levels, we can expect fluctuations not only in marine ion concentrations, but also acidity and DOC, to follow similarly geographically contrasting inter-annual frequencies in future.

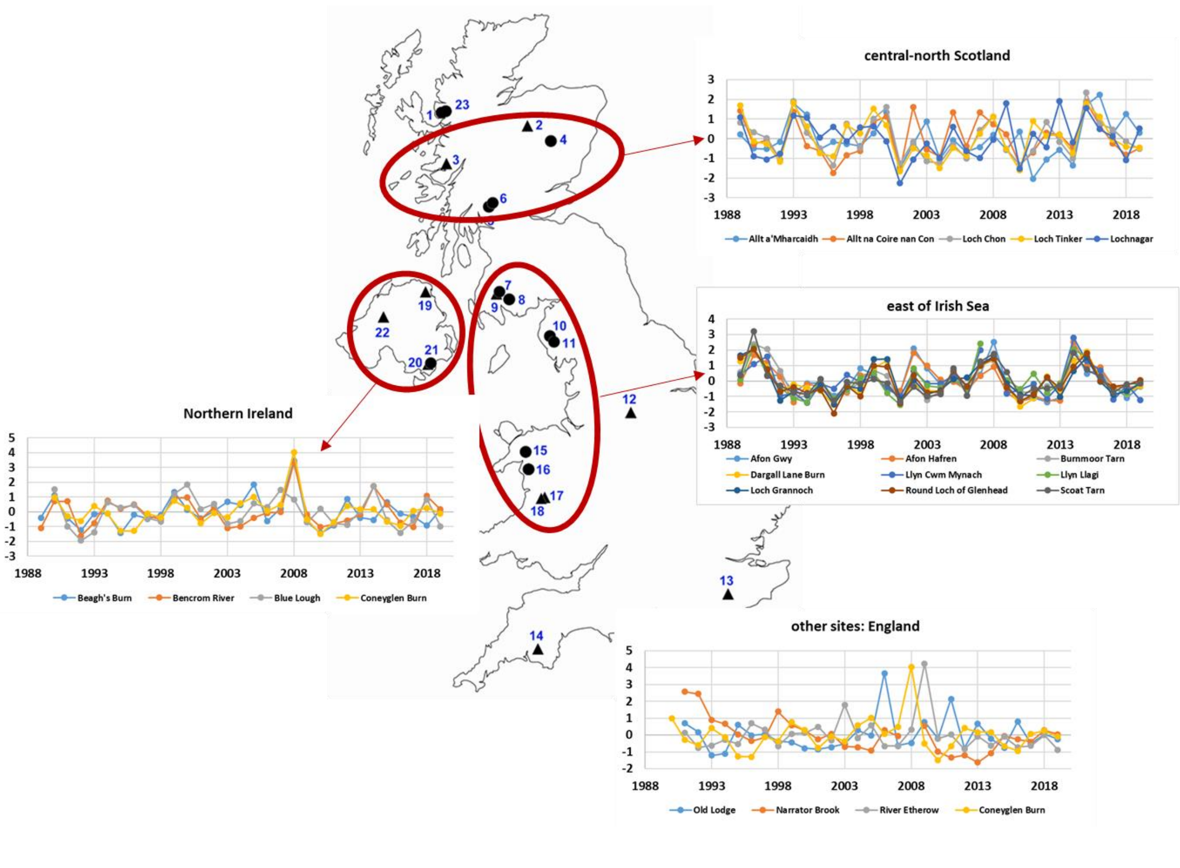

Figure 3.15. Geographical clustering of standardised annual mean marine chloride concentrations.

3.3.2.6 Trends in the relative contributions to acidity from the three strong acid anions

The potential for catchments to become increasingly burdened with reactive N, to a point of "nitrogen saturation", has been discussed in some detail in previous AWMN interpretive reports. This is important, since progress towards saturation is indicated by an increase in the leaching of NO_3^- leaching, first on a seasonal basis and eventually throughout the year. Any increase in N leaching over time, therefore, would partly counteract any recovery in acidity resulting from reductions in S, N and HCl deposition. This theoretical long-term behaviour has been incorporated within the dynamic acidification model FAB (see Section 5.1). As explained in Section 3.3.2.1., there is little evidence for an increase in NO_3^- leaching to UWMN waters. Nitrate concentrations have not changed monotonically at the majority, while trends at seven of the eight sites that have experienced significant change have been negative.

While contributions to surface water acidity from NO_3^- have historically been small relative to non-marine SO_4^{2-} and non-marine Cl^-, now that both of the latter have fallen to very low levels, NO_3^- is making an increasingly important contribution to total acidity at some sites. This is illustrated in Figure 3.16 (trends in median concentrations of non-marine SO_4^{2-}, NO_3^- and an estimate of non-marine Cl^- concentration), and Figure 3.17 (trends in percentages of the total non-marine acid anion concentration). In these figures, non-marine Cl^- concentration has been determined by i) assuming it follows site-specific linear relationships with non-marine SO_4^{2-} throughout the monitoring period, ii) regressing total Cl^- against non-marine SO_4^{2-} concentration to provide a prediction of the overall trend in non-marine Cl^- (on the assumption that marine Cl^- inputs have not changed over the full monitoring period– see Section 3.3.2.5), and iii) deducting the site specific median Cl^- concentration for the most recent 10 years of data, on the assumption that this "baseline" level is representative of marine Cl^- only – on the grounds that the burning of coal with a high chlorine content was phased out several years ago.

It is important to note that in Figure 3.16 the y-axis limits are specific to the range of acid deposition at each site, so the magnitude of change is not directly comparable, but the plot shows very strong declines in non-marine SO_4^{2-} and non-marine Cl^- (by inference), and less pronounced and more directionally variable changes in NO_3^-. Figure 3.17 shows that while percentage contributions from non-marine SO_4^{2-} and NO_3^- to total acidity have become more similar, non-marine SO_4^{2-} has remained the dominant acidifying anion in the majority of UWMN waters. The main exceptions are Blue Lough, where a moorland fire in 2011 led to a prolonged period of elevated NO_3^- ((Evans et al., 2016) and see Appendix: Section 21.2), Beagh's Burn, where although NO_3^- now appears to dominate, all three anions are close to the current limit of detection and therefore pose a negligible influence, and both Bencrom River and the Round Loch of Glenhead, where NO_3^- and non-marine SO_4^{2-} concentrations are significantly higher than in Beagh's Burn and comprise approximately 50% of the overall contribution each.

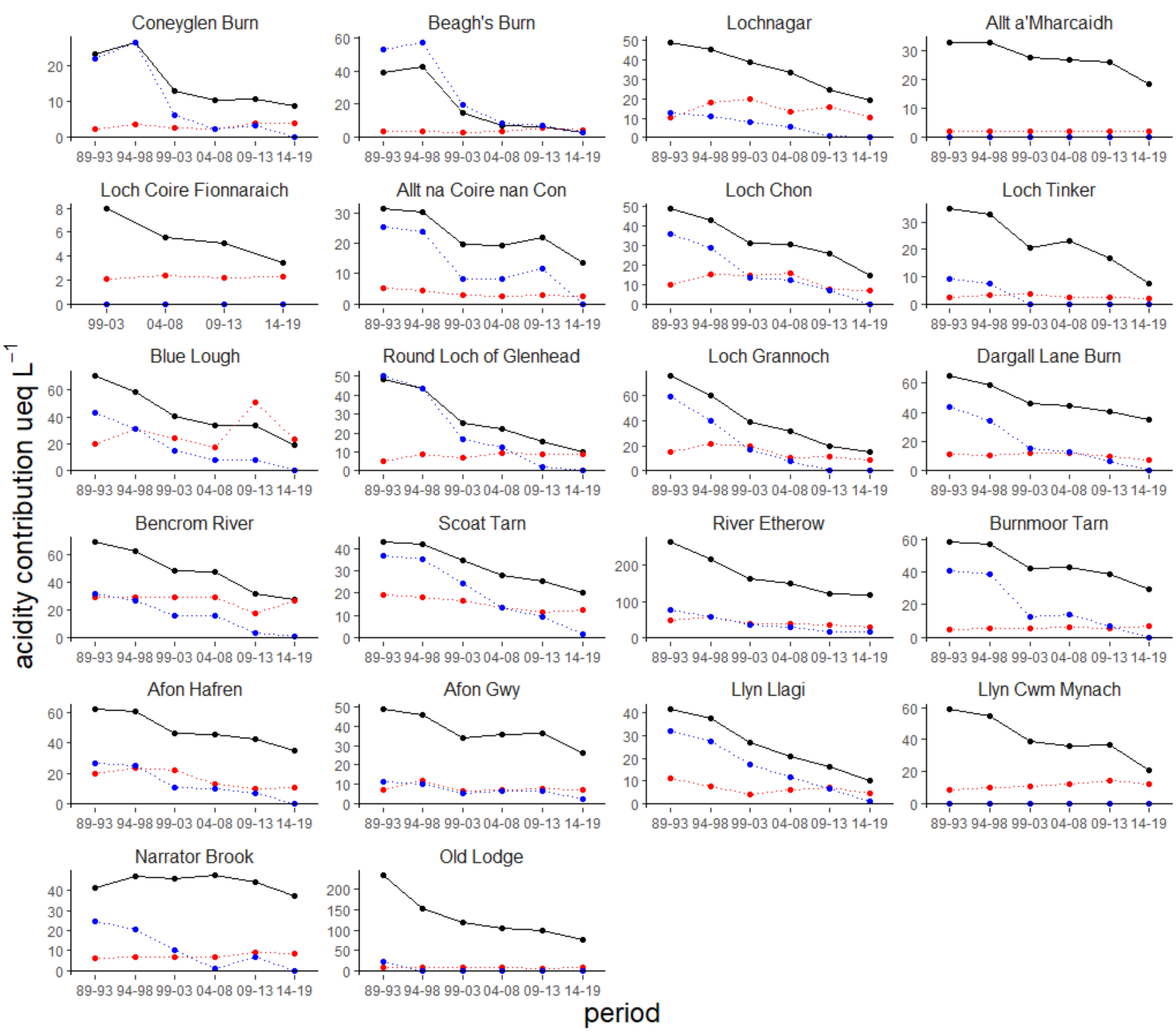

Figure 3.16. Trends in contributions for surface water acidity from nitrate (red), non-marine sulphate (black) and an estimate of non-marine chloride (blue). Data represent 5-6 year median concentrations.

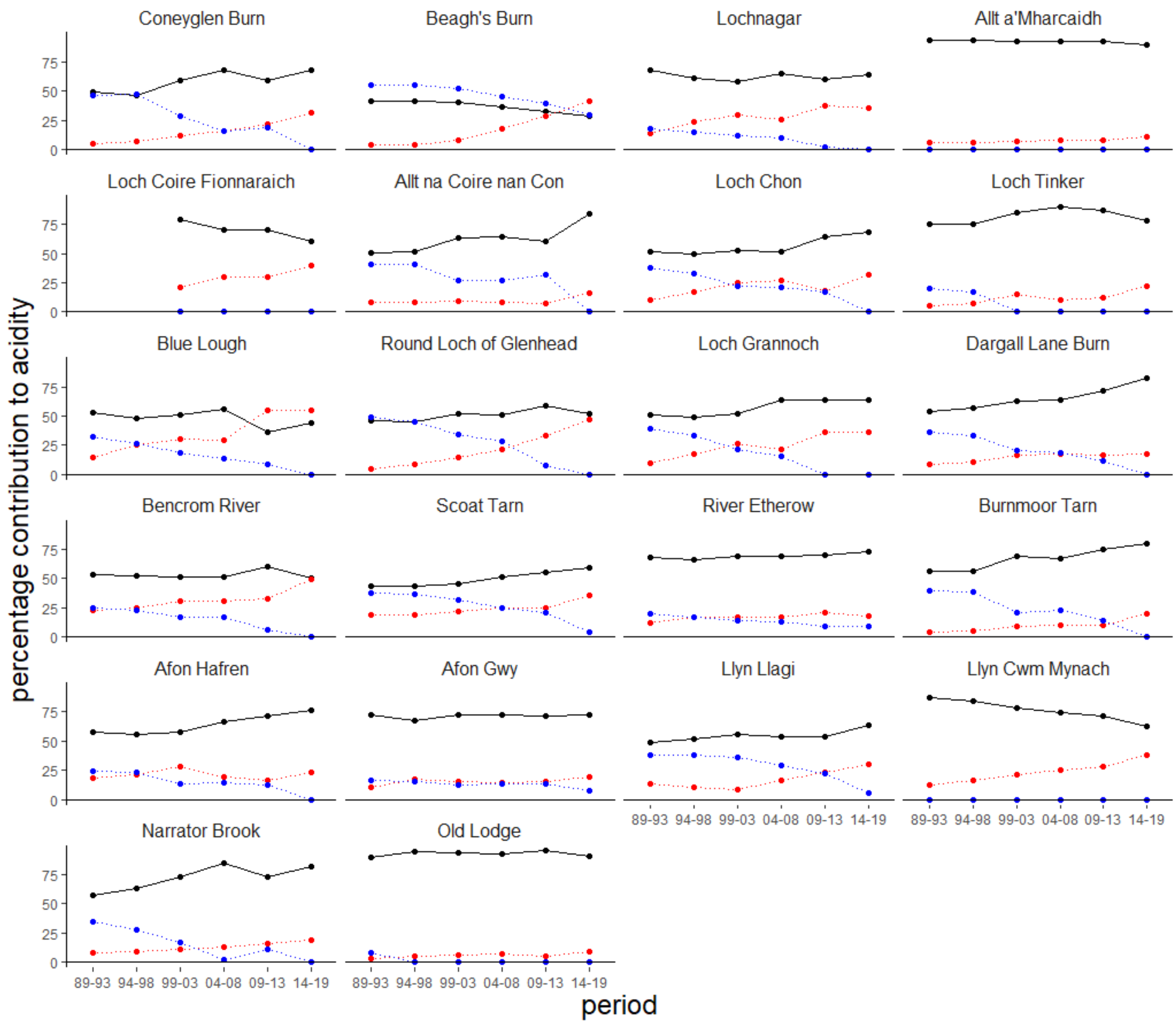

Figure 3.17. Trends in contributions to surface water acidity from nitrate (red), non-marine sulphate (black) and an estimate of non-marine chloride (blue), expressed as percentages of the sum of their contributions. Data represent 5-6 year median concentrations.

3.3.2.7 Trends in acidity extremes in UWMN streams

Largely because of the short water residence times of their catchments, the chemistry of most UWMN streams tends to be considerably more variable than that for UWMN lakes. This variability is driven largely by hydrological fluctuations. Rates of runoff and soil wetness determine the relative proportion of precipitation that reaches the aquatic system via surficial flow paths, i.e. through or over more acidic, organic-rich soil layers, relative to more chemically buffered groundwater. Separately, sporadic inputs from seasalts (most common during the winter months) can also lead to temporary spikes in acidity (Section 3.3.2.5). Although these extremes in water chemistry can be difficult to characterise with a monthly sampling regime, monthly sampling should be sufficient to characterise changes in these extremes over multi-annual scales.

Temporary surges in acidity, or “acid episodes” pose potential threats to acid-sensitive species such as salmonids and certain macroinvertebrate taxa that are sensitive to elevated levels of Al^{3+} and H^{+} ions, even over relatively short periods, depending for example on life cycle stage (Kroglund et al., 2008; Teien et al., 2004). It has been argued that the continued occurrence of acid episodes may be preventing biological recovery of chemically improving waters (Kowalik et al., 2007). On the other hand, if the acidity of extreme events is both limiting recovery and declining over time, any reduction in the severity of acid episodes should increase opportunities for sustained recolonization by more acid-sensitive taxa. In this section, therefore, we consider trends in extremes in acidity metrics (i.e. streamwater pH and labile aluminium), by determining linear trends in 5th, median and 95th percentile values for each stream site during each 5-year period since 1989.

Figure 3.18 demonstrates considerable variation between sites in the prevalence of pH trends across the pH distribution range. This in part reflects initial pH levels (pH responses to reductions in acid deposition are most sensitive in the pH 4.5 – 6.5 range), and the strength of the acid deposition trend. Streamwater pH in the low deposition sites, Coneyglen Burn, Allt na Coire nan Con, Allt a'Mharcaidh and Beagh's Burn, shows no evidence of linear change in median concentration or in the least acidic (i.e. 95th) percentile class. The same is largely true for the most acidic (i.e. 5th) percentile class, with the exception of Coneyglen Burn, where there is a clear, if gradual, upward trend in pH.

Similarly, for this group of sites, these is no indication of trend in Al^{3+} concentration in the least acidic (i.e. 5th) percentile, which is nearly always below the limit of detection (Figure 3.19). However in this case, clear downward trends are apparent in the most acidic (95th) labile aluminium percentile at Beagh's Burn and Allt na Coire nan Con. In both cases, initial extreme concentrations at these sites were sufficiently high to be potentially harmful to some acid-sensitive aquatic biota, but have since fallen to more benign levels.

The remaining (higher deposition) sites show upward trends in pH within all percentile groups. In the case of Afon Hafren, Afon Gwy, and Bencrom River and Narrator Brook, these trends roughly parallel each other, while median streamwater pH of Dargall Lane Burn and the River Etherow has increased more rapidly than the pH extremes. Old Lodge, the most acidic UWMN stream, is unusual in that pH has changed most rapidly in the least acidic (95th) percentile class. It is important to note, however, that pH is a logarithmic measure of H^+ concentration. In all of these cases, rates of decline in H^+ concentration in the most acidic (i.e. high flow) class are greater than those during more benign conditions.

More generally, the sites in the higher deposition grouping show the most rapid reduction in Al^{3+} concentration in the most acidic (95th) percentile class. The exception here is Narrator Brook, where there is no obvious trend in Al^{3+} in any percentile class. Figure 3.19 shows that, for the majority of sites, Al^{3+} concentration trends in the different percentile classes had almost converged at very low concentrations by the time measurements ceased in 2016. The exceptions in this case are Afon Gwy, Afon Hafren, Bencrom River and the River Etherow, where, by 2016, there was still a sizeable difference in labile aluminium concentrations during periods of high flow and/or seasalt deposition events, relative to more benign, and more ground-water influenced, conditions. It is noteworthy here, that extreme (95th percentile) Al^{3+} concentrations in the more acidified forested Afon Hafren have fallen at approximately twice the rate of the paired moorland site, the Afon Gwy, but by 2016 remained roughly 150% higher.

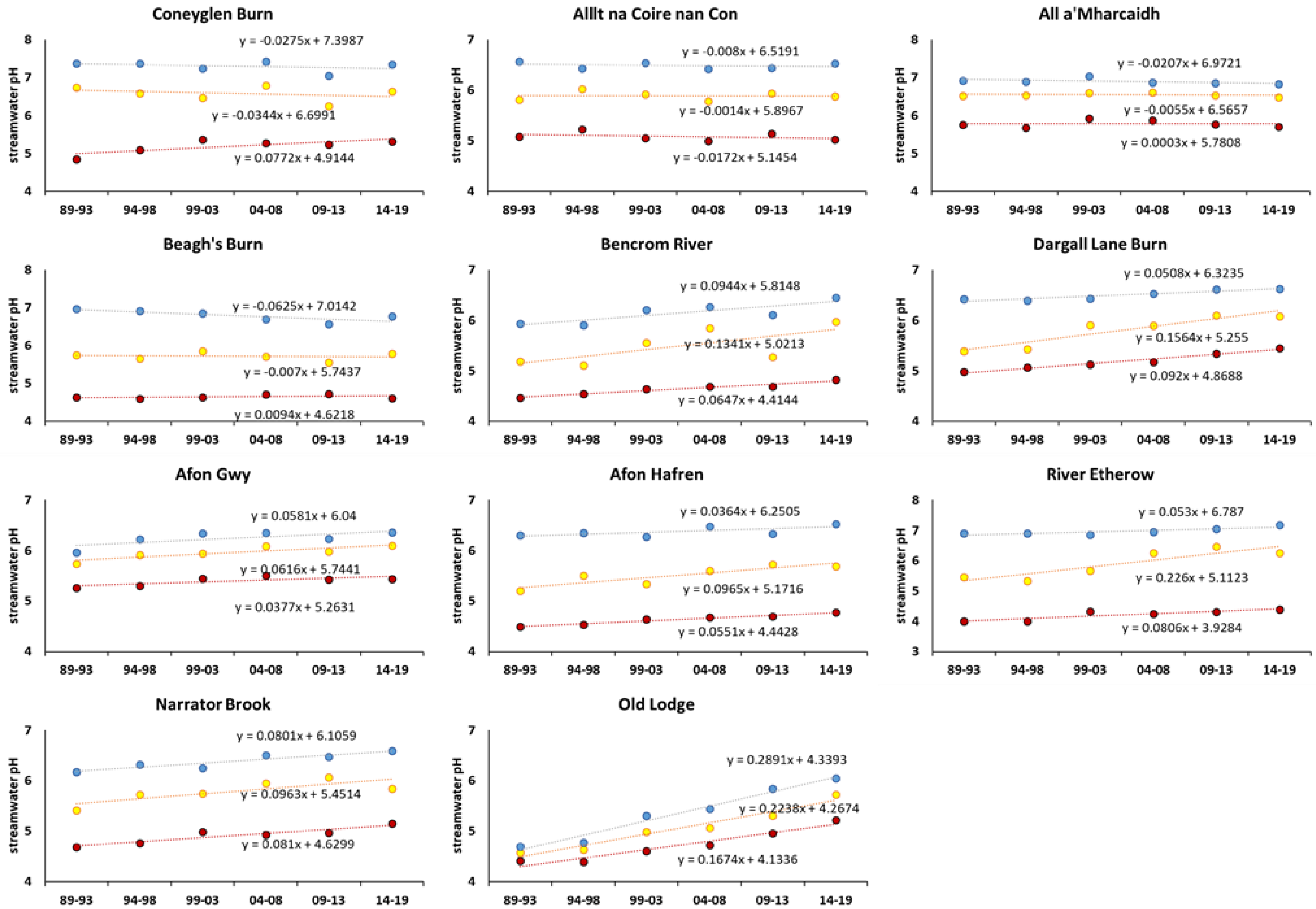

Figure 3.18. Linear trends in 5th (red), 50th (yellow) and 95th (blue) percentile pH for UWMN streamwaters. Linear trend equations are based on a 5-year time unit, so that trend slopes should be multiplied by 2 to convert them to units of pH units per decade.

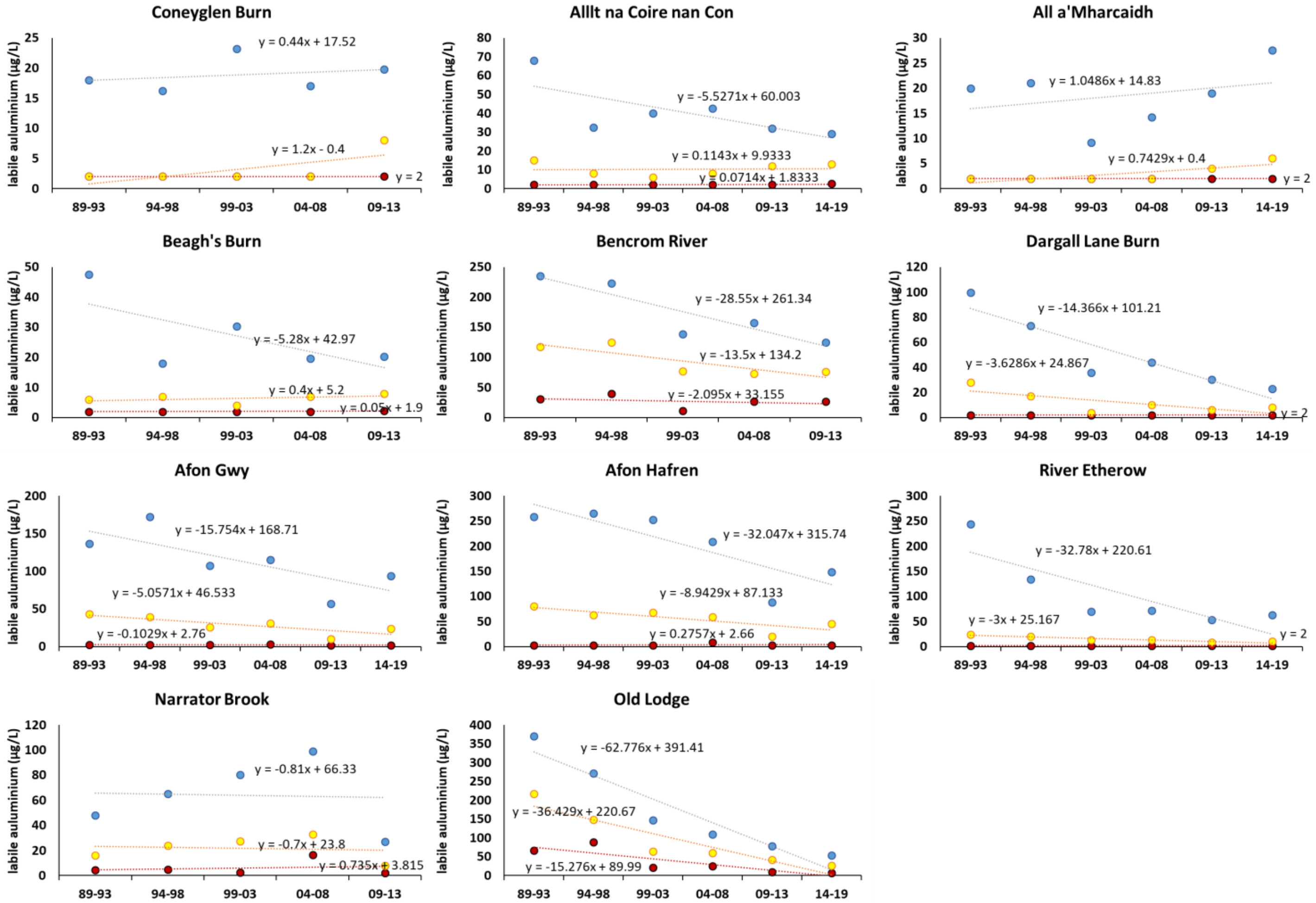

Figure 3.19. Linear trends in 5th (red), 50th (yellow) and 95th (blue) percentile labile aluminium concentrations for UWMN streamwaters. Note for most sites labile aluminium measurements ceased in 2016. Linear trend equations are based on a 5-year time unit, so that trend slopes should be multiplied by 2 to convert them to units of µg L^{-1} labile aluminium per decade.

3.4 Water chemistry trends summary

In summary, regardless of location, the catchments of all UWMN sites have experienced major declines in the deposition of S and HCl over the past three decades. The deposition of oxidised N species has also fallen substantially, but this has been counteracted at some sites by gradual increases in the deposition of reduced N species.

The CBED model estimates that the acid deposition load contributed by oxides of S and N to UWMN catchments fell by 65% between 1990 and 2017, and by 2017 was only around 50% of the load received by the most northerly "low deposition control" catchment (i.e. Loch Coire nan Arr) at the time the network was established. Deposition loads declined most in the southern Pennines (River Etherow catchment), and least to UWMN catchments in the far north and north-west of the UK. The majority of other sites from southern Scotland southwards showed similar, intermediate reductions.

Non-marine SO_4^{2-} fluxes in the runoff from UWMN sites declined at broadly similar rates to reductions in S deposition fluxes. In general, SO_4^{2-} concentrations showed a similar spatial pattern of decline to the pattern in fluxes, but rates of reduction in concentrations were relatively more rapid in waters with easterly locations as a consequence of lower rates of runoff, and in forested catchments as a consequence of historically enhanced rates of pollutant interception by forest canopies.

Chloride concentrations in UWMN sites fell at a comparable rate to non-marine SO_4^{2-}, indicating shared dominant pollution sources historically.

Although trends in total N deposition mostly lacked clear direction (CBED data for reduced available from 1999 only), downward trends in NO_3^- concentration in UWMN waters were detectable in seven of the 23 sites analysed. Total N deposition was estimated to have fallen at some of the seven sites to show downward trends in NO_3^- but not all of them. A more unifying characteristic of these sites is that they have been the most acidic on the network, and it is possible that the NO_3^- trends are more related to an increased capacity of their recovering catchment soils to retain and cycle N deposition than changes in N deposition per se.

Over the last decade, non-marine SO_4^{2-} has remained the dominant acidifying anion in most UWMN waters, non-marine Cl^- (although more challenging to estimate) is thought to have reached a negligible level at most sites, while the relative contribution to acidity from NO_3^- (but not the concentration of NO_3^-) has often increased, but remains of secondary importance at most sites.

The large reductions in acid anion concentration across the UWMN have been partially balanced by reductions in base cations, but also by reductions in Al^{3+} in the most acidified waters, reductions in H^+ ions (i.e. increases in pH) increases in organic acids (i.e. DOC), and, in the least acid-sensitive waters, increases in Gran alkalinity, indicative of a rise in bicarbonate concentrations. Particularly pronounced increases in Gran alkalinity in several Scottish sites since around 2014, appear to be linked to a prolonged period of below-average water tables and consequent increased contributions from groundwater, but further years of data are required to verify this.

The more rapid reduction in acid anion concentrations experienced by forested catchments, relative to paired moorland sites, is reflected in more rapid reductions in acidity metrics (e.g. H^+, Al^{3+} and ANC), although in two of the three pairs, water in the forested catchments has remained slightly more acidic.

Concentrations of DOC have increased across the network as a consequence of the rising solubility of soil organic matter as soil water ionic strength has declined. The resulting increase in organic acidity has partially offset the expected increase in water pH. In some of the UWMN lakes, the increase in water colour associated with the rise in DOC is estimated to have brought about a major reduction in the proportion of the lake bed that remains within the theoretical photic zone (i.e. the depth range within which aquatic photosynthesis is possible – see site-specific reports on chemistry trends in the Appendix).

As a consequence of the changes above, Acid Neutralising Capacity (ANC) has increased significantly in all but the least acidified sites, and in many cases has shifted from being predominantly negative during the first few years of monitoring, to largely exceeding the UK's adopted "critical limit" of 20 μeq L^{-1}. In a minority of sites, ANC remains predominantly below this limit, and at one site, Blue Lough, the very low weathering potential of the underlying geology is likely to prevent water chemistry ever reaching this limit. Trends in ANC, and the limitations of the current critical limit concept are considered in further details in Section 6.2.

Streamwater acidity during acid episodes, that occur during both high discharge- and sea salt deposition-events, has declined substantially in all sites that have experienced significant reductions in acid deposition. These episodes are becoming increasingly benign, and this should be conducive to the gradual re-colonisation of the historically more acidified streams by acid-sensitive taxa.

The water chemistry of the majority of UWMN sites has always been strongly influenced by sea salts, and as pollutant levels continue to fall, the importance of major storm events that generate sea salt aerosol has increasingly come to dominate short term fluctuations in surface water ionic strength, acidity, dissolved organic matter inputs and fluxes and associated water colour. There is no indication of any directional change in sea salt inputs, that could, for example, be linked to changes in climate, over the UWMN monitoring period.

Over the decade since UWMN water chemistry time series were last formally assessed, therefore, acid deposition to acid-sensitive lake and stream catchments across the UK has continued to decline, and the chemical quality of lake and stream water has continued to respond positively. This is creating the conditions for ecological improvements across all the formerly acidified UWMN sites. Evidence for actual biological responses is explored in the following two chapters.

4 Epilithic diatom trend summary

Authors: Stephen Juggins, Roger Flower, Ewan Shilland, Gina Henderson, Rick Battarbee & Don Monteith

4.1 Introduction

Diatoms played a pivotal role in the "acid rain" debate. The diatom record in lake sediments enabled the timing and extent of lake acidification to be reconstructed (Battarbee et al., 2010; Charles et al., 1990), and allowed various competing hypotheses concerning the causes of lake acidification to be evaluated (Battarbee et al., 2010). Diatoms are also one of the main groups of aquatic organisms used to monitor contemporary water quality in lakes and streams. In Europe, the diatom phytobenthos is one of the biological quality elements used to assess the ecological status of fresh waters, including acidity and acidification (Andrén and Jarlman, 2009; Juggins et al., 2016). In both stream and lake systems experimental studies have shown that diatoms respond sensitively to pH and pH-related environmental factors, and that forms, concentrations and interactions of Al and DOC, as well as pH can have a large influence on diatom species composition and biomass (e.g. Gensemer, 1991; Smith, 1990). These findings are corroborated by field studies (e.g. Genter, 1995; Hirst et al., 2002) and by the statistical analysis of diatom-chemistry training sets (Birks et al., 1990; Kingston et al., 1990). Experimental studies also show species composition can change rapidly in response to a change in water chemistry (Cameron, 1995; Hirst et al., 2004; Jüttner et al., 2021).

Diatoms are found in a range of different habitats in streams and lakes, each supporting highly diverse floras. In upland waters the epilithic community (diatoms growing on rocks and stones) is usually the most common and diverse. Rock and stone substrates also provide a stable habitat that is temporally and spatially consistent, so diatom composition is less influenced by other factors such as host plant specificity or sediment chemistry as they are in epipthytic (plant) or epipelic (mud) diatom communities respectively (Eminson and Moss, 1980; King et al., 2006). Consequently, the epilithic diatom community is used for monitoring in the UK UWMN.

Central questions that we address from an analysis of the 30-year epilithic diatom records with respect to reduced acid deposition are:

- Have there been any significant changes in diatom assemblages across the network?
- Are there differences between lakes and streams in terms of the extent of change?
- How can the different responses at individual sites be explained with reference especially to changes in water chemistry (including pH, NO_3^-, DOC and labile aluminium)?

4.2 Epilithic diatom methods

4.2.1 Field and laboratory methods

Lake and stream sites were sampled once a year, normally between July and early September. For lakes, three spatially discrete littoral locations, uninfluenced by inflow streams, were selected around the shore. Sample collection follows the European standard developed for compliance with the EU Water Framework Directive (CEN, 2004) for stream and a modified version of this standard for lakes

(King et al., 2006). For streams three sampling locations, equally-spaced along a 50m reach, and again not directly influenced by inflow streams or other local disturbance, were identified. At each location five permanently submerged cobble-sized stones, ideally from a depth >30 cm (lakes) or below the minimum flow level (streams), were selected and epilithic diatoms removed by vigorous brushing with a clean toothbrush into an open sample tray. The bulk sample for each sampling location (i.e. from the 5 stones) was then homogenised and transferred to a sample tube. For most of the duration of UMWN, samples have been preserved with 2–3 drops of Lugol's iodine, but more recently with ethanol.

Diatom samples were prepared for microscopy by cleaning with hydrogen peroxide (Battarbee et al., 2001). Microscope slides were prepared using Naphrax high refractive index mounting medium, and 500 individual diatom valves were identified and counted using a light microscope at x 1000 magnification.

4.2.2 Statistical methods

Diatom epilithon counts were aggregated across the three replicate samples collected at each site for each year, and the resulting counts converted to percentage relative abundances.

A number of different analyses were performed to (1) quantity the magnitude and test significance of a trend in the diatom assemblage data, and to visualize the pattern of the trend (linear, non-linear monotonic, step), and (2) examine the degree to which changes in the diatom community can be explained by changes in water chemistry.

The magnitude of diatom composition turnover, or beta-diversity, over the sampling period was quantified using detrended canonical correspondence analysis (DCCA) with Year as a constraining variable. The gradient length of the first axis gives a measure of turnover scaled in SD units, with a turnover of 1 SD units representing an approximately 50% change in species composition over the sampling period and a turnover of 2 SD units representing a complete exchange of species (Hill and Gauch, 1980; ter Braak and Verdonschot, 1995). Redundancy analysis (RDA), with sampling year as an explanatory variable, was used to test for a linear trend in assemblage composition at each site. The presence of a trend was determined using a restricted permutation test in which the ordering of samples was maintained with starting samples selected via random cyclic shifts of the time series. The single constrained eigenvalue from each RDA (RDA1) quantifies the fraction of **total variance** in the diatom data that can be explained by a linear temporal trend. RDA1 was compared to an equivalent measure from an unconstrained PCA (PCA1) to calculate the fraction of the **main pattern of variance** in diatom data that can be explained by a temporal linear trend. Finally, a principal curve (PrC) was fitted to the diatom data at each site to summarise the trajectory of change. A principal curve is a non-linear curve fitted through the data in multivariate space and can provide a more parsimonious fit than other ordination methods if there is a single dominate gradient (Simpson and Birks, 2012). Diatom percentage data were square-root transformed prior to RDA/PCA/PrC analyses to yield ordinations based on Hellinger's distance, which is more appropriate for ecological community data (Legendre and Gallagher, 2001). In addition to distance-based methods (RDA/PCA/PrC) we also tested the diatom data for trend using a model-based approach to fit separate generalized linear models (GLMs) to each taxon with year as the explanatory variable and using a quasibinomial link to model the proportional abundance of each taxon (Wang et al., 2012). Significance of the trends was assessed using a restricted permutation test as for RDA and a Pseudo-R2, analogous to RDA1% variance explained, was calculated according to McFadden (1974). This model-based multivariate-GLM (mGLM) provides an alternative to RDA to test community-level trends and has the additional advantage that it also provides a significance test of the trend for each individual taxon (Wang et al., 2012).

To explore the extent to which the trends at each site can be accounted for by changes in pH, we calculated the diatom acidification metric (DAM; Juggins et al., 2016) for each sample. This metric encapsulates the pH range of the constituent taxa, and ranges from zero, for an assemblage dominated by acidiobiontic taxa (i.e. those most common at pH less than 5), to 100 for an assemblage dominated by taxa most abundant at pH greater than 7. For streams we used DAM as described in Juggins et al. (2016) and, because some taxa common in lakes are not recorded in the original DAM metric, we used a modified version for lakes based on species optima from the SWAP lake-sediment diatom calibration dataset (Birks et al., 1990b). The significance of trends in DAM at each site was assessed using a Sen's slope estimator (Wilcox, 2010), and visualized using a smoother based on a generalized additive model (GAM) with spline smother and a first order autoregressive CAR(1) process for the residuals. Periods along the trend where there is a significant increase or decrease in DAM were identified by computing the 95% point-wise confidence intervals of the first derivative of the fitted smooth function (see Monteith et al. (2014) for details). The same technique was used to highlight periods of significant change in the PrC scores.

To explore the potential effects of other water chemistry variables on the diatom community time-series we used a series of RDAs to calculate the variance in the diatom data explained (in a statistical sense) by alkalinity, DOC, labile-Al, and NO3. This is referred to as the total (or marginal) effect of each variable. We also used a series of partial RDAs, to calculate the unique (or conditional effect) of each variable with the effect of pH partialled out. That is, the additional effect of the variable independent of any shared effect with pH. The significance of the total and unique effects was assessed by a restricted permutation test as described above.

In all joint diatom-chemistry analyses, water chemistry data was expressed as the mean of months 3-9 for lakes and 5-9 for streams, rather than annual mean or seasonal mean, as this aggregation period explained, on average, the maximum variance in the diatom data.

All statistical analyses were performed using R software for statistical (R Core Team, 2020) with the following additional packages: vegan (PCA and RDA: Oksanen et al., 2022), princurve (PrC: Hastie and Stuetzle, 1989), darleq3 (DAM: Juggins et al. 2016), mvabund (mGLM: Wang et al. 2016).

4.3 Epilithic diatom results

Results of the community-level DCCA, PCA / RDA and mGLMs together with their associated significant tests are shown in Table 4.1. Time series plots showing trends in the most abundant taxa at each site are shown in the Appendix. All sites except Loch Coire Fionnaraich, Allt na Coire nan Con, Loch Grannoch, Burnmoor Tarn and Coneyglen Burn show significant trends in species composition as assessed by RDA. The analogous trend test based on mGLMs yields very similar results except for Burnmoor Tarn (significant) and Narrator Brook (not significant). The variance explained for RDA1 and mGLM pseudo-R^2 are strongly correlated ($r=0.85$, $p \le 0.001$) indicating close agreement in the two methods. Species turnover varies from 0.55 at Loch Coire Fionnaraich (with only 18 years of data) and

0.8 at Burnmoor Tarn to 2.3 at the River Etherow. Fourteen sites have species turnover greater than 1 SD unit, indicating an approximately 50% change in species composition at these locations.

The ratio between the first RDA and PCA eigenvalues (RDA1/PCA1) indicates the variance in the diatom data explained by a linear trend as a proportion of the total explainable by an RDA model. Values range from 0.11 and 0.18 for Loch Coire Fionnaraich and Allt na Coire nan Con respectively to 0.86 for the River Etherow. Sixteen sites have a RDA1/PCA1 ratio over 0.5, indicating locations where a linear change with time is the dominant pattern of variation in the species data.

Results of the principal curve analysis are shown in Figure 4.1, with GAM smoothers added to highlight parts of the series showing periods of significant species turnover. Thus, the RDA and mGLMs described above test for a linear trend across the whole sampling period whereas the principal curve plus GAM smoother gives insights into how the rate of diatom community varies across the series, including periods of little or no change. The 23 sites exhibit a range of compositional change patterns: 4 show no significant periods of change, 11 show a sustained rate of turnover throughout the monitoring period, or at least the last 20 years, 3 show sustained change in the early part of the record but little or no in the last c. 8-10 years, and 5 show more complex patterns of turnover. These patterns are further discussed on a per site basis in the Appendix.

RDA1 and the RDA1/PCA1 ratio encapsulate the strength and significance of the linear trend with time at each site. RDA1-pH (Table 4.1) gives similar information but for the changes in the diatoms community directly related to changes in lake- or stream-water pH. Diatom community change is significantly related to pH at 12 sites ($p \leq 0.05$). All except Coneyglen Burn have a significant linear temporal trend. At 10 UWMN sites the RDA1-pH / PCA1 ratio is greater than 0.5, indicating that the response to pH is the main pattern of variation in the species data.

Trends in the diatom acidification metric (DAM) are shown in Figure 4.2. The y-axis scaling is the same for each site, so the slope of the fitted GAM smoother gives a relative measure of the rate of pH-related change in the diatoms communities through time. Patterns of variation vary across the network and are consistent with the results of the RDA-pH significance test. Of the 12 sites to show significant responses to pH, all but Narrator Brook exhibit significant and sustained increases in DAM over the whole (6 sites) or part (2 sites) of the sampling period.

Table 4.1: Results of redundancy analysis (RDA), multivariate GLMs (mGLM), detrended canonical correspondence analysis (DCCA), and diatom acidification metric (DAM). See text for explanation.

No.	Site Name	N	Turn-over	PCA1	RDA1	RDA1 p-value	RDA1 / PCA1	mGLM Pseudo-R2	mGLM p-value	RDA1-pH	RDA1-pH p-value	RDA1-pH / PCA1	DAM slope	DAM p-value
1	Loch Coire nan Arr	20	0.97	31	**18.5**	**0.05**	0.6	**0.07**	**0.05**	5.8	0.53	0.19	0.08	0.72
26	Loch Coire Fionnaraich	18	0.55	41.5	4.6	0.56	0.11	0.02	0.61	5.7	0.39	0.14	-0.2	0.24
2	Allt a'Mharcaidh	31	1.21	24.8	**16.1**	**0.03**	0.65	**0.07**	**0.03**	7.9	0.07	0.32	-0.19	0.13
3	Allt na Coire nan Con	31	0.83	39.8	7.2	0.23	0.18	0.03	0.06	5.5	0.07	0.14	**-0.44**	**0.01**
4	Lochnagar	31	1.76	44	**30.5**	**0.03**	0.69	**0.07**	**0.03**	**22.2**	**0.03**	0.5	**0.34**	**< 0.01**
5	Loch Chon	31	1.89	44.9	**36.1**	**0.03**	0.8	**0.11**	**0.03**	**34.5**	**0.03**	0.77	**0.88**	**< 0.01**
6	Loch Tinker	31	0.89	21.3	**11.3**	**0.03**	0.53	**0.04**	**0.03**	4.8	0.23	0.23	**0.13**	**0.03**
7	Round Loch of Glenhead	31	0.99	36.1	**19.6**	**0.03**	0.54	**0.05**	**0.03**	**18.5**	**0.03**	0.51	**0.14**	**< 0.01**
8	Loch Grannoch	31	1.18	37.5	12.1	0.61	0.32	0.06	0.06	12.8	0.17	0.34	**0.14**	**0.02**
9	Dargall Lane Burn	31	1.04	36.2	**25.6**	**0.03**	0.71	**0.08**	**0.03**	**18.0**	**0.03**	0.5	**0.37**	**< 0.01**
10	Scoat Tarn	31	1.11	14.8	**12.7**	**0.03**	0.86	**0.06**	**0.03**	**10.8**	**0.03**	0.73	0.02	0.7
11	Burnmoor Tarn	31	0.8	17.3	9.5	0.16	0.55	**0.04**	**0.03**	3.3	0.4	0.19	**0.17**	**0.02**
12	River Etherow	31	2.34	45.5	**39.3**	**0.03**	0.86	**0.06**	**0.03**	**13.4**	**0.03**	0.29	0.45	0.33
13	Old Lodge	31	1.31	31.5	**23.2**	**0.03**	0.74	**0.08**	**0.03**	**23.7**	**0.04**	0.75	**0.96**	**< 0.01**
14	Narrator Brook	30	0.87	33.3	**15.8**	**0.03**	0.48	0.04	0.2	**9.2**	**0.04**	0.28	0.57	0.06
15	Llyn Llagi	31	1.78	37.2	**30.3**	**0.03**	0.81	**0.09**	**0.03**	**26.8**	**0.03**	0.72	**0.77**	**< 0.01**
16	Llyn Cwm Mynach	31	1.17	22.1	**16.9**	**0.03**	0.76	**0.07**	**0.03**	4.1	0.43	0.19	0.13	0.18
17	Afon Hafren	31	1.58	51.5	**40.1**	**0.03**	0.78	**0.11**	**0.03**	7.4	0.17	0.14	**1.03**	**< 0.01**
18	Afon Gwy	28	0.78	42.6	**23**	**0.04**	0.54	**0.06**	**0.04**	7.7	0.18	0.18	**0.75**	**< 0.01**
19	Beagh's Burn	31	1.51	23.5	**11.9**	**0.03**	0.51	**0.04**	**0.03**	4.7	0.07	0.2	-0.54	0.13
20	Bencrom River	31	0.75	42.4	**18.5**	**0.03**	0.44	**0.05**	**0.03**	**13.5**	**0.03**	0.32	**0.17**	**< 0.01**
21	Blue Lough	30	1.37	48.6	**34.3**	**0.03**	0.71	**0.1**	**0.03**	**26.4**	**0.03**	0.54	**0.25**	**< 0.01**
22	Coneyglen Burn	30	1.39	25.5	9.4	0.13	0.37	0.03	0.13	**9**	**0.04**	0.35	**-0.66**	**0.01**

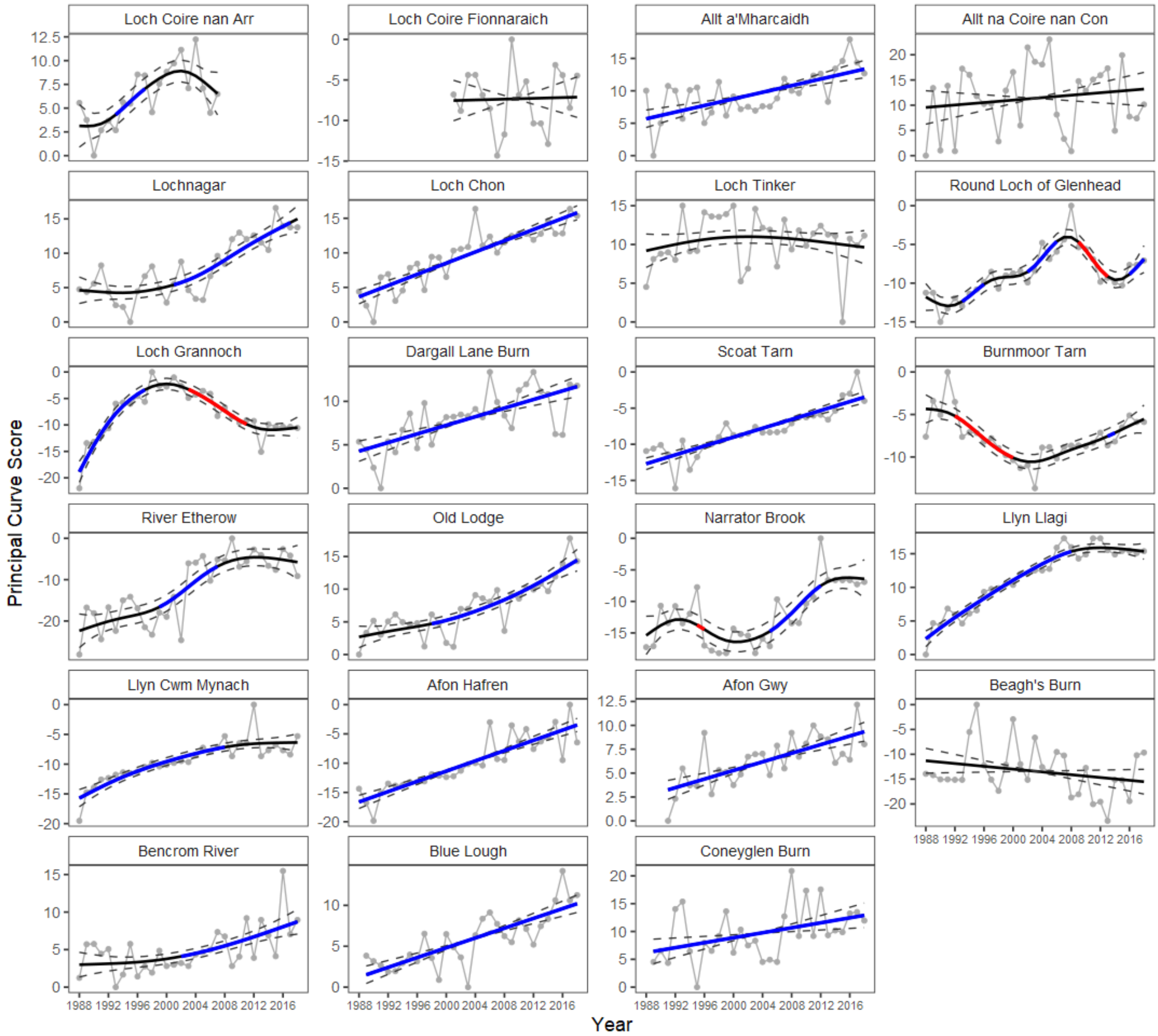

Figure 4.1. Principal curve (PrC) trajectories for each site, with GAM smoother highlighting periods of significant species change (blue = significant increase; red = significant decrease).

Results of the variance partitioning are shown in Figure 4.3. The height of the bars reflect the total variance explained by each water chemistry variable. This total is decomposed into two components: the fraction of variance uniquely explained by a variable (light shading) and the fraction shared or confounded by pH (dark shading). Red boxes indicate significant total or unique fractions ($p \leq 0.05$). No attempt has been made to adjust p-values for multiple comparisons so type-I errors will be inflated. Nevertheless, the p-values and the effect size (i.e. magnitude of the total and unique variance explained by each variable) are helpful in identifying sites where diatoms may be responding to chemical changes independent of changes in acidity. Results of these analyses are discussed in the Appendix.

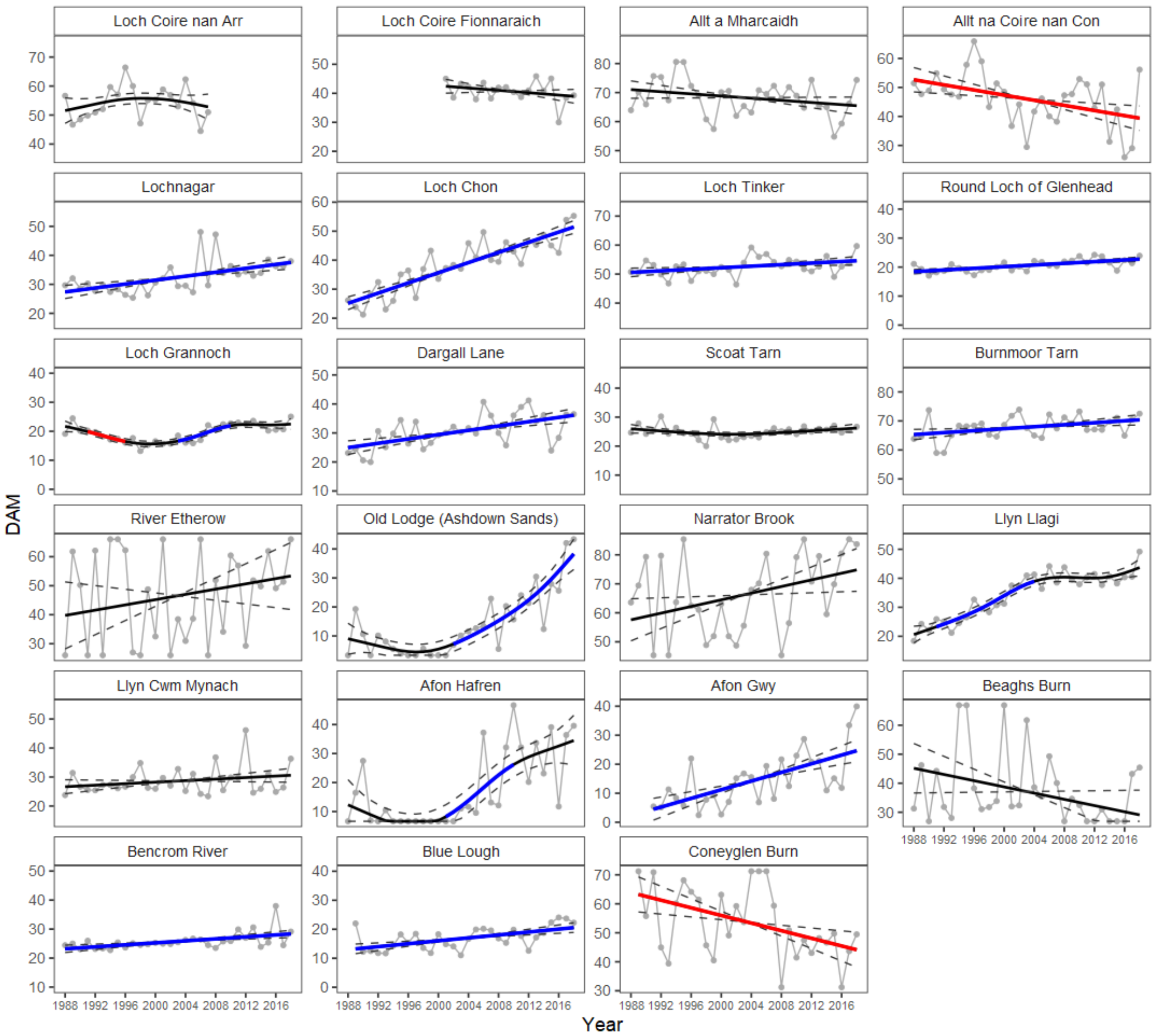

Figure 4.2. Trends in diatom acidification metric (DAM) for each site, with GAM smoother indicating periods of significant change (blue = significant increase; red = significant decrease).

Figure 4.3. Results of variance partitioning showing the fraction of variance in the diatom assemblages explained by each chemistry variable. The height of the bars represents the total effect of each variable, "unique" refers to the additional contribution the variable conditional on pH, and "shared" refers to the joint effect shared, or confounded with pH. ALK = Gran alkalinity; LAL = labile aluminium concentration; DOC = Dissolved Organic Carbon; NO3 = nitrate concentration. Red boxes indicate significant total or unique fractions ($p \leqslant 0.05$).

4.4 Epilithic diatom discussion

Of the 22 UWMN sites, four can be considered control sites in areas of low acid deposition (i.e. Lochs Coire nan Arr/Coire Fionnaraich, Allt a'Mharcaidh, Allt na Coire nan Con and Coneyglen Burn) and one is a well-buffered control in an area of moderate deposition (Burnmoor Tarn). The remaining 17 sites have been significantly impacted to varying degrees by acid deposition. The overall pattern of recovery is summarized in Table 4.2 where floristic changes are compared to site type (steam or lake, moorland or forested), deposition class, and observed pH change.

Table 4.2. Summary of diatom trends for the period 1988-2018. Diatom-Trend indicates a significant trend in diatom species and Diatom-pH indicates a significant response to changing pH. For both, S, M, L indicate small, moderate or large diatom responses, defined as variance explained of less than 0.5, 0.5-0.7, and greater than 0.7 respectively. Chem-pH indicates a significant trend in lake- or stream-water pH.SO_4 deposition classes after Fowler et al. (2005: 1=high, 4=low). Forested sites shaded green.

Site	code	SO4 Dep	Type	Control	Diatom-Trend	Chem-pH	Diatom-pH
Loch Coire nan Arr	Arr	4	Lake	Y	M		
Loch Coire Fionnaraich	Fion	4	Lake	Y			
Allt a'Mharcaidh	Mhar	4	Stream		M		
Allt na Coire nan Con	Con	4	Stream				
Lochnagar	Naga	3	Lake		M	Y	M
Loch Chon	Chon	3	Lake		L	Y	L
Loch Tinker	Tink	3	Lake		L		
Round Loch of Glenhead	RLGH	3	Lake		L	Y	M
Loch Grannoch	Gran	3	Lake		S	Y	S
Dargall Lane Burn	Darg	3	Stream		L	Y	M
Narrator Brook	Scoa	3	Stream		S	Y	S
Llyn Llagi	Burn	3	Lake		L	Y	L
Llyn Cwm Mynach	Eth	3	Lake		L		S
Beagh's Burn	OldL	3	Stream		M	Y	
Bencrom River	Narr	3	Stream		S	Y	S
Blue Lough	Lag	3	Lake		L	Y	M
Coneyglen Burn	Myn	3	Stream	Y			
Scoat Tarn	Hafr	2	Lake		L	Y	L
Burnmoor Tarn	Gwy	2	Lake	Y			
Old Lodge	Beag	2	Stream		L	Y	L
Afon Hafren	Benc	2	Stream		L	Y	S
Afon Gwy	Blue	2	Stream		M	Y	S
River Etherow	Cone	1	Stream		L	Y	S

None of the "control" sites show a significant trend in measured pH. Two sites, Loch Coire nan Arr (note short time series) and Allt a'Mharcaidh, show a significant diatom trend that does not appear to be related to pH variation as assessed in this section. At Loch Coire nan Arr the changes are difficult to interpret due the relatively short record, but may be linked to disturbances following water level regulation and the installation of a dam in the late 1990s (this site was replaced in the network by Loch Coire Fionnaraich in 2001). Although no significant relationship was established with water pH, it is possible that the changes in the Allt a'Mharcaidh diatom community may reflect the very gradual decline in median pH and 95th percentile (i.e. low flow) pH (Section 3.3.2.7), that may in turn have resulted from the increase in organic acidity (as reflected by the rise in DOC). Similar, apparently counter-intuitive changes in diatom assemblages in Allt na Coire nan Con and Coneyglen Burn, as indicated by significant negative trends in the DAM metric, may also be indicative of the effect of a rise in organic acidity at these sites. In both cases again, there is a very subtle downward trend in median and 95th percentile pH (Section 3.3.2.7), likely driven by the increase in organic acidity, despite the fact that Coneyglen Burn streamwater pH during more acidic (high flow / high sea salt) conditions, most common during the winter months, has clearly increased.

At the acidification-impacted sites (i.e. non-control) the epilithic diatom assemblages show a progressive change in composition consistent with trends in increasing lake- or stream-water pH. Of the 14 sites that show a significant increase in pH, all also exhibit a significant trend in diatoms that broadly reflects a transition to less acid tolerant taxa. Across the UWMN lake sites there is a strong correlation between the magnitude of diatom species change over the period of monitoring (i.e. turnover) and the magnitude of pH change (r=0.70, p=0.01; Figure 4.4, left). This relationship is strongly linear with two obvious outliers: Round Loch of Glenhead (RLGH) and Scoat Tarn (Scoa). At Round Loch of Glenhead, diatom changes in the early part of the record are consistent with recovery, but acidiobiontic taxa have again increased at the site over the last decade, suggesting that recovery has since stalled. This is strangely inconsistent with the water chemistry record; the increase in lake water pH began to level off close to the start of the century, but certainly shows no sign of reversal. At Scoat Tarn, diatom community change is continuous and sustained over the monitoring period (as has the pH), but is very muted compared to other similarly buffered sites in the network such as Lochnagar.

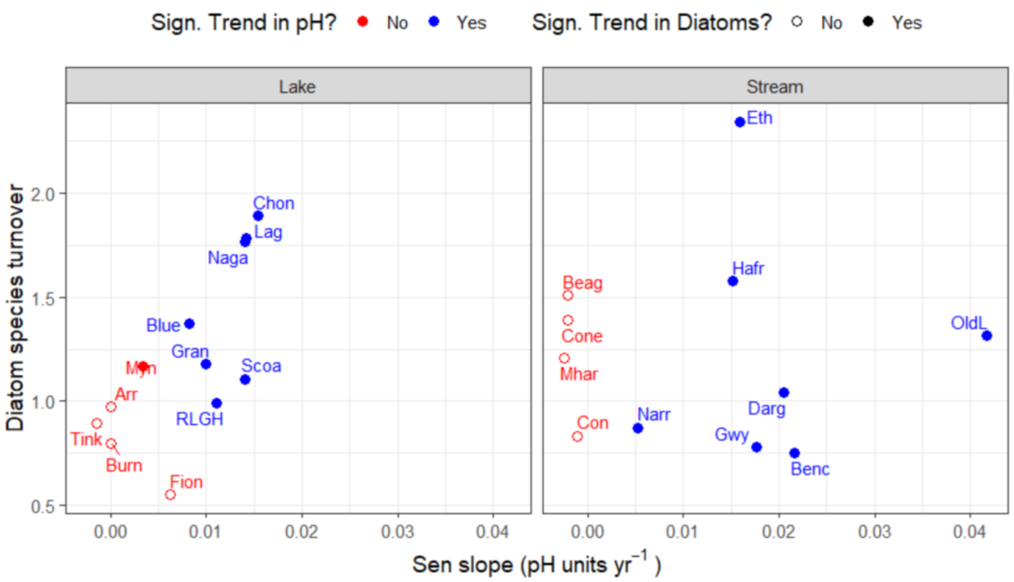

Figure 4.4. Relationship between the magnitude of diatom species change (turnover) and the magnitude of pH change at lake (left) a stream (right) sites.

The relationship between the absolute magnitude of diatom species change and pH change is not significant for streams (r=0.01, p=0.97; Figure 4.4, right). The stream diatom flora show much greater inter-annual variation than the lake flora, reflecting not only the degree of recovery but also responsiveness to antecedent flow conditions and related short-term variation in chemistry. The inter-annual variation also differs between stream sites, depending on catchment characteristics and the degree of episodicity. For example, the Afon Gwy and River Etherow have a similar median pH (5.86 and 5.80 respectively) and similar rates of overall pH change (0.018 and 0.016 pH units yr^{-1}) but Afon Gwy is much less variable chemically, and shows much less inter-annual biological variation (Figure 4.22; Appendix Sections 18.3 and 12.3). The diatom turnover metric captures the absolute magnitude of species change which, for the UWMN lakes, is primarily related to the linear trend in time, but at stream sites it also includes a component related to the inter-annual variability which confounds the relationship with pH recovery.

Differences in rates of biological recovery of paired forest / moorland sites largely mirror differences in chemical recovery. In three out of four cases (Loch Chon vs Loch Tinker, Afon Hafren vs Afon Gwy and Loch Grannoch vs Round Loch of Glenhead) diatom turnover has been larger in the forested sites (Figure 4.5), and this is consistent with the more rapid rates of decline in acid deposition, acid anion concentrations, hydrogen ion and labile aluminium concentrations and more rapid increase in ANC (Section 3.3.2.4). Indeed the forested Loch Chon shows the highest diatom recovery turnover of all UWMN lakes sites. In contrast, the moorland Loch Tinker shows no significant trend in pH and only small (but still significant) diatom changes that cannot yet be attributed to chemical change.

For the more tenuously "paired" Llyn Llagi and Llyn Cwm Mynach, the pattern is reversed. Again, diatom recovery effectively mirrors the rate of pH recovery, but it is the moorland Llyn Llagi that exhibits substantial chemical and biological recovery and the forested Llyn Cwm Mynach shows only marginal biological change (and no pH recovery). These sites are relatively distant geographically, and major forest disturbance in the Llyn Cwm Mynach is likely to have had deleterious impacts of lake acidity over the monitoring period.

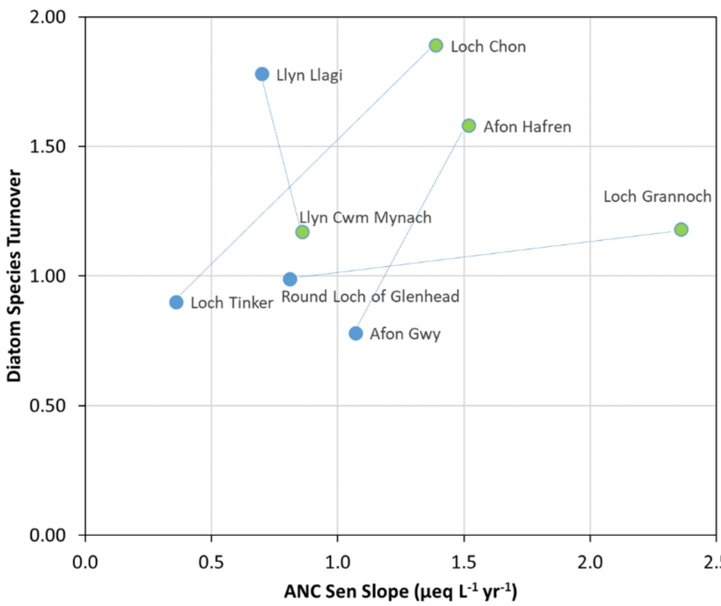

Figure 4.5. Relationship between diatom species turnover and rate of ANC change for the eight paired forest / moorland sites. Forested sites indicated as green points and moorland sites as blue points

The rate of increase of lake- and stream-water pH, and the associated diatom response is clearly variable across the network as a whole and within areas of similar acid deposition (Table 4.2). The timing of recovery is also variable. Of the "non-control" lake sites, five (Lochnagar, Loch Chon, Loch Tinker, Scoat Tarn and Blue Lough) show sustained assemblage change consistent with recovery, four (Llagi, Mynach, RLGH and Grannoch) show recovery in the early part of the monitoring record but a rather stable flora over the last 10 or so years, and one (Llyn Cwm Mynach) shows no recovery and possibly even continued acidification (Figures 4.1, 4.2 and Appendix Section 16). The inherently greater inter-annual variability in stream diatom assemblages makes it more difficult to identify periods of sustained change at stream sites. Accepting this caveat, there is evidence for differential responses among steam sites, and that while biological recovery has been sustained at some (Dargall Lane, Old Lodge, Afon Gwy and Bencrom Burn) it has also stalled at others (River Etherow, Narrator Brook, Afon Hafren and Beagh's Burn). At some sites (Llyn Llagi, Narrator Brook), the cessation of biological recovery in recent years is consistent with the slowing of chemical recovery. At other locations diatom recovery may be confounded by the rise in organic acidity associated with increasing DOC (e.g. Afon Hafren, River Etherow, and RLGH). Understanding the mechanisms that underlie such spatial and temporal differences in the rate of biological recovery among sites will require further investigation.

Table 4.3. Assessment of the degree of recovery at lake sites based on comparison of the 2018 epilithic diatom flora with the pre-acidification lake-sediment record.

No.	Name	Indicator for recovery	Interpretation
1	Loch Coire nan Arr	*A. minutissima* present throughout	Control, not acidified
26	Loch Coire Fionnaraich	NA	Control, not acidified
4	Lochnagar	*A. minutissima* present in the pre-acidification flora and has not returned.	Not recovered
5	Loch Chon	*E. incisa* & *N. leptostriata* and other acid indicators have disappeared, *B. vitrea*, *A. minutissima* returned.	Close to pre-acidification flora
6	Loch Tinker	*A. minutissima* and *F. virescens* var. *exigua* present throughout but have not returned to pre-acidification numbers.	Close to pre-acidification flora
7	Round Loch of Glenhead	*T. quadriceptata* and other acid indicators still present, *A. minutissima* and *B. vitrea*, which dominated pre-acidification flora not returned.	Not close to pre-acidification flora
8	Loch Grannoch	*T. quadriceptata* has disappeared from record but *B. vitrea* and *T. flocculosa*, which dominated pre-acidification flora are still absent or rare.	Not close to pre-acidification flora
10	Scoat Tarn	*T. binalis* and other acid indicators still present, *A. minutissima* which dominated pre-acidification flora are still absent or rare.	Not close to pre-acidification flora
11	Burnmoor Tarn	*A.minutissima* present throughout.	Control, not acidified
15	Llyn Llagi	*T. quadriceptata* has disappeared from record and *B. vitrea* and *A. minutissima*, which dominated pre-acidification flora, have returned but the latter only in low numbers.	Close to pre-acidification flora

No.	Name	Indicator for recovery	Interpretation
16	Llyn Cwm Mynach	*P. fibula, E. incisa* and other acid indicators still present, with the acidiobiontic *T. binalis* increasing in recent years. *A. minutissima, Fragilaria virescens* var. *exigua* and *C. microcephela*, which were common in the pre-acidification flora are rare or absent.	Not close to pre-acidification flora
21	Blue Lough	*T. quadriceptata, T. binalis, S. hemicyclus* and other acidobiontic taxa, absent in the pre-acidification flora, are still present.	Not close to pre-acidification flora

Some sites in the network show a remarkable degree of biological recovery. Loch Chon and the River Etherow, for example, have evolved from a chronically acidified state with a flora dominated by acid tolerant taxa to one characterized by acidiphilous (acid loving) diatoms indicative of naturally acid soft waters. This transition raises the question of the extent to which the contemporary diatom communities are fully recovered from acidification. For lake sites we can address this question by comparing the current epilithic diatom flora with that recorded in the pre-acidification levels of sediment cores from the same sites described in Juggins et al. (1996) and Battarbee et al. (2014). Lake sediments aggregate diatoms from a range of lacustrine habitats, including the epilithon. A direct quantitative comparison is therefore not appropriate, but a qualitative comparison of key acid tolerant and acid sensitive taxa (indicating acidification and recovery respectively) provides a qualitative measure of distance to the target pre-acidification flora. Results of this comparison are shown in Table 4.3. Only three sites (Loch Chon, Loch Tinker and Llyn Llagi) have current diatom assemblages that show sufficient recovery in terms of reduction and disappearance of key acidification indicators and appearance and increase in key acid sensitive indicators to be considered close to a pre-acidification flora. The remaining 6 non-control sites, although showing varying degrees of recovery, are still characterized by acidobiontic taxa indicative of acute acidification and lack acid sensitive taxa that were present in the pre-acidification flora. A more robust comparison of contemporary and pre-acidification communities is provided by the comparison of pre-acidification lake sediments with modern sediment trap samples. This was last explored for UWMN lakes by Battarbee et al. (2014b) and will be re-visited once the UWMN sediment trap diatom record is fully up to date.

The question of the degree of recovery is more difficult to address for stream sites as they lack direct evidence of the pre-acidification flora. An alternative approach is to compare their current diatom floras to those of the non-acidified control sites, again with specific focus on acid tolerant and sensitive taxa. Of the non-control stream sites, Narrator Brook is the only one to support a diatom flora dominated by acid sensitive taxa characteristic of naturally acid soft waters. The River Etherow comes close to this target on occasion but at this site the record of acid sensitive diatoms shows considerable inter-annual variation, suggesting the flora is highly dependent on recent flow conditions, with a circumneutral flora dominating after extended periods of low discharge when water chemistry is well buffered. The remaining stream sites still have a flora that contains, and is often dominated by, acid-tolerant taxa indicative of acidification by strong acid anions, with only modest and often fluctuating numbers of acid sensitive taxa.

Overall, these results indicate that while biological recovery of epilithic diatom communities is underway at most UWMN sites, and extensive at some, it is still largely incomplete and there is potential for further improvement. The apparent reduction, and even cessation, in the rate of biological recovery at over half the network sites during the last 10 or so years is perhaps surprising, but broadly consistent with a general flattening out of acid inputs and corresponding acidity. It is likely that as direct acid deposition effects begin to dwindle, the effect of other factors on water pH, such as changes in hydrology and episodicity, nutrient enrichment (from N deposition and catchment land-se), climate and dissolved organic matter inputs will become increasingly important in influencing the epilithic diatom community, and this is therefore a critical area for future research.

5 Aquatic macroinvertebrate summary

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5.1 Introduction

Macroinvertebrates in fresh waters include a wide variety of animal groups including flatworms, snails, leeches, worms, crustaceans, and insects. Inferring the ecological condition of rivers and lakes from the diversity of macroinvertebrates they support has a long history worldwide (Friberg et al., 2011). Freshwater macroinvertebrates are routinely used to assess the impacts of a variety of forms of pollution including acidity and acidification.

Macroinvertebrates have been sampled from the Upland Waters Monitoring Network sites since the inception of the network in 1988. The taxonomic data has previously revealed widespread directional community changes with evidence of recovery from acidification at around half of the streams and lake sites (Murphy et al., 2014). Acid Neutralising Capacity (ANC) had increased at all 10 sites exhibiting directional community change, and at a further seven sites where no biological recovery was detected. At the time, following the first 20 years of monitoring, it was concluded that the match between chemical and biological recovery was clearly incomplete, with biological recovery appearing to lag improvements in atmospheric and water chemistry.

Here, we present the results of a further eight years of UWMN biological monitoring of freshwater macroinvertebrates. We assess whether the modest signal of biological recovery from acidification has been sustained or even strengthened over that period. Specifically, we ask:

1. Have there been any directional temporal changes in benthic macroinvertebrate assemblages across the network?
2. Do such changes indicate recovery from acidification?
3. Are there any systematic differences between lakes and streams in their response to changes in water chemistry?
4. Has biological recovery in macroinvertebrate communities now matched the extent and pace of chemical recovery in the UWMN?

5.2 Aquatic macroinvertebrate methods

5.2.1 Sampling and laboratory processing

The UWMN has sampled the benthic macroinvertebrate community at most stream and lake sites since 1988. There have been some interruptions to time series due to years when sampling was not always possible, e.g. due to Foot and Mouth outbreak in 2001 (Table 4.1).

In April–May of each year, five, one-minute kick (streams) or sweep (lakes) samples are taken at each site (beginning in the south of the UK) with a 330 µm mesh net, with the objective of obtaining consistent replicate samples from the same habitat year after year. Thus, stony riffles are always sampled in streams and lake samples are taken from stony or sandy littoral habitat (0.3–0.5m depth), including sweeping through rooted macrophytes, where present. The samples are preserved in the field in 70% industrial methylated spirit (latterly absolute alcohol), until sorting and identification to the lowest possible taxonomic level (mostly to species), according to standard UWMN protocols (Patrick et al., 1991). Benthic sampling is undertaken in late spring to assess the macroinvertebrate community immediately following the months in the annual hydrograph when sustained or brief periods of high stream discharge and associated acid episodes were most likely (Wade et al., 1989; Weatherley and Ormerod, 1987).

5.2.2 Statistical Analysis

As an initial step in the analysis of macroinvertebrate data for this report, trends in the number of discrete taxa recorded at each site over the time series were quantified. Macroinvertebrate abundance data from replicate samples taken on each occasion at each site were pooled. The data were then harmonised to a consistent taxonomic level across each site time series. As taxon richness is a function of the number of individuals captured at a site, rarefaction was used to estimate species richness for the same number of individuals (Hurlbert, 1971). The number of individuals in the least numerous pooled sample in each site time series was used as the standardised sample size. Non-parametric Mann-Kendall tests were applied to determine the likelihood of monotonic change in richness over time, with the strength of trends being described by the Sen slope statistic.

The magnitude of macroinvertebrate compositional turnover (or β-diversity) over the monitoring period was estimated using detrended canonical correspondence analysis (DCCA) with sampling year as the sole constraining variable. The gradient length of the first ordination axis gives a measure of turnover scaled in standard deviation (SD) units, with a turnover of 1 SD unit representing an approximately 50% change in species composition over the sampling period and a turnover of 2 SD units representing a complete exchange of species (Hill and Gauch, 1980; ter Braak and Verdonschot, 1995).

To assess whether there had been directional change in the macroinvertebrate community assemblage at each site, further ordination techniques were used. Principal components analysis (PCA) was first undertaken to define the direction of the strongest gradient in assemblage composition (PCA axis 1) relative to the total amount of variation in the community. This first unconstrained PCA axis eigenvalue (PCA_1) provides a measure of the maximum proportion of the biological variation that a single constraining variable could account for in a subsequent redundancy analysis (RDA). A Redundancy Analysis (RDA) was then carried out, in the first instance with sampling year as the only explanatory variable. The ability of the constraining variable to fully account for the dominant gradient of biological change was assessed by comparing the proportion of the total variation accounted for by PCA axis 1 (% PCA_1) with the proportion accounted for by RDA axis 1 (% RDA_1).

The presence of a trend in the community data was determined using a restricted permutation test to assess the significance of the variance explained by sample year (effectively the first ordination axis of the RDA). The chronological ordering of samples (by year) in the permutation test was maintained but the 'starting sample' was selected via random cyclic shifts of the time series. This is a conservative significance test, as the maximum number of permutations is equal to the number of annual samples within each time series (15–29), which for most sites was just beyond the limit of detection of trends at the 95% level. Directional change does not necessarily indicate biological recovery, but it does imply a consistent shift in assemblage composition. Additional RDAs were also carried out with mean pH, ANC, and alkalinity as sole explanatory variables to assess to what extent the changes in community composition were associated with variation in preceding acid chemistry. Means were calculated on seasonal lake water chemistry samples collected over the preceding 12-month period (June-May) and on monthly stream water chemistry samples collected over the preceding 8-month period (Oct-May).

Prior to DCCA, PCA and RDA ordinations, the macroinvertebrate abundance data from the replicate samples taken on each occasion at each site were pooled. The data were then harmonised to a consistent taxonomic level across each site time series and converted to relative abundance. For the PCA and RDA analyses the data were square root-transformed to reduce the influence of dominant taxa. All taxa recorded were included in the analyses, including those recorded only once in the time series, since such rare taxa could be important in identifying change.

To identify biological responses more directly attributable to reductions in acidifying deposition, we calculated two diagnostic indices from the macroinvertebrate data: the lake acidification macroinvertebrate metric (LAMM) for lake sites (WFD-UKTAG, 2008); and the acid waters indicator community index (AWICsp) for stream sites (Murphy et al., 2013). LAMM and AWICsp are indices used by UK government agencies to assess the impact of acidification in fresh waters. LAMM assigns a sensitivity score to each taxon and then calculates an abundance-weighted average for all scored taxa captured in a sample. Similarly, AWICsp assigns a sensitivity score to each of 48 stream macroinvertebrate taxa with the final AWICsp index value being the average for all scored taxa captured in a sample. LAMM and AWICsp scores were calculated for each lake and stream site in each year from the pooled list of taxa from replicate kick samples. Non-parametric Mann-Kendall tests were applied to determine the likelihood of monotonic change in index values over time, with the strength of trends being described by the Sen slope statistic.

Finally, to assess the relationship between the magnitude of chemical recovery trends, and the magnitude of community change and biological recovery we tested for significant correlations between calculated Sen slopes for pH, ANC and alkalinity with estimates of taxon turnover and calculated Sen slopes for LAMM and AWICsp.

Rarefaction of taxon richness, PCA and RDA were carried out using the “vegan 2.5.7” package (Oksanen et al., 2022), and trend analyses were carried out with the “trend 1.1.4” package (Pohlert, 2020). DCCA were carried out using Canoco 4.5 (Braak and Smilauer, 2002). Trend plots and correlations were run in Minitab 19.

Table 5.1 Sampling for benthic macroinvertebrates at Upland Waters Monitoring Network sites in each year between 1998 and 2016.

Lakes		1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
001	Loch Coire nan Arr	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●									
025	Loch Coire Fionnaraich															●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
004	Lochnagar	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
005	Loch Chon	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
006	Loch Tinker	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
007	Round Loch of Glenhead	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
008	Loch Grannoch	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●		●	●	●	●	●
010	Scoat Tarn	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
011	Burnmoor Tarn	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
015	Llyn Llagi	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
016	Llyn Cwm Mynach	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
021	Blue Lough		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●
Streams																														
002	Allt a Mharcaidh	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
003	Allt na Coire nan Con	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
009	Dargall Lane	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
012	River Etherow	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
013	Old Lodge	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
014	Narrator Brook	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●				●	●	●	●	●	●
017	Afon Hafren	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
018	Afon Gwy				●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
019	Beaghs Burn	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●					●	●	●	●	●
020	Bencrom River	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●
022	Coneyglen Burn		●	●	●	●	●	●	●	●	●	●	●	●		●	●	●	●	●	●				●	●	●	●	●	●

5.3 Aquatic macroinvertebrate results

A total of 236 macroinvertebrate taxa were recorded over the first 28 years of monitoring and 616 sampling occasions at the 23 UWMN lake and stream sites,. Loch Chon had the highest taxon inventory (109) and Bencrom River the lowest (34). Macroinvertebrate taxon richness increased over the period at only two of the lakes (Loch Tinker and Llyn Llagi) and five of the streams. There was a decline in taxon richness at Burnmoor Tarn, and no monotonic trend in richness at the other sites between 1988 and 2016 (Table 5.2, Figure 5.1). Loch Tinker gained taxa at a rate of one every five years, and the trend has continued right up to 2016 (Figure 5.1). In contrast, Burnmoor Tarn lost, on average, one taxon every seven years. At Llyn Llagi, gains in taxa were most rapid during the first half of the monitoring period, after which numbers largely plateaued (Figure 5.1). Macroinvertebrate communities in the two stream sites in southern England (Narrator Brook and Old Lodge) increased in richness by approximately one taxon every 5 years, with the increase being sustained at Old Lodge right up to 2016, while tailing off around 2003 at Narrator Brook. Contrasting trends in taxon richness were observed for the paired forest-moorland Welsh streams, the Afon Hafren and Afon Gwy, despite similar numbers at the start of monitoring. In the more acidified and afforested Afon Hafren, richness increased steadily (one taxon every seven years) over the 28 years, whereas no change in richness was observed in the Afon Gwy over the same period. The River Etherow, in the south Pennines, and Bencrom River in the Mourne Mountains (also moorland catchments) had more modest increases in taxon richness. In the River Etherow the increase in richness was sustained at a consistent rate (one taxon every 12 years), while at Bencrom River the increase in richness only became apparent over the last decade of monitoring (Table 5.2, Figure 5.1).

Lakes and streams exhibited similar ranges of taxa turnover over the monitoring period. Scoat Tarn and Allt a'Mharcaidh showed relatively low levels of turnover whilst more substantial shifts in composition were evident at Llyn Llagi and Beagh's Burn (Table 5.2). At five lakes and seven streams taxa turnover was greater than the 1 SD unit – indicative of an approximate 50% change in species composition (Table 5.2).

Significant directional change in macroinvertebrate community composition was observed at 12 sites: six lakes and six streams (Table 5.3). Consistent linear temporal trends were most apparent at Loch Chon, Round Loch of Glenhead, Scoat Tarn, Narrator Brook, Afon Gwy and River Etherow (Figure 5.2). More variable, but still broadly linear, change was evident in the Old Lodge community. Distinctly asymptotic relationships with time occurred at Loch Tinker, Llyn Llagi, Llyn Cwm Mynach, and Coneyglen Burn (Figure 5.2). At these sites most of the directional change occurred in the first half of the monitoring period. At Llyn Llagi there appeared to be a sudden shift in community composition in the late 1990s, before and after which there was relatively little directional change (Figure 5.2). At Beagh's Burn, the clearest directional change occurred after 2005. However, this site was not sampled from 2008-2011 so these patterns should be interpreted with caution. At nine of the 12 sites to show significant directional change, taxa turnover was also particularly clear (greater than 1 SD unit) – thus demonstrating broad agreement between the two approaches in the quantification of temporal trends.

A comparison of RDA analyses conducted for this report with that carried out on the first 20 years of data (Murphy et al., 2014) revealed the following. Four sites showed no directional change in either analysis and six sites showed a significant temporal trend in both. Six sites in the latest analysis showed directional trends after providing no evidence of change after the first 20 years. However, a further six sites that had shown significant trends over the first 20 years no longer show evidence of directional change after 28 years. An asymptotic pattern of change was obvious at each of these latter six sites with no consistent shift in community composition over the past eight years following an earlier period of more substantial changes (Figure 5.2).

The maximum variance in the assemblage that could be explained by a hypothetical linear variable (% PCA_1) was compared with the variance explained by linear change in the following four explanatory variables (% RDA_1 time, % RDA_1 pH, % RDA_1 ANC, and % RDA_1 alkalinity) at each site (Table 5.3). Directional temporal change (% RDA_1 time) (i.e. describing purely linear change over time) was most often the best explanatory variable. Allt na Coire nan Con and the Dargall Lane Burn were the only sites where no significant directional change in the macroinvertebrate community was observed but there was a significant association with one or more of the measures of acid chemistry (Table 5.3). The variance explained by ANC was significant but small at Allt na Coire nan Con. However, at the Dargall Lane Burn all three measures of acid chemistry exceeded 70% of the maximum possible explanatory power. One or more chemical variable were significantly associated with variation in the biological community at only four of the lakes (Loch Chon, Loch Tinker, Round Loch of Glenhead and Llyn Llagi) and six of the streams (Table 5.3). At lake sites, pH was the acid chemistry variable most often found to be significantly associated with variation in assemblage composition, whereas in streams ANC was the dominant explanatory variable, being significant at six of the 11 sites (Table 5.3).

A significant increasing trend in diagnostic index scores, indicative of a reduction in acidification stress on biota, was recorded at 14 of the UWMN sites; seven lakes and seven streams (Table 5.2). Nine of the 10 sites that exhibited a significant increasing trend after 20 years (Murphy et al., 2014) maintained that trend after 28 years. A further five sites that had not shown a significant trend in score after 20 years showed a significant trend after 28 years. The greatest rates of increase in the LAMM metric were at Round Loch of Glenhead and Loch Chon where, by 2016, values were at or exceeding levels observed in other non-acidified “control” lakes in the network (Figure 5.3). More modest rates of increase were evident at Blue Lough and Llyn Cwm Mynach, but also at non-acidified Burnmoor Tarn; all three having asymptotic response curves with increases most pronounced prior to 2005 (Figure 5.3). LAMM values at Blue Lough were low throughout, but particularly so over the first 10 years of monitoring when they were often at the minimum possible score (2.0). In contrast, LAMM values at Burnmoor Tarn confirm that the site was never greatly affected by acidification with values initially varying around 5.0: over the past 10 years they have usually been greater than 5.6, possibly due to sustained increases in alkalinity at the site. Llyn Cwm Mynach lies between Blue Lough and Burnmoor Tarn on the gradient of acid stress. There were relatively small but significant increases in LAMM scores at Llyn Llagi over the monitoring period. This is consistent with the relatively small improvements in acid chemistry at this site. Loch Grannoch has also seen a small but significant increase in LAMM scores, with most of the increase taking place in the first decade of monitoring (Figure 5.3).

Lochnagar and Scoat Tarn were the only UWMN lakes that did not show evidence of macroinvertebrate recovery despite evidence of chemical recovery from acidification (Table 5.2, Figure 5.3). In Lochnagar the increase in NO_3^- concentration in the early years of monitoring almost nullified the effect on water acidity of declining S deposition, and ANC and pH only started to rise in from around 2010. However, it is also likely that the remote and climatically extreme environment of this site will impose additional restraints on biological recovery. Despite recent improvements in acid chemistry, by 2016, when the last macroinvertebrate samples analysed in this report were collected, the ANC of Scoat Tarn was still negative, while mean labile aluminium concentrations remained above 20 µg L^{-1}. It is possible that chemical improvements at this site have not yet been sufficient to enable significant macroinvertebrate recovery.

Seven UWMN streams underwent significant increases in AWICsp scores; only the low deposition montane Allt a'Mharcaidh and two stream sites in Northern Ireland continue to indicate no consistent change in AWICsp scores over the monitoring period (Table 5.2, Figure 5.3). A decreasing trend in AWICsp scores was evident at the low deposition Coneyglen Burn in Northern Ireland, although this may have been influenced by a few recent sampling occasions when only 2-3 AWICsp scoring taxa were recorded. The strongest rate of recovery was seen in the River Etherow where AWICsp values have gone from among the lowest in the network in the late 1980s to among the highest in 2016. Alkalinity and ANC have also recovered strongly at this site, while labile aluminium concentrations fell substantially over the first 20 years of monitoring (see Appendix Section 12.2).

The only stream site with more pronounced change in acid chemistry than the River Etherow was Old Lodge. Initially, AWICsp values of around 3 were consistent with Old Lodge being the most acidic stream on the network (e.g. highly negative ANC and a mean pH of 4.5). There have been major improvements in water chemistry over the past 28 years, most notably in declining labile aluminium concentration and rising pH and ANC over the first 20 years. The macroinvertebrate community now includes some moderately acid-sensitive taxa, e.g. *Isoperla grammatica,* but AWICsp values still average below 4 (Figure 5.3). At the other five stream sites, modest improvements in AWICsp follow significant sustained shifts in ANC over the entire monitoring period from negative or near-negative values to maintained positive ANC charge balances. This was seen both at relatively mildly acidified sites, e.g. Allt na Coire nan Con and Narrator Brook, and at more impacted sites, e.g. Dargall Lane and Afon Hafren.

The absence of change in AWICsp at Beagh's Burn is consistent with the lack of change in acidity over the monitoring period at this chemically benign site. At Bencrom River, AWICsp values were markedly consistent at around 4.3 across the monitoring period despite modest improvements in ANC and, more latterly, in pH and alkalinity (Figure 5.3). In common with Scoat Tarn and Loch Grannoch, however, labile aluminium concentrations were still relatively high by 2016. Nevertheless, there are indications from the rarefied taxon richness that the community at Bencrom River may be beginning to respond to the increases in buffering capacity (Figures 5.1 & 5.2).

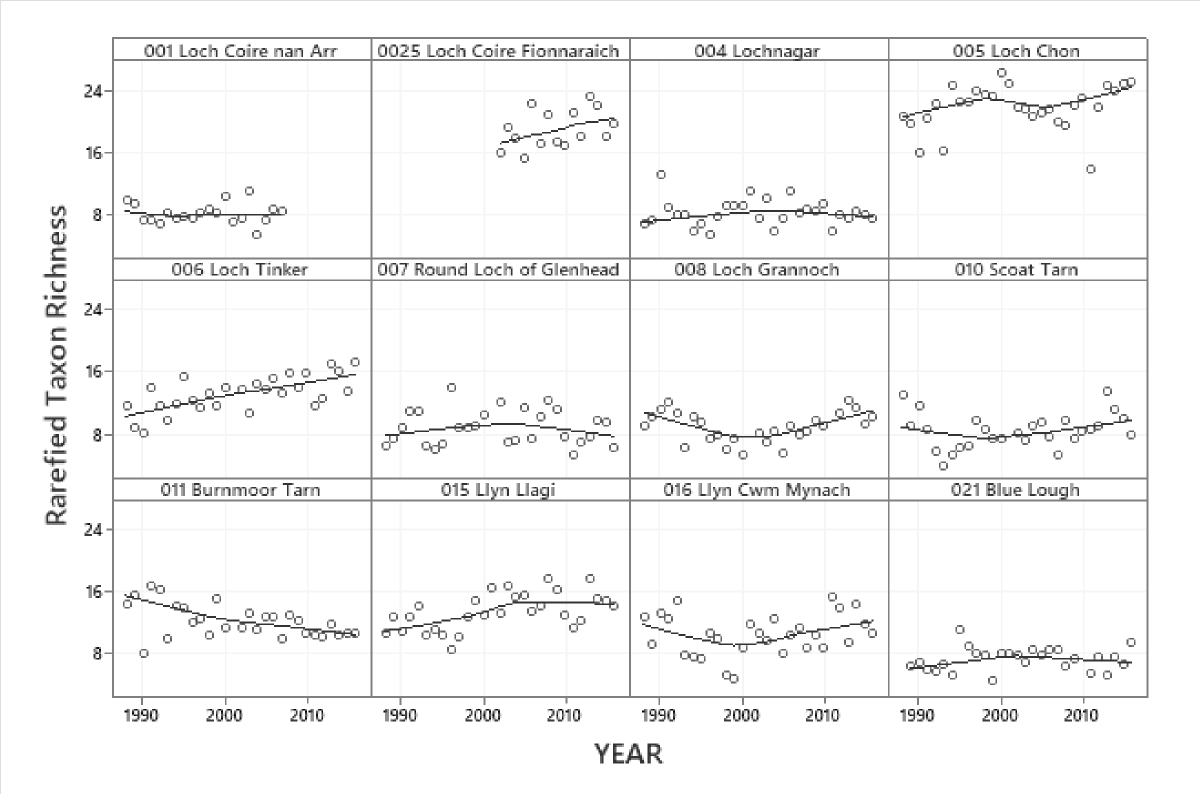
There were significant positive correlations between the magnitude of change in mean Gran alkalinity and that of change in diagnostic index scores (LAMM or AWICsp), both across all sites (Figure 5.4, Table 5.4) and for lakes and stream sites separately (Table 5.4). There was also a significant positive correlation between the magnitude of change in mean pH and change in the diagnostic index scores, but only when considering all sites together. There were no significant associations between the magnitude of change in ANC and the magnitude of biological changes at sites over the monitoring period (Table 5.4).

Table 5.2. Analysis of taxonomic turnover over time, and monotonic trends in rarefied taxon richness, LAMM and AWICsp at UWMN lake and stream sites over the monitoring period. Taxa turnover over the monitoring period is given by the gradient length (in standard deviation units) of the first ordination axis of a detrended canonical correspondence analysis, with sampling year as the sole constraining variable. The Sen slope statistic gives the linear rate of change in the metric per year. Rarefied taxon richness and LAMM/AWICsp values in bold are statistically significant ($p < 0.05$).

		Taxa turnover	Rarefied taxon richness		LAMM / AWICsp	
Lakes		**DCCA axis 1 (SD)**	**Sen slope**	***p***	**Sen slope**	***p***
001	Loch Coire nan Arr	1.13	0.018	0.871	-0.029	0.074
025	Loch Coire Fionnaraich	0.95	0.227	0.138	-0.032	0.075
004	Lochnagar	0.72	0.008	0.750	-0.010	0.488
005	Loch Chon	1.28	0.085	0.149	**0.075**	**<0.001**
006	Loch Tinker	0.81	**0.213**	**0.000**	0.005	0.465
007	Round Loch of Glenhead	0.58	0.016	0.707	**0.087**	**<0.001**
008	Loch Grannoch	0.87	0.040	0.479	**0.021**	**0.033**
010	Scoat Tarn	0.23	0.090	0.186	0.003	0.797
011	Burnmoor Tarn	1.14	**-0.142**	**0.009**	**0.039**	**0.001**
015	Llyn Llagi	1.40	**0.153**	**0.005**	**0.022**	**0.005**
016	Llyn Cwm Mynach	1.30	0.056	0.442	**0.031**	**0.008**
021	Blue Lough	0.71	0.022	0.559	**0.040**	**0.033**
Streams						
002	Allt a'Mharcaidh	0.40	0.054	0.358	0.010	0.068
003	Allt na Coire nan Con	0.89	0.041	0.399	**0.021**	**0.002**
009	Dargall Lane Burn	1.00	-0.053	0.050	**0.030**	**<0.001**
012	River Etherow	1.09	**0.086**	**0.010**	**0.070**	**<0.001**
013	Old Lodge	1.03	**0.213**	**0.001**	**0.032**	**0.011**
014	Narrator Brook	1.17	**0.234**	**0.030**	**0.026**	**<0.001**
017	Afon Hafren	0.78	**0.156**	**0.001**	**0.022**	**0.001**
018	Afon Gwy	1.02	-0.036	0.234	**0.024**	**0.015**
019	Beagh's Burn	1.33	0.012	0.834	0.002	0.833
020	Bencrom River	0.94	**0.046**	**0.046**	0.000	0.573
022	Coneyglen Burn	1.15	-0.040	0.472	**-0.033**	**0.030**

Table 5.3. Analysis of change in macroinvertebrate community composition over the monitoring period for UWMN lake and stream sites. PCA_1 is the eigenvalue of the first PCA axis; RDA_1 time, RDA_1 pH, RDA_1 ANC, and RDA_1 Alkalinity are the eigenvalues of the first RDA axis (constrained by time, mean pH, ANC and alkalinity respectively); %PCA_1, % RDA_1 time, % RDA_1 pH, % RDA_1 ANC and % RDA_1 Alkalinity are the variances in the taxa data explained by PCA axis 1, and RDA axis 1 constrained by time, mean pH, ANC and alkalinity; p is the exact permutation p. Values in bold indicate those sites where the constraining variable can account for a significant proportion of the biological variation represented in the first axis of the ordination.

Lakes		**PCA_1**	**% PCA_1**	**RDA_1 time**	**% RDA_1 time**	***p***	**RDA_1pH**	**% RDA_1 pH**	***p***	**RDA_1 ANC**	**% RDA_1 ANC**	***p***	**RDA_1 Alkalinity**	**% RDA_1 Alkalinity**	***p***
001	Loch Coire nan Arr	0.088	34.1	0.043	16.6	0.150	0.008	3.1	0.789	0.009	3.3	0.842	0.005	1.9	1.000
025	Loch Coire Fionnaraich	0.052	36.9	0.034	24.3	0.067	0.011	7.8	0.267	0.005	3.5	1.000	0.008	5.5	0.667
004	Lochnagar	0.094	46.1	0.018	8.7	0.172	0.008	4.3	0.500	0.014	7.1	0.214	0.004	2.2	0.750
005	Loch Chon	0.062	30.3	**0.049**	**23.8**	**0.034**	**0.035**	**17.0**	**0.036**	**0.036**	**17.2**	**0.036**	0.034	16.6	0.071
006	Loch Tinker	0.038	28.5	**0.023**	**17.8**	**0.036**	**0.015**	**11.2**	**0.037**	0.008	6.4	0.148	**0.016**	**12.2**	**0.037**
007	Round Loch of Glenhead	0.044	50.9	**0.028**	**31.8**	**0.036**	0.023	26.3	0.111	0.018	20.1	0.111	0.020	22.2	0.074
008	Loch Grannoch	0.064	36.5	0.019	11.1	0.296	0.009	5.2	0.654	0.013	7.4	0.462	0.007	3.9	0.769
010	Scoat Tarn	0.013	39.8	**0.009**	**28.9**	**0.036**	**0.007**	**21.2**	**0.037**	0.002	7.0	0.185	0.004	11.6	0.185
011	Burnmoor Tarn	0.096	38.1	0.045	17.9	0.143	0.016	6.5	0.333	0.015	6.3	0.370	0.026	10.5	0.148
015	Llyn Llagi	0.079	41.7	**0.060**	**31.9**	**0.034**	**0.048**	**25.6**	**0.036**	0.025	13.3	0.071	**0.027**	**14.4**	**0.036**
016	Llyn Cwm Mynach	0.073	41.6	**0.049**	**27.7**	**0.034**	0.016	9.1	0.071	0.009	5.4	0.393	0.012	7.0	0.071
021	Blue Lough	0.080	53.2	0.020	13.2	0.296	0.020	14.3	0.160	0.004	3.1	0.640	0.020	14.4	0.160
Streams															
002	Allt a'Mharcaidh	0.028	38.1	0.005	6.1	0.552	0.004	5.5	0.179	0.003	4.3	0.393	0.005	6.2	0.179
003	Allt na Coire nan Con	0.079	29.2	0.021	7.9	0.207	0.014	5.1	0.286	**0.022**	**8.3**	**0.036**	0.016	6.0	0.107
009	Dargall Lane Burn	0.040	31.9	0.027	21.7	0.071	**0.031**	**25.7**	**0.037**	**0.027**	**22.3**	**0.037**	**0.027**	**22.7**	**0.037**
012	River Etherow	0.050	30.4	**0.039**	**23.8**	**0.034**	0.017	10.3	0.107	**0.030**	**18.5**	**0.036**	**0.024**	**15.4**	**0.038**
013	Old Lodge	0.077	42.1	**0.031**	**16.8**	**0.034**	**0.022**	**12.5**	**0.038**	**0.021**	**11.7**	**0.038**	**0.022**	**12.7**	**0.038**
014	Narrator Brook	0.049	32.3	**0.034**	**22.4**	**0.040**	0.011	8.8	0.429	**0.017**	**13.0**	**0.048**	0.014	10.8	0.095
017	Afon Hafren	0.050	38.3	0.023	17.6	0.071	0.012	9.6	0.074	0.017	12.8	0.148	0.006	4.6	0.259
018	Afon Gwy	0.047	35.8	**0.027**	**20.5**	**0.040**	**0.015**	**11.2**	**0.040**	**0.016**	**12.2**	**0.040**	**0.012**	**9.1**	**0.040**
019	Beagh's Burn	0.151	60.8	**0.068**	**27.3**	**0.040**	0.030	11.9	0.167	0.008	3.2	0.542	0.025	9.7	0.167
020	Bencrom River	0.069	39.1	0.026	14.6	0.107	0.003	1.8	1.000	0.014	8.5	0.148	0.005	3.0	0.741
022	Coneyglen Burn	0.090	41.5	**0.048**	**21.9**	**0.042**	0.005	2.2	0.909	0.012	5.3	0.636	0.007	3.1	0.773



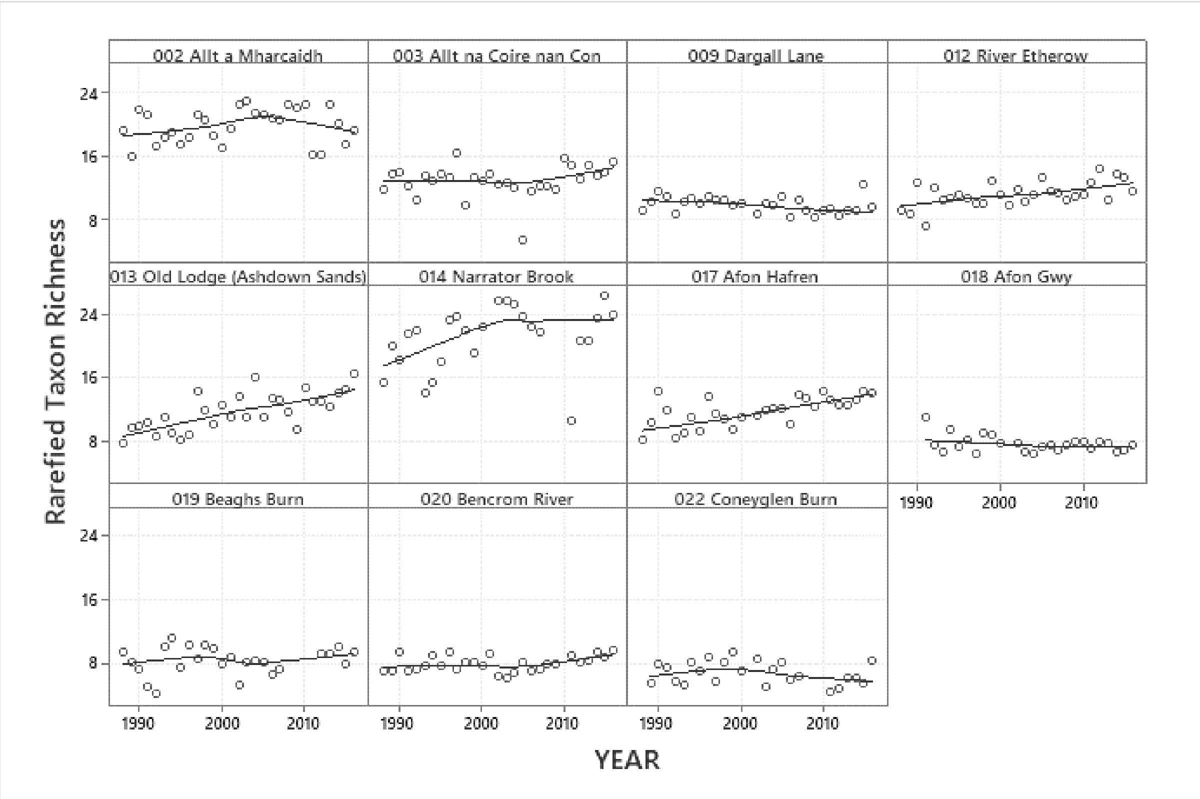


Figure 5.1. Variation in rarefied taxon richness at each of the UWMN lake and stream sites. The solid line represents a LOESS smoother (degree of smoothing = 0.75, number of steps = 2).

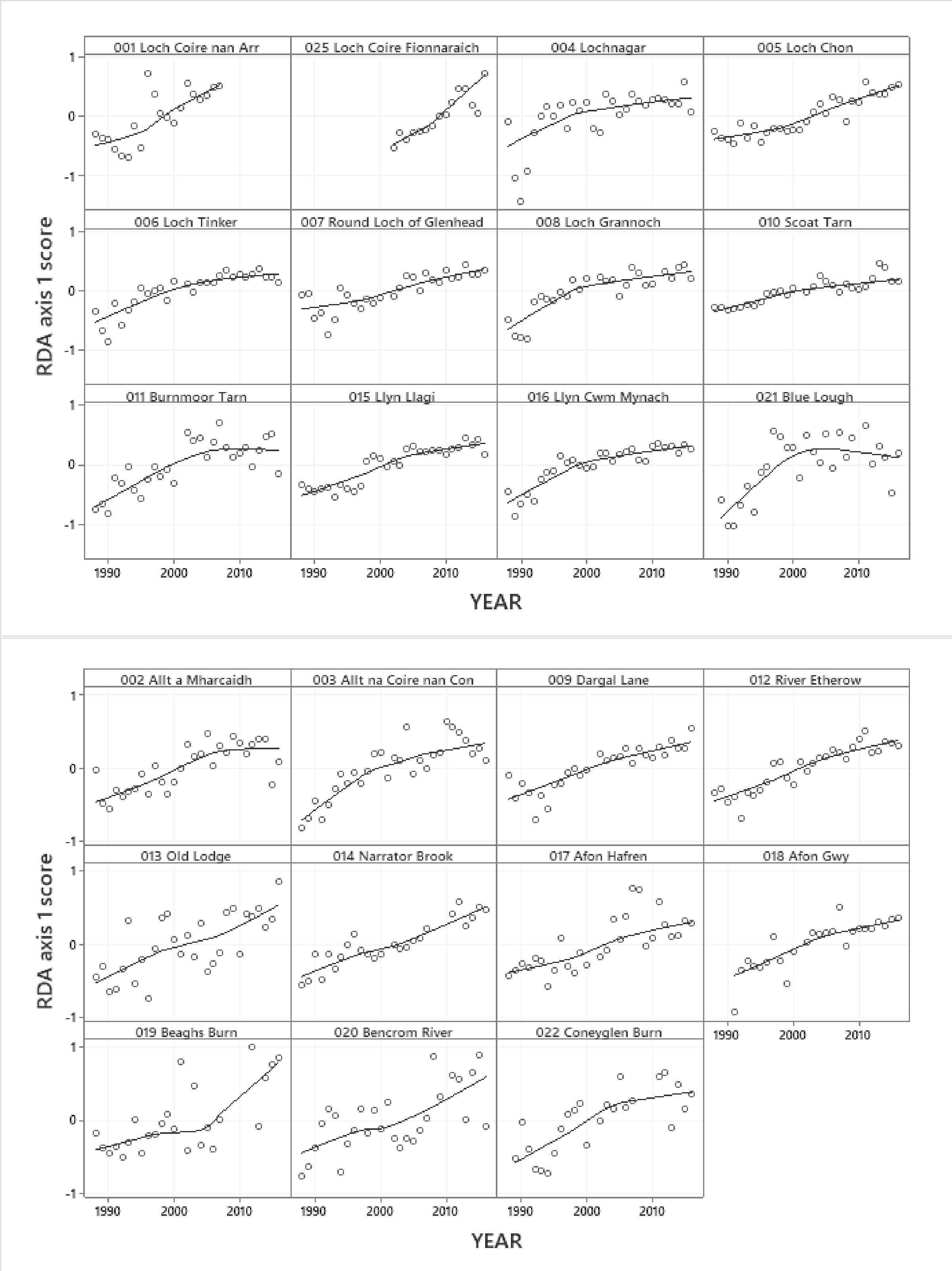


Figure 5.2. Variation in axis 1 scores from redundancy analysis fitted to macroinvertebrate data from each of the UWMN lake and stream sites, constrained by sampling year. The solid line represents a LOESS smoother (degree of smoothing = 0.75, number of steps = 2).

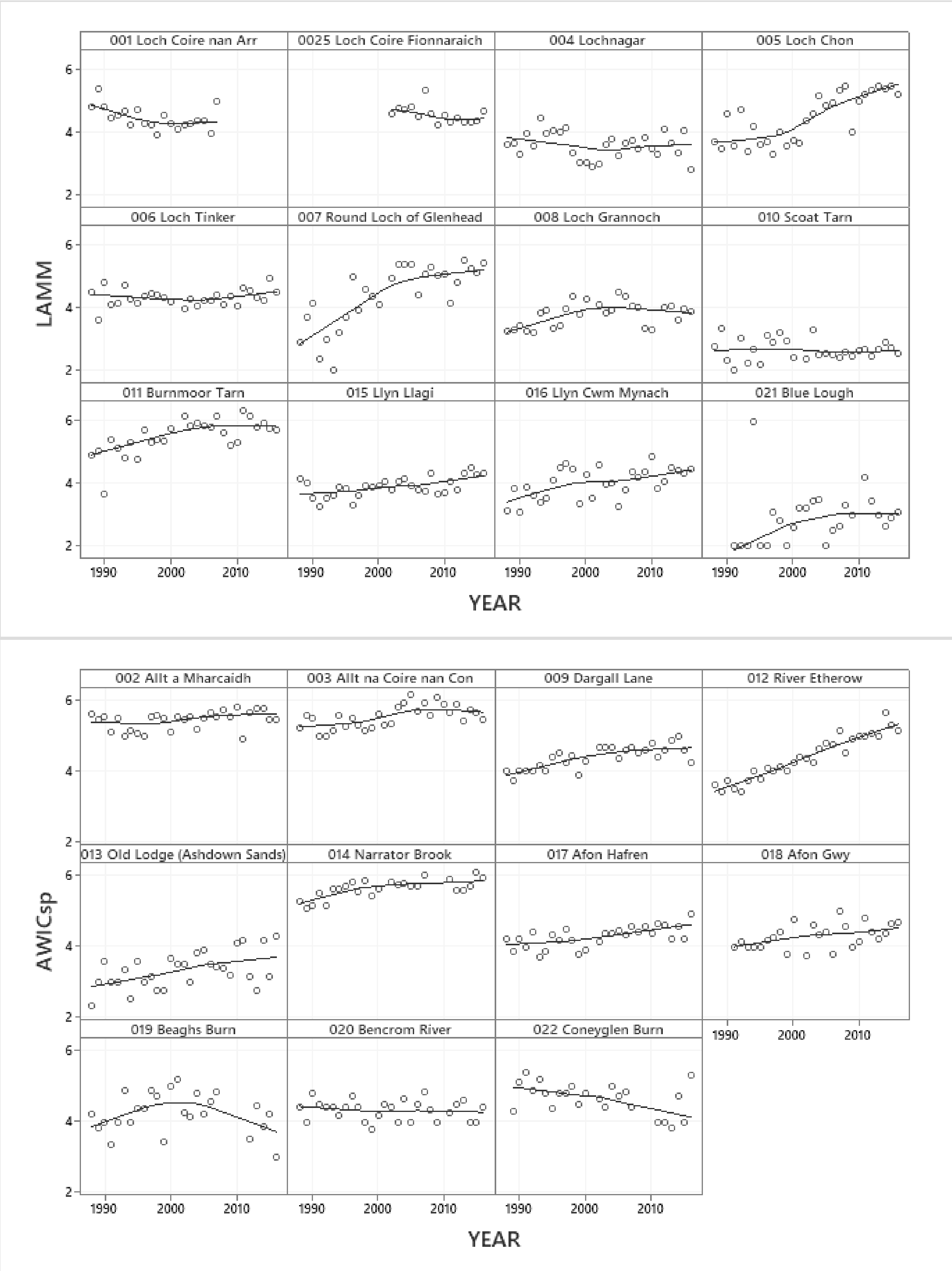


Figure 5.3. Variation in LAMM and AWICsp values at each of the UWMN lake and stream sites, respectively. The solid line represents a LOESS smoother (degree of smoothing = 0.75, number of steps = 2).

Table 5.4. Correlations between the magnitude of chemical recovery trends (Sen slopes for pH , ANC and alkalinity) and the magnitude of community change and biological recovery (taxa turnover and Sen slopes for LAMM and AWICsp). Correlation coefficients in bold are significant at p <0.05.

	pH (unit yr^{-1})	**ANC (µeq l^{-1} yr^{-1})**	**Alkalinity (µeq l^{-1} yr^{-1})**
All Sites (n = 23)			
Taxa Turnover	-0.083	0.158	0.078
Diagnostic Index (unit yr^{-1})	**0.415**	0.342	**0.445**
Lakes (n = 12)			
Taxa Turnover	-0.294	0.143	-0.025
LAMM (unit yr^{-1})	0.424	0.382	**0.634**
Streams (n = 11)			
Taxa Turnover	0.079	0.154	0.097
AWICsp (unit yr^{-1})	0.503	0.479	**0.606**

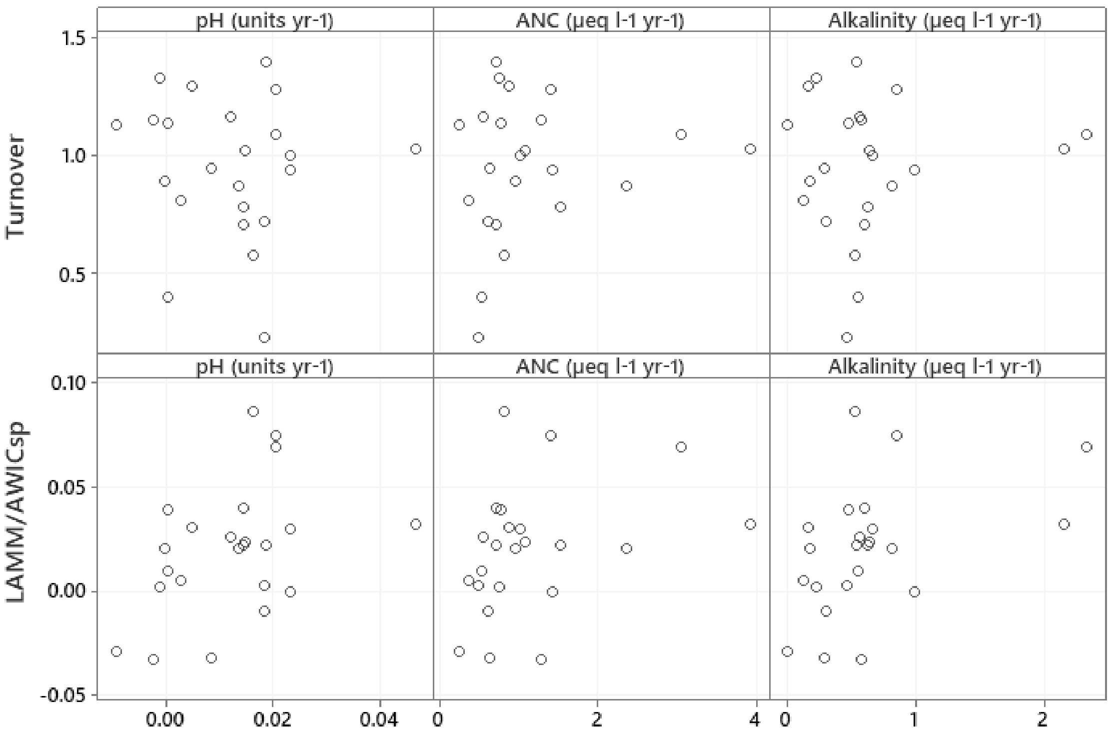


Figure 5.4. Relationships between magnitude of change in annual averages of pH, ANC and alkalinity and magnitude of change in diagnostic index scores and taxa turnover in the macroinvertebrate community across all 23 UWMN sites.

5.4 Aquatic macroinvertebrate discussion

After 28 years of monitoring at UWMN lakes and streams, biological recovery trajectories are evident at 14 of the 19 sites that show distinct chemical recovery trends. This compares with 10 out of 19 sites with improving acid chemistry after 20 years of monitoring (Monteith et al., 2014; Murphy et al., 2014). The spatial extent of biological recovery is therefore still not currently as wide as observed in the water chemistry records, but there are clear signs that biological responses are gathering pace. In general, the more pronounced the rate of increase in pH and Gran alkalinity at a site, the greater the rate of recovery in the biological community. There is no indication of a systematic difference in the extent to which lakes and streams are responding to reductions in acidification of fresh waters. Similar patterns of recovery are seen in both lentic and lotic habitats.

At most of the lake and stream sites in historically low acid deposition regions (e.g. Loch Coire Fionnaraich, Allt a'Mharcaidh) and those situated on more chemically buffered geology (e.g. Burnmoor Tarn), there has been relatively little change in assemblage composition over time. The majority of sites that had been subject to relatively moderate levels of acid deposition are now showing chemical and biological recovery trends of varying strengths. For some (e.g. Blue Lough) the improvement has been modest but for other sites (e.g. Loch Chon, Round Loch of Glenhead, and Dargall Lane) there has been a substantial change in the community, with acid-sensitive taxa becoming well-established. Some of the most acidified sites (e.g. Old Lodge, Afon Gwy, River Etherow), have undergone considerable shifts in community composition in response to improving acid conditions. The River Etherow has undergone a remarkable transformation from a species-poor community dominated by acid-tolerant taxa, to one supporting a much more diverse macroinvertebrate community, including an increasing number of acid-sensitive taxa. There have been exceptions though; Scoat Tarn, in the Lake District, Lochnagar in Scotland, and Bencrom River in Northern Ireland have been relatively slow to recover chemically and biologically from past acidification. Understanding the mechanisms that cause such differences in the rate of recovery among sites is a critical area of research that needs further work.

We found that the rate of change in diagnostic indices of acidification stress (LAMM/AWICsp) was correlated with the rate of increase in pH and Gran alkalinity, but not ANC. Nevertheless, rates of change in ANC and Gran alkalinity are themselves reasonably well correlated and variation in ANC could account for a significant proportion of variation in macroinvertebrate community composition at six of the 11 stream sites, though at only one of the lake sites. Since both variables are essentially indicators of a spectrum of chemical changes that range from reductions in labile aluminium and hydrogen ion concentrations to increases in bicarbonate ions, it is difficult to make generalisations regarding possible physiological or ecological mechanisms. At some sites, chemical recovery is dominated by change in a subset of these metrics, while other sites have experienced these changes sequentially. Consequently, our results are indicative of a broad response by the UWMN macroinvertebrate communities to improvements in a range of indicators of acidity/alkalinity.

It is not possible to confidently assert if and when a river or lake macroinvertebrate community has fully recovered from acidification. While there are tentative reference values set out for LAMM, these are based solely on two humic (i.e. DOC) site classes only, and without any consideration for other critical aspects of the lake water chemistry, geography or underlying geology (WFD-UKTAG, 2008). More accurate site-specific reference values for biotic indices of acidification status would require more stressor-independent environmental parameters to be taken into consideration in any predictive model. Such a model is not yet available in the UK. Alternatively, in lakes at least, it may be possible to reconstruct the pre-acidification macroinvertebrate community from remains in sediment cores. Nevertheless, it is clear from the monitoring data that there is potential for further chemical and biological recovery. At several recovering lake and river sites (Lochnagar, Loch Grannoch, Scoat Tarn, Afon Gwy and Old Lodge), there have been marked increases in Gran alkalinity over the past 5-10 years that may well stimulate additional responses in the macroinvertebrate community.

As discussed previously (Monteith et al., 2005; Murphy et al., 2014) there are a number of possible obstacles to biological recovery keeping pace with chemical recovery. These include variability in the chemical recovery trend (Kowalik et al., 2007), limitations on the dispersal of acid-sensitive colonists from unimpacted source areas (Gray and Arnott, 2011), hysteresis in the recovery trajectory due to biological interactions within the acid-tolerant assemblage (Monteith et al., 2005), and climate change or other effects disrupting a straightforward recovery from acidification (Johnson and Angeler, 2010). Further analysis may be able to determine if any of these mechanisms are having a substantial influence on the rate of biological recovery and whether there is any prospect for the community structures of the more acidified sites to ever fully return to those that characterised the sites prior to acidification. A recent study analysing recovery from acidification in 55 rivers and 34 lakes across Europe found that macroinvertebrate diversity was positively associated with reductions in acid components of the water, but negatively correlated with increases in air temperature (Velle et al., 2016). As environmental stress from acidification continues to decline in response to emissions policy, upland waters macroinvertebrate communities may experience stronger impacts from climate in the years to come.

6 Evidence for recovery from acidification and links to policy

Author: Don Monteith

6.1 Introduction

In the previous sections we have shown that the water chemistry, and particularly the acidity, of the majority of the UWMN sites has been responding to reductions in acid deposition throughout the last three decades, and even within the most recent years of monitoring in many cases. It is also clear that the biological communities assessed in this report (epilithic diatoms and macroinvertebrates) are changing in a manner broadly consistent with biological recovery from acidification – the ultimate aim of atmospheric emissions control policy with respect to acidified waters.

In this section we a) review how the observed chemical and biological changes relate to chemical reference targets most relevant to policy, and b) consider the factors that might explain variation between sites with respect to the current distance between observations and targets, and the prospects for further chemical and biological recovery.

There are various pieces of international legislation pertinent to the restoration of the ecological health of acidified surface waters. These fall under the auspices of the United Nations Economic Commission for Europe (UNECE), and the European Union (EU) (via the National Emissions Ceilings Directive (NECD) and Water Framework Directive (WFD)), and are detailed in the 20 Year UWMN Interpretive Report (Kernan et al., 2010). While the UK government, following Brexit, is no longer a signatory to EU directives, it is committed to maintaining a "level playing field" with respect to most EU environmental legislation, and to implementing atmospheric emissions policies and supporting monitoring and research in the spirit of the NECD and WFD.

The UNECE Convention on Long Range Transboundary Air Pollution (CLRTAP) developed the concept of Critical Loads as a means of setting appropriate atmospheric emissions controls. Critical Loads quantify the maximum atmospheric deposition load (S + N) that can be applied to specified receptor environments or organisms without resulting in “harmful effects” (Nilsson and Grennfelt, 1988). In the case of Critical Loads for freshwater acidity, the harmful effect threshold (or the Critical Limit) is based largely on a study by Lien et al. (1996), who established a relationship between Acid Neutralising Capacity (ANC) and evidence of damage to fish (particularly brown trout) and aquatic macroinvertebrate populations in Norwegian waters. Consequently, the UK adopted an ANC critical limit (or ANC_{crit}) of 20 μeq L^{-1}, which corresponds approximately to a 10% probability of damage to brown trout populations in the Norwegian dataset. Critical Load Exceedance is then defined as the amount acid deposition must be reduced by to achieve an ANC value of 20 μeq L^{-1} (or 0 μeq L^{-1} in the case of waters with geologies that render them naturally acidic) by reducing some combination of S and N deposition.

The 20 μeq L^{-1} ANC_{crit}, therefore, provides an initial reference point with which to gauge the chemical recovery progress and ecological viability of UWMN waters. It is important to recognise, however, that this is a relatively generic assessment threshold, and various caveats must be noted regarding its application. First, the Norwegian waters assessed by Lien et al.(1996) are predominantly relatively clear lakes, i.e. with low DOC concentrations. The potential for strong acids from organic compounds to contribute to water acidity is ignored in the ANC calculation, but significantly higher ANC concentrations are likely to be required to avoid the same level of acidity-related biological damage in browner, i.e. more organic acid influenced, waters. Second, the study is based largely on one-off water samples collected from lakes in the autumn and therefore considered representative of annual average chemistry. It does not, therefore take into account the temporal variation in ANC that can be substantial in headwater streams particularly. Sensitive organisms in running waters with a mean of 20 µeq L^{-1} could still be vulnerable to highly acidic episodes – for example, during spates or following sea salt deposition events. Finally, the limit of 20 µeq L^{-1} ANC is perhaps most relevant to Al^{3+} and H^+ ion toxicity thresholds for brown trout and some sensitive gill-breathing macroinvertebrate species. Other freshwater taxa are likely to be limited by other water chemical characteristics that may also have changed as a direct consequence of change in the acid deposition load: for example, the availability of bicarbonate, and/or increased inputs of organically bound nutrients or changes in the underwater light environment associated with rising DOC levels. Further ecological change in response to broader chemical improvements might, therefore, be expected where there is the chemical potential for ANC to advance significantly beyond the 20 µeq L^{-1} threshold. This is particularly relevant to the WFD's focus on achieving "good ecological status". The main diagnostic tool deployed under the WFD is the Ecological Quality Ratio (EQR) which is used to quantify how far ecological communities deviate from theoretical "high status" reference sites. Determination of what constitutes an appropriate reference site is challenging, and a number of methods have been adopted for different surface water typologies, pressures and ecological indicators.

Under the UNECE's second sulphur protocol, the recommended methodology for determining the Critical Load for surface water acidity was the Steady State Water Chemistry (SSWC) model (Henriksen et al., 1992). The later, process-informed, mass balance model, the First-order Acidity Balance Model (FAB; Posch et al., 1997), built on the SSWC by incorporating theoretical N dynamics, i.e. the theoretical process of progressive soil N accumulation, resulting in first seasonal, and ultimately year-round, nitrate leaching. The FAB model determines separate critical loads for S and N. Both models were used to provide the Critical Load estimates that underpinned the UNECE Gothenburg protocol (1999). The FAB model remains the recommended method, although it is only applied by the UK, Norway, Sweden, Finland and the Swiss canton Ticino.

The most commonly applied biogeochemical tool for determining how UK catchment soils and surface waters have responded, and will respond, to changes in acid deposition, from pre-industrial days into the future, is the dynamic model MAGIC (Model for Acidification of Groundwater in Catchments (Cosby et al., 1985). It is used to predict how future emission scenarios will affect surface water chemistry, and to calculate the reduction in acid deposition required to meet a specific ANC target. The parameterisation of MAGIC has been developed over time, as monitoring time series have grown and key biogeochemical processes regarding the nature of chemical recovery have become better understood. In early years, MAGIC did not factor in increases in organic acidity in response to reductions in acid deposition, and this may account for some discrepancies between its estimates of pre-industrial pH with those provided by palaeoecological (diatom-based) approaches (Battarbee et al., 2005). In the 20 Year UWMN Interpretive Report, Kernan et al. (2010) provide MAGIC-based estimates for pre-acidification "baseline" ANC values for all UWMN sites, and the same values are referred in the following sections.

6.2 Classification of progress toward chemical recovery targets

Various recovery targets for UK Upland Waters were reviewed in the UWMN 20 Year Interpretive Report. Achieving the ANC_{crit} of 20 µeq L^{-1} satisfies UNECE requirements but, for reasons discussed above, may be insufficient to facilitate the full return of aquatic ecosystems to a pre-acidified condition. Ecologically-based recovery targets may seem more intuitive, but determination of appropriate reference conditions involve a number of assumptions that are difficult to substantiate. In the case of the WFD, all acid-sensitive waters are considered within a single class, i.e. alkalinity < 200 µeq L^{-1}, but it is clear from earlier sections and the site-specific summaries in the Appendix that waters that fall beneath this limit vary hugely in terms of physical and chemical properties and are likely to have supported a wide range of ecological communities prior to acidification.

Figure 6.1 presents the ANC data as time series, with a Generalised Additive Model (GAM) trend line fitted according to the approach of Monteith et al. (2014) to summarise non-linear change over time. The coloured sections of the trend lines indicate periods when the first derivative of the GAM curve is significantly different from zero - blue indicating periods of significant increases in ANC. Of the chemically “benign” sites, Loch Coire nan Arr, Loch Coire Fionnaraich, Beagh’s Burn, and Loch Tinker, show no long-term trend in ANC. ANC levels in the Allt a’Mharcaidh have been stable throughout most of the monitoring period, but show an uptick since around 2014. This recent change in chemistry may be linked to a period of relatively low precipitation and river levels in northern Scotland and Northern Ireland, resulting in relatively high contributions to runoff from more chemically buffered groundwater. Burnmoor Tarn and Coneyglen Burn are the only sites within the “benign” grouping that have experienced progressive (albeit very slight) increases in ANC over time. Burnmoor Tarn is the only UWMN site in a more atmospherically polluted region of the UK that has been sufficiently well buffered geologically to resist acidification, and unlike most other UWMN lakes, palaeoecological pH reconstruction provides no evidence of pH change over the past two centuries (Battarbee et al., 2014b). The Gran alkalinity of Burnmoor Tarn has also increased slightly but significantly over the monitoring period (see Section 3.3.2), indicating an increase in bicarbonate concentration that must therefore be considered to be part of the wider chemical recovery process. A rise in bicarbonate has the potential to influence aquatic biota through increasing availability of inorganic carbon to plant species with a preference for bicarbonate over CO_2 as a primary carbon source for photosynthesis (Farmer, 1990), and to shell forming macroinvertebrate taxa.

In the following sub-sections we consider the latest UWMN data in the context of various recovery target-setting approaches, and use the latter to classify the chemical recovery status of individual sites. The approaches include hydro-chemical measures and lake palaeoecological pH reconstruction. Figure 6.2 summarises the distribution of ANC values in UWMN waters within 5-6 year periods, to illustrate how ANC has changed over time relative to ANC_{crit}, and MAGIC-based estimates of pre-industrial ANC, i.e. ANC in 1800, as presented previously in Kernan et al.(2010).

6.2.1 ANC_{crit}-based site classification

This classification, based on interpretation of Figure 6.2, groups sites according to how the distribution of ANC values at each site has changed over time relative to an ANC of 20 µeq L^{-1}. By considering not only the change in the median, but also the distribution around it, the approach recognises the potential importance of episodically low ANC values in hampering biological recovery in some circumstances. The sites are grouped as follows:

a) Chemically benign: Sites where ANC has rarely if ever been recorded below 20 µeq L^{-1} and shows little or no increase in ANC over time: Coneyglen Burn, Beagh's Burn, Allt a'Mharcaidh, Loch Coire nan Arr, Loch Coire Fionnaraich, Loch Tinker and Burnmoor Tarn.
b) Mildly acidified recovering: Sites where ANC averaged around or above 20 µeq L^{-1} in the early years of monitoring and has since increased to a point where measurements now very rarely fall below this threshold: Allt na Coire nan Con and the River Etherow.
c) Moderately acidified – strong recovery: Sites where ANC was predominantly less than 20 µeq L^{-1} in the early years of monitoring and has since increased to average significantly greater than 20 µeq L^{-1}: Loch Chon, Llyn Llagi, Llyn Cwm Mynach, Old Lodge, Bencrom River, and Narrator Brook.
d) Moderately acidified – moderate recovery: Sites where the ANC was predominantly less than 20 µeq L^{-1} in the early years of monitoring and has since increased to average around 20 µeq L^{-1}, while a significant proportion of samples still register below this threshold: Round Loch of Glenhead, Loch Grannoch, Dargall Lane Burn, Afon Hafren and Afon Gwy.
e) Strongly acidified – weak recovery: Sites where ANC was routinely negative in the early years of monitoring and, while it has increased since, most samples still have an ANC below 0 µeq L^{-1}: Lochnagar, Scoat Tarn and Blue Lough.

The ANC values of the very low deposition site, Loch Coire nan Arr, where monitoring terminated in 2008, and its replacement site, Loch Coire Fionnaraich, are both generally consistent with the "benign" category, in that ANC values below 20 µeq L^{-1} are rare. Occasional negative ANC values recorded in Loch Coire Fionnaraich are associated with high marine ion levels, and therefore naturally driven sea salt deposition events. In our classification we have ignored the major reduction in ANC at Loch Coire nan Arr in the final period of monitoring of the site, when it is likely that chemical change was dominated by water level fluctuations caused by the dam installation.

It is important to note that while the acid anion deposition flux to UWMN sites over recent years has fallen to very low levels in a recent historical context: i) it remains disproportionately higher in the more heavily acidified regions; and ii) where deposition fluxes of acidity are now falling below rates of geological alkalinity generation through weathering, gradual restoration of soil base cation saturation should lead to further gradual increases in ANC for many years to come.

6.2.2 Dynamic $ANC_{crit\text{-}ORG}$-based site classification

In contrast to the previous approach, where ANC trends were compared against a fixed ANC_{crit}, in this classification we take into account a theoretical contribution from organic acids to water acidity in order to determine the level of ANC necessary to provide protection for acid-sensitive biological elements. According to the calculations of Lydersen et al. (2004), the ANC_{crit} for brown trout should be as low as 8 µeq L^{-1} for waters with a negligible DOC concentration, rise to 20 µeq L^{-1} for waters with a DOC concentration of 3.5 mg L^{-1}, and increasingly exceed 20 µeq L^{-1} for progressively DOC-rich waters. Their estimates were based on the assumptions of 1) a charge density of 10.2 µeq mg^{-1} C and 2) one third of the organic matter ion-exchange sites being permanently deprotonated – thus resulting in an organic acid contribution of 3.4 µeq mg^{-1} C.

Two important implications follow.

First, ANC_{crit} values required to protect organisms as sensitive as brown trout should be substantially higher than 20 µeq L^{-1} in the browner (higher DOC) UWMN sites, for example Loch Grannoch, the River Etherow and Old Lodge, where, median DOC concentration has been over 9 mg L^{-1} over the six years leading up to 2019. According to the Lydersen et al (2004) calculation, the equivalent ANC_{crit} (denoted from now on as $ANC_{crit-ORG}$) for surface waters with a DOC concentration of 9 mg L^{-1} would be 8 + (9 x 3.4) = 38.6 µeq L^{-1}, i.e. almost double that of the UK's ANC_{crit} value.

Second, since DOC concentrations have increased substantially over time (and often more rapidly at sites with higher initial DOC concentrations) the $ANC_{crit-ORG}$ level at all sites will also have increased as ANC levels have risen. Any prospect of biological recovery therefore depends on ANC rising more rapidly than the $ANC_{crit-ORG}$. On this basis, the difference between the measured ANC value and the dynamic (DOC concentration-dependent) $ANC_{crit-ORG}$ should provide a more physiologically appropriate metric for assessing progress towards more benign chemistry than a comparison against the static ANC_{crit}.

Trends in this differential (i.e. measured ANC - $ANC_{crit-ORG}$) at each site are illustrated in Figure 6.3 and provide a slightly different perspective on the recovery status of some sites to that presented in Section 6.2.1. In this Figure a "gap closure" of 0 µeq L^{-1}, represented by the red dotted line, indicates an ANC value equivalent to the $ANC_{crit-ORG}$. The water chemistry of sites where (and when) distributions of gap closure values lie predominantly above the red line should be relatively benign for highly sensitive elements of the biota such as brown trout and acid-sensitive mayfly species.

Application of comparable classification criteria to those set out in Section 6.2.1, but substituting the fixed 20 µeq L^{-1} ANC_{crit} with a 0 µeq L^{-1} differential between measured ANC and the dynamic $ANC_{crit-ORG}$, results in the following categorisation:

A. Chemically benign: Sites where ANC was rarely if ever lower than the $ANC_{crit-ORG}$ and shows little or no increase in ANC over time. i.e. Coneyglen Burn, Beagh's Burn, Allt a'Mharcaidh, Loch Coire nan Arr, Loch Coire Fionnaraich, Loch Tinker and Burnmoor Tarn.
B. Mildly acidified recovering: Sites where ANC averaged around or above the $ANC_{crit-ORG}$ in the early years of monitoring and has since increased to a point where samples now very rarely fall below this threshold: i.e. Allt na Coire nan Con and the River Etherow.
C. Moderately acidified – strong recovery: Sites where ANC was predominantly less than the $ANC_{crit-ORG}$ in the early years of monitoring and has since increased to average significantly greater than this threshold: i.e. Loch Chon, Llyn Llagi, Llyn Cwm Mynach, Old Lodge, Bencrom River, Dargall Lane Burn and Narrator Brook.
D. Moderately acidified – moderate recovery: Sites where the ANC was predominantly less than the $ANC_{crit-ORG}$ in the early years of monitoring and has since increased to average around it: Sites : i.e. Afon Hafren and Afon Gwy and Lochnagar.
E. Strongly acidified – weak recovery: Sites where ANC was routinely negative in the early years of monitoring and, while it has increased since, most samples still have an ANC below the $ANC_{crit-ORG}$: i.e. Scoat Tarn, Loch Grannoch, Round Loch of Glenhead and Blue Lough.

Three sites classify differently using this approach. As a consequence of its low DOC concentrations, recent ANC values for Lochnagar have averaged around the $ANC_{crit-ORG}$, while still remaining below the fixed ANC_{crit} of 20 µeq L^{-1} (resulting in an upgrading from Class E to Class D). For similar reasons, recent ANC values for the Dargall Lane Burn have averaged above the $ANC_{crit-ORG}$ while simultaneously averaging around the 20 µeq L^{-1} threshold (resulting in an upgrading from Class D to Class C). In contrast, the relatively high recent DOC concentrations in Loch Grannoch (and to a lesser extent the Round Loch of Glenhead) have raised the $ANC_{crit\text{-}ORG}$ considerably, so that the ANC of most samples at both sites remains significantly below the dynamic threshold, despite now averaging around 20 µeq L^{-1} (resulting in a downgrading from Class D to Class E).

6.2.3 Distance from MAGIC-inferred ANC baseline

Progress toward the MAGIC-derived pre-industrial baseline values, previously presented in Kernan et al. (2010), is indicated in Figure 6.2, but is perhaps more clearly illustrated in the bar plots of Figure 6.4, where mean (5-6 yearly) ANC values only are provided, with sites ranked from left to right in order of the A-E classification of Section 6.2.2. This emphasises how close recent mean ANC is to baseline values in most of the better buffered sites to the left of the figure. The main exception here is Burnmoor Tarn, the only one of these sites in a historically high deposition region, where recent mean ANC is only around half of the baseline value.

In contrast, while all the more sensitive UWMN sites are showing progressive increases in ANC, the recent (2014-2019) mean values of all but one remain substantially below the MAGIC baselines. On average, the difference between MAGIC baseline ANC and the 2014-2019 mean ANC for the fourteen more acidified sites (on the right of Figure 6.4) is 27 µeq L-1. In percentage terms, average recovery in ANC (determined as the difference between ANC in the 1989-1994 and 2014-2019 year periods, relative to the difference between the MAGIC ANC baseline and mean ANC of the 2014-2019 period) for the same group of fourteen sites was 57% (Table 6.1). While the steady reduction in the difference between MAGIC baseline ANC and measured ANC is encouraging, this has taken place over a period of substantial reductions in deposition. As deposition loads begin to flatten out, further significant progress in ANC will increasingly depend on any further reductions in the leaching of NO_3^- and the rate of recovery in base saturation of the catchment soils, both of which are likely to be much more gradual processes.

The single exception to the recovery pattern in the more sensitive and acidified group of sites is Loch Grannoch, where the recent mean is greater than the baseline value. It is currently unclear why the ANC of this site, with its heavily forested catchment, is now so high although it is known that the catchment has been subjected to substantial applications of fertiliser since it was established in the 1950s and in recent years has undergone significant physical disturbance from forest management. Importantly, as explained in the previous section, despite the relative high contemporary ANC the water acidity of Loch Grannoch remains problematic for more acid-sensitive species because of the relatively high current concentrations of organic acids. Further years of monitoring will be needed to determine if these levels are sustained.

6.2.4 Water pH relative to diatom-inferred pre-industrial pH

Sediment cores were taken from all UWMN lakes at the onset of monitoring (see Section 1.1). In the 20 year Interpretive Report, Kernan et al. (2010) presented diatom-inferred pH (DI-pH) values for UWMN lake sediments, dated by ^{210}Pb dating to around 1860, and based on the mean of three alternative diatom-inferred pH modelling methods. All of these inference models have been shown to provide reliable estimates of water pH, with a standard error of approximately +/- 0.3 pH units (Battarbee et al., 2005). We have used the same pre-industrial DI-pH values to provide a historical comparator for measured pH in UWMN lakes over the monitoring period.

Over the last three decades the water pH of the majority of UWMN lakes has gradually increased toward their respective pre-industrial DI-pH values, and in some cases has exceeded them (Figure 6.6). The lakes fall into three main groups on the basis of these pH trend – DI-pH relationships:

1) Non-acidified lakes: Sites where median pH has always been close to, or slightly above, the 1860 DI-pH, value, i.e. Loch Coire nan Arr (and by inference Loch Coire Fionnaraich), Burnmoor Tarn and Loch Tinker.
2) Acidified-recovered lakes: Sites where median pH was significantly below DI-pH but is now not significantly different from, or greater than, DI-pH, i.e. Lochnagar, Blue Lough and Llyn Llagi.
3) Acidified-recovering: Sites where median remains significantly below DI-pH, i.e. Loch Chon, Round Loch of Glenhead, Loch Grannoch, Llyn Cwm Mynach and Scoat Tarn.

These groupings are broadly consistent with those based on ANC recovery patterns discussed in earlier sections, but there are some notable differences.

First, while the ANC of Blue Lough remains, on average, well below the ANC_{crit}, and even slightly below 0 µeq L^{-1}, median measured water pH appears to have reached the diatom-inferred pre-industrial pH level. The exceptionally acidic geology underlying Blue Lough has long been recognised, and it has been suggested that 0 µeq L^{-1} is a more realistic target level than 20 µeq L^{-1}. However, the MAGIC baseline ANC value of 18 µeq L^{-1}, the lowest for any site on the network, implies some potential for further recovery.

Second, the majority of recent Lochnagar pH measurements lie significantly above the pre-industrial DI-pH value. Historically and currently, the diatom flora of this high altitude, cold and clearwater mountain lake is quite different from the lower lying acidified lakes on the network and from the majority of lakes contributing the training sets on which the diatom-pH inference models are based. It is possible, therefore, that the DI-pH of pH 5.6 underestimates the actual pre-industrial water pH of this site. There is some indication from the water chemistry trends (Appendix: Figure 4.2) that non-marine sulphate and nitrate concentrations are still declining, and it seems feasible that water pH has yet to stabilise.

Third, and finally, it is important to note that the afforestation of the Loch Grannoch and Loch Chon catchments did not occur until the mid-20th century. Given that both sites are known to have acidified more than their moorland counterparts, and that lake water pH, although rising, remains lower than the neighbouring lochs (Section 3.3.2.4), it is not surprising that the current pH remains lower than the DI-pH values for these lochs prior to forestation. While levels of S and N deposition have fallen to similarly low levels at the two sites in recent years, Loch Chon is significantly better buffered geologically - as indicated by higher concentrations of calcium), and it would seem likely that water acidity is now flattening out at a new post-recovery equilibrium. Loch Chon, arguably, should therefore be included within the “acidified-recovered” group. Loch Grannoch, on the other hand, remains significantly more acidified.

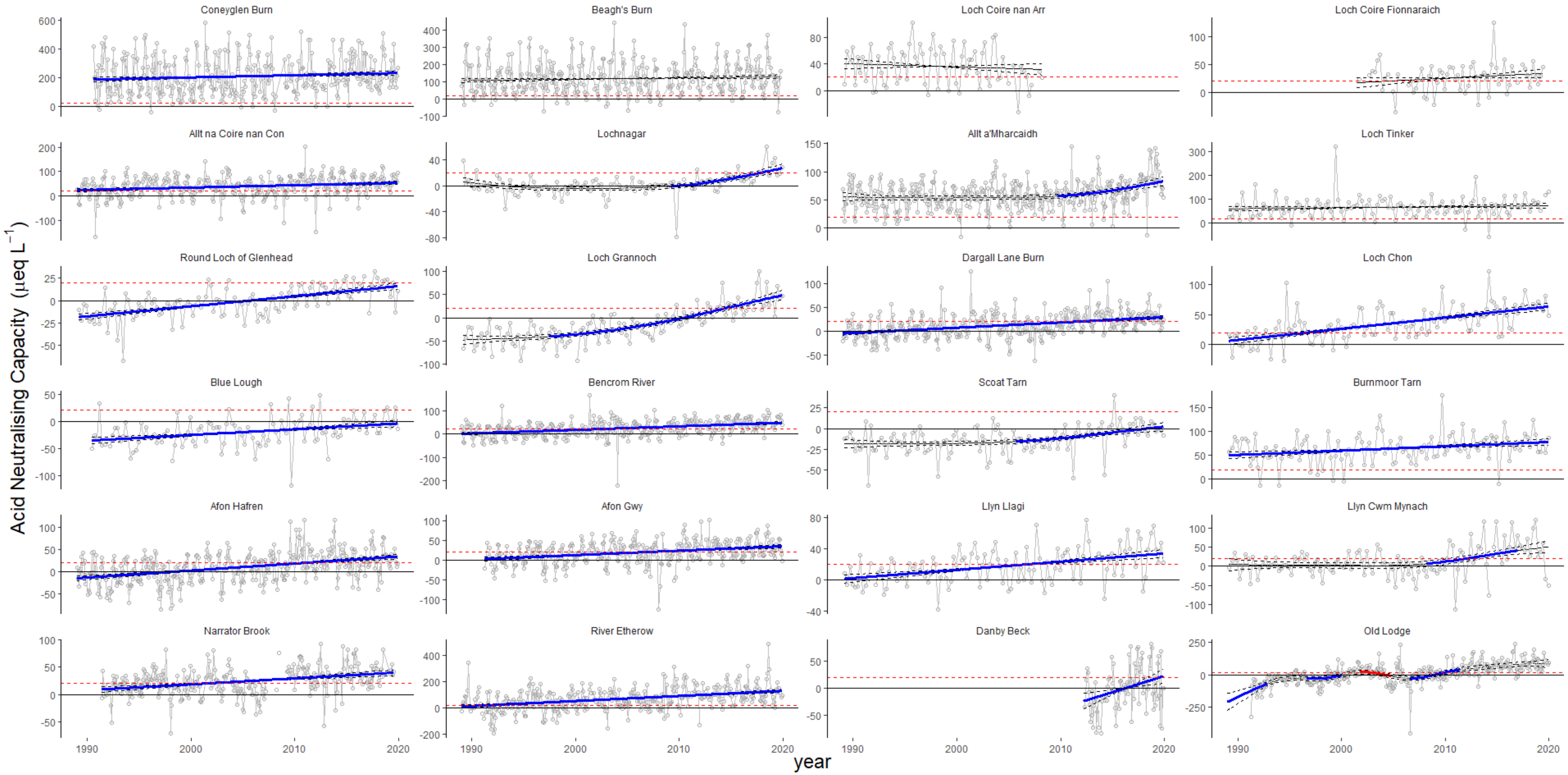


Figure 6.1. Temporal trends in Acid Neutralising Capacity in UWMN sites, with a Generalised Additive Model (GAM) smoother included to convey the long-term trends. Colouring of the GAM is used to convey when the first derivative of the GAM is significantly different from zero, with blue representing periods of significant increase in ANC, and red represents periods of significant decrease.

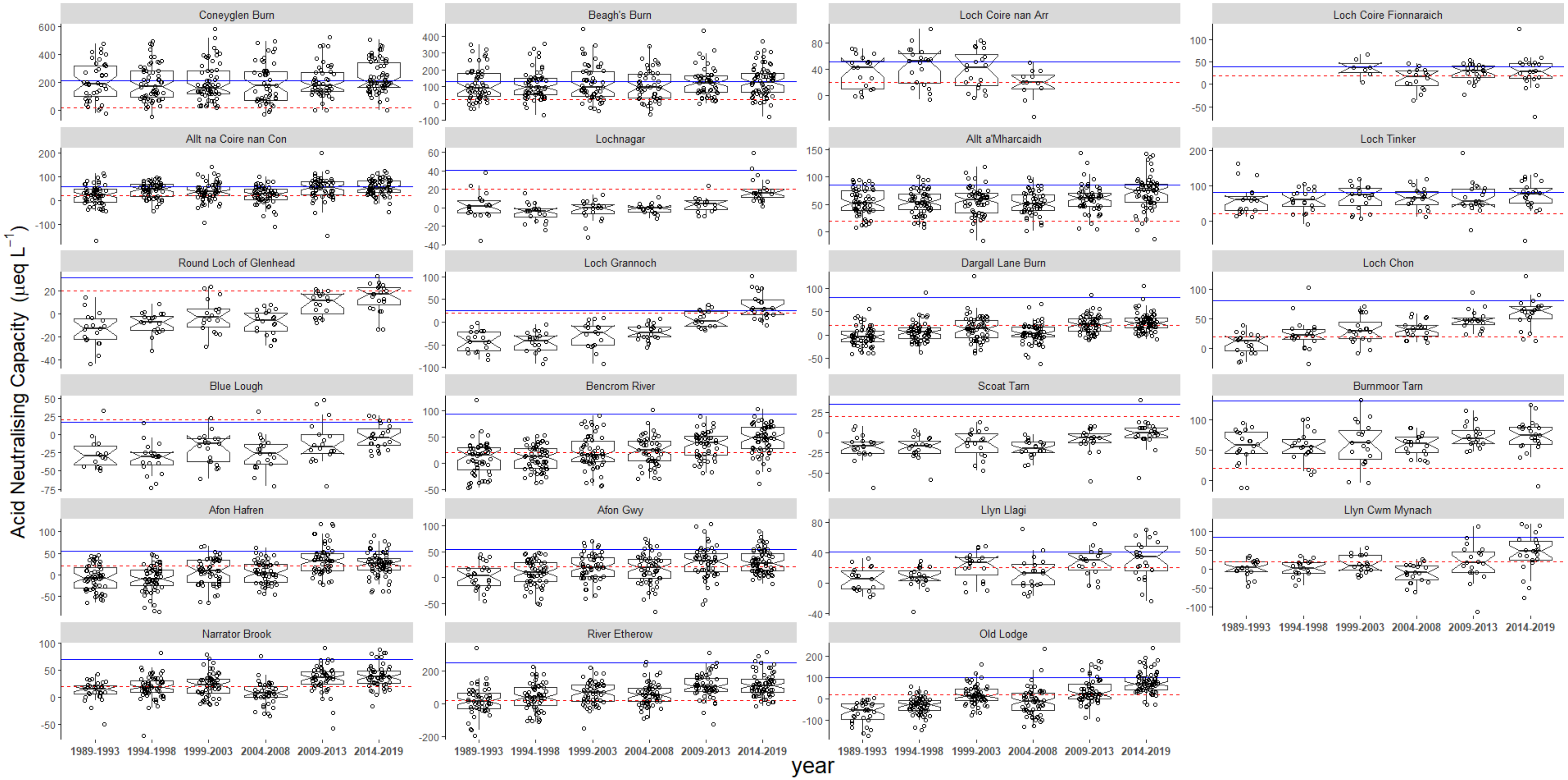


Figure 6.2 Box and whisker plots summarising the distribution of Acid Neutralising Capacity (determined as the equivalent sum of base cation concentrations minus acid anion concentrations) from 1989 – 2019. Data are grouped in 5-6 year periods . Central lines within the boxes represent the population median, edges of the box represent the 25% and 75th percential of the distribution and ends of the "whiskers" represent 5th and 95th percentiles. The width of the box "notches" represents the confidence interval on the box median. Open circles represent individual samples that are randomly jittered, i.e. they are not chronologically ordered within groups. The red dotted line represents the UK's adopted Critical Limit for ANC of 20 µeq L^{-1}. The blue solid line represents the MAGIC modelled prediction of ANC in 1800. Circles represent the ANC of individual samples. Points representing individual samples within each temporal period are jittered randomly (rather than ordered chronologically) to aid interpretation.

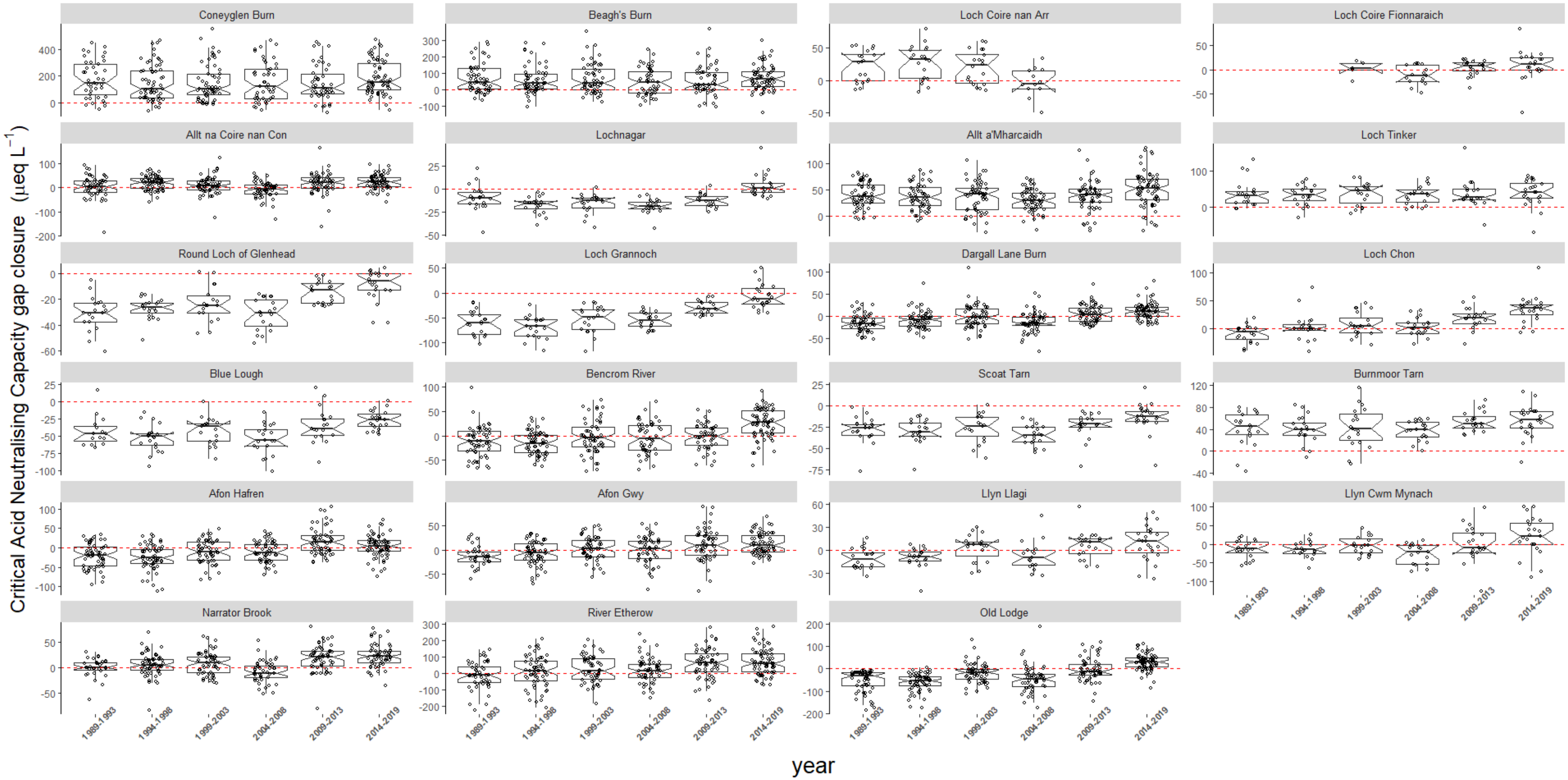


Figure 6.3 Box and whisker plots summarising the distribution of Acid Neutralising Capacity (determined as the equivalent sum of base cation concentrations minus acid anion concentrations) from 1989 – 2019 relative to the dynamic ANC$_{crit-ORG}$ value. Each point represents the difference between the measured ANC and the ANC$_{crit-ORG}$ defined in Section 6.2.2 with the red dotted line representing parity. Data are grouped in 5-6 year periods . Central lines within the boxes represent the population median, edges of the box represent the 25% and 75th percential of the distribution and ends of the "whiskers" represent 5th and 95th percentiles. The width of the box "notches" represents the confidence interval on the box median. Open circles represent individual samples that are randomly jittered, i.e. they are not chronologically ordered within groups. Points representing individual samples within each temporal period are jittered randomly (rather than ordered chronologically) to aid interpretation.

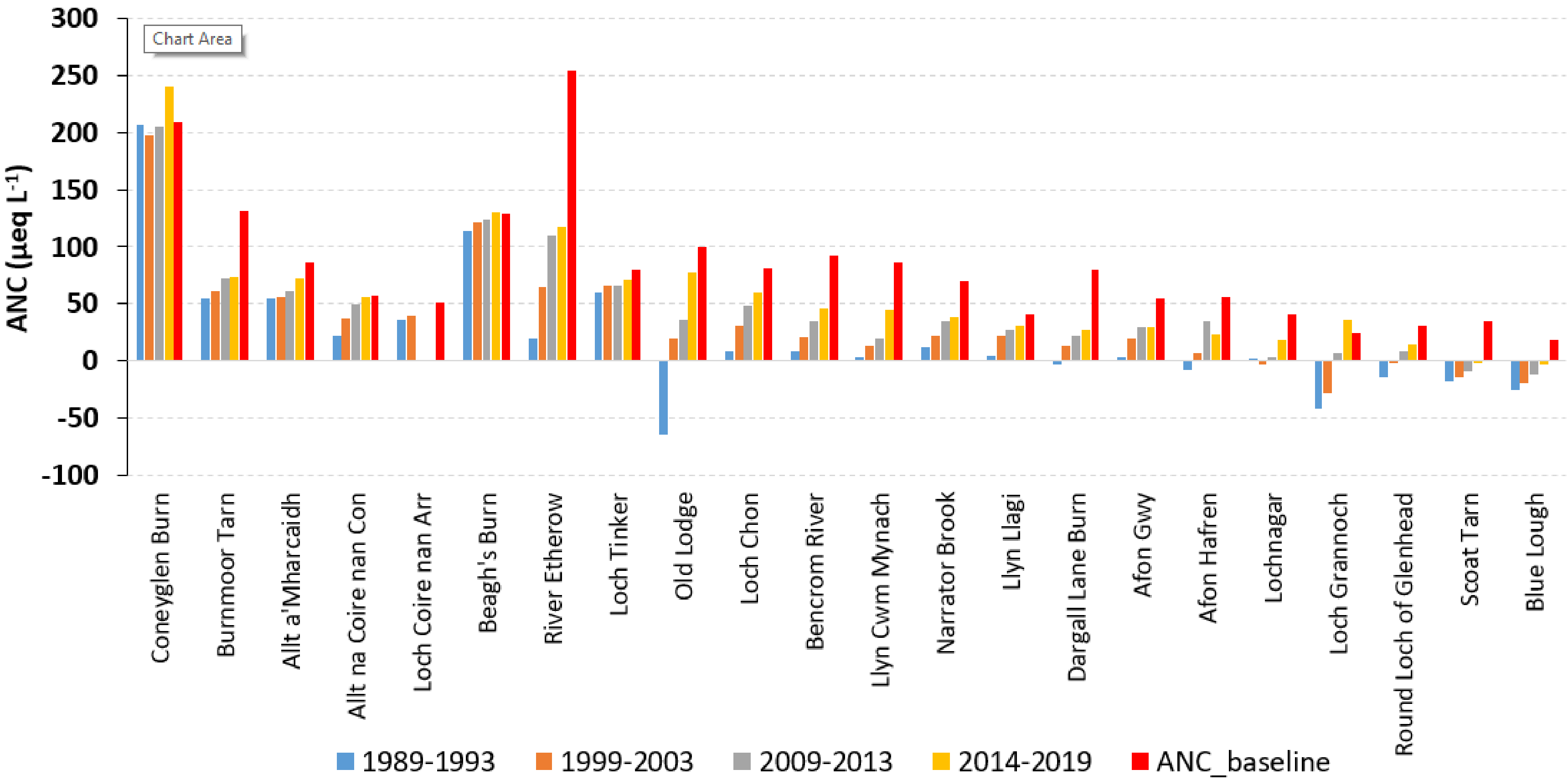


Figure 6.4. Mean five-yearly ANC values for UWMN sites and the MAGIC-inferred pre-industrial, or baseline, Acid Neutralising Capacity (red bars). Sites are ordered first according to the A-E grouping set out in Section 6.2.2 and second by mean 2014-19 ANC (left-to-right in decending order).

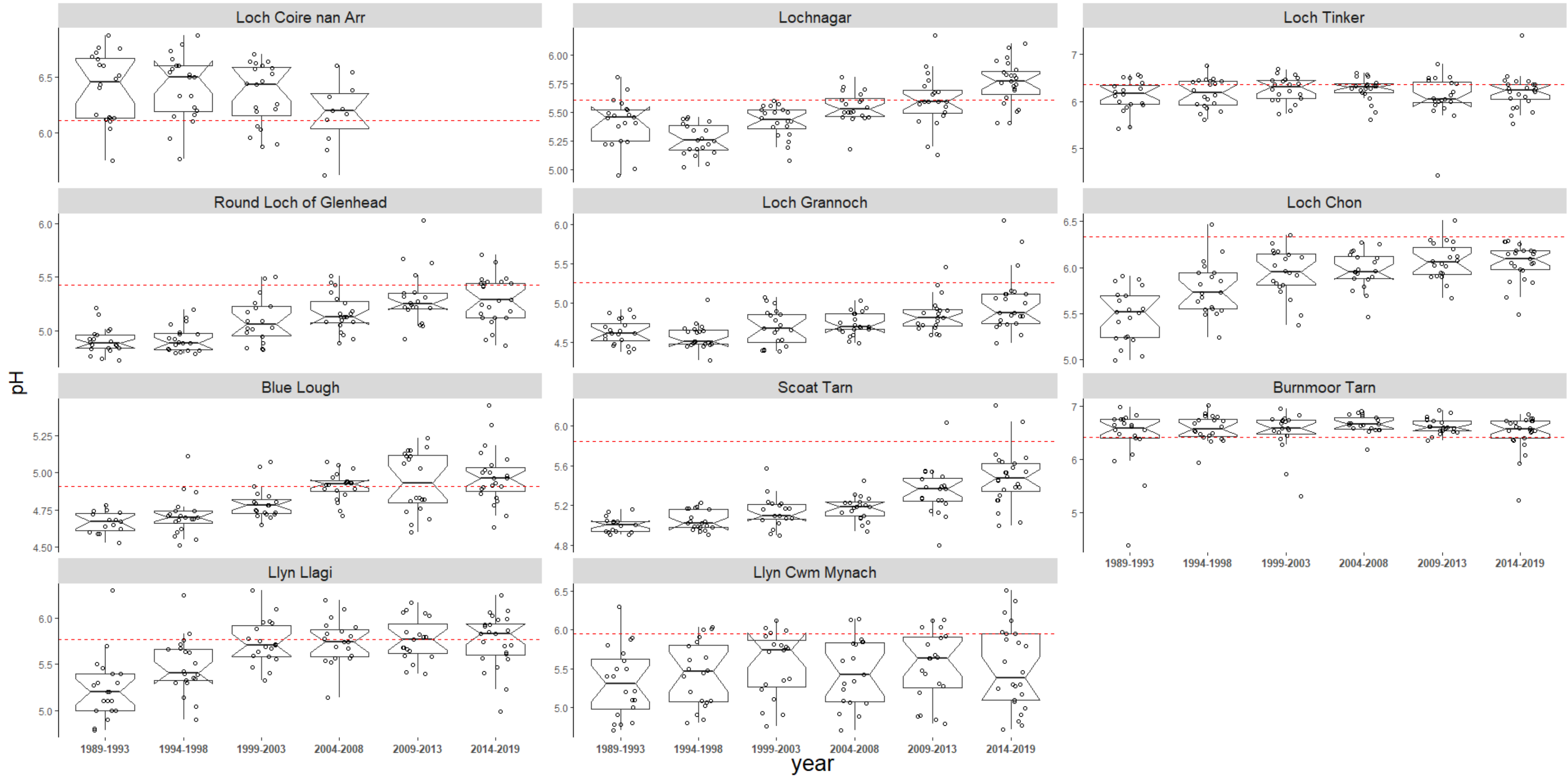


***Figure 6.5** Box and whisker plots summarising the distribution of lake water pH from 1989 – 2019 grouped in 5-6 year periods . Central lines represent the population median, edges of the box represent the 25% and 75th percential of the distribution and ends of the "whiskers" represent 5th and 95th percentiles. The width of the box "notches" represents the confidence interval on the box median. Open circles represent pH of individual samples that are randomly jittered, i.e. they are not chronologically ordered within groups. The red dotted line represents the 1860 mean diatom inferred pH of three diatom pH inference models. Points representing individual samples within each temporal period are jittered randomly (rather than ordered chronologically) to aid interpretation.*

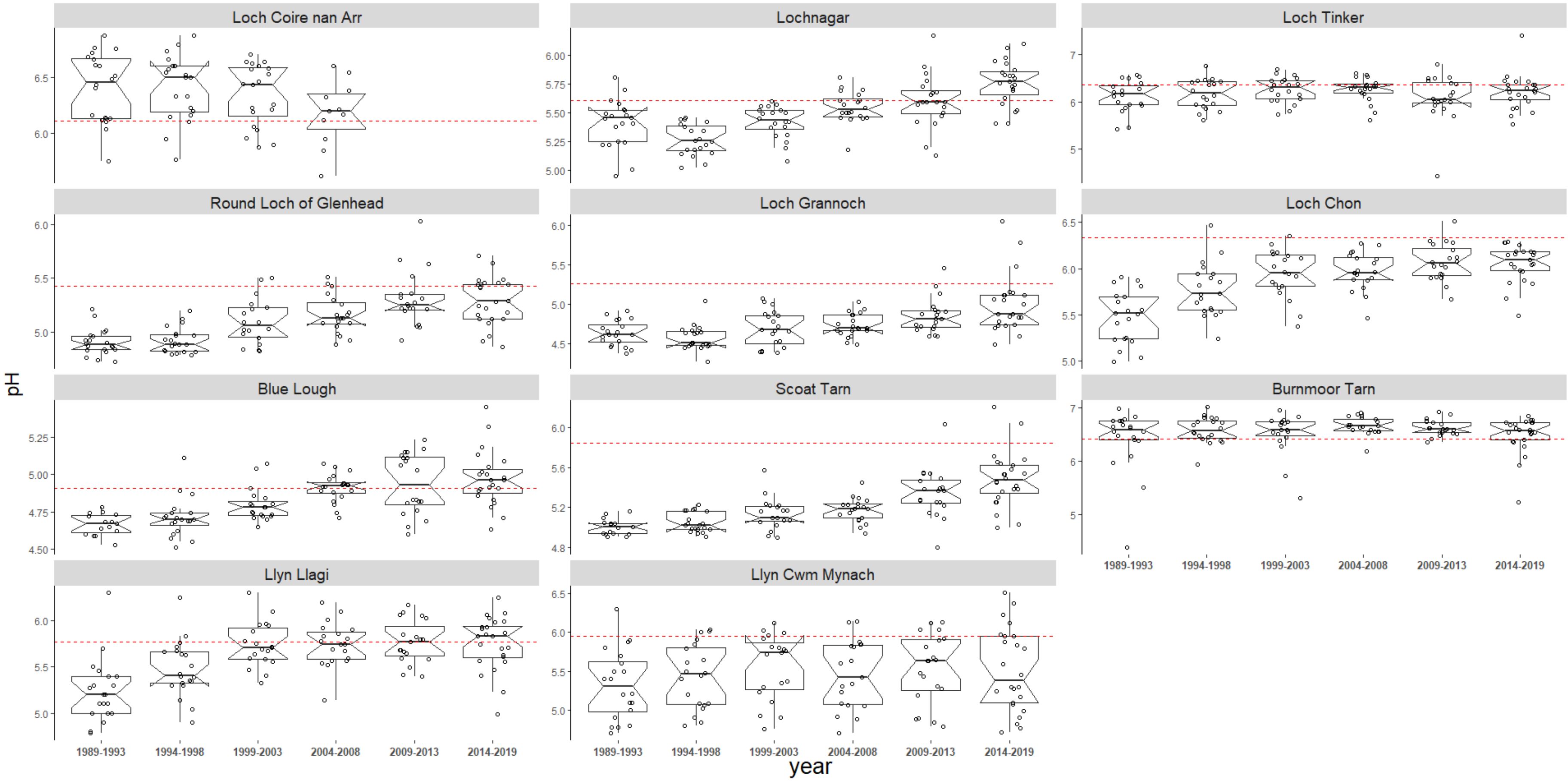


***Figure 6.6** Box and whisker plots summarising the distribution of lake water pH from 1989 – 2019 grouped in 5-6 year periods . Central lines represent the population median, edges of the box represent the 25% and 75th percential of the distribution and ends of the "whiskers" represent 5th and 95th percentiles. The width of the box "notches" represents the confidence interval on the box median. Open circles represent pH of individual samples that are randomly jittered, i.e. they are not chronologically ordered within groups. The red dotted line represents the 1860 mean diatom inferred pH of three diatom pH inference models.*

6.2.5 Summary of chemical recovery status in relation to geological sensitivity and deposition

The previous sections set out various approaches to classifying the chemical recovery status of UWMN sites, including relationships between measured ANC and ANC_{crit}, the difference between measured ANC and the dynamic (DOC-based) $ANC_{crit\text{-}ORG}$, distance from a pre-industrial baseline ANC as determined by the MAGIC model, and measured pH relative to diatom-inferred pre-industrial pH (lakes only).

There is reasonable consistency across classifications (Table 6.1), all reflecting the importance of both geographical situation and geochemical sensitivity in determining the extent of chemical change over the monitoring period. The MAGIC pre-industrial ANC "baseline" provides one measure of the sensitivity, since pre-industrial acid-base status should be indicative of a catchment's underlying geological buffering potential. The "chemically benign" sites all have MAGIC-inferred "baseline" ANC values of 80 μeq L^{-1} or more and/or are situated in the UK's lowest deposition regions in the far north of Scotland and the north of Northern Ireland. More generally, and with the exception of Llyn Llagi, the ANC of all sites with a MAGIC baseline ANC >60 μeq L^{-1} has either remained at, or returned/exceeded ANC_{crit} and $ANC_{crit\text{-}ORG}$ targets. In constrast, the ANC of most sites with a MAGIC baseline ANC of between 40-60 μeq L^{-1} is currently oscillating around these thresholds, indicating continued significant chemical risk to acid-sensitive biota, while the ANC_{crit} and $ANC_{crit\text{-}ORG}$ targets have mostly not been met at the sites with baselines below 40 μeq L^{-1}. As stated earlier, however, it is unlikely that the ANC of Blue Lough was ever as high as 20 μeq L^{-1}.

Table 6.1 UWMN chemical recovery classifications based on relationships between change in water chemistry and recovery targets represented by a) the 20 μeq L^{-1} ANC Critical Limit (ANC_{crit}), b) the ANC Critical Limit taking into account the contribution to acidity from organic acids ($ANC_{crit\text{-}ORG}$), and c) pre-industrial pH predicted by diatom-inferred pH reconstruction. Colour shading highlights small differences in classification between the two ANC-based approaches .

SITE	ANC_{crit}_class	$ANC_{crit\text{-}ORG}$	DI_pH class	MAGIC ANC baseline (μeq/L)
Loch Coire Fionnaraich	a	A	1	NA
Coneyglen Burn	a	A	NA	209
Burnmoor Tarn	a	A	1	131
Beagh's Burn	a	A	NA	129
Allt a'Mharcaidh	a	A	NA	86
Loch Tinker	a	A	1	80
Loch Coire nan Arr	a	A	1	51
River Etherow	b	B	NA	254
Allt na Coire nan Con	b	B	NA	57
Old Lodge	c	C	NA	100
Bencrom River	c	C	NA	93
Llyn Cwm Mynach	c	C	3	86
Loch Chon	c	C	3	81
Dargall Lane Burn	d	C	NA	80
Narrator Brook	c	C	NA	70
Llyn Llagi	c	C	2	41
Afon Hafren	d	D	NA	56
Afon Gwy	d	D	NA	55
Lochnagar	e	D	2	41
Scoat Tarn	e	E	3	35
R.Loch of Glenhead	d	E	3	31
Loch Grannoch	d	E	3	25
Blue Lough	e	E	2	18

Lake water pH of all four UWMN lakes classed within the “chemically benign” grouping (i.e. those shaded blue in Table 6.1, shows little indication of change over the full UWMN monitoring period, and in all cases pH levels have remained very close to the palaeoecologically-based pre-industrial DI-pH value. There is less consistency between the ANC-based groupings C-E (i.e yellow-orange-red shading) and progress towards the reference pH, but the main exceptions here, and possible explanations, have already been discussed in Section 6.2.4. Most importantly, over the period 2014-2019, the pH of three out of four of the lakes to show the weakest recovery in ANC relative to $ANC_{crit-ORG}$ (the Group E sites, Scoat Tarn, Round Loch of Glenhead and Loch Grannoch) remained significantly below the pre-industrial DI-pH value, providing further evidence of a continuing acidified state.

The role of both catchment buffering and recent rates of acid deposition in influencing the chemical recovery status summarised in Table 6.1, is illustrated in Figures 6.7 - 6.8. In these plots UWMN sites are colour-coded according to the $ANC_{crit-ORG}$ classification. We have used estimates of annual average runoff (Standardised Annual Average Rainfall (SAAR) 1961-1990) for each catchment, multiplied by the sum of mean non-marine calcium and mean non-marine magnesium concentration, in order to derive a theoretical divalent mean 2014-2019 non-marine divalent base cation flux. There are various limitations to this approach, including that a) spatial variation in the SAAR runoff estimate may not be entirely representative of spatial variation in runoff between 2014-2019, b) failure to fully account for fine-scale temporal variation in the base cation concentration of the UWMN streams particularly may lead to significant errrors in the cation flux estimate, and c) in the case of Figure 6.7, that the theoretical contribution to acidity from N deposition is over-estimated as it does not take into account N immobilisation within the soil and N losses to the atmosphere. Nevertheless, both plots provide some indication of the likely reasons behind the restricted amount of chemical recovery of sites in the D-E (or d-e) ANC-based classification classes shown in Table 6.1., and prospects for further recovery if acid deposition can be lowered further.

Figure 6.7 is based on the assumption that all deposited N (as estimated by CBED) ultimately has an acidifying influence. The acid deposition flux presented in this figure should, therefore, be considered a worst-case scenario only. In Figure 6.7, the four sites that are currently most acidifed, the Round Loch of Glenhead, Loch Grannoch, Blue Lough and Scoat Tarn (coloured red) are the only sites where total theoretical (S+N based) acid deposition flux exceeds the 2014-2019 divalent base cation loss by more than a factor of 3, i.e. they lie to the left of the 3:1 ratio indicated by the red dotted line. More broadly, the ANC of most of the sites where theoretical acid deposition is double the divalent cation flux (i.e. most of those falling to the left of the orange line) remains theoretically problematic for brown trout and similarly acid-sensitive macroinvertebrates (i.e. most sites fall into the “Strongly acidified – weak recovery” or “Moderately acidified” – moderate recovery” groups). In contrast, most sites in the “chemically benign” group currently receive less acid deposition (theoretically) from S and N than the divalent non-marine base cation generation rate. i.e. most lie to the right of the 1:1 line.

Figure 6.8 ignores all potential contributions to acidity from N deposition, and thus assumes S deposition is currently the only acidifying stressor. Given that some NO_3^- leaching continues at the majority of sites, this can be considered a “best-case” scenario. In this plot, the most severely acidified group all receive S deposition at over half of the rate of divalent base-cation leaching, while most of the sites where divalent base cation leaching is less than three times the S deposition rate fall into either the “Strongly acidified – weak recovery” or “Moderately acidified” groups.

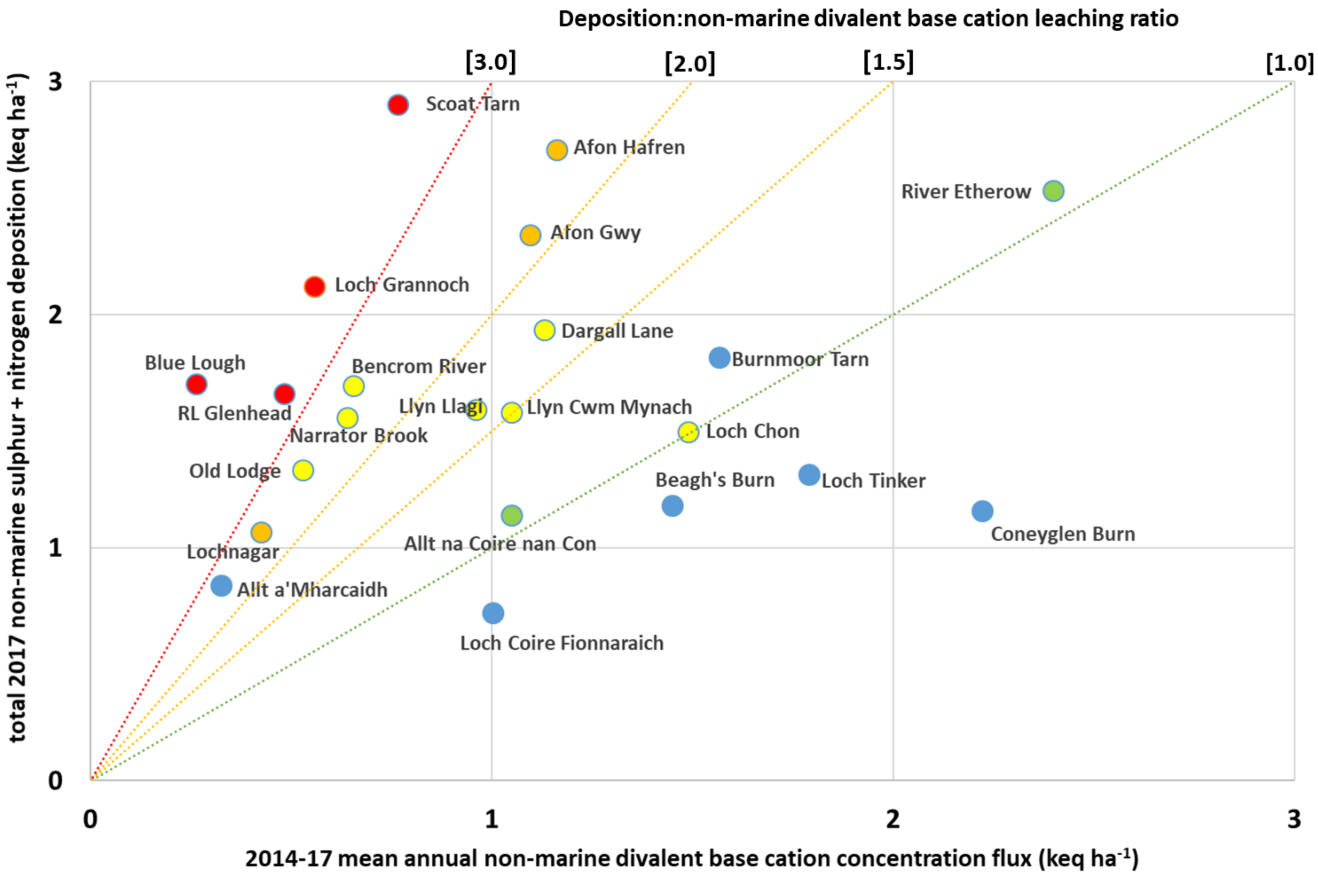


Figure 6.7 UWMN sites plotted as a function of recent (2014-19) non-marine divalent base cation (i.e. calcium + magenesium) concentration (μeq L^{-1}) and recent (2014-2017) CBED estimated deposition of acidity from sulphur and nitrogen (keq ha^{-1} yr^{-1}), assuming all deposited nitrogen is contributes to the acid load. Sites are coloured according to the dynamic $ANC_{crit-ORG}$ classification set out in Section 6.2.2.: BLUE = Class A; GREEN = Class B; YELLOW = Class C; ORANGE = Class D; and, RED = Class E. Diagonal lines are fitted largely by eye in order to best discriminate between the five site groupings, but precise positioning has been adjusted to conform with integer-based deposition:cation flux ratios.

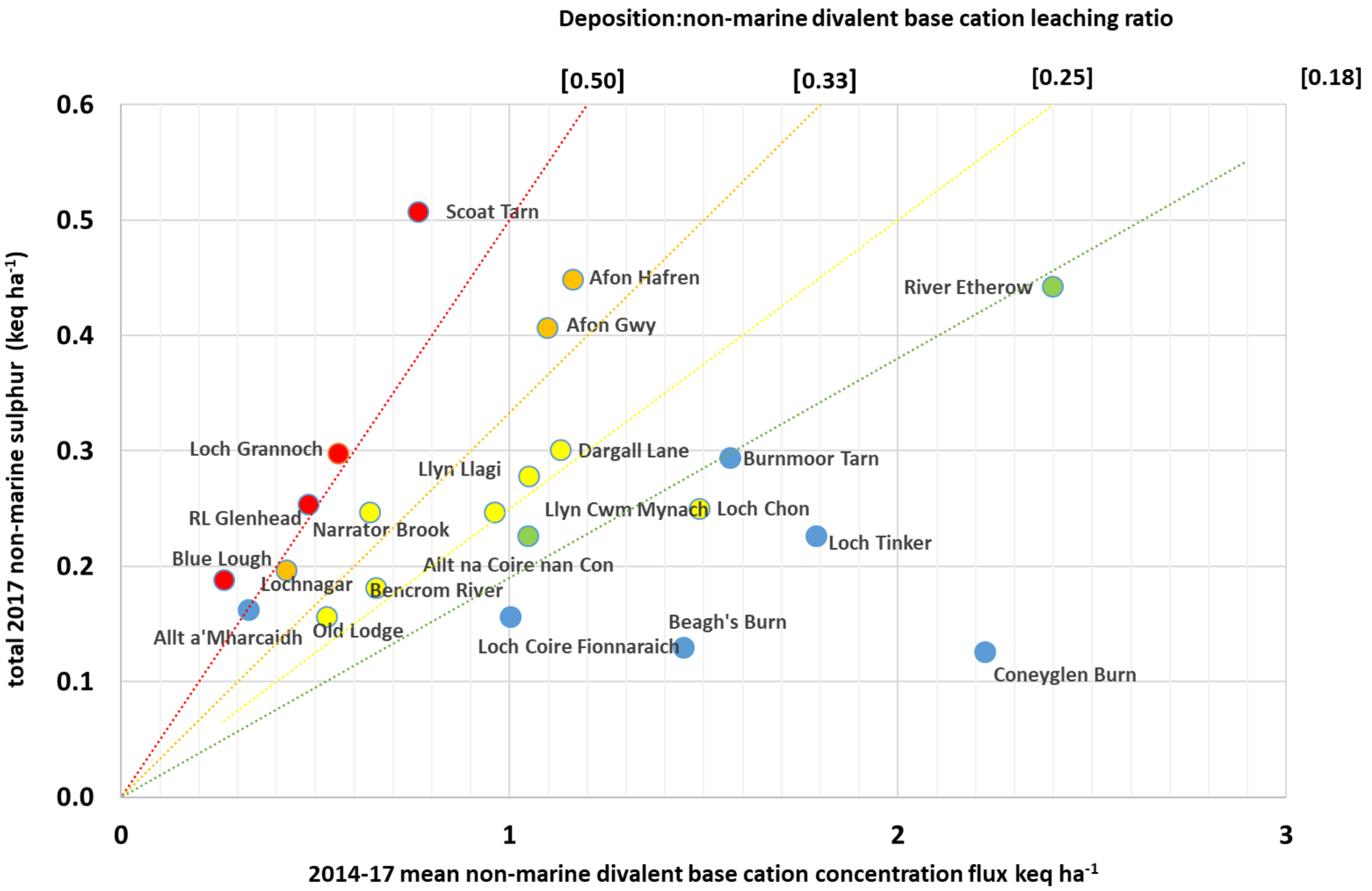


Figure 6.8 UWMN sites plotted as a function of recent (2014-19) non-marine divalent base cation (i.e. calcium + magenesium) concentration (μeq L^{-1}) and recent (2014-2017) CBED estimated deposition of acidity from sulphur only. Sites are coloured according to the dynamic $ANC_{crit\text{-}ORG}$ classification set out in Section 6.2.2.: BLUE = Class A; GREEN = Class B; YELLOW = Class C; ORANGE = Class D; and, RED = Class E. Diagonal lines are fitted largely by eye in order to best discriminate between the five site groupings, but precise positioning has been adjusted to conform with unit fraction based deposition:cation flux ratios.

The two plots (Figures 6.7 and 6.8) therefore help to make the point that, despite major reductions over the past three decades, the atmospheric deposition of acidity to the geologically sensitive Scoat Tarn, Loch Grannoch and the Round Loch of Glenhead (at least) appears to continue to be too high to bring about the improvement in water quality necessary to facilitate the re-establishment of more acid-sensitive upland freshwater taxa. The same may also be true for some sites within the "Mildly acidified recovering" and "Moderately acidified – strong recovery" groupings. For reasons discussed earlier, soil base cation via weathering status in the Blue Lough catchment may be too weak for further reductions in deposition to raise ANC as high as the ANC_{crit} or $ANC_{crit\text{-}ORG}$ levels. For most sites within these intermediate recovery groupings, significant reductions in N deposition are likely to be necessary for further significant chemical recovery to occur.

6.3 Biological change in the context of progress toward chemical recovery targets

In this report, resource constraints limited our assessment of biological change to epilithic diatom and aquatic macroinvertebrate populations only. The analyses presented in Chapters 4 and 5 demonstrate that these biological groups have undergone substantial changes in the majority of UWMN sites. For example, the epilithic diatom and macroinvertebrate communities experienced over 50 % species turnover at 14 and 12 sites respectively (out of 23). Monotonic change over time in the species assemblages has been the dominant mode of interannual variation in 16 and 12 sites respectively, and of potential explanatory variables, change in water pH has most frequently been linked with biological shifts.

Comparisons of chemical trend classifications provided in Sections 6.2.1 – 6.2.4 and biological trend statistics presented in Chapters 4 and 5 provide further insights into links between chemical and biological recovery. Table 6.2 summarises results for the linear (time) trend analysis (based on Redundancy Analysis (RDA)) and trends in the acidity metrics (DAM (diatoms), LAMM and AWICsp (macroinvertebrates) with sites ordered primarily according to their ranking in our dynamic $ANC_{crit\text{-}ORG}$ classification (Section 6.2.2). Within each $ANC_{crit\text{-}ORG}$ class, sites are further ordered with respect to the rate of change in ANC, with the weaker trends given a higher rank. The table shows that biological changes indicative of responses to changes in acidity are concentrated almost exclusively on chemically recovering sites, but also emphasises that wider biological change (i.e. significant time trends based on RDA) is not confined to sites experiencing reductions in acidity only.

Of the top five sites in the "chemically benign" grouping (Section 6.2.2), i.e. the five Group A surface waters to have undergone ANC trends of less than 0.76 $\mu eq\ L^{-1}\ yr^{-1}$, the only significant increase in a biological indicator score is for the diatom (DAM) score at Loch Tinker. The increase in the DAM metric is largely confined to the early years of monitoring, during which ANC increased, albeit over range considerable above the ANC_{crit} and $ANC_{crit\text{-}ORG}$ thresholds. In contrast, the majority of sites in Groups B-E show significant upward trends in either or both biological metrics.

Table 6.2 A comparison of the $ANC_{crit\text{-}ORG}$ classification of chemical recovery at UWMN sites (see Section 6.2.2) and summarised trends in biological acidity indicator scores and trends in the wider biological assemblages as presented in Chapters 4 & 5. Sites are ordered primarily according to the chemical classification. Secondary sorting is by the rate of change in ANC. Arrows mark the direction of statistically significant trends in acidity metrics (e.g. blue up arrow = a reduction in acidity). Curved arrows represent sites with significant but clearly non-linear trends in indicator scores, with evidence for levelling off in more recent years. Diagonal double-headed arrows denote statistically significant linear trends over time (determined by Redundancy Analysis) of undefined direction.

SITE	$ANC_{crit\text{-}ORG}$ class	DAM trend?	LAMM/AWI Csp trend?	diatom sig linear trend?	invertebrate sig linear trend	median ANC(2015-19)	median ANC_{ORG} (2015-19)	ANC trend (µeq/L/yr)
Loch Coire nan Arr	A			⤢		42.7	36.9	0.24
Loch Tinker	A	⤴		⤢	⤢	77.8	60.4	0.36
Allt a'Mharcaidh	A			⤢		76.5	68.7	0.52
Loch Coire Fionnaraich	A					28.2	18.34	0.62
Beagh's Burn	A			⤢	⤢	134.3	86.7	0.75
Burnmoor Tarn	A	⤴	⤴			72.3	62.8	0.77
Coneyglen Burn	A	↘	↘		⤢	211.8	178.8	1.28
River Etherow	B	↗	↗	⤢	⤢	108.1	75.46	0.81
Allt na Coire nan Con	B	↘	⤴			51.9	32.5	0.94
Narrator Brook	C			⤢	⤢	38.1	32.7	0.54
Llyn Llagi	C	⤴	↗	⤢	⤢	34.8	21.5	0.70
Llyn Cwm Mynach	C		↗	⤢	⤢	47.0	35.1	0.86
Dargall Lane Burn	C	↗	⤴	⤢		24.8	18.0	1.02
Loch Chon	C	↗	↗	⤢	⤢	61.2	43.9	1.39
Bencrom River	C	↗		⤢		47.9	36.3	1.43
Old Lodge	C	↗	↗	⤢	⤢	75.5	43.9	3.94
Lochnagar	D	↗		⤢		16.1	9.6	0.61
Afon Gwy	D	↗	↗	⤢	⤢	25.0	16.2	1.07
Afon Hafren	D	↗	↗	⤢		25.0	14.5	1.52
Scoat Tarn	E			⤢	⤢	-0.2	-4.62	0.48
Blue Lough	E	↗	⤴	⤢		-2.1	-17.1	0.70
Loch Grannoch	E	⤴	⤴			26.9	-4.38	2.36
Round Loch of Glenhead	E	↗	⤴	⤢	⤢	17.3	1.32	3.06

Coneyglen Burn is the only site where changes in both epilithic diatom and macroinvertebrate communities are indicative of slightly more acidic conditions. This is surprising given that Coneyglen Burn has always been a chemically well buffered site and the evidence that the acidity of acid extremes at the site has declined slightly over time (Section 3.3.2.7). It is possible, however, that median pH levels have fallen very slightly (Section 3.3.2.7; Figure 3.18) as a consequence of the stream's large long-term increase in organic acidity (i.e. DOC) despite acidity variables showing no significant long-term monotonic trends (Appendix: Section 22.2). Change in the epilithic diatom flora of Allt na Coire nan Con, another low deposition site in the northwest, is also indicative of a slight reduction in pH. Again there are hints of subtle reductions in median pH levels (Section 3.3.2.7; Figure 3.18) that could be linked to the site's large DOC increase, despite the lack of evidence for this from the Seasonal Kendall analyses (Appendix: Section 3.2).

The LAMM/AWICsp (macroinvertebrate) scores increased significantly in 13 of the 16 sites in the $ANC_{crit\text{-}ORG}$ classes B-E, indicating that improvements in the aquatic fauna are occurring almost wherever water acidity has been declining, regardless of the ambient ANC level. In around half of these cases, the scores have flattened out in recent years, but such behaviours occur in both the most acidified (Group E) sites and much less impacted sites including Burnmoor Tarn and Allt na Coire nan Con. These indications of non-linear recovery in the macroinvertebrate community may partly reflect a process of occasional, as opposed to continual, colonisation and establishment of new taxa, possibly punctuated by setbacks resulting, for example, from the influence of acid episodes. It should not, therefore, be assumed from the apparent levelling out of the scores at some sites that further biological responses to continuing improvements in water chemistry are not possible.

The clearest linear trends in the DAM (diatom) index have occurred at the sites in Groups C-E, i.e. the more acidic chemically recovering sites, and 11 out of 14 sites in this grouping show significant increases in the DAM score overall. Llyn Llagi and Loch Grannoch are the only sites across groups C-E where change in the DAM scores appears to have levelled off in recent years. In the case of Llyn Llagi this is consistent with a generally levelling off of water acidity as acid deposition reaches a very low level and NO_3^- leaching is negligible. Water pH in Loch Grannoch has also stabilised over the past decade, possibly in part due to very large increases in organic acidity offsetting benefits resulting from reductions in mineral acidity (e.g. sulphuric acid).

Within Groups C-E, only two sites show no improvement in both the DAM or LAMM/AWICsp scores, Narrator Brook and Scoat Tarn. These sites have experienced the weakest increases in ANC of any site outside the low deposition sites in Group A. Scoat Tarn has undergone a very large reduction in acid deposition, but this has been largely balanced by a decline in base cations. While labile aluminium concentrations have fallen substantially, they have only recently reached levels conducive to the recovery of more acid-sensitive species in recent years, while pH levels only began to climb significantly above pH 5 over the last decade (Appendix: Section 10.2). Narrator Brook on the other hand, is a much less acid-impacted site, but has also experienced a much weaker reduction in acid deposition, as evidenced by very low rates of change in non-marine SO_4^{2-} concentration (Appendix: Section 14.2).

Finally, biological trend analysis presented in Chapters 4 and 5, summarised in Table 6.2, also demonstrates that significant changes in epilithic diatom and macroinvertebrate communities are not confined to sites recovering from acidification only. Regardless of geographical situation and acid-sensitivity, UWMN sites have experienced significant reductions in acid deposition that have led to other significant hydrochemical changes, most particularly with respect to increases in DOC concentrations (Monteith et al., 2007). Change in the latter will have led to reductions in the penetration of photosynthetically active radiation and an increase in the flux of organically bound nutrients, both of which are likely to have had consequences for ecosystem structure and function. At some sites, a tendency for an increase in precipitation during the summer months may have also exacerbated DOC concentrations (Wit et al., 2021). Preliminary analysis of UWMN water temperature data, not considered in this report, provides little evidence that UWMN sites have undergone significant warming over the monitoring period. In the longer term, however, warming in response to global climate change would appear inevitable, and will bring with it the potential for further biological turnover that UWMN will be uniquely placed to detect and quantify. Further investigations will be necessary to determine the prevalence of these effects.

In summary, therefore, the UWMN data demonstrate that deposition-induced reductions in the acidity of the UK's acid-sensitive waters are having a pronounced influence on their aquatic ecosystems, including, but not restricted to, an increase in the representation of more acid-sensitive species. Acidity-related responses by the epilithic diatom and macroinvertebrate communities are widespread. They are not restricted to waters with an ANC of 20 µeq L^{-1} or less, but rather are occurring wherever ANC has been increasing strongly. While there is an indication of a "levelling off" of biological responses in recent years at some sites, this is not always consistent with patterns of chemical change, and in some cases, recent plateauing may be more indicative of stepped improvement rather than suggestive of achievement of complete recovery. Importantly, analysis of diatom remains in UWMN sediment traps collected up to around ten years ago indicated that although recent diatom assemblages were indicative of less acidic conditions, they remained very different from pre-industrial assemblages (Battarbee et al., 2014b). This might in part result from a chronic exhaustion of buffering that is preventing water chemistry from returning to a pre-acidification condition, but might also reflect other changes that have occurred within these waters, and particularly the increased availability of nitrogen in the form of nitrate. A repeat analysis of the most recent sediment trap data will be necessary to test if there has been any more recent reduction in those recovery gaps.

7 Conclusions

In this latest in a series of occasional interpretive reports documenting long-term trends in the chemistry and biota of UK UWMN sites, we have provided the clearest evidence yet that reductions in the atmospheric emission of S, HCl and N are bringing about progressive chemical and ecological improvements in the UK's acidified upland waters – one of the primary environmental goals of internationally agreed acid emissions controls. CBED modelling suggests that reductions in the deposition of S and HCl have contributed most to the overall reduction in acid deposition loads. Deposition of oxidised N species has also declined, but the deposition of reduced N has been increasing slightly in recent years in some regions, resulting in relatively flat trends in total N deposition to the majority of sites.

In the majority of the waters monitored over the past three decades, ANC has now reached (on average), or is exceeding, the UK's official ANC target (or ANC_{crit}) for recovering acidified waters of 20 µeq L^{-1}. Chemical and biological recovery has been occurring at almost all acid-sensitive UWMN sites where levels of acid deposition have fallen significantly, regardless of precisely where they lie on an ANC trajectory relative to the ANC_{crit} value. While there is some indication of biological recovery slowing down in recent years, this seems more to reflect a slowing down of chemical recovery as acid deposition falls to a relatively low level, rather than any particular chemical threshold being reached.

Similar improvements are being reported for long-term monitoring sites in acid-sensitive regions over much of industrialised North America and north-western Europe (as for example represented by the ICP Waters network). They are a testament to the international cooperation developed to address one of the largest transboundary pollution issues ever to arise, and serve as a demonstration of what can be achieved where there is a common international resolve to mitigate an environmental problem.

The greater pollutant interception rates of forest canopies result in sharper reductions in acid deposition to forested catchments (relative to moorland catchments) as deposition declines regionally. Consequently measures of acidity have also fallen more quickly in the waters of the forested catchments, while biological communities have also changed more rapidly, although in general the waters of the forested catchments remain more acidic than their moorland neighbours. All of the UWMN afforested catchments are undergoing substantial management-driven changes, including a gradual replacement of coniferous monocultures with mixed coniferous/deciduous stands. The UWMN data collected to date will provide robust baselines for assessing how forested watersheds respond to such practices in the coming years.

Despite the lack of evidence for clear reductions in N deposition, concentrations of NO_3^- (a secondary acidifying anion) have been declining in several of the more acidified UWMN sites. This is indicative of an increase in the soil-biological processing of N as the acidity of soils responds to the overall reduction in acid deposition - driven primarily by reductions in S and HCl deposition. To date the UWMN chemical record provides no evidence that a hypothetical long-term accumulation of atmospherically deposited N is bringing about any increase in the leaching of NO_3^-, i.e. as a consequence of soil "N saturation".

Our inclusion, for the first time, of a DOC-based correction to the critical limit ($ANC_{crit\text{-}ORG}$), to allow for the influence of organic acids on water acidity, provides a slightly different perspective on recovery prospects, and emphasises the potentially confounding influence of DOC increases on water acidity. The UWMN dataset has been pivotal in the development of scientific understanding of widely observed increases in DOC concentrations in upland waters across North America and northern Europe. The DOC trends have been attributed to the effect of declining ionic strength of soil water on the solubility of soil organic matter (Monteith et al., In press). This response appears so sensitive that, at some stream sites in the far north and west of the UK, the effect of slight reductions in ion deposition on the release of organic acidity appear to have outweighed the effect of the reduction in the deposition of acidity to largely un-acidified catchments, leading to very slight reductions in water pH within certain flow ranges.

Despite the widespread evidence for chemical improvements, the ANC of some of the most acidified sites on the network remains either below the ANC_{crit} (and/or $ANC_{crit\text{-}ORG}$) or is now averaging around these thresholds. This suggests that chemical conditions for a range of more acid-sensitive species, such as brown trout, remain unfavourable at least part of the time (for example during more acidic, high flow conditions). In recent years, these sites have been receiving the highest levels of acid deposition relative to their acidity buffering potential (as determined by the base cation flux). Although S deposition has fallen to low levels across the network, further small reductions in deposition could still prove important in the further chemical recovery of these sites toward more ecologically benign conditions.

The greatest potential to further reduce acid deposition to many of the UWMN catchments now lies in the ability to control N deposition more tightly, but precisely how effective such actions would be in influencing NO_3^- leaching remains unclear. More widely, pre-acidification ANC levels predicted by the MAGIC model for most chemically recovering UWMN sites remain substantially higher than recently measured levels. Further monitoring is therefore required to determine whether water chemistry continues to improve as weathering rates increasingly exceed deposition fluxes and facilitate a gradual replenishment of soil base saturation.

Unsurprisingly, the monitored biological groups of several of the UWMN lakes appear to remain in a more acidified state than prior to acidification. A range of potential chemical, physical and biological constraints may be limiting the rate and extent of further biological improvements, but it is also possible that some recent environmental changes, not directly linked to water acidity, are causing trajectories of biological "recovery" to deviate toward novel ecological states. For example, some waters may have developed into phosphorus limited systems that have no pre-industrial precedent as a consequence of the rise in availability of reactive nitrogen, in the form of NO_3^-, relative to pre-industrial times. It is encouraging, therefore, that NO_3^- concentrations are falling in some of the most impacted systems, bucking the expectation of increased NO_3^- leaching as a consequence of progressive soil N saturation. There is a clear need, however, to continue to monitor the development of these communities to determine the degree to which the restoration of freshwater ecological structure and biogeochemical and ecological functioning is possible. Repeat assessments of trends in the UWMN sediment trap diatom data in the context of pre-industrial diatom community structure (not provided in this report) should be very informative in this respect.

More generally, fluctuations and directional change in the biogeochemistry of UWMN sites, including concentrations and fluxes of dissolved organic matter, are becoming increasingly dependent on temporal patterns in runoff and sea salt deposition. There has been little net warming of UWMN waters over the 1988-2019 monitoring period, but UKCP18 climate change projections suggest that annual mean air temperatures across much of the UK uplands may warm by an order of 1.5 to over 4.0 °C by 2080 relative to 1980. Warming is expected to accelerate the microbial decomposition of soil organic matter and bring about further increases in DOC, particularly in the waters of the more peat dominated UWMN catchments. The uplands make a substantial contribution to the UK's overall flux of organic carbon from the land to the sea, and development of a clearer understanding of the environmental factors influence its spatial and temporal variability is important in the development of the UK's Net Zero strategy.

Warming, "browning" (by increased DOC) and any directional changes in storminess, may also change the timing and intensity of periods of lake thermal stratification, that in turn determine the extent to which lake water remains mixed and oxygenated, and influences redox processes that affect the mobility and biological availability of sediment-borne nutrients. Although not assessed in this report, the UWMN thermal profile measurements are the UK's only detailed source of long-term temperature data for upland UK lakes, and will prove increasingly valuable in determining how these systems are responding to global warming over the coming decades.

Increased dissolved organic matter concentrations will have consequences not only for the aquatic productivity of upland waters, through light limitation of photosynthesis, but also for the quality of upland drinking water resources. A large proportion of the UK's drinking water is derived from upland catchments, and water companies have been facing increasing treatment costs due to increases in DOC that, up to now, been caused primarily by deposition-driven reductions in soil water ionic strength. Highly detailed long-term upland hydrochemical records such as those produced by UWMN are already helping the UK water industry to develop a clearer understanding of the key drivers of DOC change and what the future impacts of climate change may be for these critical environmental assets.

The UK's upland waters are clearly important a) from a freshwater biodiversity perspective, since these environments currently provide important habitats, and potentially climate change refuges, for a wide range of species with a preference for cool, soft waters, b) as processors and conduits for dissolved organic carbon and nutrients from land to the oceans, and c) with respect to the availability, quality, sustainability and cost of the UK's drinking water. The first 30 years of UWMN data not only provide a record of how these systems, many of them heavily impacted by acidification, have been responding to reductions in acidity as a consequence of air quality policy measures, but also quantify wider changes in water chemistry that are likely to be having both physical (underwater light) and chemical-biological (organic acidity and organic nutrient) effects. In the longer term, further changes in N leaching, changes in climate (including warming, hydrological shifts and changes in the frequency and intensity of sea salt deposition events), and the future management of forested catchments, are all likely to influence the future physical and chemical state of these systems. The records compiled to date therefore provide unique and highly robust baselines, against which the impact of future environmental change on these vitally important habitats and resources can continue to be assessed. Such information is vital for the continued development of air and water policies, land and water management practices and the further development of scientific understanding of upland waters and their catchments.

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Appendix: Site-specific summaries of UWMN catchment characteristics and water chemical and biological trends

1a. Loch Coire nan Arr **(monitoring ceased - 2008)**

1a.1: site description

Loch Coire nan Arr was originally the most northerly of all UK Acid Waters Monitoring Network (AWMN) sites. As atmospheric pollution loads at the site were known to be low, the site was considered a “control” against which effects of reductions in acid deposition on acidified sites to the south could be assessed. Palaeoecological studies later suggested that the loch had undergone very slight acidification during the 20th century (Patrick et al., 1995). The loch supplied fresh water to a fish farm (based at Kishorn, 1.6 km to the south). In 1991, a temporary dam was installed on the loch outflow as a means of conserving the water supply to the fish farm and this was later replaced with a permanent structure with sluice that raised the average water level, while the water level was drawn down substantially at times of low rainfall. Fluctuations in water levels and the associated increase in turbidity may both have contributed to the loss of the once abundant emergent aquatic macrophyte stands at the site and an apparent worsening of water quality in the later years of monitoring. As a consequence of these impacts, AWMN monitoring was terminated in 2008. Parallel monitoring was established at the nearby Loch Coire Fionnaraich (Site 1b) in 2001. Despite having not been monitored for the past 15 years, the historical water chemistry and biological data collected at this low deposition but acidification-sensitive site provide useful sources of reference for the recovering sites on the network.

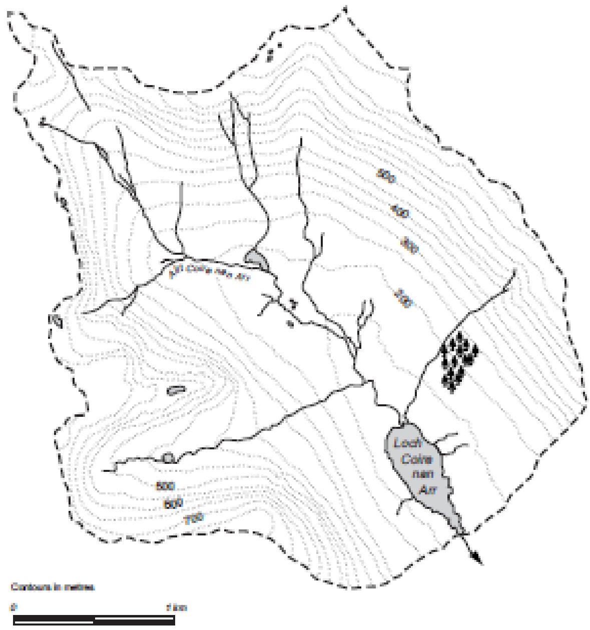


Figure 1a.1 Mapped view of the Loch Coire nan Arr catchment

Table 1a.1 Loch Coire nan Arr site characteristics

Grid Reference	NG 808422	
Lake altitude	125 m	
Maximum altitude	750 m	
Maximum depth	12.0 m	
Mean depth	4.8 m	
Volume	5.6×10^5 m^3	
Lake area	11.6 ha	
Catchment area	909 ha	
Catchment area (excl.lake)	897 ha	
Catchment:Lake ratio	77.3	
Catchment geology	Torridonian sandstone	
Catchment soils	Peat	
Catchment vegetation	Moorland – 99% Conifers <1%	
Mean annual runoff (precipitation – evaporation)	2838 mm	
	CBED estimated deposition (kg S or N ha^{-1} yr^{-1})	
	1990	**2017**
Total oxidised sulphur	20.7	14.6
Non-marine oxidised sulphur	9.9	2.5
Oxidised nitrogen	9.3	2.9
Reduced nitrogen	9.4	5.0

Table 1a.2 water chemistry summary statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	42.7		54.2		27.1		-0.19	*
xSO_4^{2-}	µeq l^{-1}	14.9		22.5		-15.0		-0.14	
Cl^-	µeq l^{-1}	252.5		665.8		124.1		-0.29	
NO^{3-}	µeq l^{-1}	2.1		8.0		2.1		0.00	
pH	pH	6.5		6.9		5.8		0.00	
Alk	µeq l^{-1}	32.0		60.0		4.0		0.00	
Cond	µS cm^{-1}	38.0		85.0		21.0		0.00	
Na^+	µeq l^{-1}	224.0		495.9		130.5		-0.26	
Ca^{2+}	µeq l^{-1}	44.4		69.9		19.0		0.00	
Mg^{2+}	µeq l^{-1}	58.0		151.4		25.5		0.00	
K^+	µeq l^{-1}	8.4		14.3		2.6		-0.02	
Lab Al	µg l^{-1}	2.0		7.0		2.0		0.00	
DOC	mg l^{-1}	1.7		3.3		0.1		0.04	*
ANC-CB	µeq l^{-1}	42.7		71.3		-2.6		0.24	

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance). Note trend slopes are for 1989-2007 only.

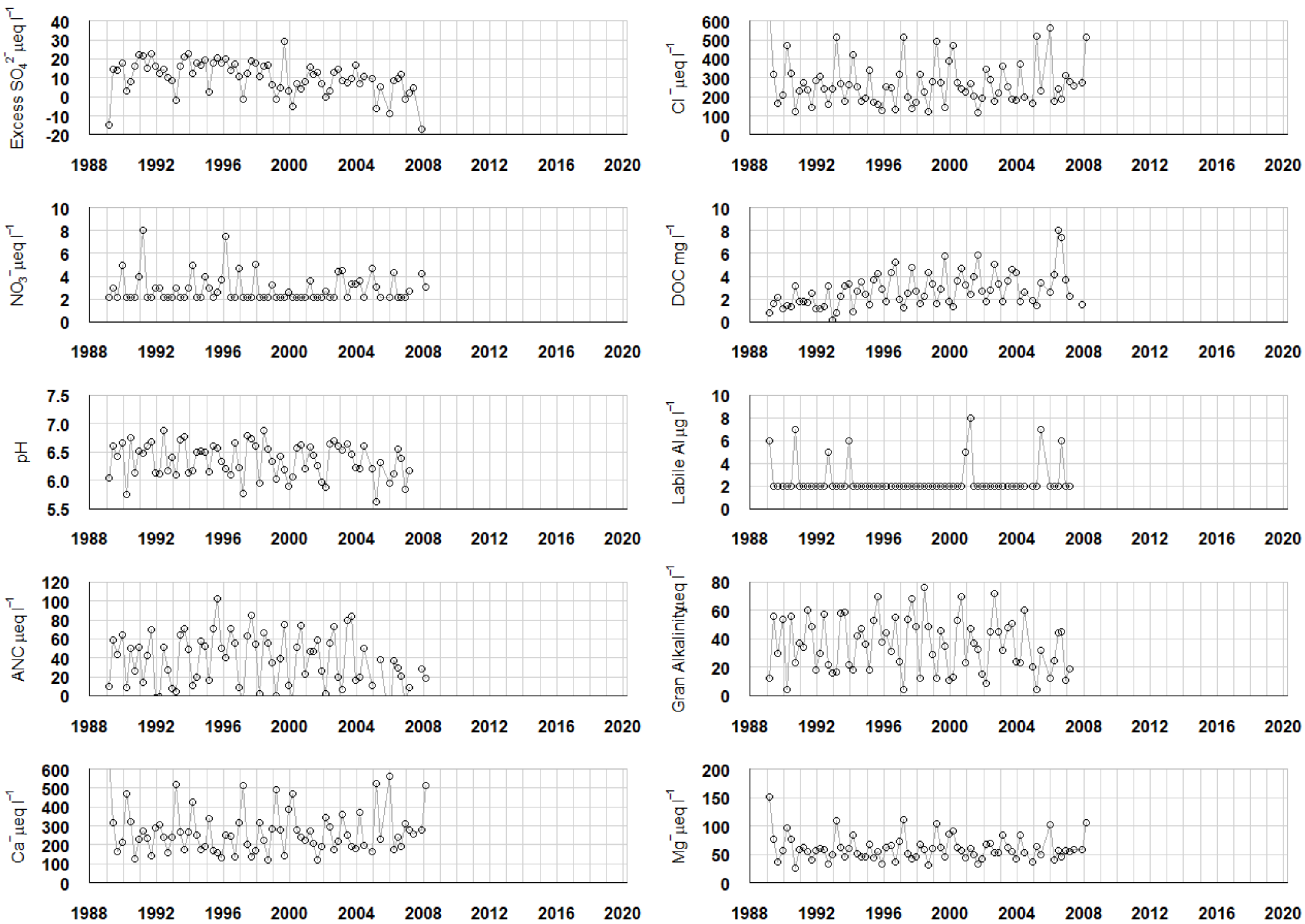


Figure 1a.2 Loch Coire nan Arr water chemistry time series for key determinands

1a.2 Loch Coire nan Arr: water chemistry trends

At the onset of monitoring, the water chemistry of Loch Coire nan Arr reflected both the relatively low levels of anthropogenic sulphur and nitrogen deposition, and the low level of buffering provided by the catchment's Torridonian sandstone geology. Thus non-marine sulphate concentration was the lowest on the network, nitrate concentrations were generally below the level of detection and divalent base cation (calcium and magnesium) concentrations were also relatively low. Sea salt-derived inputs of chloride and sodium particularly dominated the ionic strength of the loch water. Acid Neutralising Capacity (ANC) was usually positive, although regularly fell below 20 µeq L^{-1} after stormy periods and the associated high inputs of sea salt. In contrast to most sites further south, water chemistry remained largely unchanged up to the cessation of monitoring in 2007, but non-marine sulphate concentration declined slightly, reflecting a gradual reduction in sulphur deposition that, in turn, was sufficient to drive a significant increase in DOC concentration. There is some indication that the change in water level caused by the installation of the dam exacerbated the release of nitrate over a period where inputs of sea salt were also elevated. These two factors may account for a slightly depressed pH in the last 3-4 years of monitoring, i.e. up to 2008.

1a.3 Loch Coire nan Arr: epilithic diatom community trends

The epilithic diatom community of Loch Coire nan Arr underwent a significant linear trend in species composition (RDA1, mGLM) over the relatively short monitoring period, but this is not significantly related to pH (RDA1-pH, DAM slope) or other variables (Main Report: Figure 4.3). Fluctuations in water level in the years since the installation of the dam will have had a major impact on all aspects of the biology.

From the start of monitoring until 2006, the diatom epilithon of this loch were stable (Appendix: Figure 1a.3), with the relative abundances of *Brachysira vitrea* remaining similar throughout the sampling period. Some changes in relative abundances occurred with *Achnanthes minutissima* most common in the years between 1997 and 2005. Other less common diatom species disappeared from the count data after 2004 but several new species were recorded after the mid-1990s. Because of the physical disturbances, interpretation of these latter species changes is problematic.

1a.4 Loch Coire nan Arr: macroinvertebrate community trends

Over the 20 years of monitoring, there were no significant monotonic trends in the macroinvertebrate rarefied taxon richness or in the diagnostic index LAMM for Loch Coire nan Arr. Likewise, there was no directional change in macroinvertebrate community composition. The loch supported a diverse range of mayflies, including *Siphlonurus*, *Centroptilum*, *Ameletus* and Leptophlebiidae, and stoneflies such as *Nemoura* and *Siphonoperla* (Appendix: Figure 1a.4). The diversity of caddisfly fauna decreased after 2001 from 6-9 taxa to 1-2 taxa, possibly due to the later lake water level fluctuations. Gastropod and bivalve Mollusca were also recorded prior to 2001 but were absent subsequently.

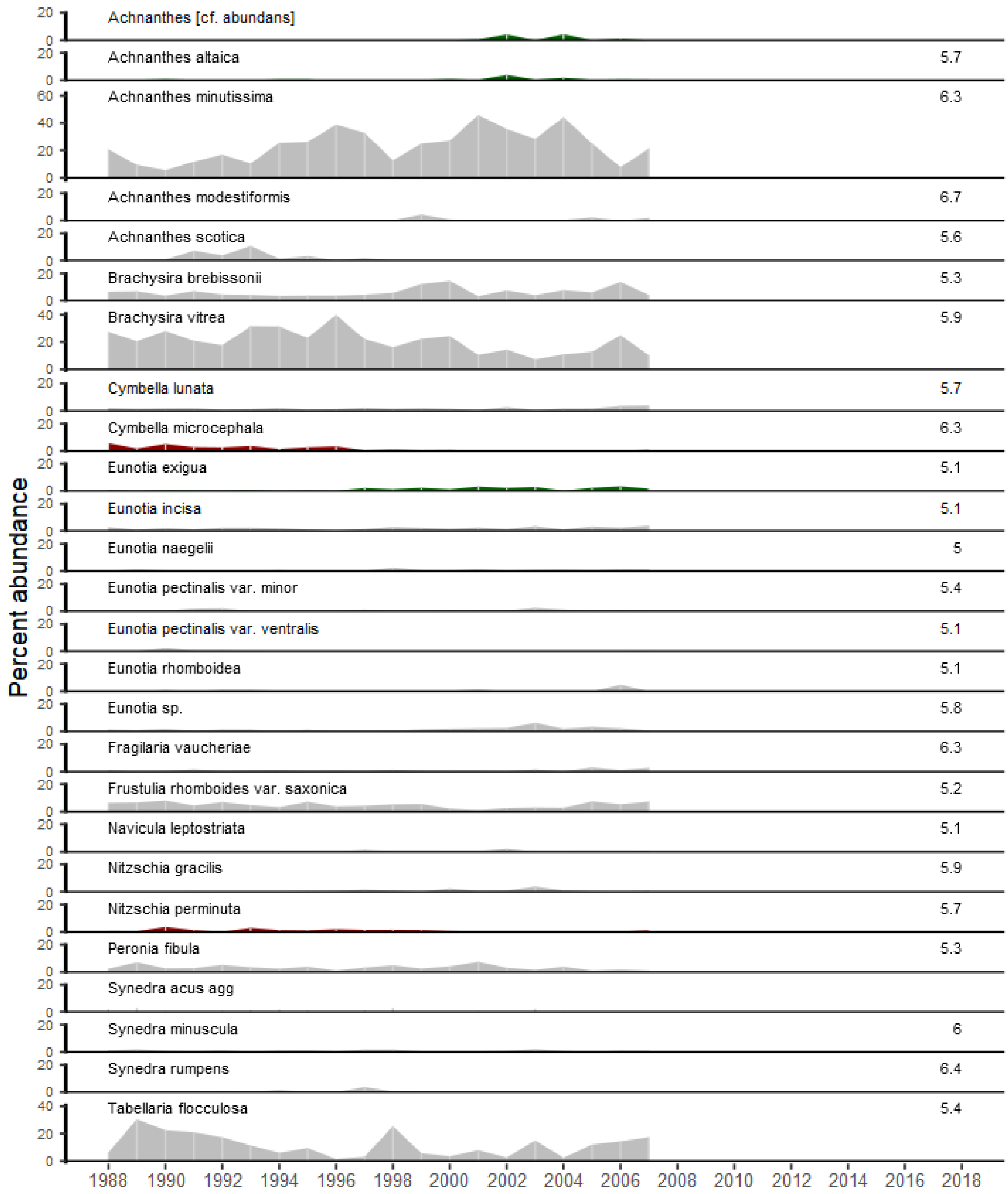


Figure 1a.3 Loch Coire nan Arr: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

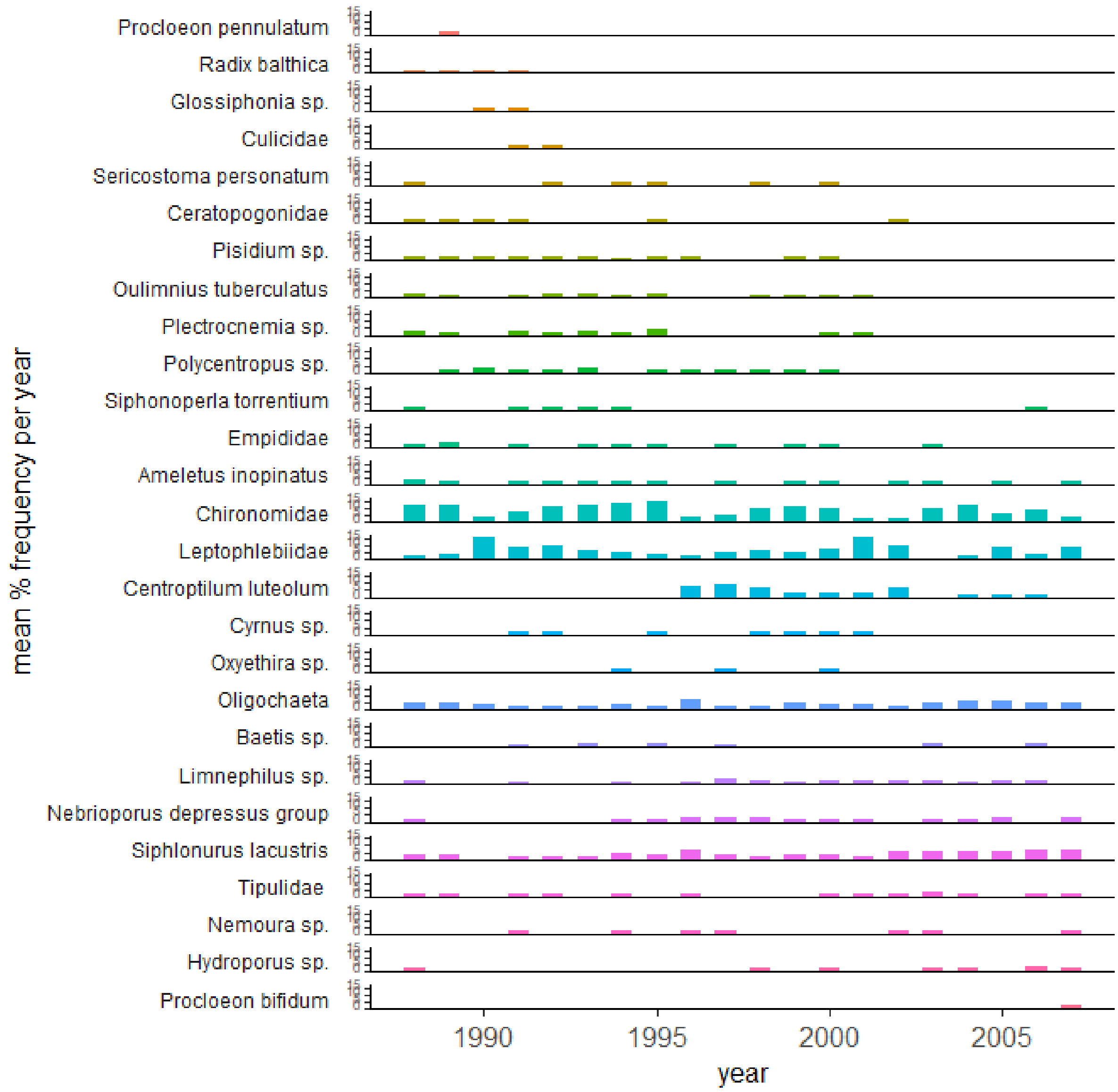
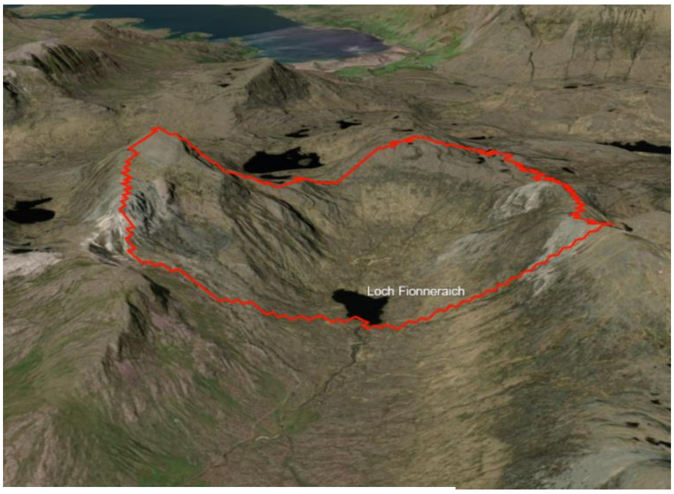


Figure 1a.4 Loch Coire nan Arr: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

1b. Loch Coire Fionnaraich

1b.1: Site description

Loch Coire Fionnaraich is located in northwest Scotland at an altitude of 236 m.a.s.l. and has been monitored since 2001, when it was identified as a suitable poorly chemically buffered low-deposition replacement for the nearby Loch Coire nan Arr. The loch is characterized by blanket peats and acid heathland vegetation including grasses and *Calluna vulgaris*, and in its steep upper catchment is dominated by exposed Torridonian sandstone outcrops.



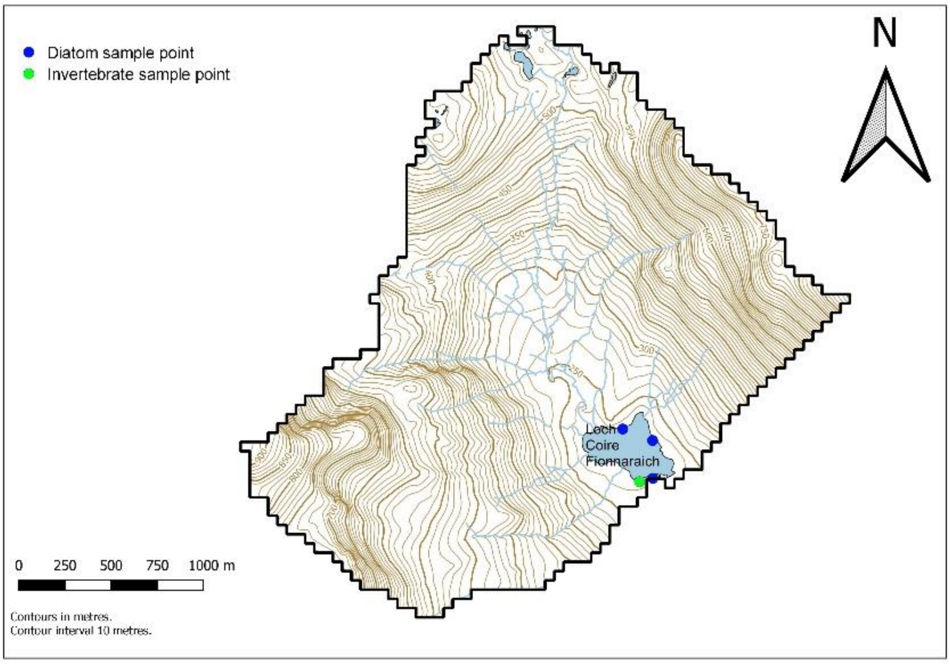


Figure 1b.1 Mapped and aerial views of the Loch Coire Fionnaraich catchment

Table 1b.1 Loch Coire Fionnaraich: site characteristics

Grid Reference	NG 945498	
Lake altitude	236 m	
Maximum altitude	962 m	
Maximum depth	14.6 m	
Mean depth	5.6 m	
Volume	52.484 x 10^4 m^3	
Lake area	9 ha	
Catchment area	560 ha	
Catchment area (excl.lake)	551 ha	
Catchment:Lake ratio	60.2	
Catchment geology	Torridonian sandstone	
Catchment soils	Peat and podzols	
Catchment vegetation	Moorland – 100%	
Mean annual runoff (precipitation – evaporation)	2838	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	20.7	14.6
Non-marine oxidised sulphur	9.9	2.5
Oxidised nitrogen	9.3	2.9
Reduced nitrogen	9.4	5.0

Table 1b.2 water chemistry summary statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}		21.7		75.6		11.0	-0.14	
xSO_4^{2-}	µeq l^{-1}		2.2		15.0		-1.1	-0.09	
Cl^-	µeq l^{-1}		173.5		376.2		85.2	-1.16	
NO^{3-}	µeq l^{-1}		2.1		7.1		2.1	0.00	
pH	pH		5.9		6.3		5.2	0.00	
Alk	µeq l^{-1}		25.1		48.2		-3.3	0.29	
Cond	µS cm^{-1}		27.0		53.8		14.5	-0.09	
Na^+	µeq l^{-1}		165.7		317.9		72.2	-0.02	
Ca^{2+}	µeq l^{-1}		26.0		33.3		12.4	0.01	
Mg^{2+}	µeq l^{-1}		35.4		72.6		21.1	-0.13	
K^+	µeq l^{-1}		6.6		9.9		2.4	0.04	
Lab Al	µg l^{-1}		2.0		3.0		2.0	0.00	
DOC	mg l^{-1}		2.9		6.0		0.9	-0.02	
ANC-CB	µeq l^{-1}		28.1		59.0		-72.4	0.62	

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance). Note trend slopes are for 2001-2019 only. No trends significant at p<0.05.

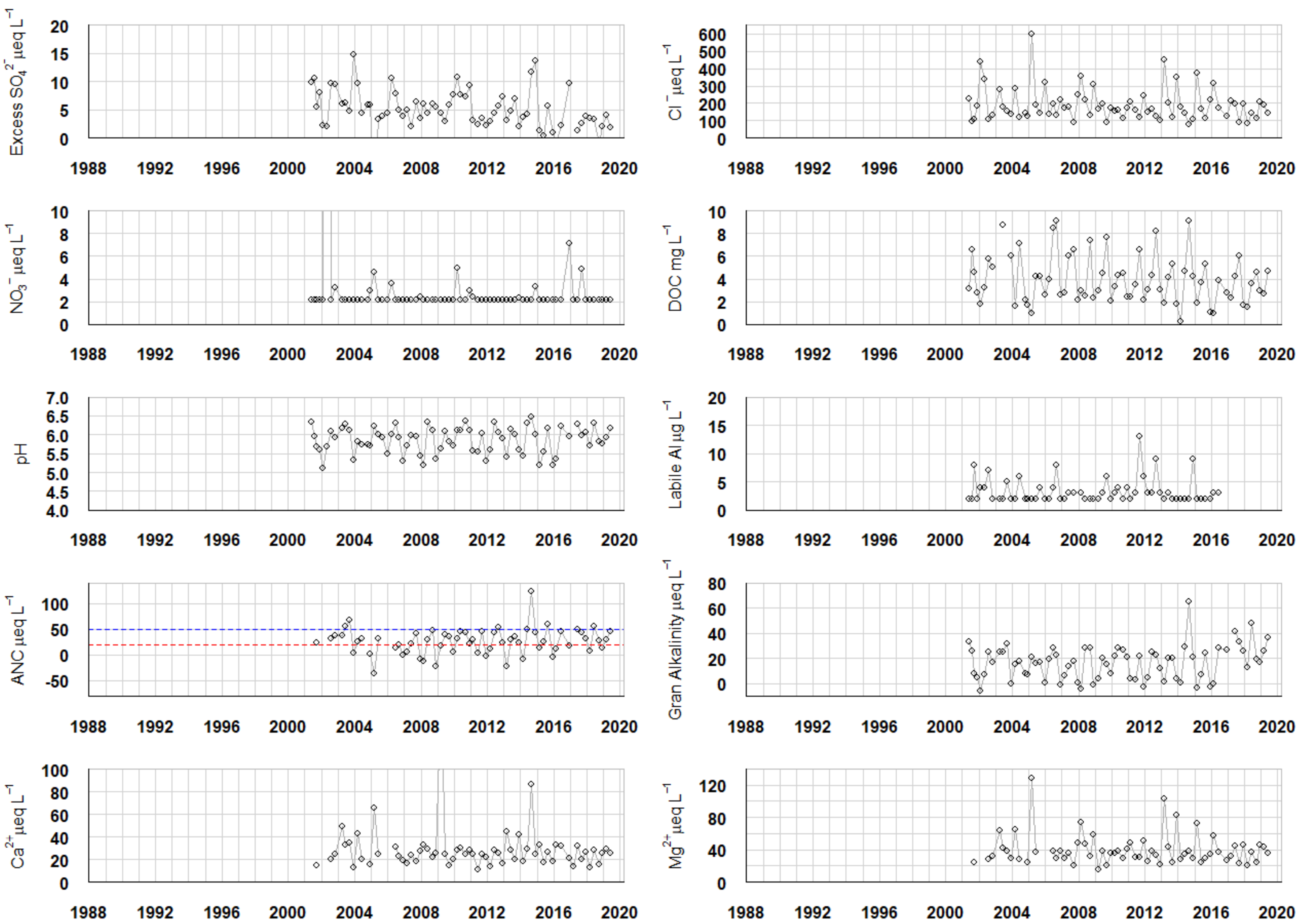


Figure 1b.2 Loch Coire Fionnaraich water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L-1; blue dotted line is set to a higher limit of 50 µeq L-1.

1b.2 Loch Coire Fionnaraich: water chemistry trends

In common with the neighbouring Loch Coire nan Arr, the water chemistry of Loch Coire Fionnaraich is again reflective of a geologically poorly buffered, low deposition site. The only notable difference in chemistry is that DOC concentrations were generally around 50% higher than in Loch Coire nan Arr over the period where monitoring occurred in parallel. Since monitoring began in 2001, non-marine sulphate concentrations have averaged around 5 μeq L^{-1} and the nitrate concentration of most samples falls below the laboratory detection limit. Despite this, there is still a hint of a reduction in non-marine sulphate over time, although this was not statistically significant. Indeed, none of the chemistry variables analysed showed significant trends over the past two decades. Chloride and sodium concentrations again demonstrate the dominance of sea salt inputs on ionic strength. Water pH of this un-acidified site oscillates between around 5.0 and 6.5, while ANC varies mostly between around 0 and 50 μeq L^{-1}, with the most acidic conditions again associated with periods of higher sea salt inputs.

1b.3 Loch Coire Fionnaraich: epilithic diatom community trends

Unsurprisingly, the acid-sensitive and oligotrophic diatoms *Brachysira vitrea* and *Tabellaria flocculosa* are common in both Loch Coire Fionnaraich and Loch Coire nan Arr. Along with these taxa, the flora is characterised by fluctuating numbers of *Achnanthes minutissima*, *Peronia fibula* and *Frustulia rhomboides* var. *saxonica* (Appendix: Figure 1b.3) . Although there is some inter-year fluctuation in the abundance of these taxa, there are no significant trends in the diatom data, nor are any of the fluctuations related to short term variability in water chemistry (Main Report: Figure 4.3).

1b.4 Loch Coire Fionnaraich: macroinvertebrate community trends

It is also not surprising, given the absence of significant change in water chemistry, that there is no indication of a temporal shift in the macroinvertebrate assemblage of Loch Coire Fionnaraich, either in terms of taxon richness or the LAMM diagnostic index. The consistent presence of moderately acid-sensitive taxa such as the freshwater snail *Radix balthica*, the mayflies *Siphlonurus lacustris* and Baetidae, and the minute freshwater clam *Pisidium*, is consistent with the absence of significant acidification stress. Assessment of the extent of directional change in assemblage composition showed that the time-constrained first RDA axis could account for 24% of the variation in the biological data. However, the bootstrap test, in which the years of samples are randomized, was unable to determine the significance of this change due to the relatively short time series. There are indications that insect diversity may be increasing but further years will be necessary to verify this.

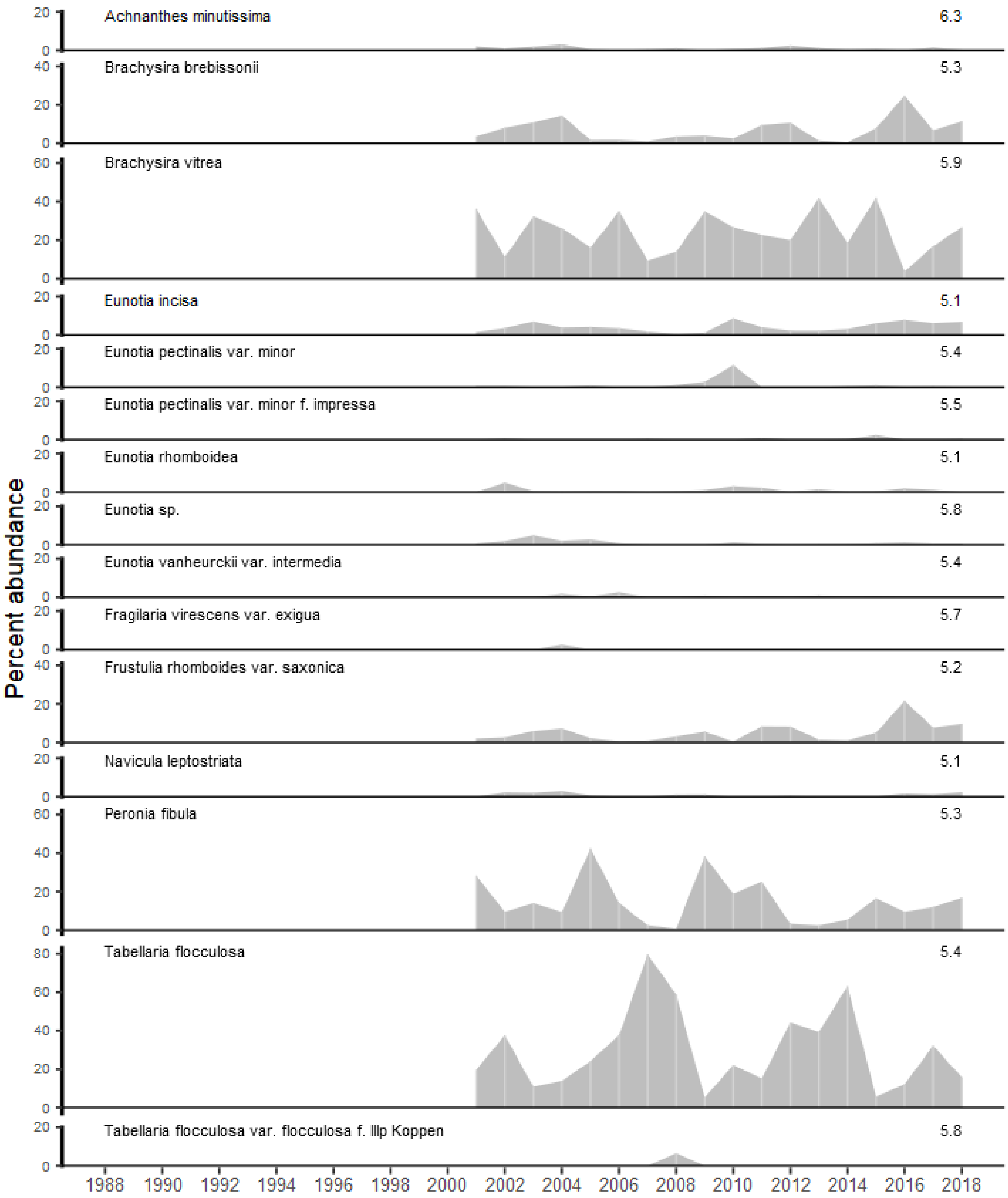


Figure 1b.3 Loch Coire Fionnaraich: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

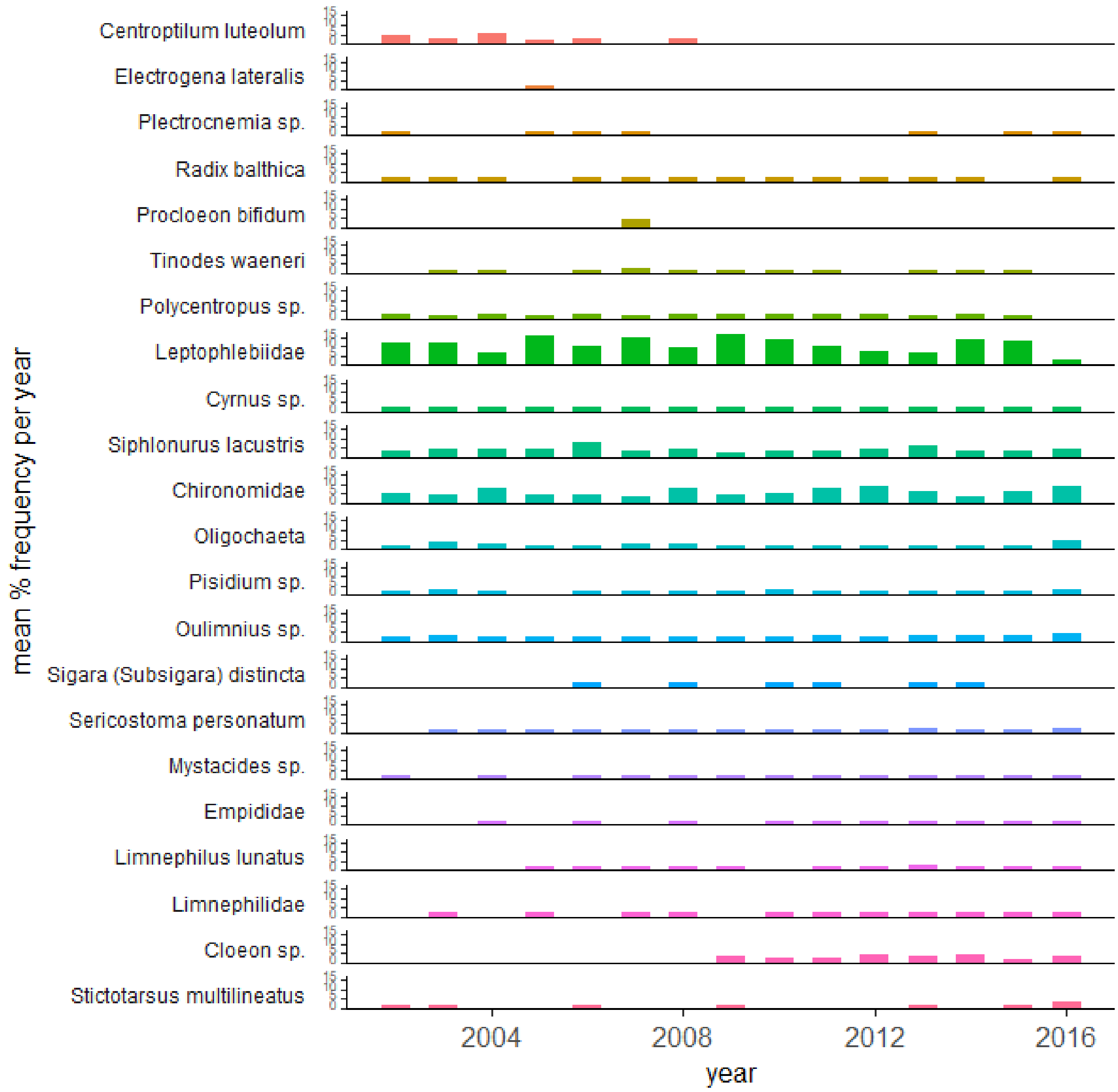
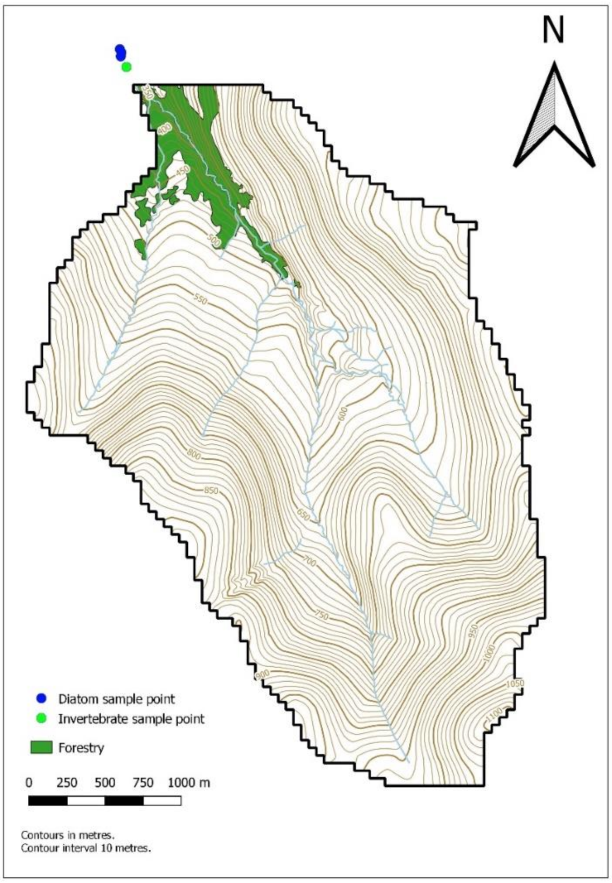


Figure 1b.4 Loch Coire Fionnaraich: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

9.1 2. Allt a'Mharcaidh

2.1 Site description

The Allt a'Mharcaidh, in the western Cairngorms of northeast Scotland, is a high altitude, well-buffered mountain stream subject to occasional acid episodes. No clear physical changes have been observed in the study catchment since the onset of monitoring in 1988. The Allt a'Mharcaidh was studied as part of the SWAP project (e.g. Ferrier & Harriman, 1990) and is a UK Environmental Change Network (ECN) site.



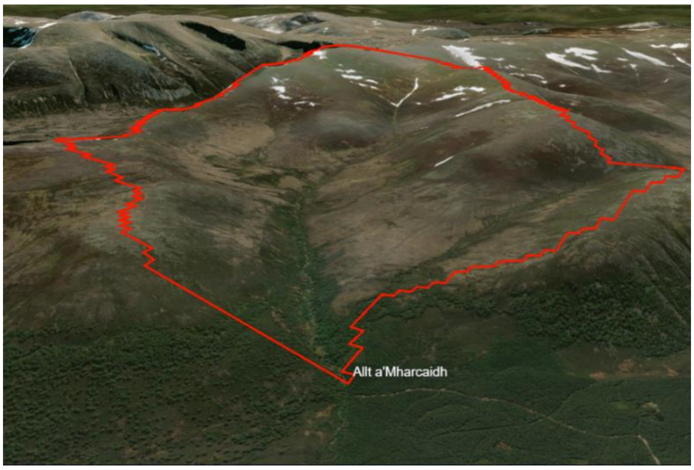


Figure 2.1 Mapped and aerial views of the Allt a'Mharcaidh

Table 2.1 Allt a'Mharcaidh site characteristics

Grid Reference	NM 881045	
Catchment area	998 ha	
Minimum catchment altitude	325 m	
Maximum catchment altitude	1111m	
Catchment geology	Granite	
Catchment soils	Alpine & peaty podsols, blanket peat	
Catchment vegetation	Moorland c. 94% Conifer woodland c. 4%	
Mean annual runoff (precipitation – evaporation)	773 mm	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	12.6	7.6
Non-marine oxidised sulphur	9.2	2.6
Oxidised nitrogen	4.7	3.9
Reduced nitrogen	6.8	5.6

Table 2.2 Allt a'Mharcaidh water chemistry summary statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	44.8	30.1	58.3	51.6	33.3	16.7	-0.54	**
xSO_4^{2-}	µeq l^{-1}	33.2	19.2	46.3	36.0	19.0	-3.8	-0.52	**
Cl^-	µeq l^{-1}	104.4	106.4	259.5	321.6	81.8	80.1	-0.24	**
NO^{3-}	µeq l^{-1}	2.1	2.1	3.0	8.1	2.1	2.1	0.00	
pH	pH^{-1}	6.5	6.5	7.1	7.1	5.1	5.0	-0.00	
Alk	µeq l^{-1}	40.0	68.0	82.0	214.0	-4.0	-8.7	0.55	**
Cond	µS cm^{-1}	23.0	25.0	38.0	47.3	17.0	18.6	0.00	
Na^+	µeq l^{-1}	134.9	137.0	213.2	223.5	91.4	104.2	-0.20	*
Ca^{2+}	µeq l^{-1}	42.7	43.4	60.4	103.8	27.9	28.5	-0.08	
Mg^{2+}	µeq l^{-1}	28.8	28.8	50.2	63.9	18.9	20.2	-0.06	**
K^+	µeq l^{-1}	6.8	7.9	14.6	27.6	2.6	3.8	0.01	
Lab Al	µg l^{-1}	2.0	6.0	29.0	30.0	2.0	2.0	0.00	
DOC	mg l^{-1}	1.7	2.3	5.8	9.2	0.1	0.3	0.04	**
ANC-CB	µeq l^{-1}	53.1	76.5	95.1	142.1	7.7	-137.5	0.52	*

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

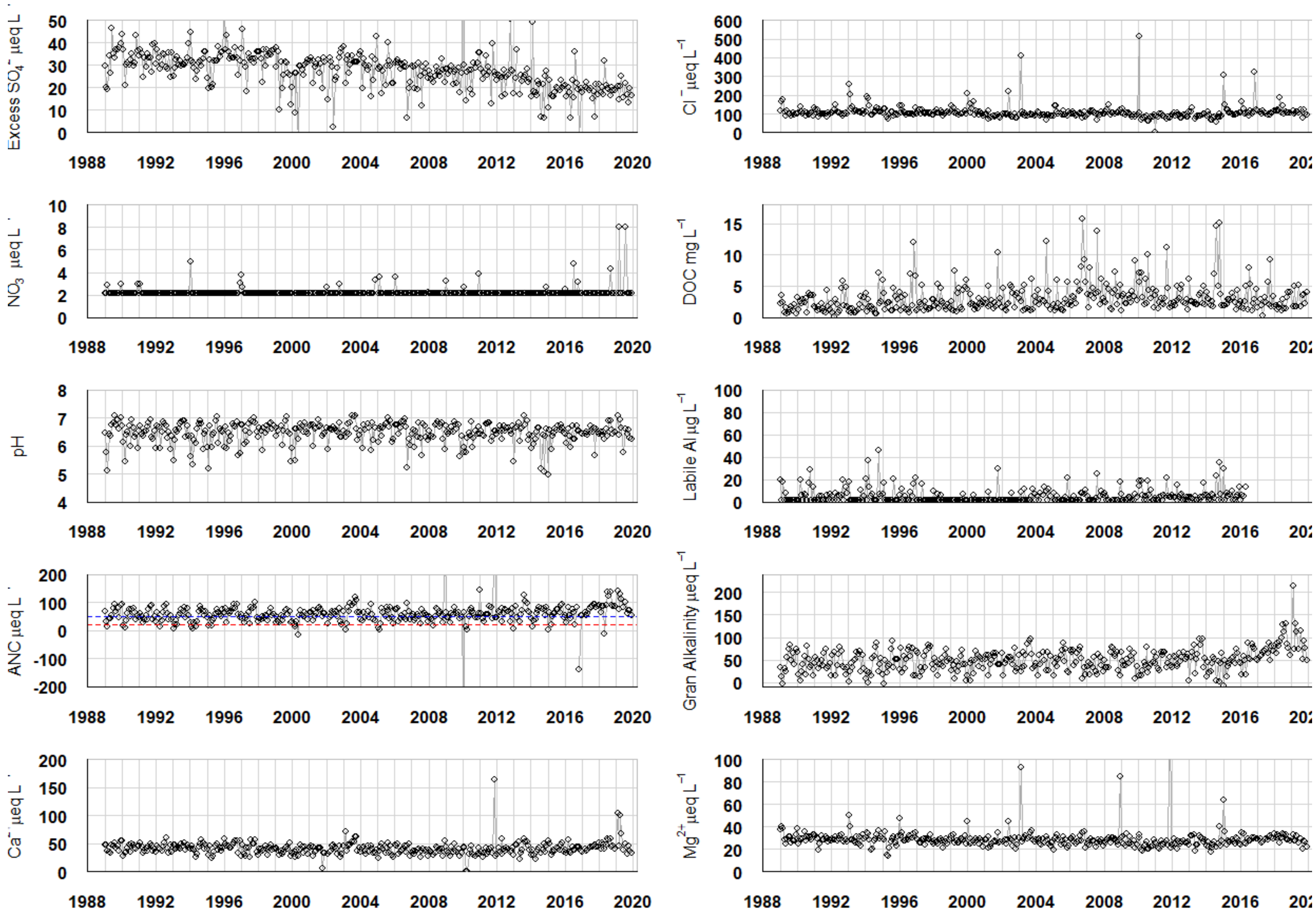


Figure 2.2 Allt a'Mharcaidh water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 μeq L^{-1}; blue dotted line is set to a higher limit of 50 μeq L^{-1}.

2.2 Allt a'Mharcaidh: water chemistry trends

In contrast to the sites to the west, the Allt a'Mharcaidh stream had considerably higher concentrations of non-marine sulphate at the onset of monitoring despite similarly low estimated levels of non-marine sulphur deposition. This is due to considerably lower rates of runoff in the east of Scotland. The concentrating effect has helped accentuate a very clear, and relatively linear, downward trend in non-marine sulphate over time. In common with the north-western sites, however, nitrate concentrations have remained mostly below limits of detection, reflecting the relatively low levels of reactive nitrogen deposition in the region. Although the Allt a'Mharcaidh shows similar concentrations of divalent base cations to the north-western sites, marine ion inputs are much lower, implying stronger buffering from the underlying geology. Water pH has consequently remained at pH 6 or above in most samples over time, with pH dipping to pH 5 only on very rare occasions, Acid Neutralising Capacity has almost invariably been positive (mostly above the UK ANC_{crit} level of 20 µeq L^{-1}), and Gran Alkalinity has oscillated mostly between 10 and 100 µeq L^{-1}. There is an indication of an increase in both Gran Alkalinity and ANC since 2016, but this appears to be linked to an extended period of exceptionally low flow and a resulting larger contribution from more ion-rich groundwater. Like most other sites on the UWMN, DOC concentrations have risen progressively, and maximum DOC concentrations have almost doubled over time, a feature that can be linked directly to the reduction in ion deposition over the same period.

2.3 Allt a'Mharcaidh: epilithic diatom community trends

The composition of the epilithic diatom flora of the Allt a'Mharcaidh has changed significantly during the thirty-one year monitoring period (RDA1, mGLM; Main Report: Figure 4.3). The common species *Synedra minuscula, Achnanthes minutissima*, and to lesser extent *Tabellaria flocculosa*, are present throughout the sampling period. *Fragilaria vaucheriae* underwent a clear and statistically significant decline from around 2010 and was replaced by a significant increase *Gomphonema angustatum* agg (Appendix: Figure 2.3). Species turnover over the monitoring period was 1.2 SD units, indicating around 50% species replacement.

Numerical analysis suggests that the small but significant change in community composition is not related to change in pH (RDA1-pH, DAM; Main Report: Figure 4.3). Variance partitioning with other water chemistry variables indicates significant relationships with labile aluminium and nitrate concentration, although both these variables have remained at very low concentrations relative to most other sites and therefore seem to be unlikely direct drivers of community variation.

2.4 Allt a'Mharcaidh: macroinvertebrate community trends

The Allt a'Mharcaidh is among the most macroinvertebrate species-rich streams on the Network. The macroinvertebrate community features persistent populations of acid-sensitive caddisflies (*Glossosoma*), and mayflies such as *Baetis*, *Rhithrogena* and *Electrogena,* as well as abundant populations of more moderately sensitive stoneflies such as *Perlodes microcephalus*. It is notable that the stream has supported large numbers of animals throughout the monitoring period with an average of 800 individuals per replicate sample, 60% more abundant than the next most numerous community, that of the River Etherow. Despite the relatively stable conditions at the site, there was a slight but not significant ($p < 0.068$) indication, from variation in AWICsp scores, that the macroinvertebrate assemblage may have benefitted from a slight reduction in acid stress. This is reflected in the recent addition of the caddisfly *Sericostoma personatum,* the mayfly *Ecdyonurus* and beetle *Esolus* to the community and the loss of the stoneflies *Nemoura* and *Leuctra hippopus* from the site.

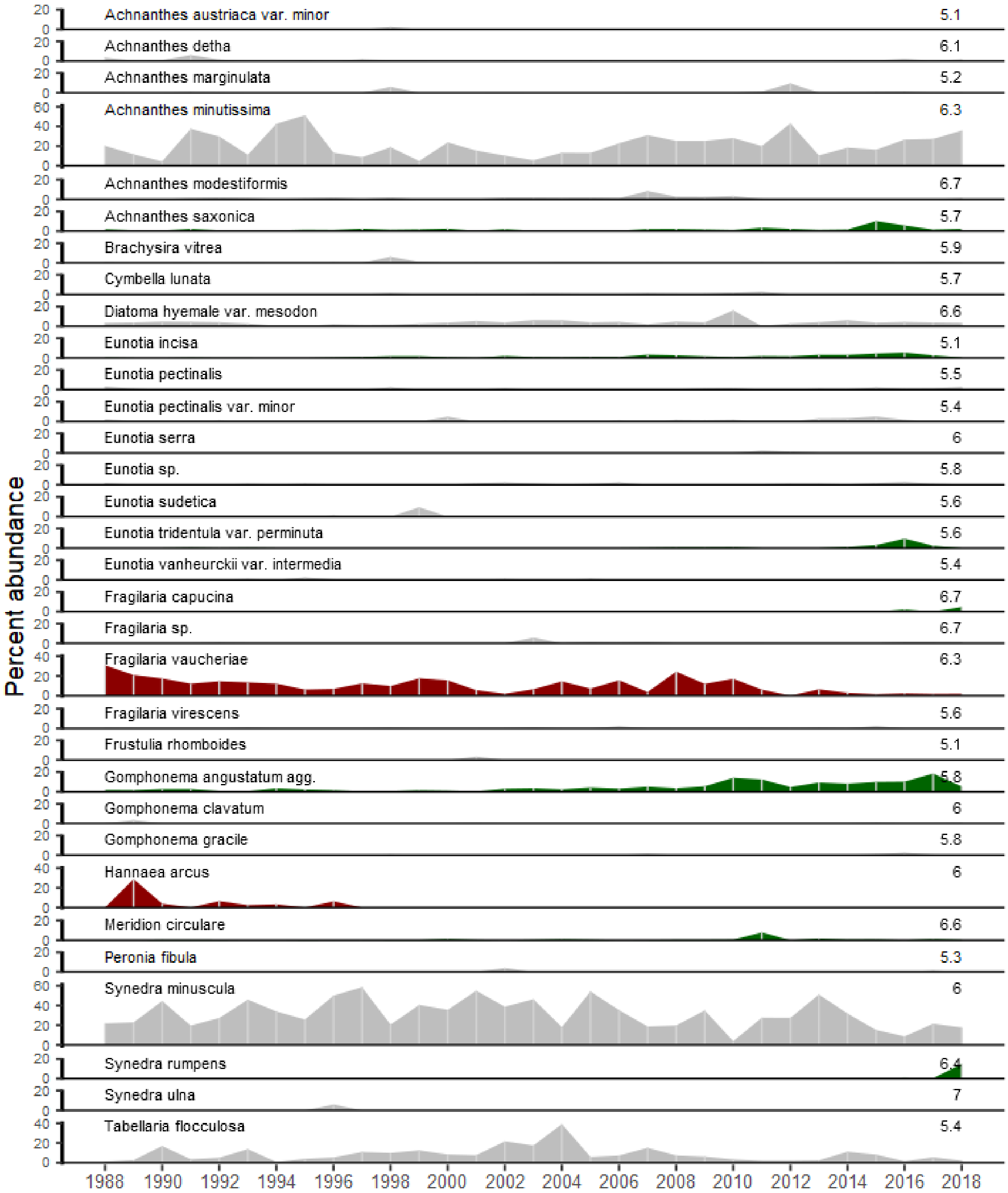


Figure 2.3 Allt a'Mharcaidh: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

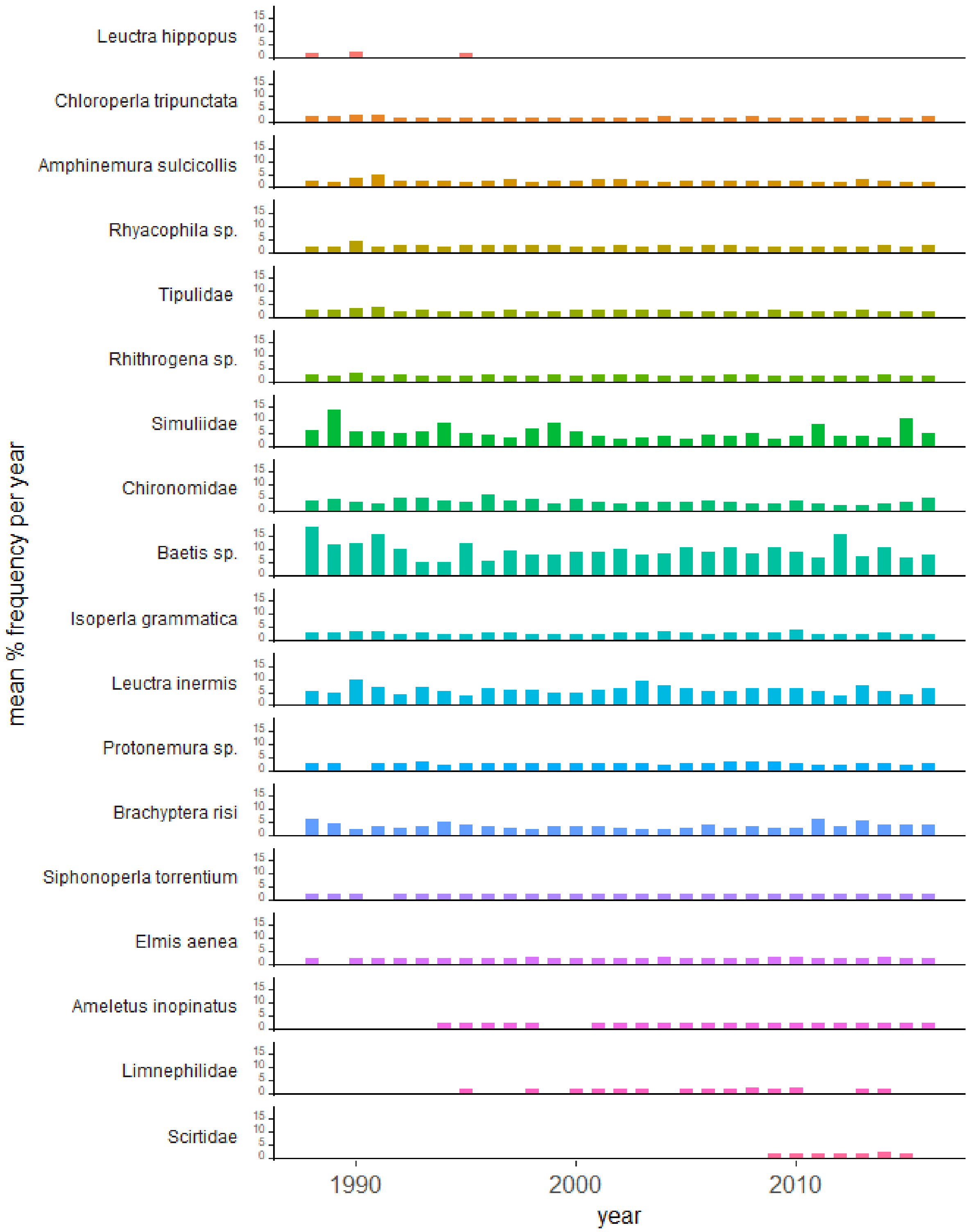


Figure 2.4 Allt a'Mharcaidh: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

3. Allt na Coire nan Con

3.1 Site description

Allt na Coire nan Con, in the Strontian region of northwest Scotland, is a fast flowing stream within a partially forested catchment. The bulk of the catchment was planted (predominantly with spruce and larch) around 1970. In 1988, approximately 48% of the catchment was covered by the Glenhurich Forest, which is managed by the Forestry and Land Scotland's Lochaber Forest District. The forest is dominated by Sitka spruce (*Picea sitchensis*) and Lodgepole pine (*Pinus contorta*) planted in the early 1920s and 1930s. Grazing on the upper slopes is confined to deer. Considerable felling and some re-planting was carried out in the mid 1990's, including areas close to the survey and sampling stretches**.** Felling reduced the proportion of conifer forest to 35% of the catchment by 2007 and under the Forest Design Plan this trend is expected to continue until it reaches a level of around 20% by 2050. The reduction in conifer cover involves part conversion to open space, mainly through a lowering of the tree line to reduce pollutant scavenging and improve landscaping, and a larger scale change to broadleaved woodland. The latter is targeted to riparian buffer zones in an effort to protect water quality and enhance biological recovery. Native broadleaves will be established over 75% of the riparian corridor through natural regeneration, supplemented by planting where necessary.

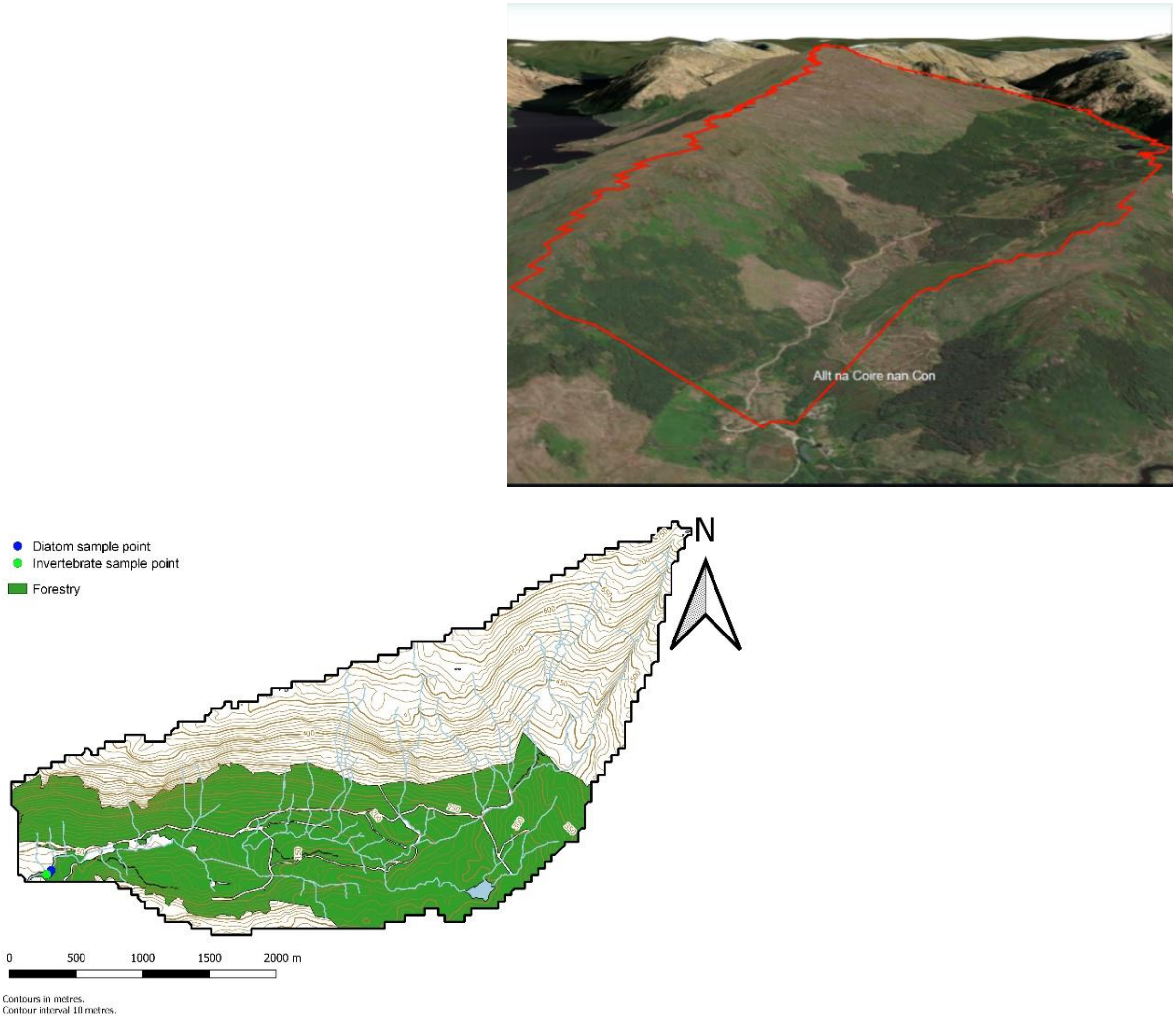


Figure 2.1 Mapped and aerial views of the Allt na Coire nan Con catchment

Table 3.1 Allt nan Coire nan Con site characteristics

Grid Reference	NM 793688	
Catchment area	790 ha	
Minimum catchment altitude	10 m	
Maximum catchment altitude	756 m	
Catchment geology	Schists and gneiss	
Catchment soils	Peaty podsols,	
Catchment vegetation	Conifers 42% Moorland 54%	
Mean annual runoff (precipitation – evaporation)	2262 mm	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	29.2	19.0
Non-marine oxidised sulphur	16.4	3.6
Oxidised nitrogen	17.6	5.1
Reduced nitrogen	23.9	7.7

Table 3.2 Allt nan Coire nan Con water chemistry summary statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope $year^{-1}$**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	60.4	40.2	110.4	71.2	37.5	17.2	-0.88	**
xSO_4^{2-}	µeq l^{-1}	27.9	10.8	81.7	44.0	-7.0	-4.4	-0.71	**
Cl^-	µeq l^{-1}	287.7	235.4	818.1	678.6	132.6	126.9	-1.71	**
NO^{3-}	µeq l^{-1}	3.0	2.1	17.1	27.4	2.1	2.1	0.00	**
pH	pH	5.8	5.9	6.7	6.7	5.0	4.6	-0.00	
Alk	µeq l^{-1}	12.5	31.1	80.0	104.8	-7.0	-14.9	0.17	**
Cond	µS cm^{-1}	47.5	40.2	108.0	95.7	20.0	24.2	-0.16	**
Na^+	µeq l^{-1}	267.5	228.1	569.9	518.7	152.3	77.4	-1.08	**
Ca^{2+}	µeq l^{-1}	57.4	44.0	107.3	84.8	27.4	17.8	-0.48	**
Mg^{2+}	µeq l^{-1}	68.3	53.0	168.6	138.9	26.3	6.4	-0.34	**
K^+	µeq l^{-1}	8.9	7.4	15.6	16.0	2.6	2.3	-0.02	*
Lab Al	µg l^{-1}	15.0	13.0	98.0	47.0	2.0	2.0	0.00	
DOC	mg l^{-1}	3.1	5.7	7.9	14.1	0.1	1.0	0.11	**
ANC-CB	µeq l^{-1}	25.2	51.9	113.4	123.2	-166.4	-49.3	0.94	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

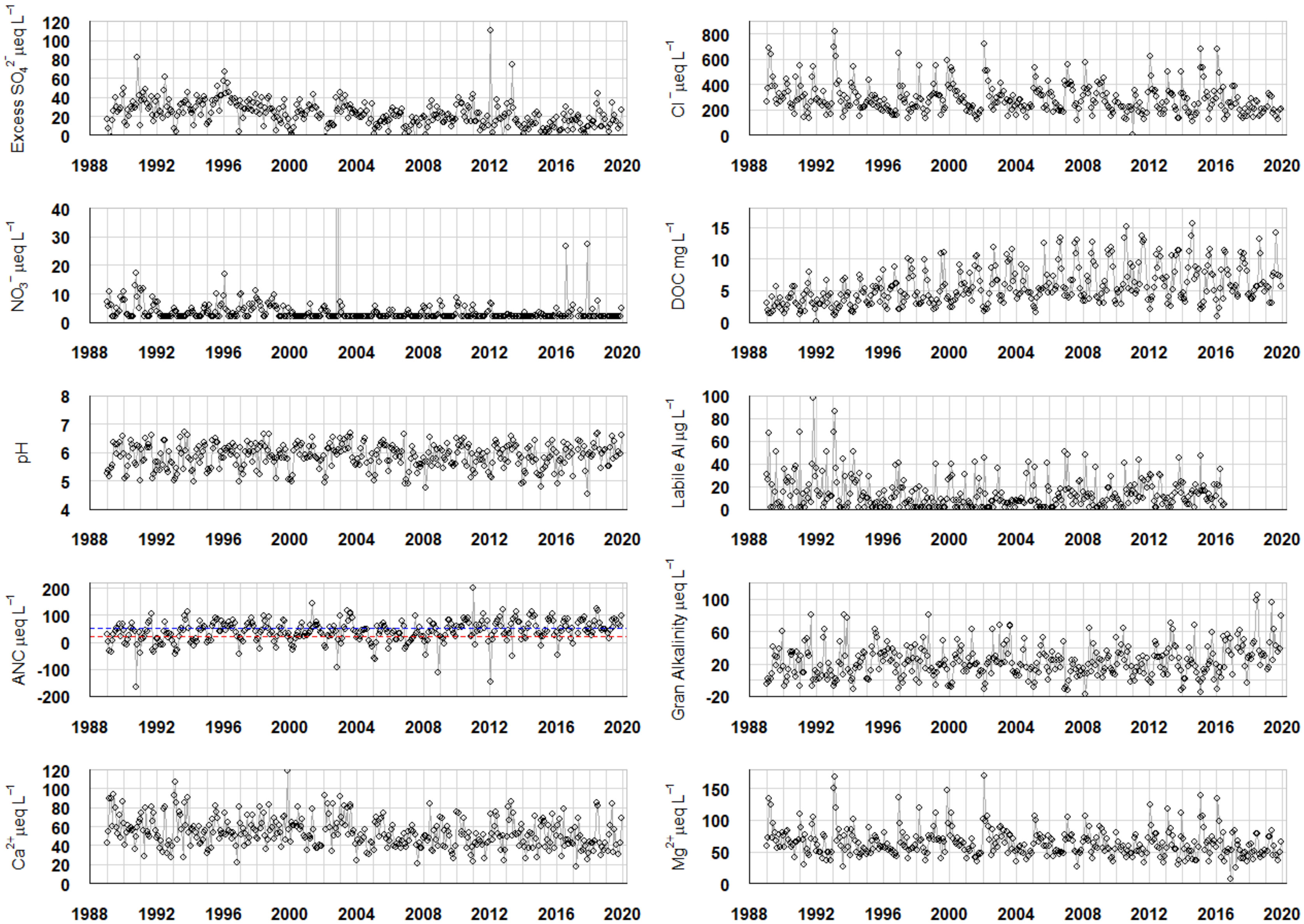


Figure 3.2 Allt na Coire nan Arr water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

3.2 Allt nan Coire nan Con: water chemistry trends

Although situated only 70 km south of Loch Coire Fionnaraich, Allt na Coire nan Con has received higher acid deposition loads historically, both due to its closer proximity to larger emission sources, and because of the enhanced pollutant interception provided by the forest canopy. Increased interception of reactive nitrogen may also explain regularly detectable levels of nitrate, particularly in the early years of monitoring. Large fluctuations in chloride and sodium concentrations emphasise the strong influence of sea salt deposition at this coastal site, although it is also clear that, in the long-term, average chloride concentrations have been declining – reflecting a reduction in the deposition of hydrochloric acid.

Higher concentrations of divalent base cations relative to the sites to the north are indicative of slightly stronger geological buffering, but over the first decade of monitoring labile aluminium concentrations were repeatedly recorded at potentially biologically harmful levels of 50 µg L^{-1} or above. Since then, and until monitoring of this determinand ceased in 2016, labile aluminium concentrations have generally been lower, but continued to rise regularly above 40 µg L^{-1}. Until around a decade ago, ANC was frequently negative during sea salt deposition events, but has since been positive in most samples, and the long-term upward trend is statistically significant. There is no indication that pH (varying between pH 5.0 and 6.5) has changed over time. However, the apparent influence of a recent drought observed for Allt a'Mharcaidh again provides the most likely explanation for a recent uptick in pH, Gran Alkalinity and ANC. DOC concentrations have increased dramatically at this site, largely as a consequence of the reduction in ion deposition, with median concentrations almost doubling between the first and last five years of monitoring.

3.3 Allt nan Coire nan Con: epilithic diatom community trends

The diatom flora at Allt na Coire nan Con was dominated throughout the monitoring period by *Achnanthes saxonica and Tabellaria flocculosa*, with lesser numbers of *Synedra minuscula* and *Gomphonema angustatum* agg., *Achnanthese minutissima* and *Eunotia incisa*. The latter has become more abundant since 2000, but there is considerable inter-year fluctuation in this and other taxa, and no significant overall trend or any significant trend in the dominant taxa (Main Report: Table 4.1 and Figure 4.1, Appendix: Figure 3.3). DAM scores show a significant decline, although again there is considerable fluctuation around the downward trend (Main Report: Figure 4.2). This reduction seems to be driven by the increase in *Eunotia incisa* which has a SWAP pH optimum of 5.1, somewhat lower than the other common taxa at this site. The increase in *Eunotia incisa* is consistent with the observed increase in stream water DOC, but further data are needed to clarify the underlying causes of this and other diatom species changes at the site.

3.4 Allt nan Coire nan Con: macroinvertebrate community trends

Despite the evidence for slight improvements in water chemistry in Allt na Coire nan Con, there have been no significant temporal trends in macroinvertebrate taxon richness (Main Report: Figure 5.1) or directional change in assemblage composition at the site (Main Report: Figure 5.2 and Table 5.3). The community features a relatively rich diversity of mayflies, stoneflies, water beetles and caddisflies including taxa from across the gradient of acid sensitivities, from the highly acid-sensitive caddisfly (*Silo pallipes*), and moderately sensitive beetle (*Limnius volkmari*) to the moderately acid-tolerant stonefly (*Isoperla grammatica*) (Appendix: Figure 3.4). There is, however, a modest signal of a reduction in acid stress, with a small but significant increase in what were already high AWICsp scores, particularly over the first 20 years of monitoring – broadly coincident with the period of substantial labile aluminium decline. Over this period a number of additional acid-sensitive taxa became established at the site, e.g. *Electrogena lateralis*, *Hydraena*, and *Elmis aenea*.

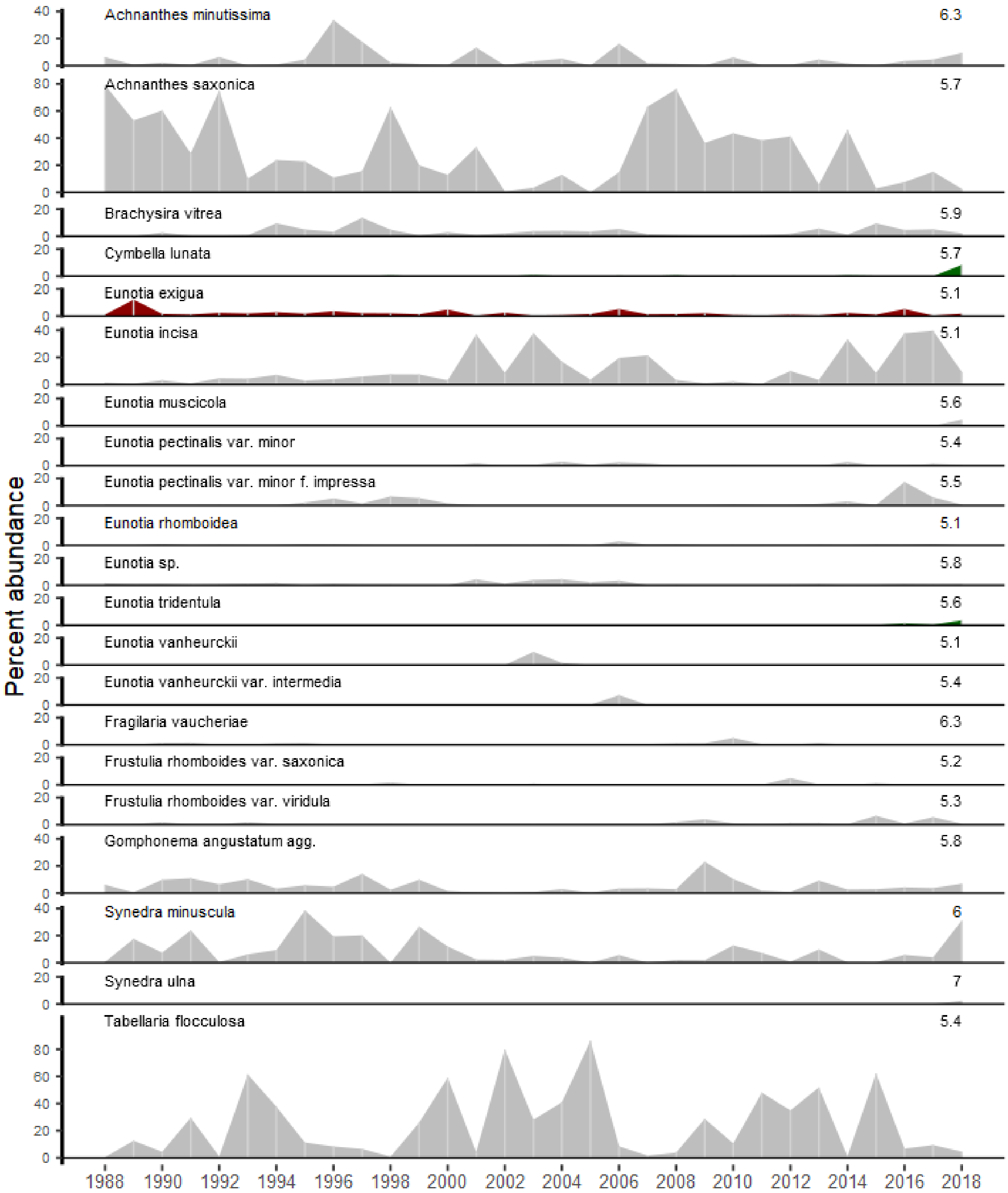


Figure 3.3 Allt na Coire nan Con: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

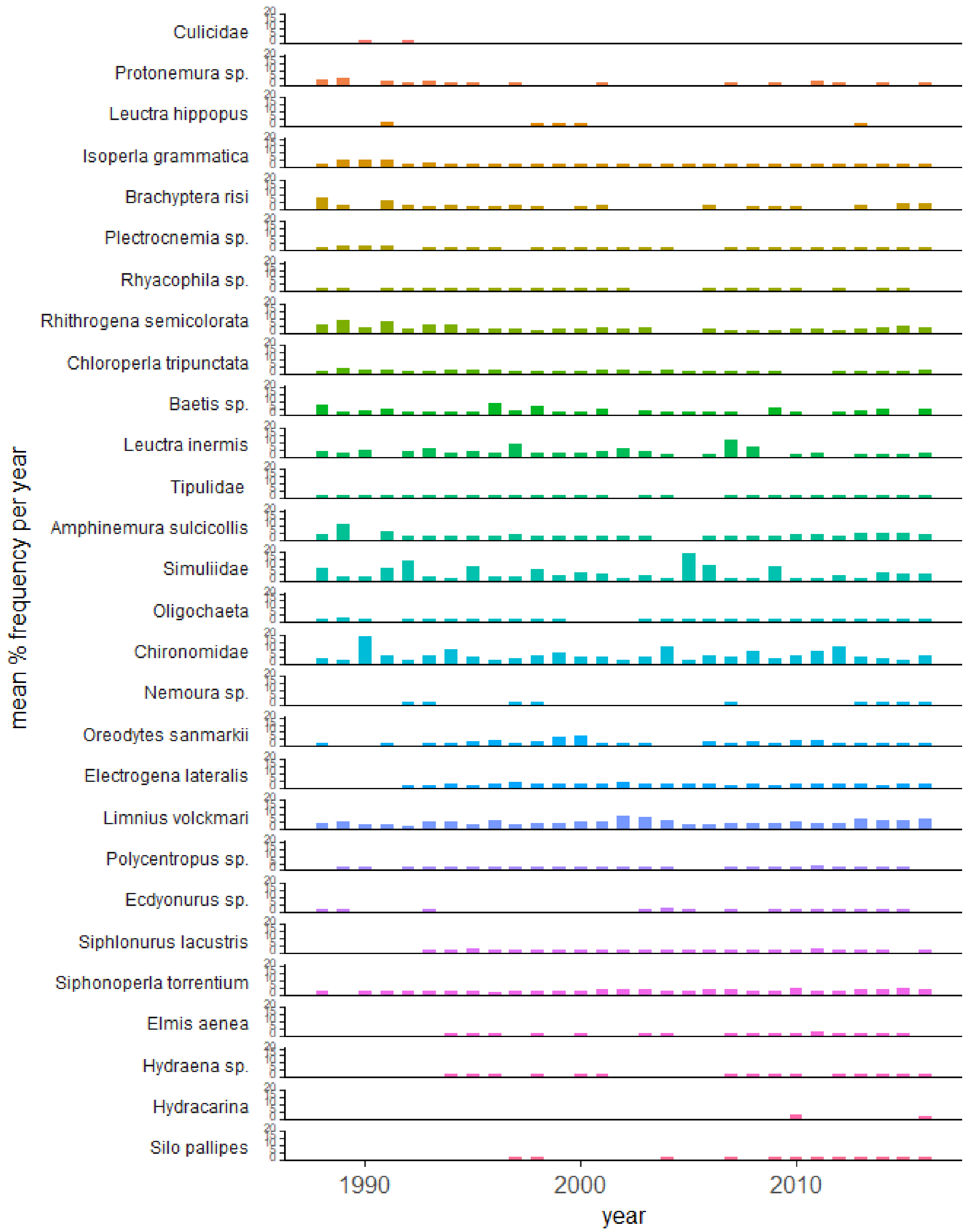
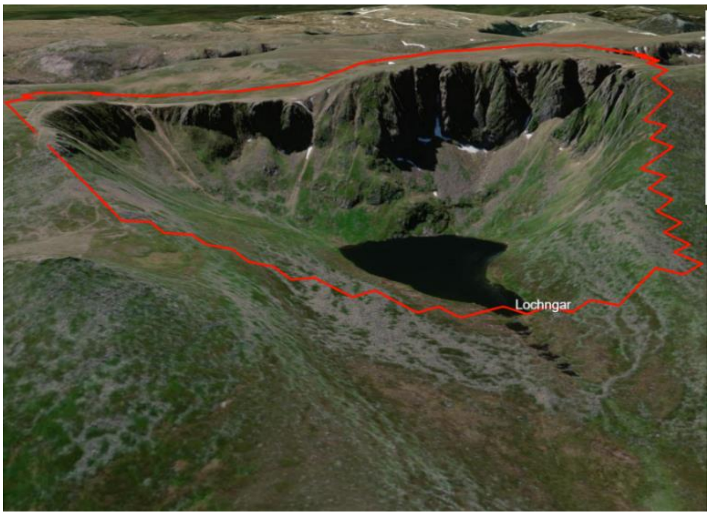


Figure 3.4 Allt na Coire nan Con: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

4. Lochnagar

4.1 Site description

At an altitude of 785 m in the Grampian Mountains of northeast Scotland, Lochnagar is the highest of the UWMN lakes. Palaeoecological pH reconstruction indicates that Lochnagar acidified from around pH 5.6, in the mid-nineteenth century, to around pH 5.0 by the 1940s (Patrick et al. 1989, Patrick et al. 1995). Although prone to a considerable duration of ice cover during some winters, the extent of the freezing period has been highly variable in recent years. Scientific work at Lochnagar increased after its inclusion in the EU funded mountain lakes projects AL:PE, MOLAR, CHILL and EMERGE, and a comprehensive overview of the natural history of the loch and related scientific research is presented by Rose (2017). There have been no physical disturbances in the catchment, other than occasional scree falls from the corrie backwall, since the onset of monitoring in 1988.



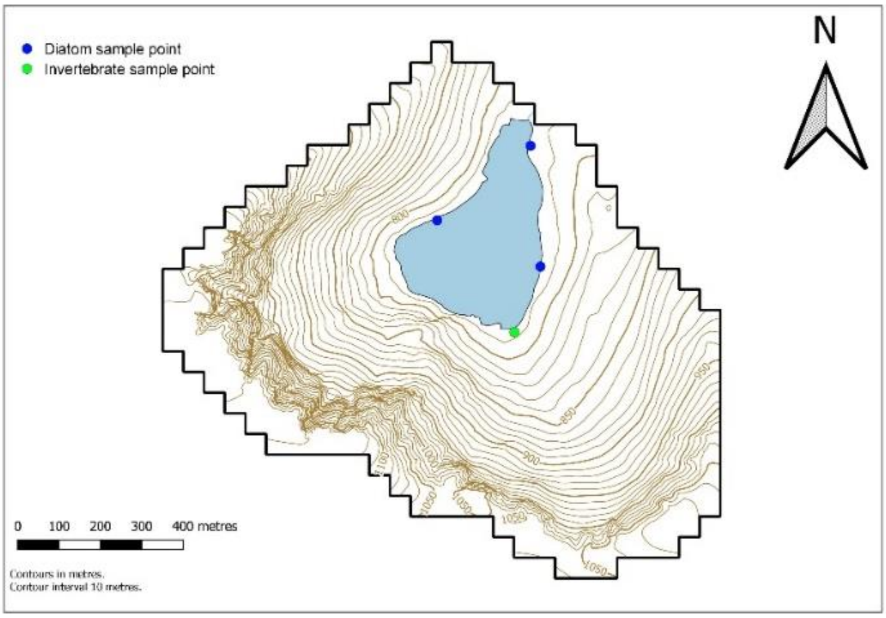


Figure 2.1 Mapped and aerial views of Lochnagar catchment

Table 4.1 Lochnagar site characteristics

Grid Reference	NO 252289	
Lake altitude	785 m	
Maximum altitude	1145 m	
Maximum depth	26 m	
Mean depth	8.4 m	
Volume	8.2 x 10^5 m^3	
Lake area	9.8 ha	
Catchment area	108.5 ha	
Catchment area (excl.lake)	91.9 ha	
Catchment:Lake ratio	9:37	
Catchment geology	Granite	
Catchment soils	Peats	
Catchment vegetation	Alpine - moorland	
Mean annual runoff (precipitation – evaporation)	1295 mm	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	13.8	6.3
Non-marine oxidised sulphur	11.4	3.1
Oxidised nitrogen	7.4	5.1
Reduced nitrogen	11.9	7.1

Table 4.2 Lochnagar water chemistry summary statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	58.3	26.3	85.4	30.5	54.2	21.7	-1.19	**
xSO_4^{2-}	µeq l^{-1}	49.4	18.9	74.5	21.6	44.8	15.2	-1.11	**
Cl^-	µeq l^{-1}	86.0	71.1	166.4	91.6	67.7	33.6	-0.59	**
NO^{3-}	µeq l^{-1}	11.5	10.4	21.0	15.5	2.1	6.4	-0.22	**
pH	pH	5.5	5.8	5.8	6.1	5.0	5.4	0.01	**
Alk	µeq l^{-1}	2.0	16.0	12.0	29.0	-10.0	2.0	0.30	**
Cond	µS cm^{-1}	21.5	15.7	35.0	19.0	4.0	13.7	-0.22	**
Na^+	µeq l^{-1}	91.4	74.3	174.0	117.0	74.0	68.3	-0.56	**
Ca^{2+}	µeq l^{-1}	27.9	17.4	49.9	31.9	21.5	13.9	-0.37	**
Mg^{2+}	µeq l^{-1}	32.9	22.6	54.3	28.8	4.1	17.9	-0.40	**
K^+	µeq l^{-1}	7.2	5.2	19.4	8.5	2.6	3.8	-0.03	**
Lab Al	µg l^{-1}	8.0	6.0	137.0	16.0	2.0	4.0	-0.04	
DOC	mg l^{-1}	0.9	1.9	2.1	4.0	0.2	0.7	0.03	**
ANC-CB	µeq l^{-1}	1.9	16.1	37.9	59.5	-35.4	1.9	0.61	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

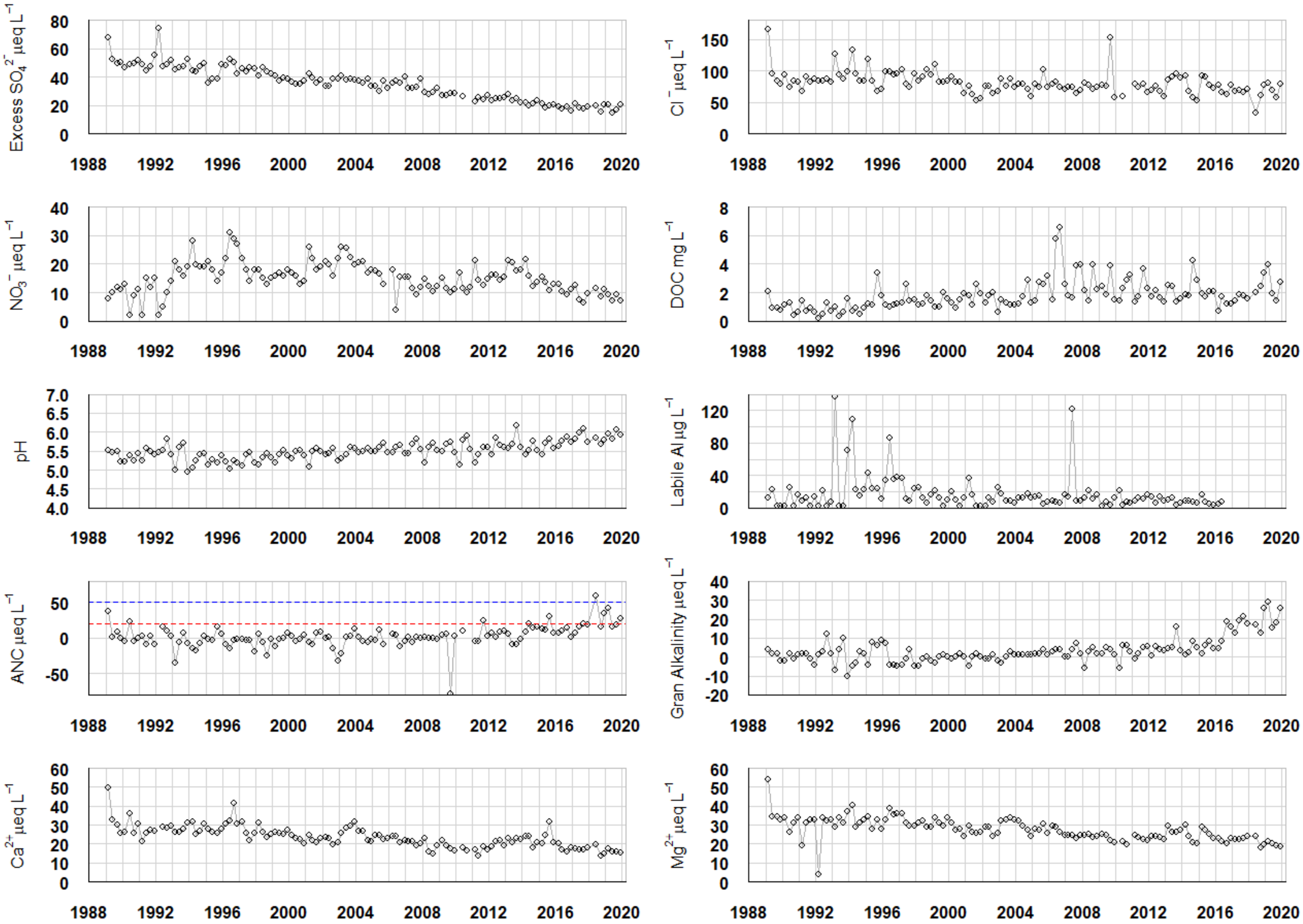


Figure 4.2 Lochnagar water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

4.2 Lochnagar: water chemistry trends

The CBED deposition estimates for non-marine sulphur deposition to Lochnagar at the onset of monitoring are only marginally higher than for the “control” lochs to the north-west. In common with Allt a’Mharcaidh, however, the lower runoff in this easterly region has resulted in higher concentrations of non-marine sulphate in loch water, and consequently a relatively rapid rate of decline. Also in contrast with the lochs to the north-west, nitrate concentrations in Lochnagar have been above limits of detection throughout the monitoring period, reflecting the sparse soil cover and low temperatures that limit the capacity of the catchment’s soils to retain incoming reactive nitrogen deposition, in addition to the concentrating effect of the low runoff. Over the first 20 years of monitoring, nitrate concentrations increased over a period when oxidised nitrogen deposition in the region also rose, and the increased contribution to water acidity was sufficient to almost entirely offset the substantial reduction in sulphate concentration over the same period. This resulted in no net change in water pH or ANC, while labile aluminium concentrations first increased before falling again to relatively benign levels. Consequently, Lochnagar remained in a strongly acidified condition over the first two decades, with pH rarely rising above 5.5 and ANC consistently below 20 µeq L^{-1} and often negative.

Nitrate concentrations in Lochnagar began to fall again around 2005, since when pH and ANC have edged upwards. Over the last 10 years, pH has rarely been recorded below 5.5, and has on occasions exceeded 6.0., while ANC is now mostly positive and has occasionally exceeded the UK ANC_{crit} of 20 µeq L^{-1}. Because of its easterly location, Lochnagar receives much lower levels of sea salt deposition than the majority of UWMMN sites, and this makes the influence of declining inputs of hydrochloric acid on the water chemistry, in the form of a substantial and relatively linear decline in chloride concentration, more obvious. The overall drop in pollutant ion deposition is reflected in a decline in electrical conductivity from 21.5 to 15.7 µS cm^{-1} from the first to the last five years of monitoring. Very low ionic concentrations pose a potential threat to a range of aquatic biota, although Norwegian studies have suggested that water with an electrical conductivity of above 10 µS cm^{-1} should not pose a threat to most aquatic organisms inhabiting oligotrophic waters.

The water of Lochnagar was exceptionally transparent at the onset of monitoring, as indicated by a median DOC concentration over the first 5 years of only 0.9 mg L^{-1}. Since then concentrations have approximately doubled. Based on our understanding of the relationship between DOC concentration and the depth of penetration of photosynthetically active radiation (PAR), the DOC increase will have reduced the amount of the loch bed lying above the photic zone (i.e. depth at which PAR is 1% of that at the loch surface) from 100% to approximately 75% (Monteith pers. comm).

4.3 Lochnagar: epilithic diatom community trends

The epilithic diatom assemblages sampled in this loch were dominated for the first 20 years of monitoring by *Achnanthes marginulata* and *Tabellaria flocculosa.* (Appendix: Figure 4.3). There is some inter-annual variability, but *Tabellaria flocculosa* (SWAP pH optimum = 5.4) began to increase, and *Achnanthes marginulata* (optimum = 5.2) and *Eunotia incisa* (optimum = 5.1) decline, from around 2008, i.e. roughly coincident with the increase in pH and ANC. Other minor taxa with pH optima < 5.5, such as *Achnanthes* [*altaica* var. *minor*] and varieties of *Achnanthes austriaca* also show significant declines and disappear from the record at this time. The overall trend in species replacement is significant at the community level (RDA1, mGLM; Main Report: Table 4.1). Diatom turnover is 1.8, indicating a near-complete turnover of taxa over the monitoring period.

There is a significant increase in DAM (Main Report: Table 4.1) and an overall significant relationship with measured lake pH (Main Report: Figure 4.3). Furthermore, the RDA1-pH / PCA ratio is 0.5, indicating that the response to pH is the dominant effect observed in the diatom data. Both the PRC and DAM trajectories (Main Report: Figures 4.1 & 4.2) indicate relative stability for the first part of the monitoring period but more rapid and sustained recovery with a transition to a less acid flora after 2005.

4.4 Lochnagar: macroinvertebrate community trends

The macroinvertebrate community at Lochnagar remained relatively stable and species poor over the 28 years of monitoring (Appendix: Figure 4.4), with an assemblage dominated by non-biting midges (Chironomidae); cranefly larvae; a diverse range of stoneflies including *Capnia*, *Siphonoperla* and *Nemurella*; and Polycentropodidae and Limnephilidae caddis flies. The combination of the improvement in water chemistry being a relatively recent phenomenon only, Lochnagar's remoteness from other standing waters and relatively low water temperatures, may all contribute to the absence of a clear response in the fauna to chemical improvements. A further few years of relatively benign chemistry may be necessary before a consistent response in the fauna becomes detectable.

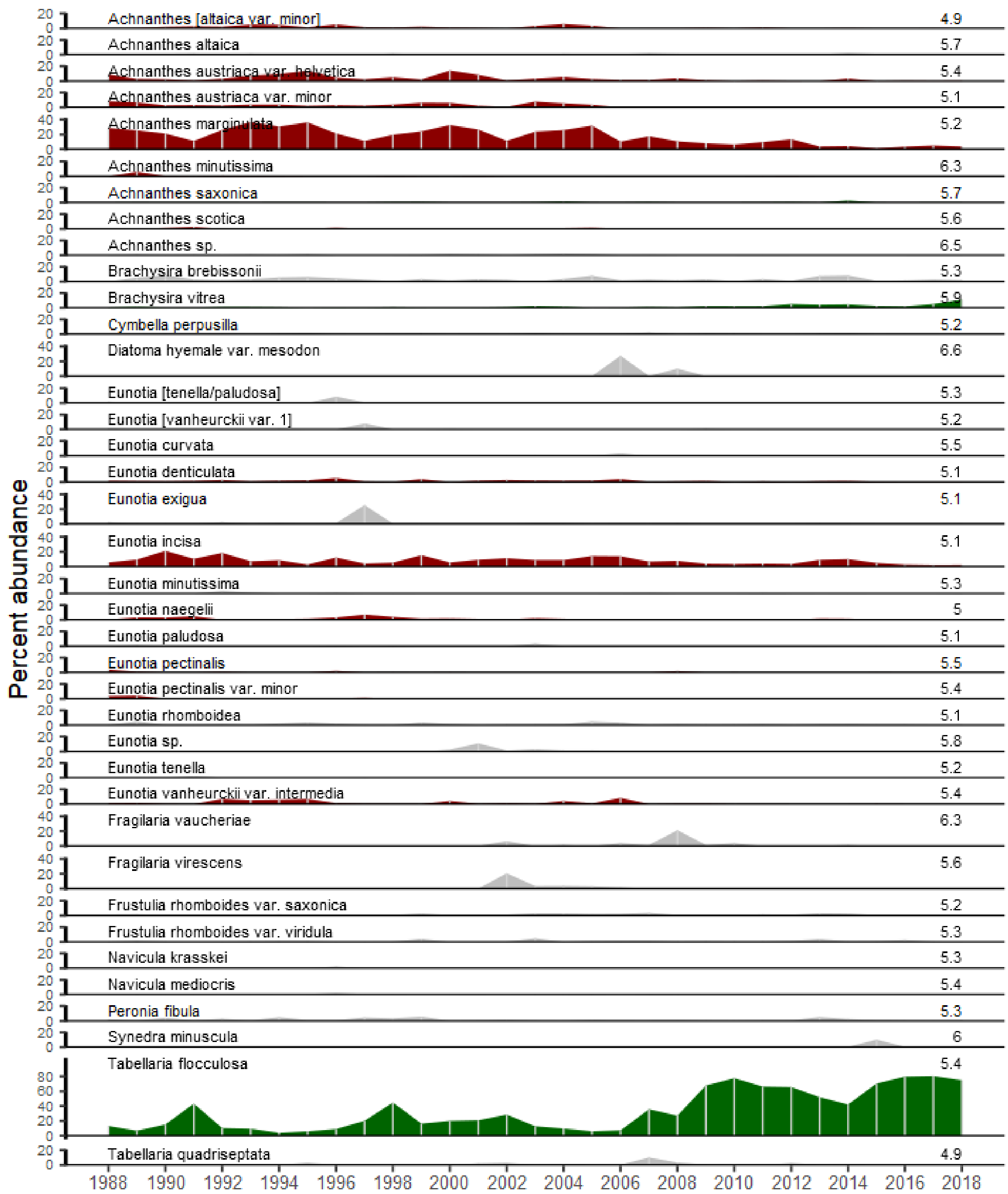


Figure 4.3 Lochnagar: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species

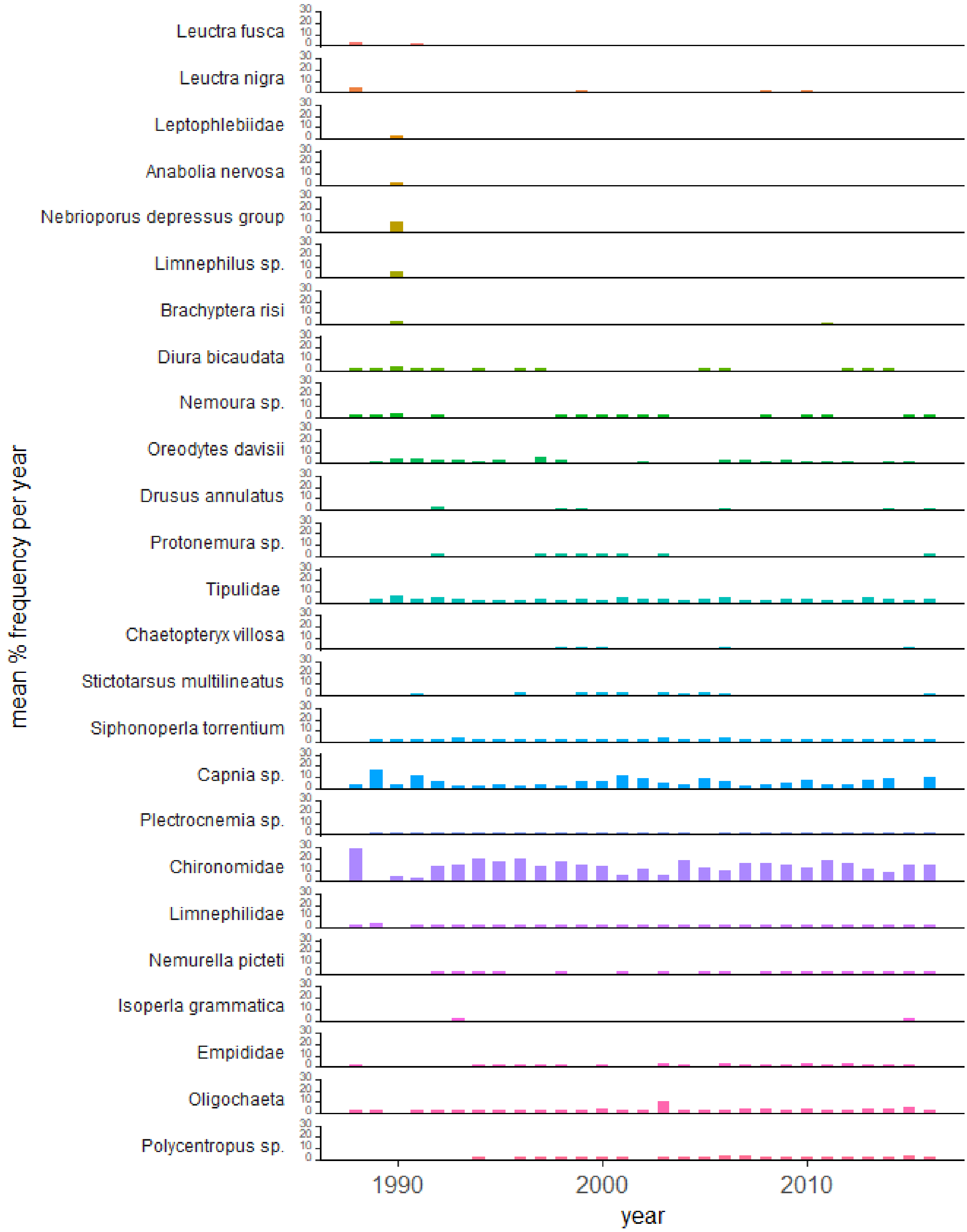


Figure 4.4 Lochnagar: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

5. Loch Chon

5.1 Loch Chon site description

Loch Chon is a relatively large loch in the Trossachs region of central Scotland. Today large areas of the catchment are covered by mature coniferous forest. Its recent palaeoecological history was studied in the SWAP programme (Battarbee & Renberg, 1990). This work suggested that the loch had acidified substantially over the previous 150 years, with the pH falling from around 6.4 to around 5.0 by 1992 (Patrick et al., 1989; Kreiser et al., 1990). An accelerated rate of acidification in recent decades was attributed to afforestation of the catchment. In 1995, a small forestry access road was constructed parallel to the west shore, but felling to date has been largely restricted to small areas to the northwest of the site. The Loch Chon catchment forms part of Loch Ard Forest. This is managed by Forestry and Land Scotland who are working to create a riparian woodland habitat network involving the conversion of conifer stands to native broadleaves within a minimum 20 m wide buffer zone along either side of all permanent watercourses. The upper tree line will be reduced below the 300 m contour, increasing the proportion of open space from 40% in the 1980s to 57% by 2050. Overall conifer cover will be reduced from an initial 53% to 21%.

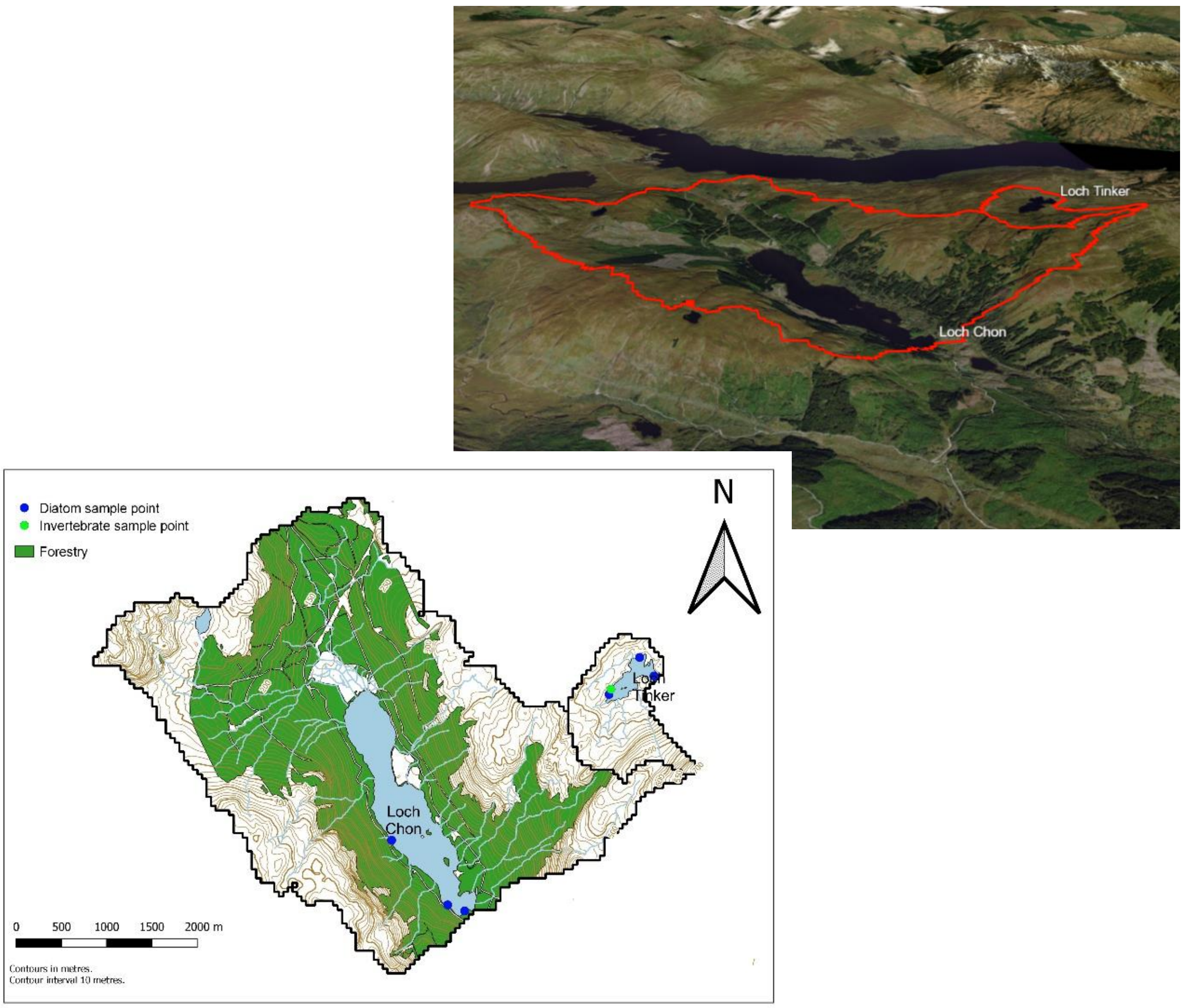


Figure 4.1 Mapped and aerial views of the Loch Chon catchment

Table 5.1 Loch Chon site characteristics

Grid Reference	NN 421051	
Lake altitude	100 m	
Maximum altitude	1145 m	
Maximum depth	25 m	
Mean depth	7.6 m	
Volume	7.3 x 10^6 m^3	
Lake area	100 ha	
Catchment area	108.5 ha	
Catchment area (excl.lake)	1570 ha	
Catchment:Lake ratio	15:7	
Catchment geology	Mica schist and grits	
Catchment soils	Peaty gleys peaty podzols	
Catchment vegetation	Conifers – 50% Moorland – 50%	
Mean annual runoff (precipitation – evaporation)	2179 mm	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	26.3	13.0
Non-marine oxidised sulphur	18.9	4.0
Oxidised nitrogen	14.3	6.5
Reduced nitrogen	30.1	11.0

Table 5.2 Loch Chon water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	75.0	34.6	91.7	49.3	60.4	29.2	-1.38	**
xSO_4^{2-}	µeq l^{-1}	48.9	14.7	60.8	20.8	33.4	8.9	-1.14	**
Cl^-	µeq l^{-1}	238.4	185.9	411.9	388.6	152.3	129.2	-1.29	**
NO^{3-}	µeq l^{-1}	10.0	7.9	16.0	13.9	2.1	2.1	-0.18	**
pH	pH	5.5	6.1	5.9	6.3	5.0	5.5	0.02	**
Alk	µeq l^{-1}	5.5	42.8	15.0	61.4	-8.0	5.2	0.86	**
Cond	µS cm^{-1}	40.5	34.7	61.0	57.6	29.0	28.8	-0.18	**
Na^+	µeq l^{-1}	193.6	164.9	304.5	281.8	143.6	129.2	-1.02	**
Ca^{2+}	µeq l^{-1}	77.6	68.9	94.3	93.0	64.4	60.9	-0.25	**
Mg^{2+}	µeq l^{-1}	47.3	44.3	72.4	76.0	37.8	38.0	-0.19	**
K^+	µeq l^{-1}	5.9	8.0	12.5	11.3	2.6	4.8	0.00	
Lab Al	µg l^{-1}	19.0	8.0	69.0	13.0	2.0	4.0	-0.02	
DOC	mg l^{-1}	2.7	5.1	5.3	9.6	1.7	2.1	0.08	**
ANC-CB	µeq l^{-1}	12.0	61.2	38.9	91.2	-24.8	12.9	1.39	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

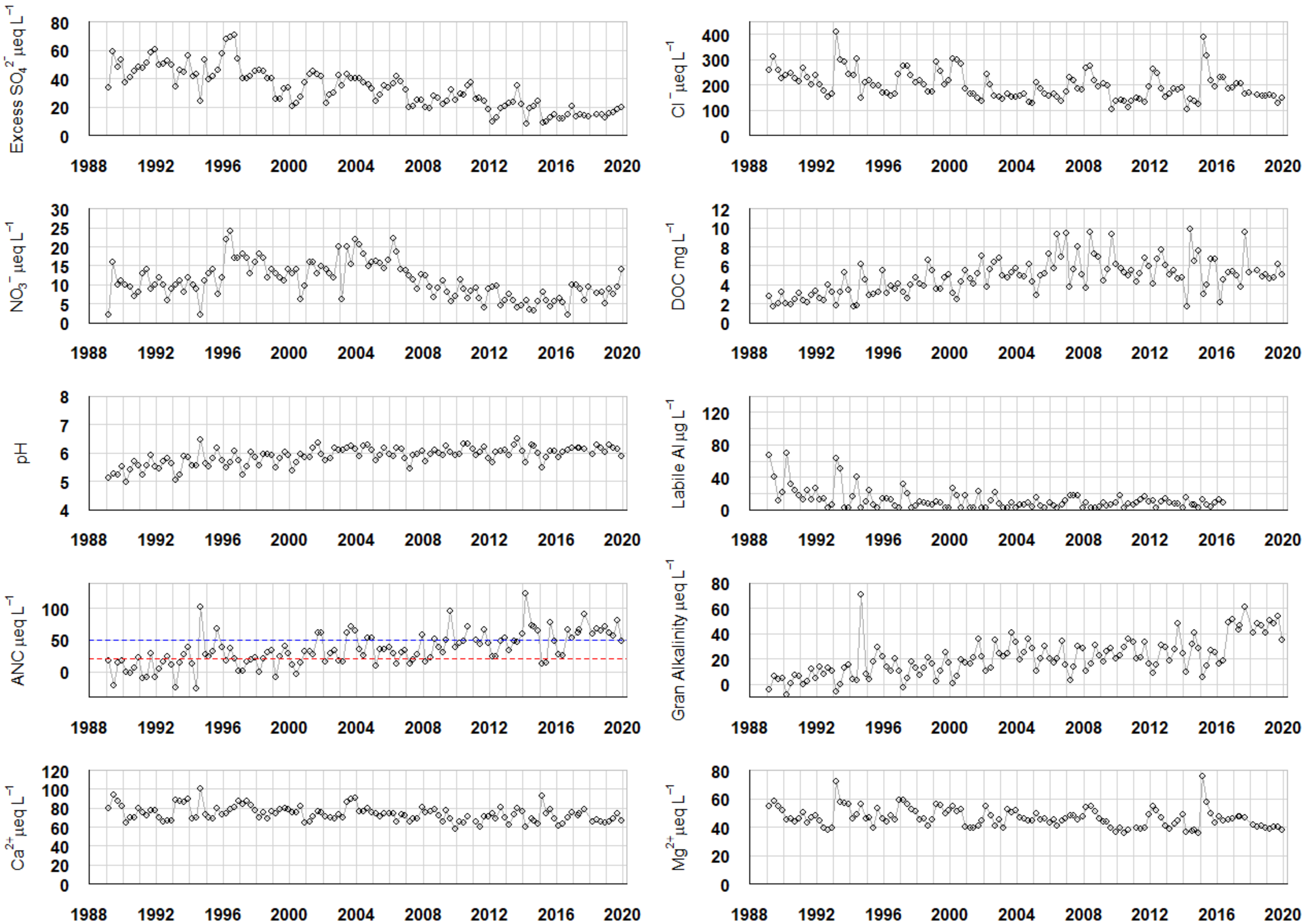


Figure 5.2 Loch Chon water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

5.2 Loch Chon: water chemistry trends

Historically, Loch Chon received considerably higher levels of both sulphur and nitrogen deposition than the Scottish UWMN sites further north, but higher rates of runoff relative to Lochnagar have resulted in similar non-marine sulphate concentrations and rates of reduction over time. For much of the monitoring period concentrations of non-marine sulphate have also been much higher than for the neighbouring moorland site, Loch Tinker, demonstrating the role of forestry in enhancing pollutant interception. Also in common with Lochnagar, nitrate concentrations have remained detectable throughout the year and increased over the first 20 years, reaching similar concentrations to sulphate (in equivalence terms) before falling substantially more recently. While low temperatures and sparse soil cover are likely to have contributed to the elevated nitrate concentrations in Lochnagar, enhanced interception of reactive N by the forest, and possibly also partial by-passing of the underlying soils provided by the the forest drainage system, provide more plausible explanations for the phenomena in Loch Chon; nitrate concentrations have rarely been detectable in the neighbouring non-forested Loch Tinker.

The Loch Chon catchment is vulnerable to frequent and sizeable inputs of sea salt, as evidenced by the large variation in chloride concentration. Chloride concentrations also show a reduction over time of similar magnitude to non-marine sulphate (a consequence of the reduction in hydrochloric acid deposition). Despite the increase in nitrate over the first half of the record, the larger declines in non-marine sulphate and chloride resulted in an increase in water pH at this time. Over the first five years of monitoring, loch water pH normally ranged between 5.0 and 5.5, ANC was normally less than 20 μeq L^{-1} and often slightly negative, while labile aluminium concentration ranged from around 10 to 70 μg L^{-1}, with the highest concentrations normally triggered by seasalt episodes. By 2004, pH was averaging around 6.0, ANC was exceeding 20 μeq L^{-1} in most samples and frequently exceeding 50 μeq L^{-1}, while labile aluminium concentrations had fallen to biologically benign median concentrations of less than 10 μg L^{-1}. Since 2004, pH and ANC have largely levelled out. In common with several other Scottish sites, however, they underwent a further increase from around 2016, together with a surge in Gran alkalinity (indicative of an increase in bicarbonate). This is most likely a temporary change, linked to an extended period of low rainfall, reduced water tables and an increase in the proportional contribution to run-off from more ion-rich water groundwater.

Median DOC concentrations approximately doubled between the first and most recent five-year period, from 2.7 to 5.1 mg L^{-1}, although short term DOC maxima have increased at a much greater rate, with concentrations regularly exceeding 8 mg L^{-1} since 2006. The associated change in water colour is likely to have had a profound effect on the proportion of the lake bed where photosynthesis is possible (i.e. the photic zone). Changes in the DOC median concentration are estimated to have reduced the area of the loch bed within the photic zone from around 80 to 20%, with the occasional recent DOC peaks potentially reducing this still further to around 2% of the loch bed.

5.3 Loch Chon: epilithic diatom community trends

The epilithic diatom community of Loch Chon showed clear changes in the abundances of common species during the monitoring period – taxa with low pH optima being replaced by others with higher pH optima. The early part of the record was dominated by *Navicula leptostriata* (SWAP pH optimum = 5.1), *Achnanthes marginulata* (optimum = 5.2), and *Eunotia incisa* (optimum = 5.1). These, together with other low-pH taxa such as *Tabellaria binalis* f. *elliptica* (optimum = 5.0), *Eunotia exigua* (optimum = 5.1) and *Frustulia* [cf. *oldenburgiana*] (optimum = 4.7), show significant reduction and have been replaced by increasing proportions of *Tabellaria flocculosa* and *Brachysira vitrea* (optimum = 5.4 and 5.9 respectively). The acid-sensitive species *Achnanthes minutissima* (optimum = 6.3) appears in the late 1990s and shows a significant increase from around 2003. Diatom turnover is 1.9, indicating a near-complete turnover of taxa over the duration of the monitoring period.

Numerical analysis indicates that the trends in diatom abundances are significant at the community level (RDA1, mGLM; Main Report: Table 4.1) and that these changes are strongly related to an increase in pH (RDA1-pH, DAM; Main Report: Table 4.1). Plots of PrC and DAM scores indicate a sustained species recovery across the whole monitoring period with relatively little inter-annual variability (Main Report: Figures 4.1 & 4.2). Variance partitioning indicates a significant relationship between diatom assemblage change and alkalinity, labile Al, and DOC, but the conditional effects of these variable is not significant, indicating that the trends in the diatom data can be accounted for by the observe increase in lake-water pH alone (Main Report: Figure 4.3).

5.4 Loch Chon: macroinvertebrate community trends

Loch Chon supports the most diverse lake macroinvertebrate community on the UWMN with rarefied richness rarely dropping below 20 (Main Report: Figure 5.1). The assemblage has featured a notably diverse range of lesser water boatmen (Corixidae), beetles and caddisflies (Appendix: Figure 5.4). Despite the relatively species rich starting point, there has been a shift in community composition over the monitoring period, consistent with a recovery from acidification. This is characterised by the establishment of acid-sensitive taxa such as the aquatic amphipod *Gammarus*, the mayfly *Caenis luctuosa*, and stonefly *Leuctra geniculata*, accompanied by the loss, or reduced abundance, of more acid-tolerant taxa such as the water boatman *Callicorixa wollastoni* and the tube making caddis *Holocentropus*.

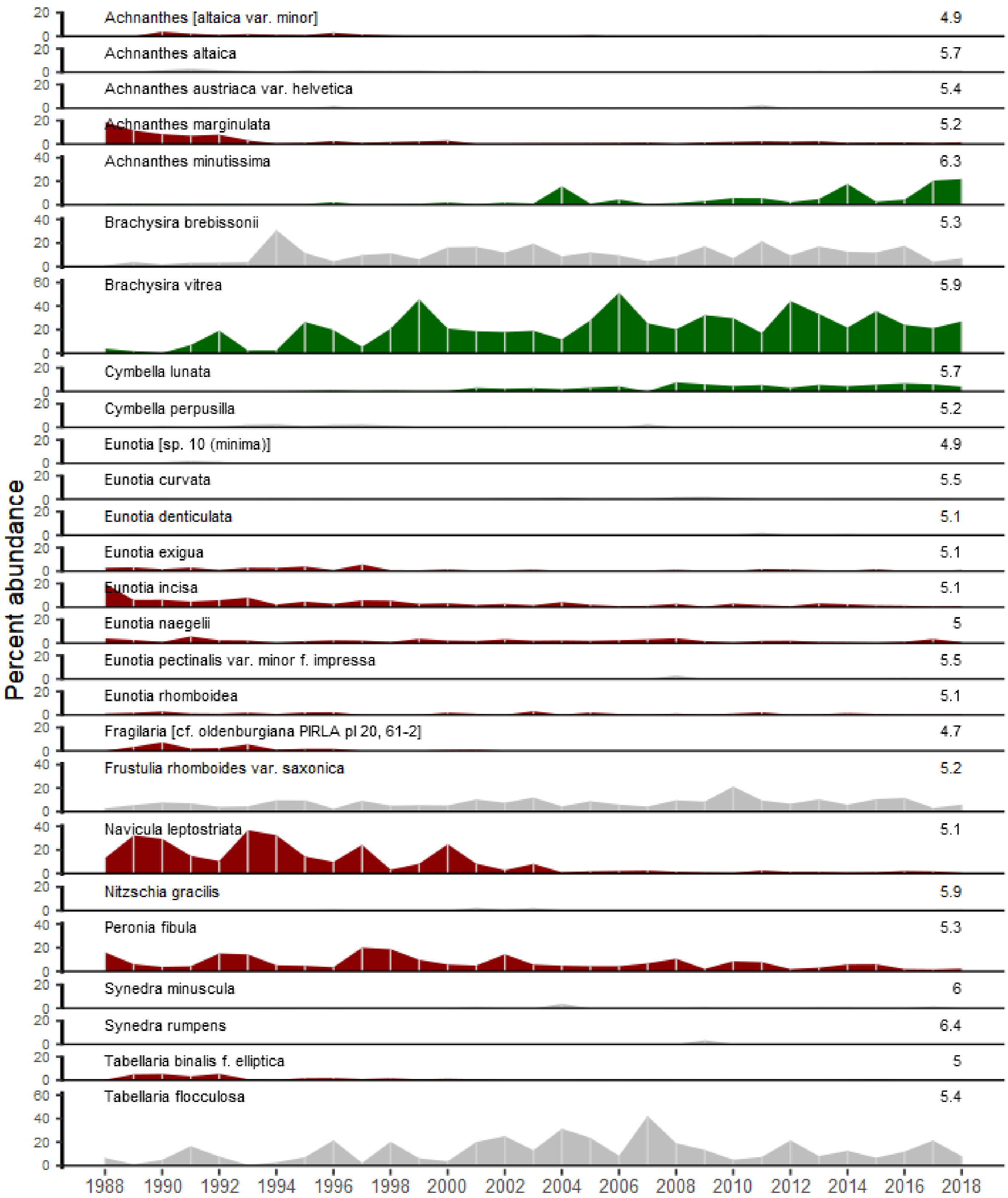


Figure 5.3 Loch Chon: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

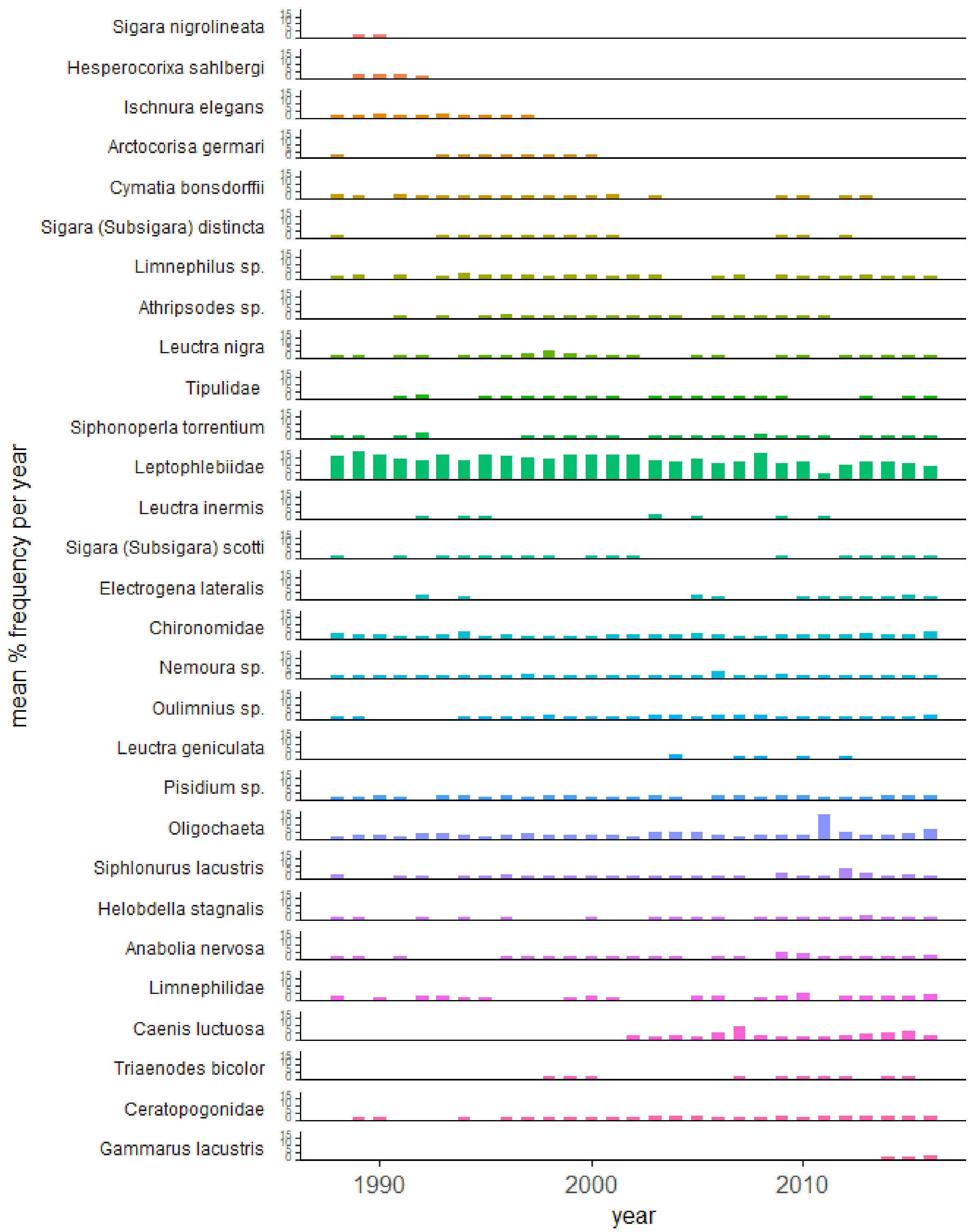
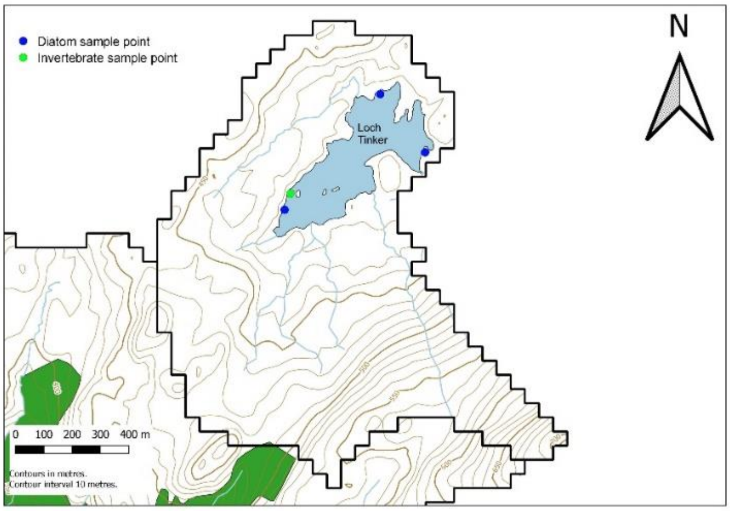


Figure 5.4 Loch Chon: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 2% of the assemblage in any year.

6. Loch Tinker

6.1 Loch Tinker site description

Loch Tinker lies in a non-forested peaty moorland catchment to the east of Loch Chon but at significantly higher altitude. The two sites have been used as a experimental / control pair to examine the influence of forestry on acidification (Kreiser et al. 1990) and other aspects of water quality. In that study, pH reconstruction using the fossil diatom assemblage of sediment cores suggested that the loch had acidified from around pH 6.5 in the mid-19th century, to around pH 5.5 by the early 20th century, since when it had remained relatively stable. This is a rather unusual chronological pattern for acidified lakes in the UK, the majority of which exhibit steady or accelerated acidification during the 20th century that roughly parallels the increase in the acid deposition load. Much of the change in the fossil assemblage is driven by a reduction in the planktonic species *Cyclotella kuetzingiana*. There has been no physical disturbance within the catchment of the loch during the monitoring period.



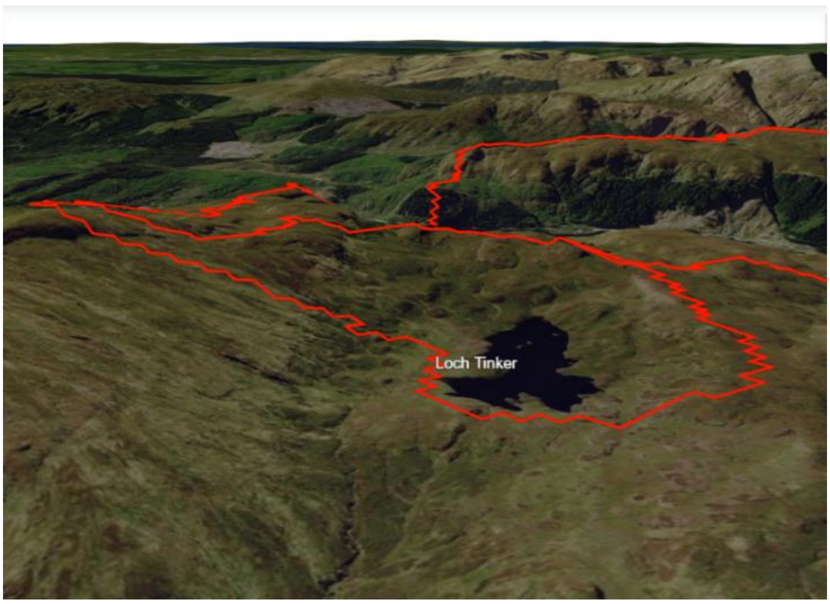


Figure 5.1 Mapped and aerial views of the Loch Tinker catchment

Table 6.1 Loch Tinker site characteristics

Grid Reference	NN 445068	
Lake altitude	420 m	
Maximum altitude	705 m	
Maximum depth	25 m	
Mean depth	9.8 m	
Volume	4.0 x 10^5 m^3	
Lake area	11.3 ha	
Catchment area	123.3 ha	
Catchment area (excl.lake)	112 ha	
Catchment:Lake ratio	9:9	
Catchment geology	Mica schist and grits	
Catchment soils	Blanket peats	
Catchment vegetation	Moorland	
Mean annual runoff (precipitation – evaporation)	2179 mm	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	23.9	12.1
Non-marine oxidised sulphur	17.0	3.6
Oxidised nitrogen	10.3	5.5
Reduced nitrogen	22.8	9.8

Table 6.2 Loch Tinker water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	54.2	19.7	70.8	166.8	39.6	11.4	-1.10	**
xSO_4^{2-}	µeq l^{-1}	35.6	6.2	49.6	134.6	18.0	2.6	-0.95	**
Cl^-	µeq l^{-1}	139.6	118.8	440.1	370.0	90.3	71.7	-0.49	*
NO^{3-}	µeq l^{-1}	2.1	2.1	6.0	5.3	2.1	2.1	0.00	*
pH	pH	6.2	6.3	6.6	7.4	5.4	5.5	0.00	
Alk	µeq l^{-1}	30.5	52.0	96.0	798.0	-2.0	5.1	0.12	
Cond	µS cm^{-1}	30.5	27.2	62.0	133.6	21.0	18.6	-0.16	**
Na^+	µeq l^{-1}	132.7	115.7	321.9	380.2	91.4	78.7	-0.64	**
Ca^{2+}	µeq l^{-1}	82.3	70.8	126.7	548.9	49.9	48.9	-0.50	**
Mg^{2+}	µeq l^{-1}	42.4	38.0	87.2	306.0	31.3	22.7	-0.32	**
K^+	µeq l^{-1}	6.9	6.6	18.2	20.1	2.6	3.2	0.00	
Lab Al	µg l^{-1}	2.0	2.0	14.0	5.0	2.0	1.0	0.00	
DOC	mg l^{-1}	4.0	5.1	7.4	10.9	1.9	1.9	0.04	**
ANC-CB	µeq l^{-1}	59.0	77.8	162.2	775.9	10.4	26.3	0.36	

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

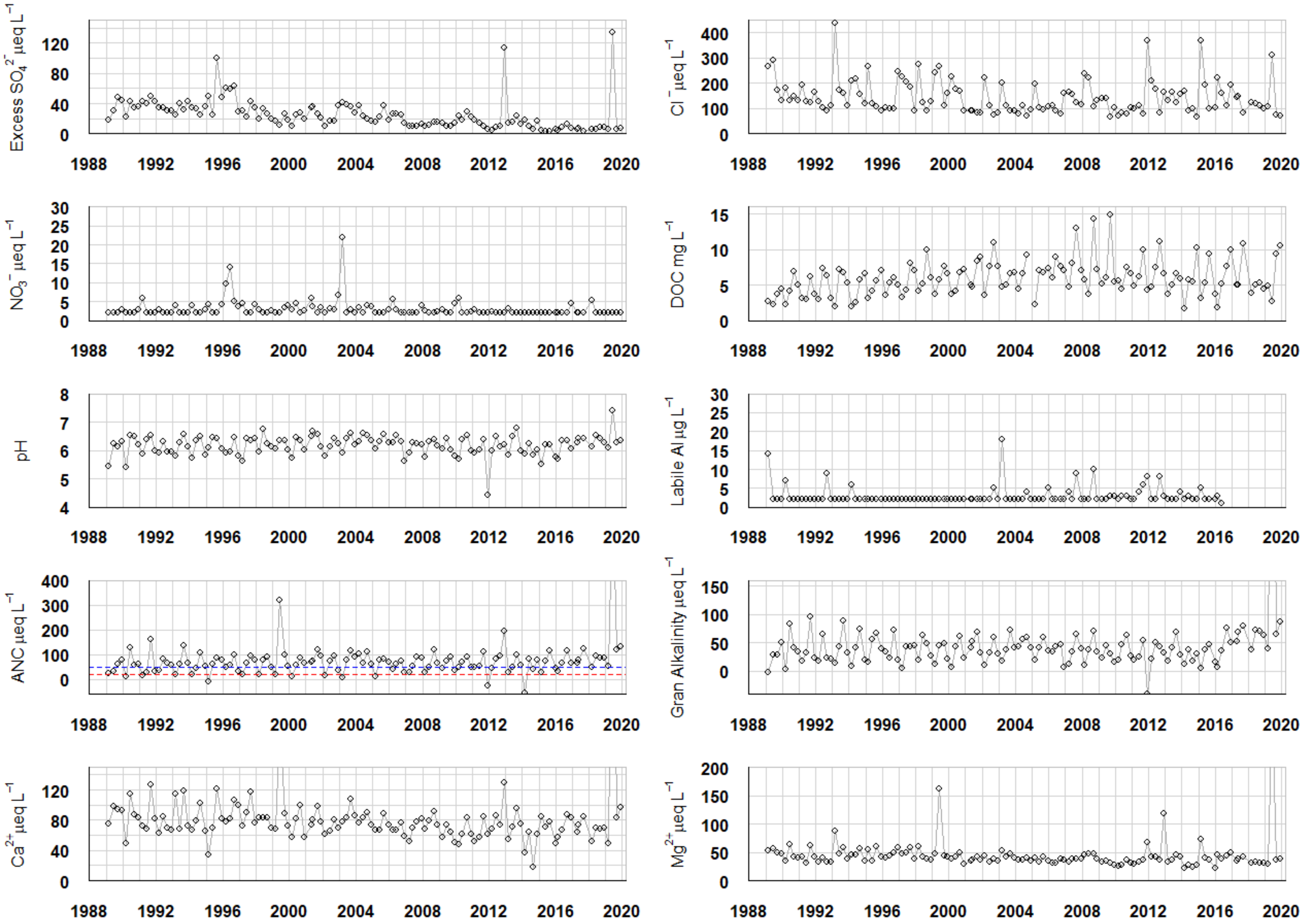


Figure 6.2 Loch Tinker water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

6.2 Loch Tinker: water chemistry trends

Despite receiving significantly lower atmospheric inputs of acidity than the neighbouring, and afforested, Loch Chon, and exhibiting lower concentrations of acid anions, the slightly higher concentrations of calcium and magnesium, and considerably higher levels of Gran Alkalinity, demonstrate that Loch Tinker has been much better protected against acidification. While concentrations of non-marine sulphate, chloride and nitrate have all fallen significantly, the reduction is balanced by similar reductions in base cations and there has therefore been no detectable long-term directional effect on loch water pH, Gran Alkalinity or ANC, while labile aluminium concentrations remained mostly below the limit of detection until measurements ceased in 2016. Despite this, Gran Alkalinity shows the same short-term rise seen in other Scottish sites from around 2016 and attributed to the influence of drought.

In common with Loch Chon, chloride concentrations exhibit both substantial between sample variability, a function of substantial sea salt inputs, and a long term downward trend as a consequence of the decline in hydrochloric acid deposition. Nitrate concentrations are mostly below the limit of detection but were elevated during the relatively cold winter and spring of 1996. Relatively high concentrations of DOC in Loch Tinker reflect the peat dominated catchment of Loch Tinker, and they have risen substantially over the monitoring period, by far the most significant chemical change in Loch Tinker over the 30 years.

As is the case throughout the network, the increase in DOC appears to be tightly linked to the reduction in pollutant deposition to the catchment soils. The absence of trends in acidity over the monitoring period therefore provide an opportunity to consider the potential ecological importance of an increase in DOC per se. Median DOC has increased from 4.0 to 5.1 mg L^{-1}. This is estimated to have reduced the percentage of the lake bed within the photic zone from around 90% to 70%, and during late summer DOC peaks, from around 70% to 40% of the bed (Monteith pers. comm.). The lack of evidence for a major acidification recovery response in the water chemistry record, despite moderate levels of buffering, brings into question the palaeoecological inferences discussed in Section 6.1., and whether the key shift in the diatom assemblage (i.e. the loss of the planktonic *Cyclotella* species) may actually be more closely linked to changes in dissolved organic matter and/or water transparency than a change in pH.

6.3 Loch Tinker: epilithic diatom community trends

Compared to the nearby Loch Chon, changes in the diatom community at Loch Tinker are modest, with a turnover of only 0.89. The record has been dominated by *Brachysira vitrea* (SWAP pH optimum = 5.9) and *Achnanthes minutissima* (optima = 6.3) with lesser numbers of *Brachysira brebissonii* (optimum = 5.3), and *Frustulia rhomboides* var. *saxonica* (optimum = 5.2) throughout. The overall community level trend is significant but the overall effect of the trend (i.e. variance accounted) is relatively small at just over 50% (RDA1/PCA1, Main Report: Table 4.1). The appearance and sustained occurrence, albeit at low numbers, of *Cymbella microcephela* is one of the few taxon-specific significant trends (Appendix: Figure 6.3).

There are no significant relationships between diatom assemblage change and pH or other water chemistry variables but there is a significant but small uniform increase in the DAM score over the sampling period. This probably reflects the increase in *Cymbella microcephela* and slightly greater abundance of the acid sensitive *Achnanthes minutissima* from around 2000. In summary, there is some evidence for subtle changes in the diatom flora that are consistent with a subtle changes in water chemistry (e.g. rising DOC) but additional data is needed to confirm this.

6.4 Loch Tinker: macroinvertebrate community trends

The absence of any trend in acidity in Loch Tinker is reflected in the lack of a temporal trend in the macroinvertebrate LAMM diagnostic index of acidification impacts ((Main Report: Figure 5.3 and Table

5.2)). However, there have been significant changes in the macroinvertebrate community, particularly between 1988 and 2000 when the relative abundance of Oligochaeta (aquatic worms) and *Pisidium* (bivalve Mollusca) declined while that of a range of caddisflies and Chironomidae (non-biting midges) increased (Appendix: Figure 6.4). There has also been a gradual but continual increase in taxon richness right up to 2016. Whether this could be linked to the increased inputs of dissolved organic matter and associated nutrients requires further exploration.

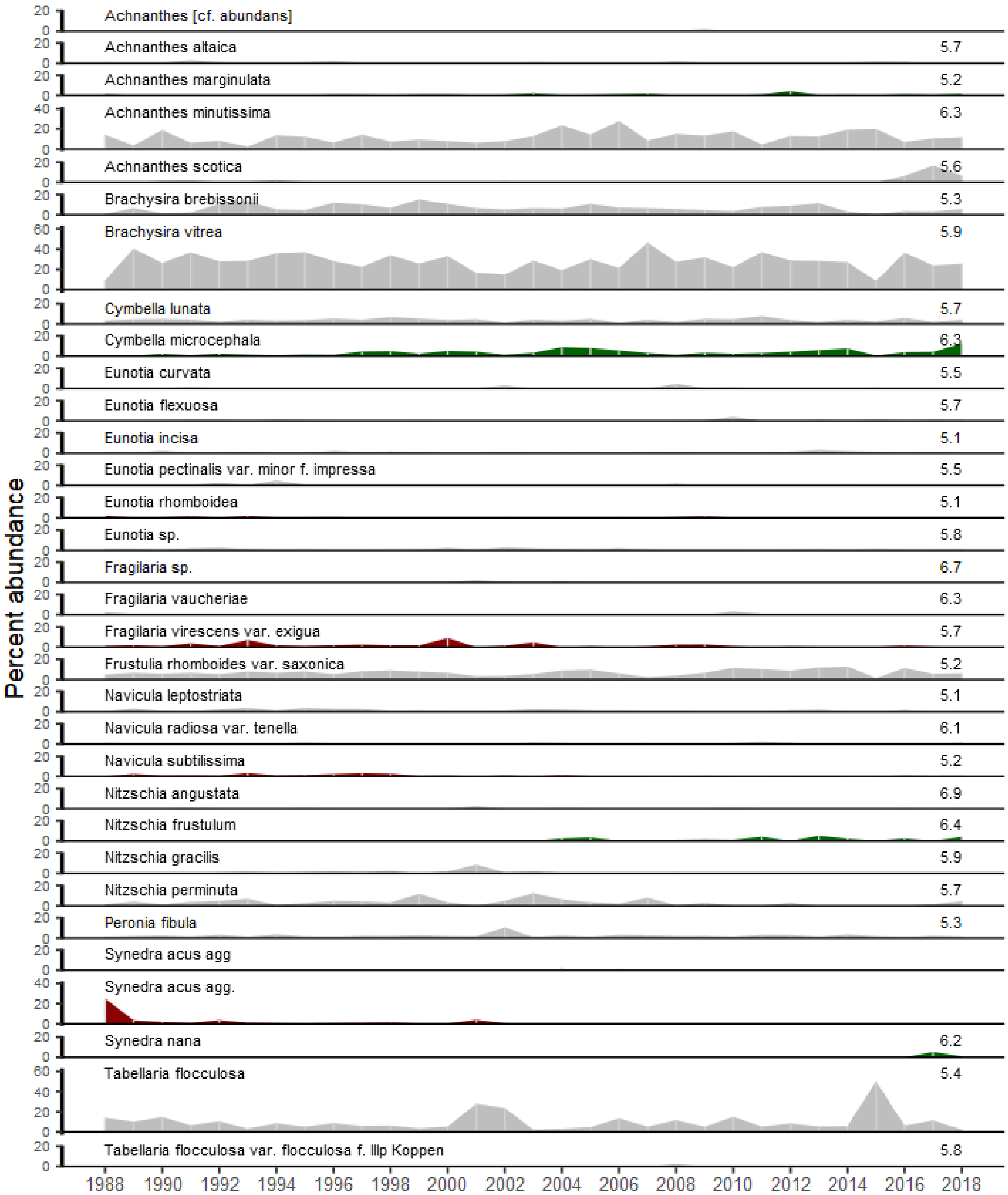


Figure 6.3 Loch Tinker: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

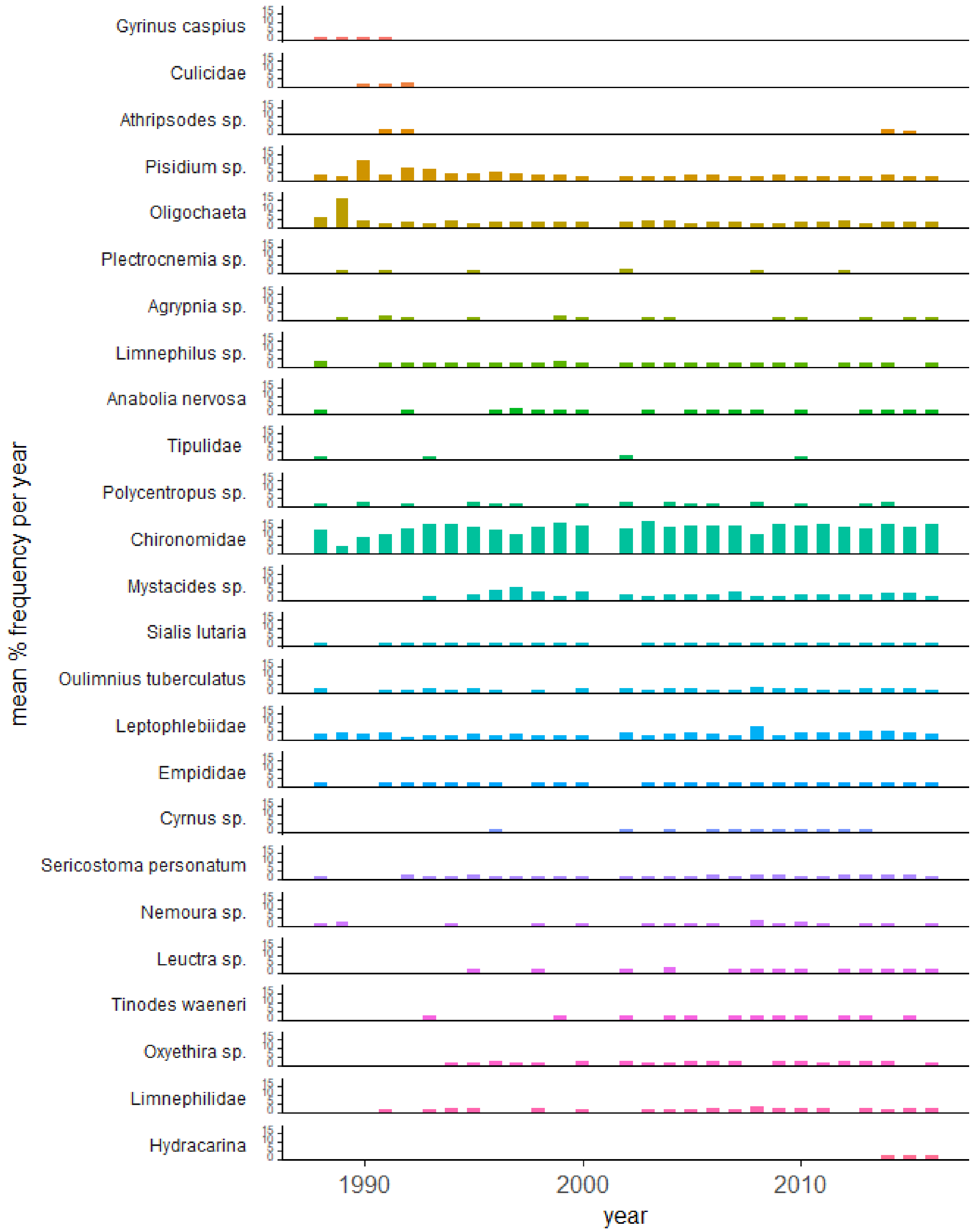


Figure 6.4 Loch Tinker: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

7. Round Loch of Glenhead

7.1 Site description

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

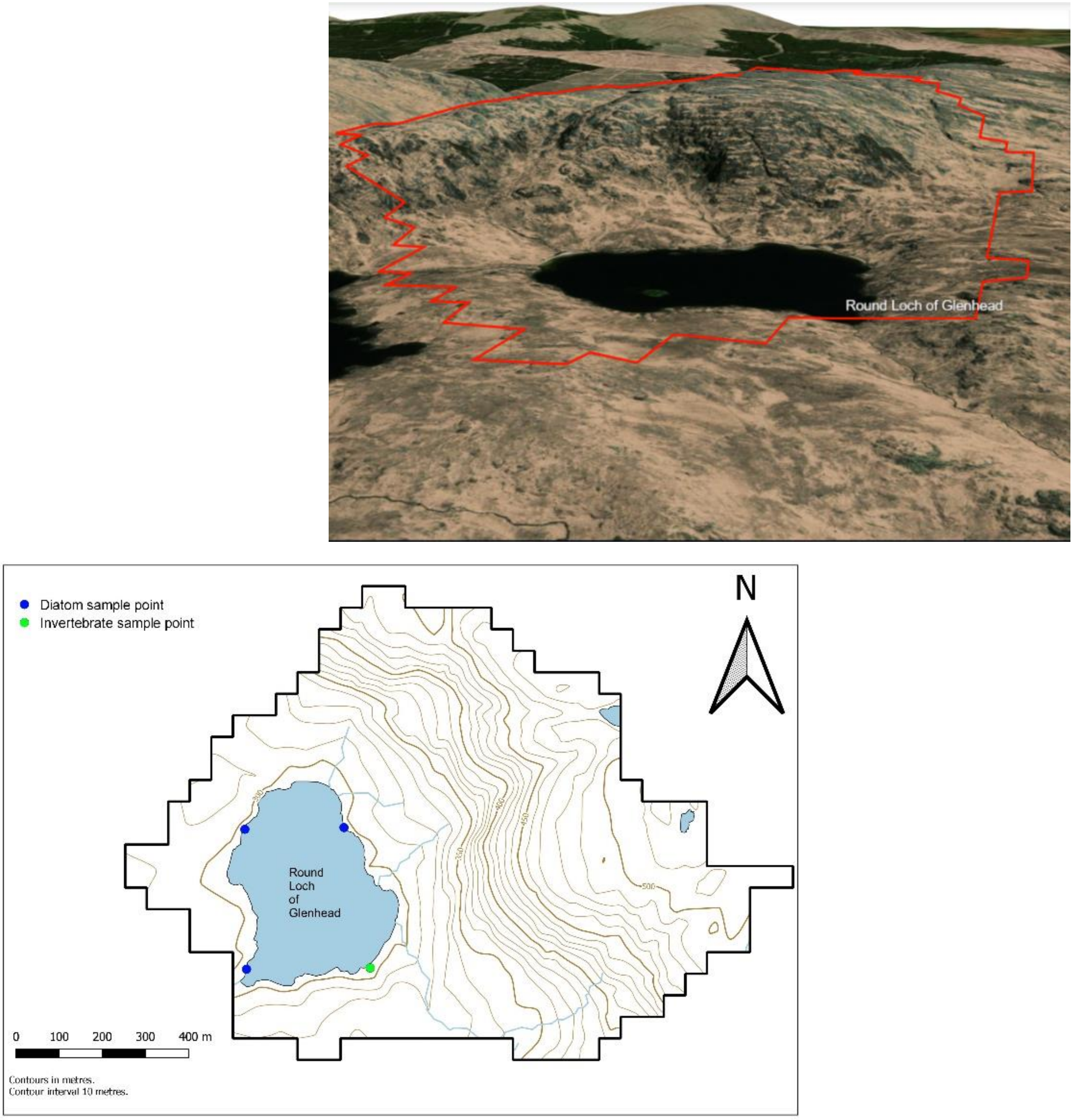


Figure 7.1 Mapped and aerial views of the Round Loch of Glenhead catchment

Table 7.1 Round Loch of Glenhead site characteristics

Grid Reference	NX 450804	
Lake altitude	295 m	
Maximum altitude	525 m	
Maximum depth	13.5 m	
Mean depth	4.28 m	
Volume	5.3 x 10^5 m^3	
Lake area	12.5 ha	
Catchment area	107.6 ha	
Catchment area (excl.lake)	95.1 ha	
Catchment:Lake ratio	7:5	
Catchment geology	Tonalite, tonalite/granite	
Catchment soils	Peat, peaty podsols	
Catchment vegetation	Moorland	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	28.2	11.1
Non-marine oxidised sulphur	19.9	4.1
Oxidised nitrogen	10.9	5.4
Reduced nitrogen	28.9	14.3

Table 7.2 Round Loch of Glenhead water chemistry statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope $year^{-1}$**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	69.8	25.9	87.5	38.1	58.3	16.5	-1.50	**
xSO_4^{2-}	µeq l^{-1}	46.2	9.0	63.0	20.2	36.1	5.6	-1.29	**
Cl^-	µeq l^{-1}	225.7	157.5	299.0	257.9	135.4	104.4	-0.82	**
NO^{3-}	µeq l^{-1}	5.0	9.8	9.0	23.4	2.1	2.1	0.06	**
pH	pH	4.9	5.4	5.2	5.7	4.7	4.9	0.01	**
Alk	µeq l^{-1}	-12.0	7.7	-3.0	18.0	-22.0	-9.3	0.52	**
Cond	µS cm^{-1}	39.5	28.7	49.0	41.6	28.0	20.4	-0.28	**
Na^+	µeq l^{-1}	193.6	145.0	248.0	216.1	139.2	104.0	-0.96	**
Ca^{2+}	µeq l^{-1}	36.4	24.1	41.9	31.2	25.0	20.2	-0.29	**
Mg^{2+}	µeq l^{-1}	48.5	35.2	61.7	55.1	32.9	28.1	-0.26	**
K^+	µeq l^{-1}	7.9	6.6	12.8	8.7	2.6	3.7	-0.03	**
Lab Al	µg l^{-1}	69.5	16.5	111.0	28.0	32.0	11.0	-0.23	
DOC	mg l^{-1}	2.8	4.7	3.7	6.5	1.9	2.6	0.05	**
ANC-CB	µeq l^{-1}	-13.3	17.3	14.7	32.8	-67.1	-13.9	0.81	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

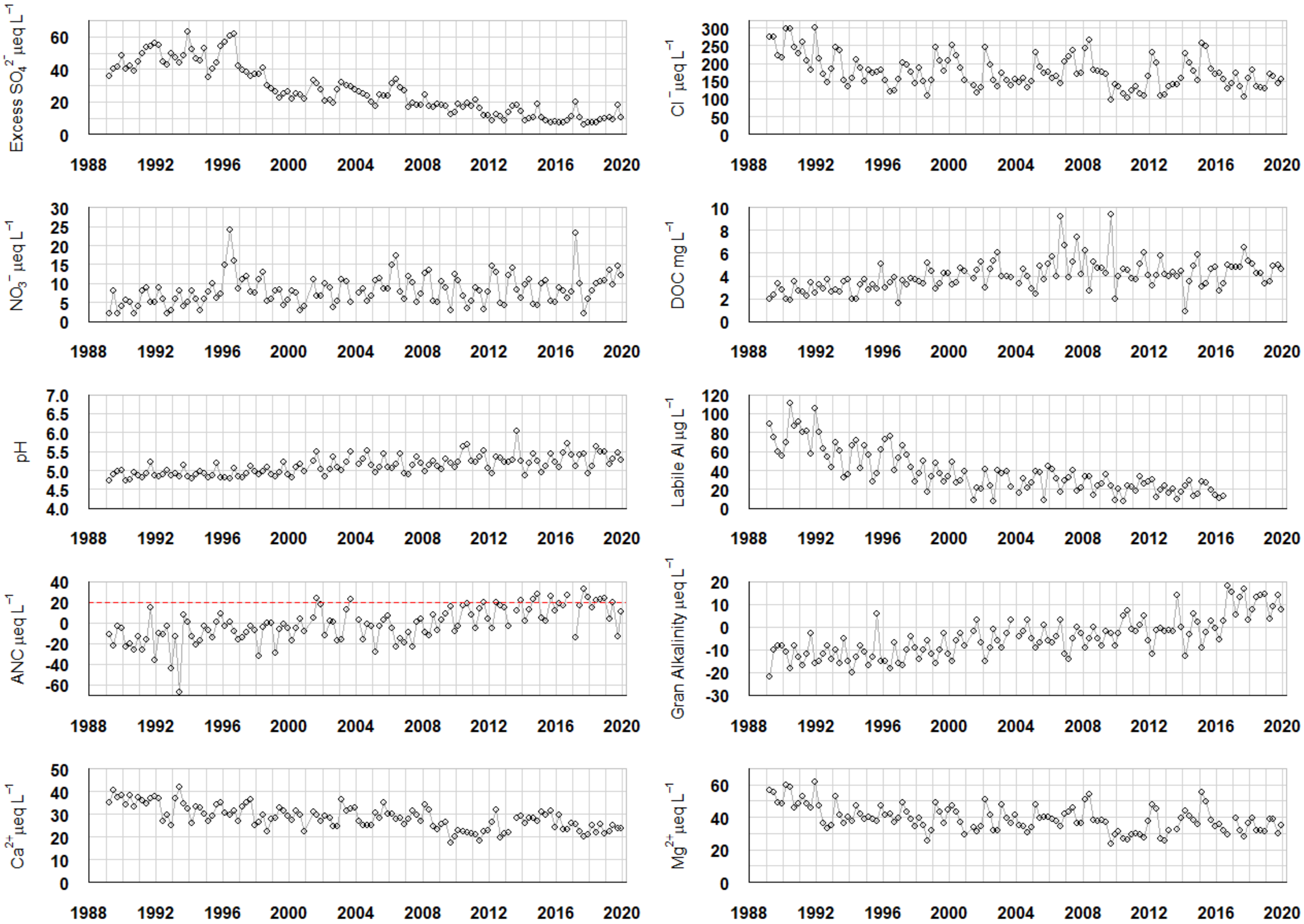


Figure 7.2. Round Loch of Glenhead water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

7.2 Round Loch of Glenhead: water chemistry trends

Concentrations of non-marine sulphate in the Round Loch of Glenhead fell from a 1989-1993 median of 46.2 µeq L^{-1} to 9.0 µeq L^{-1} by 2015-2019, a similar fall proportionally to the reduction in the CBED estimate for non-marine sulphur deposition. Chloride concentrations (in terms of equivalence) declined by about two thirds of the reduction in non-marine sulphate. In contrast, and despite the CBED estimate for a major decline in reduced and oxidized nitrogen deposition, nitrate concentrations rose over the first decade of monitoring and have remained relatively high throughout the year, so that nitrate currently makes a similar contribution to residual acidity to that of the historically dominant anion, i.e. non-marine sulphate. Inter-annual fluctuations in nitrate concentrations in UWMN surface waters have previously been linked to variation in the North Atlantic Oscillation (Monteith et al., 2000); nitrate concentrations tend to peak in the spring, and higher annual peaks tend to follow colder and drier winters.

The Round Loch of Glenhead was one of the most acidic and acidified sites on the monitoring network when monitoring was initiated, but despite the increase in nitrate, the much larger combined decline in non-marine sulphate and chloride has driven a considerable reduction in acidity over the past three decades. Between the first and most recent five-year periods, the pH of the loch increased from a median of 4.9 to 5.4, labile aluminium concentrations fell from highly toxic to relatively benign levels (until measurements ceased in 2016), and ANC shifted from being almost permanently negative to mostly positive, with recent levels oscillating mostly between 0 and 30 µeq L^{-1}. Over the same period, the already low calcium concentrations have fallen by about one third, and magnesium and electrical conductivity by a quarter. As a consequence of the reduction in ion deposition, median DOC concentrations have risen sharply, from 2.8 to 4.7 mg L^{-1}, and this will have had a significant impact on the light environment of the loch. On the basis of a relationship previously established between DOC concentration and the depth of penetration of photosynthetically active radiation (PAR) (Monteith pers. comm.), the increase in DOC is estimated to have reduced the photic depth of the loch (i.e. the depth at which photosynthesis is sustainable) from around 10 to 6 metres.

7.3 Round Loch of Glenhead: epilithic diatom community trends

The epilithic diatom community of the Round Loch of Glenhead has undergone substantial change during the monitoring period (Appendix: Figure 7.3). Over the first two decades the assemblage was dominated by the acidobiontic species *Tabellaria quadriseptata* (SWAP pH optimum = 4.9) and to a lesser extent *Eunotia incisa* (optimum = 5.1). In the late 1990s, the assemblage gradually transitioned to one increasingly dominated by *Navicula leptostriata* (optimum = 5.1) - changes consistent with a response to reduced acidity. Rather surprisingly, however, *Navicula leptostriata* then declined from around 2010, while T*abellaria quadriseptata* and *Eunotia incisa* increased again, although the increase in these low pH optima taxa has been accompanied by an increase in *Tabellaria flocculosa* (optimum = 5.4).

Numerical analysis indicates that the trends in several of these species are significant, as is the overall community-level trend. The effect size of the trend (RDA1/PCA1) is 54%, and overall turnover is 0.99. Together, these results indicate a significant but modest species replacement over the sampling period. Both DAM and RDA1-pH (Main Report: Table 4.1) indicate the trends in diatom assemblage change are significantly related to pH, but the effect is small with pH accounting for only 19% of the explainable variance in the diatom data. Change in lake-water DOC explains a significant unique fraction of variance in the diatom data, suggesting a response to DOC independent of pH at this site.

Overall, the diatom data suggests a modest recovery that is consistent with the modest decrease in acidity recorded in the water chemistry. However, the return of significant proportions of *Tabellaria quadriseptata* since 2010 is currently unexplained.

7.4 Round Loch of Glenhead: macroinvertebrate community trends

There is an unambiguous signal of recovery from acidification in the macroinvertebrate community at Round Loch of Glenhead, consistent with the improvement in water chemistry. LAMM scores have increased from very low levels in the early 1990s to levels close to those seen in unimpacted clear water lakes by 2016 (Main Report: Figure 5.3 and Table 5.2). While the loch remains relatively acidic, its macroinvertebrate community features increasing numbers of acid-sensitive taxa such as the shell forming freshwater snail *Radix balthica,* the bivalve mollusc *Pisidium*, and the acid-sensitive mayfly *Siphlonurus lacustris*.

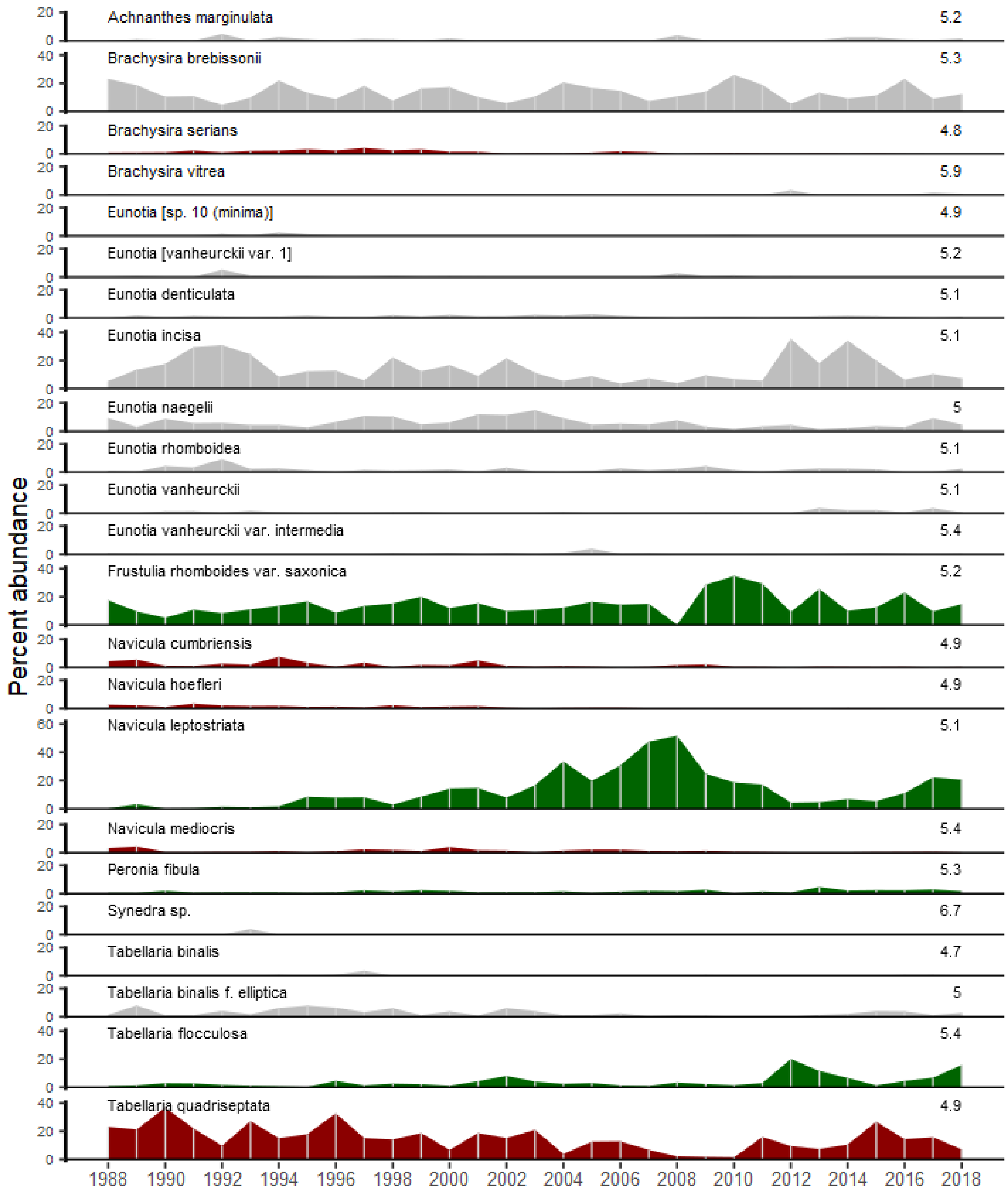


Figure 7.3 Round Loch of Glenhead: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species

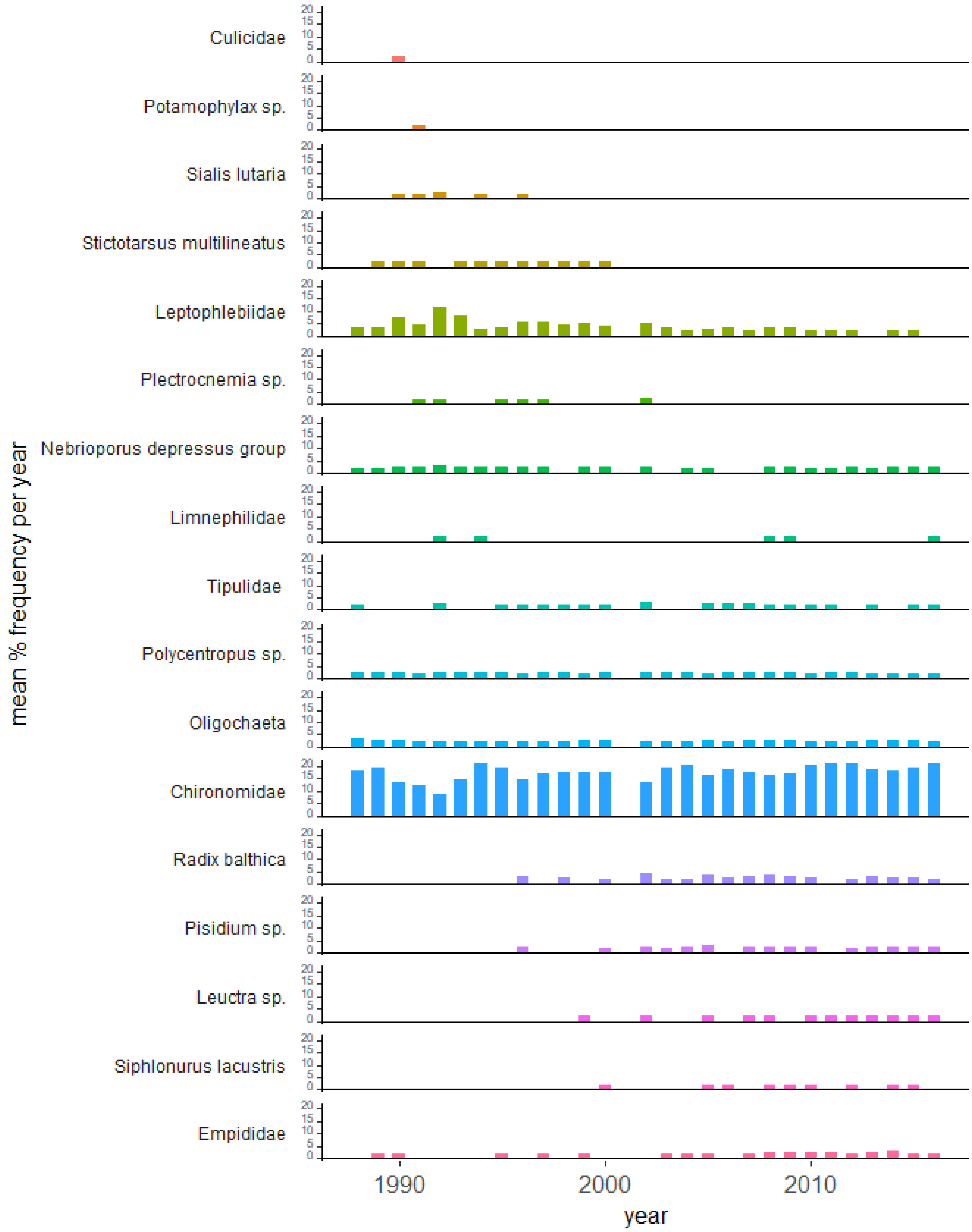
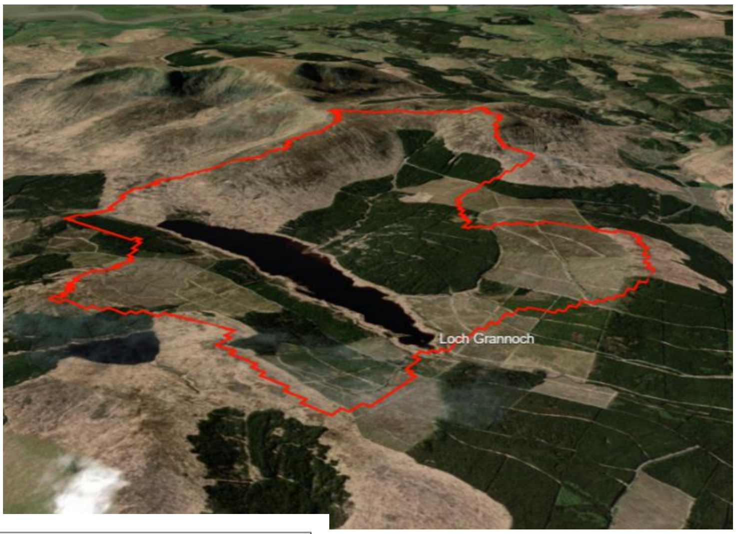


Figure 7.4 Round Loch of Glenhead: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

8. Loch Grannoch

8.1 Loch Grannoch site description

Loch Grannoch is a large loch in the Galloway region of southwest Scotland. In contrast to the neighbouring site, Round Loch of Glenhead, a large proportion of the catchment is under managed coniferous forest, part of which is approaching maturity. Flower et al. (1990) observed a floristic difference between the diatom assemblage of a surface sediment sample, taken in 1988, and that of the upper layers of a sediment core taken two years previously. This was attributed to phosphorus and potassium fertiliser application in the catchment which peaked in 1985 and is likely to have raised nutrient levels in the Loch. The Loch Grannoch catchment comprises two forests, Round Fell on the west side and Fleet Basin to the east, both of which lie within the Forestry Commission's Galloway Forest District. The forests have separate design plans, with both seeking to lower the tree line below 300 m, partly to reduce the pollutant scavenging effect but also to improve foraging habitat for raptors. Significant areas of native broadleaved woodland will be planted to form riparian buffer zones along the main inflowing streams. The net effect of these changes will be to reduce the proportion of conifer cover from 64% in the 1980s to 29% by 2050, There has been a significant amount of felling in the catchment on the eastern side and northern end over the last decade.



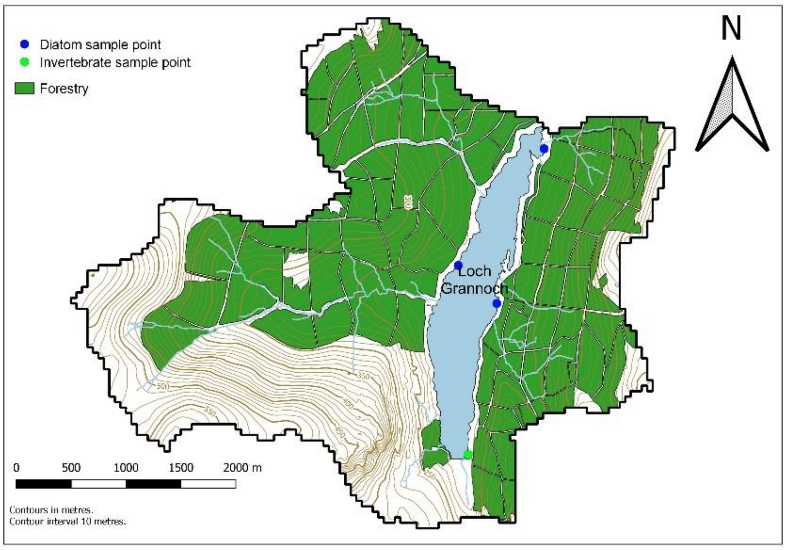


Figure 8.1 Mapped and aerial views of the Loch Grannoch catchment

Table 8.1 Loch Grannoch site characteristics

Grid Reference	NX 542700	
Lake altitude	210 m	
Maximum altitude	585 m	
Maximum depth	20.5 m	
Mean depth	6.4 m	
Volume	7.4 x 10^6 m^3	
Lake area	114.3 ha	
Catchment area	1401.3 ha	
Catchment area (excl.lake)	1287 ha	
Catchment:Lake ratio	11:3	
Catchment geology	Granite	
Catchment soils	Peats, peaty podsols, peaty gleys, skeletal soils	
Catchment vegetation	Conifers – 70% Moorland – 30%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	29.0	12.2
Non-marine oxidised sulphur	20.7	4.8
Oxidised nitrogen	14.8	7.4
Reduced nitrogen	39.0	18.1

Table 8.2 Loch Grannoch water chemistry statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	98.9	33.4	129.1	53.8	79.2	18.1	-2.29	**
xSO_4^{2-}	µeq l^{-1}	71.2	11.0	106.3	36.4	52.0	4.7	-2.02	**
Cl^-	µeq l^{-1}	273.6	203.2	426.0	332.1	189.0	128.9	-1.56	**
NO^{3-}	µeq l^{-1}	9.0	7.8	33.0	13.4	2.1	4.3	-0.21	**
pH	pH	4.6	5.0	4.9	6.1	4.4	4.6	0.01	**
Alk	µeq l^{-1}	-25.0	2.9	0.0	39.2	-46.0	-26.6	0.81	**
Cond	µS cm^{-1}	52.5	36.4	78.0	57.6	31.0	14.9	-0.49	**
Na^+	µeq l^{-1}	234.9	185.6	313.2	270.5	182.7	149.2	-1.19	**
Ca^{2+}	µeq l^{-1}	53.4	40.5	62.4	55.4	38.4	28.5	-0.33	**
Mg^{2+}	µeq l^{-1}	57.2	47.5	75.7	63.4	41.1	35.9	-0.22	**
K^+	µeq l^{-1}	5.4	7.2	10.7	13.8	2.6	3.2	0.10	**
Lab Al	µg l^{-1}	201.0	51.0	552.0	70.0	125.0	38.0	-0.66	
DOC	mg l^{-1}	3.6	9.2	5.5	19.7	2.9	5.7	0.16	**
ANC-CB	µeq l^{-1}	-43.0	26.9	-1.5	100.6	-83.1	-6.6	2.36	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

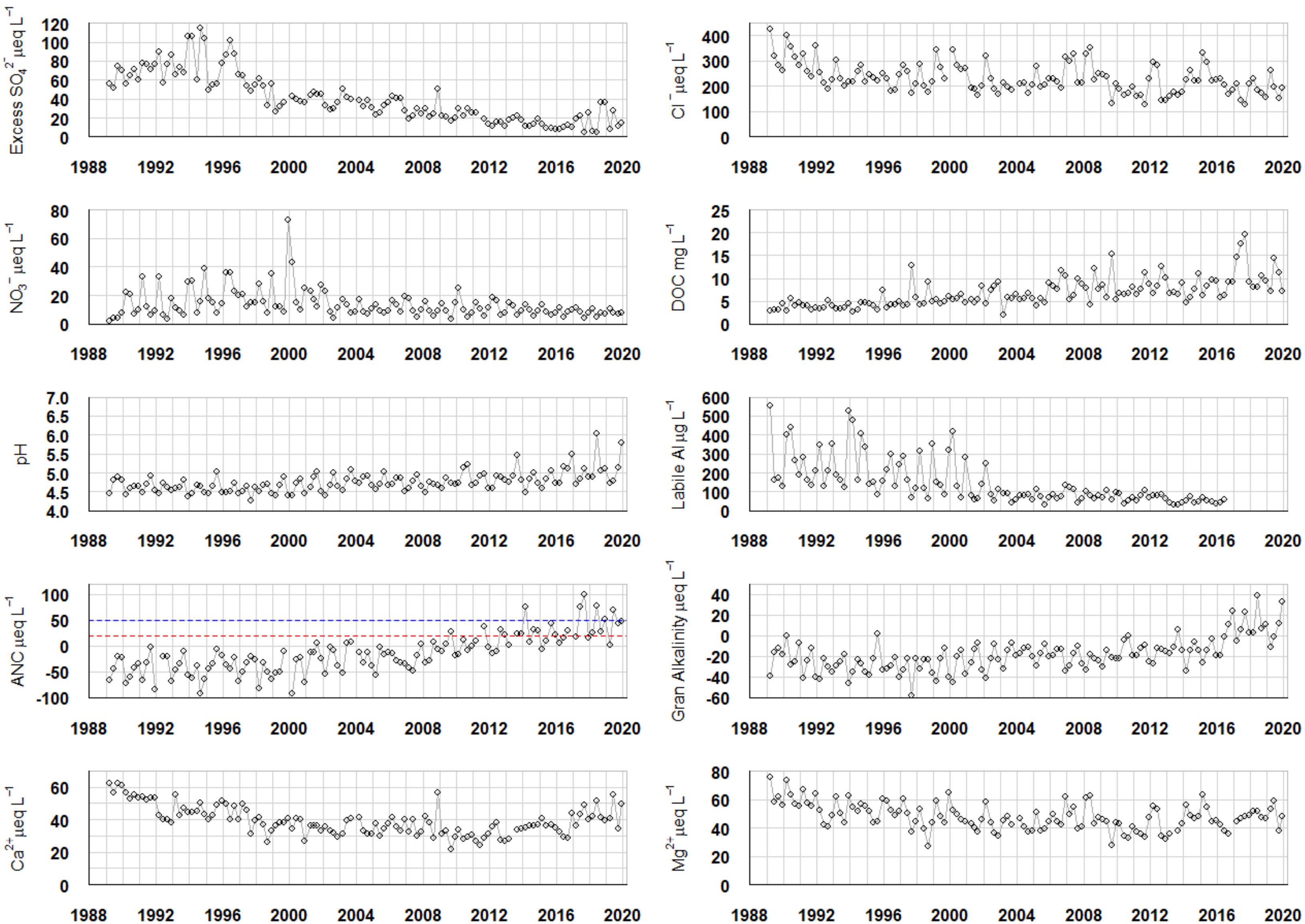


Figure 8.2. Loch Grannoch water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

8.2 Loch Grannoch: water chemistry trends

The presence of a forest canopy over much of the Loch Grannoch catchment has caused both greater loads of acid deposition historically, and greater rates of deposition decline over the past 30 years, relative to the neighbouring Round Loch of Glenhead. Non-marine sulphur deposition is estimated by the CBED model to have declined by approximately 75% from 1990-2017, and this is reflected in an 84% reduction in the loch water concentration of non-marine sulphate, with median concentrations over 2015-2019 around two thirds that experienced by the low deposition “control” site Loch Coire nan Arr at the onset of monitoring.

Chloride concentration has fallen at a slightly slower rate than non-marine sulphate, a consequence of the reduction in hydrochloric acid deposition, and in contrast to most Scottish sites, nitrate concentration has also fallen significantly over the three decades, despite it climbing over the first decade. Importantly, the seasonal nitrate concentration pattern has changed over time from year-round leaching over the first two decades, indicative of nitrogen saturated catchment soils, to seasonal leaching, where nitrate is retained during the growth season, and since 2016, nitrate concentrations have been approaching the limit of detection. These reductions in nitrate leaching have occurred despite the considerable physical disturbance in the catchment associated with felling and other forest management that can often exacerbate surface water concentrations.

The large reduction in acid anion inputs have resulted in a substantial reduction in loch water acidity. Over the first 15 years of monitoring, concentrations of labile aluminium frequently exceeded 200 µg L^{-1}, a level likely to impose acute toxicity to salmonids and a wide range of acid sensitive macroinvertebrates, with the highest concentrations associated with periods of significant sea salt inputs. By around 2004, labile aluminium concentrations had dropped to more stable levels of circa 100 µg L^{-1}, and by 2016, when aluminium measurements were curtailed, concentrations were averaging around 50 µg L^{-1}. Between the first and most recent five-year period, loch water pH rose from 4.6 to 5.0 and ANC from -43.0 to 26.9. In recent years loch water ANC has been positive in most samples but is still occasionally recorded at below 20 µeq L^{-1}. Consequently, while the water chemistry of Loch Grannoch has undergone one of the most spectacular recoveries of all sites on the network, it remains in a significantly acidified state.

Concentrations of DOC have almost trebled, rising by a remarkable rate of 1.6 mg L^{-1} per decade. The sharp rate of increase is likely due to multiple factors, but primarily the particularly rapid reduction in pollutant deposition to this forested catchment that has increased the solubility of soil organic matter. Rates of reduction in ion inputs will also have been enhanced by the partial removal of the canopy over recent years, as this will have brought down pollutant and sea salt interception rates further. Finally forest disturbance is known to exacerbate DOC concentrations in runoff, partly by increasing inputs of low molecular weight, non-coloured compounds. Regardless of sources however, secchi disc transparency of Loch Grannoch has fallen consistently over the monitoring period, from over 3 metres in the early years of monitoring to less than 2 metres by 2013 (Shilland pers. comm.).

8.3 Loch Grannoch: epilithic diatom community trends

The epilithic diatom assemblages of Loch Grannoch have shown considerable fluctuations in species representation (Appendix: Figure 8.3). Initiallly the assemblage was dominated by *Eunotia exigua* (SWAP pH optimum=5.1), *Eunotia incisa* (optimum = 5.1), *Achnanthes* [*altaica* var. *minor*] (optimum = 4.9), *Frustulia rhomboides* var. *saxonica* (optimum = 5.2) and *Pinnularia subcapitata var. hilseana* (optimum = 5.0). After 1993, the acidobiontic species *Tabellaria quadriseptata* (optimum = 4.9) became temporarily dominant until 2006, a change most likely associated with a temporary increase in nitrate and consequent reduction in pH. Floristic changes in the upper levels of a sediment core collected from Loch Grannoch in the late 1980s had been attributed to the influence of fertilizer applied to sections of the forest in the mid-1980s (Flower *et al*., 1990). Representation of *Tabellaria quadriseptata* declined strongly after 2006 since when *E. incisa* has dominated the assemblage again, with lesser proportions of *Frustulia rhomboides* var. *saxonica* and *Brachysira brebissonnii* (optimum = 5.3). The post-2006 reduction in *T. quadriseptata* suggests a response to decreasing acidity. The RDA linear trend test is not significant although a test for non-linear change is ($p \leq 0.05$) (Main Report: Table 4.1). This suggests a more complex pattern of species change with a trend that reverts, in part, to a species composition characteristic of the earlier part of the record – and observation also supported by trends in the PrC scores (Main Report: Figure 4.1).

RDA-chemistry tests indicate no significant relationship between change in diatom composition and measured water chemistry (Main Report: Table 4.1). Again, however, the non-linear changes in both chemistry and the diatom assemblage are likely to have restricted the likelihood of establishing a strong correlation between spot sampled chemistry and the annual diatom samples. It is therefore possible that some of the changes in the early part of the record are not directly related to recovery from acidification, but the decrease in *T. quadriseptata* since 2006 suggests a small but significant response to declining acidity at this site in the latter half of the monitoring period.

8.4 Loch Grannoch: macroinvertebrate community trends

In contrast with its moorland pair, the Round Loch of Glenhead, the forested Loch Grannoch shows a more modest indication of biological recovery from acidification. There have been no significant increases in taxon richness and no directional change in community composition over the 28 years (Main Report: Figures 5.1 & 5.2). While increases in ANC and alkalinity exceed or equal those at the Round Loch of Glenhead, labile aluminium and H^+ concentrations have remained relatively high, and this may account for the modest rate of recovery in the macroinvertebrate community. The assemblage is dominated by aquatic worms (Oligochaeta), non-biting midges (Chironomidae), Leptophlebiidae mayflies, and a range of caddisflies and water boatmen (Corixidae). The latter group has undergone a distinct shift from relatively high representation of the acid-tolerant species, *Callicorixa wollastoni* and *Arctocorisa germari* prior to 2000, to an assemblage featuring mostly *Sigara scotti* and *S. venusta*, both also acid-tolerant. However, moderately acid-sensitive taxa such as the caddisfly, *Mystacides,* and the predatory fly family, Empididae, were beginning to appear consistently later in the time series. Recent years have also seen the appearance of the acid-sensitive freshwater snail *Potamopyrgus antipodarum* and the mayfly *Caenis* in 2015 and 2016, indicative of potential early steps towards more substantial biological recovery.

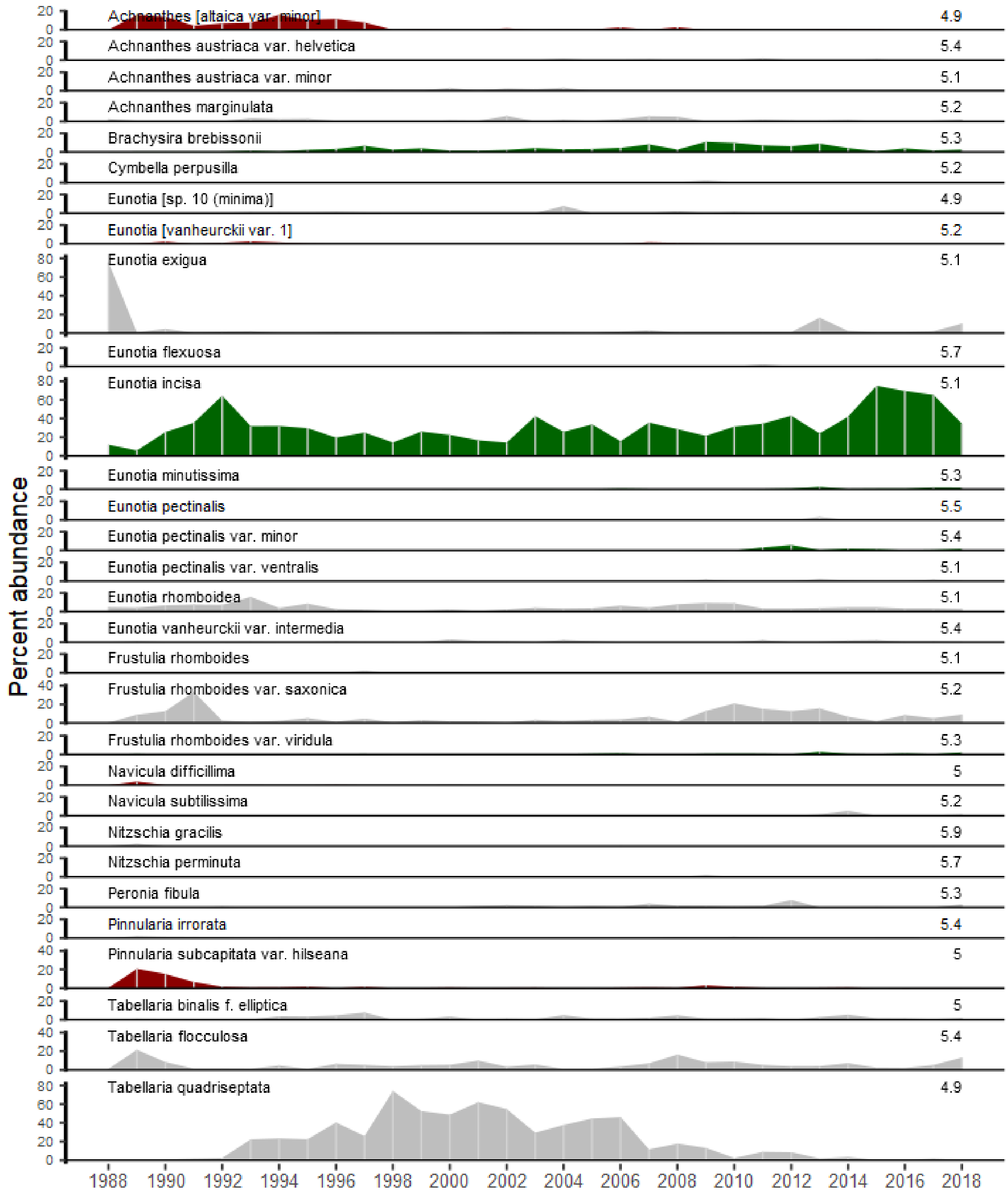


Figure 8.3 Loch Grannoch: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

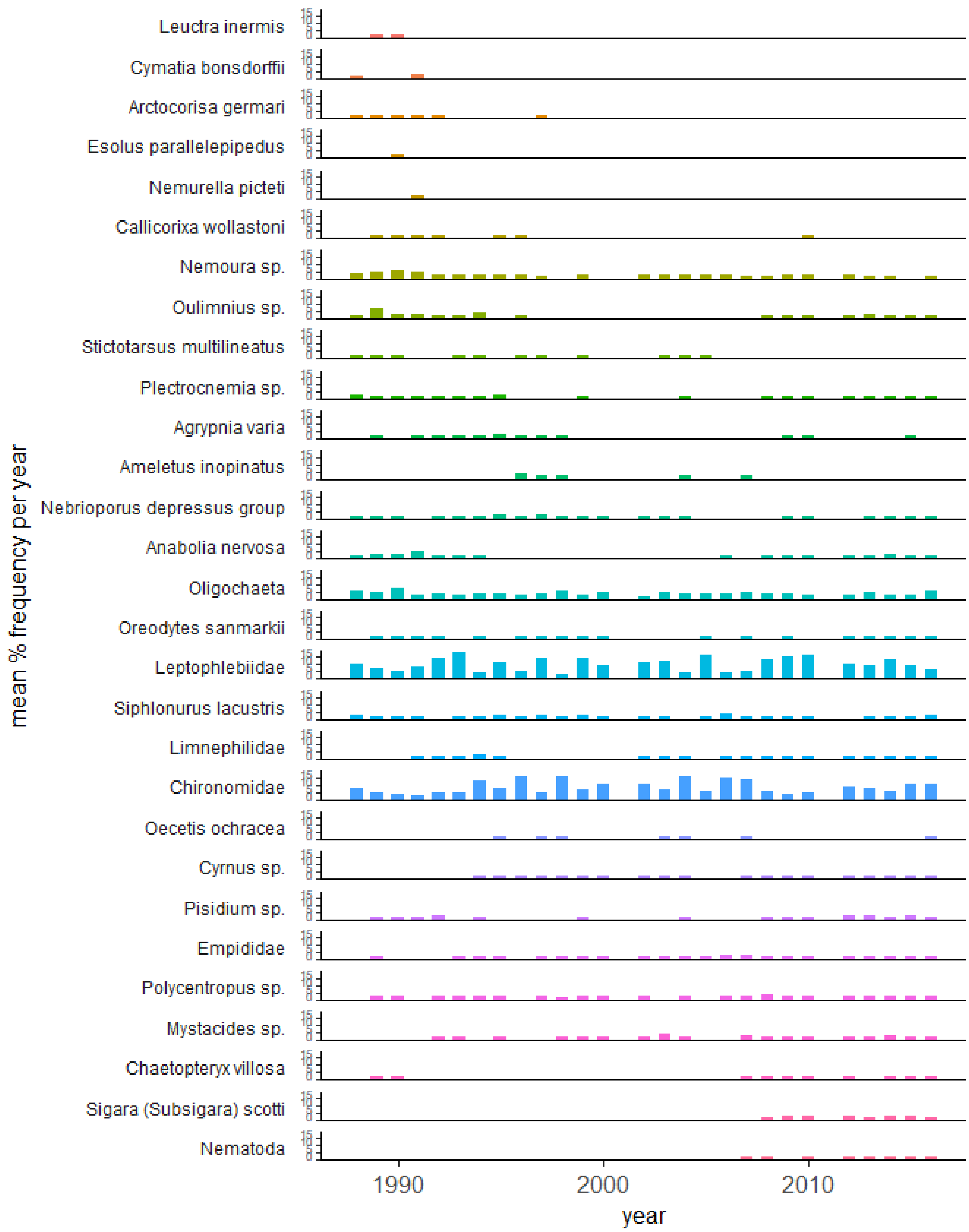
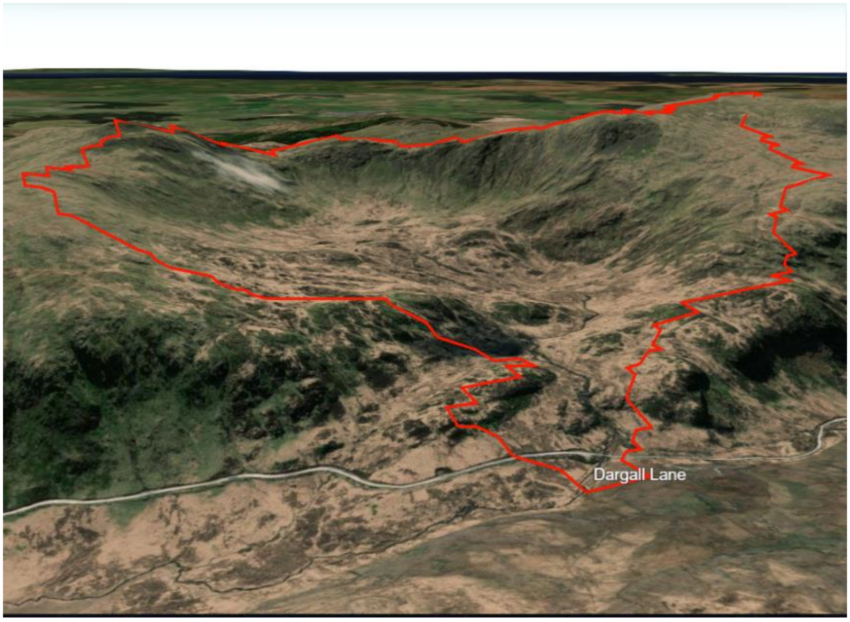


Figure 8.4 Loch Grannoch: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

9. Dargall Lane Burn

9.1 Site description

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



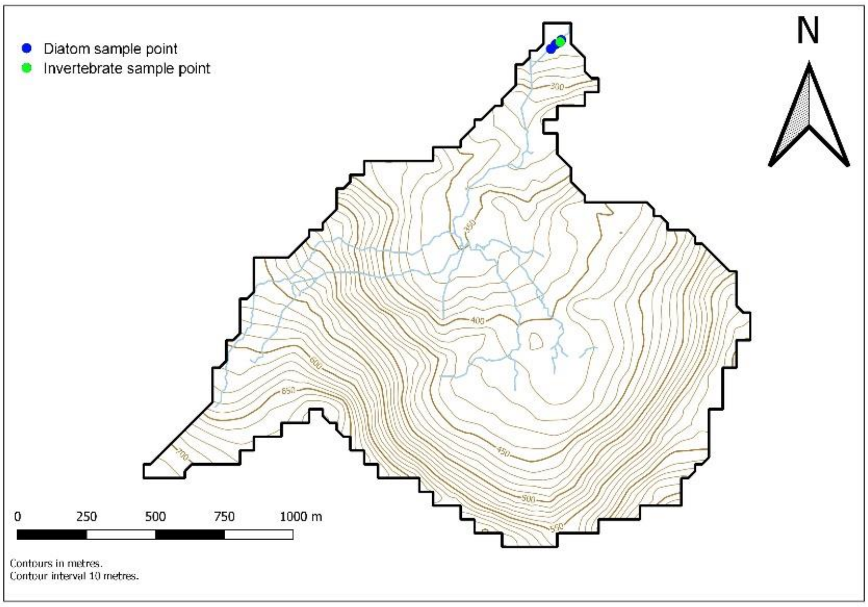


Figure 9.1 Mapped and aerial views of the Dargall Lane Burn catchment

Table 9.1 Dargall Lane Burn site characteristics

Grid Reference	NX 449786	
Catchment area	210 ha	
Minimum catchment altitude	225 m	
Maximum catchment altitude	716 m	
Catchment geology	Greywackes, shales, mudstones, black shale	
Catchment soils	Podsols, peaty gleys, blanket peat	
Catchment vegetation	moorland	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	26.5	13.1
Non-marine oxidised sulphur	18.7	4.8
Oxidised nitrogen	10.1	6.3
Reduced nitrogen	26.7	16.5

Table 9.2 Dargall Lane Burn water chemistry statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope $year^{-1}$**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	81.2	49.8	110.4	75.0	54.2	30.8	-1.23	**
xSO_4^{2-}	µeq l^{-1}	62.1	33.4	90.8	63.9	32.7	17.3	-1.01	**
Cl^-	µeq l^{-1}	200.3	143.7	366.7	306.5	115.7	79.0	-1.69	**
NO^{3-}	µeq l^{-1}	4.0	6.9	42.9	23.1	2.1	2.1	0.00	
pH	pH	5.4	6.1	6.4	6.8	4.9	5.4	0.02	**
Alk	µeq l^{-1}	0.0	24.5	41.0	69.0	-12.0	1.6	0.67	**
Cond	µS cm^{-1}	36.0	29.4	59.0	47.9	25.0	17.5	-0.25	**
Na^+	µeq l^{-1}	180.5	142.9	282.8	246.6	117.5	87.4	-1.31	**
Ca^{2+}	µeq l^{-1}	53.4	38.5	80.3	64.6	23.0	20.8	-0.36	**
Mg^{2+}	µeq l^{-1}	54.7	45.0	83.1	75.6	28.8	25.8	-0.33	**
K^+	µeq l^{-1}	9.3	8.3	17.1	15.8	2.6	1.8	-0.04	**
Lab Al	µg l^{-1}	28.0	8.0	133.0	28.0	2.0	1.0	-0.04	
DOC	mg l^{-1}	1.2	2.0	5.9	4.7	0.3	0.9	0.04	**
ANC-CB	µeq l^{-1}	-3.3	24.8	56.0	77.3	-39.9	-2.0	1.02	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

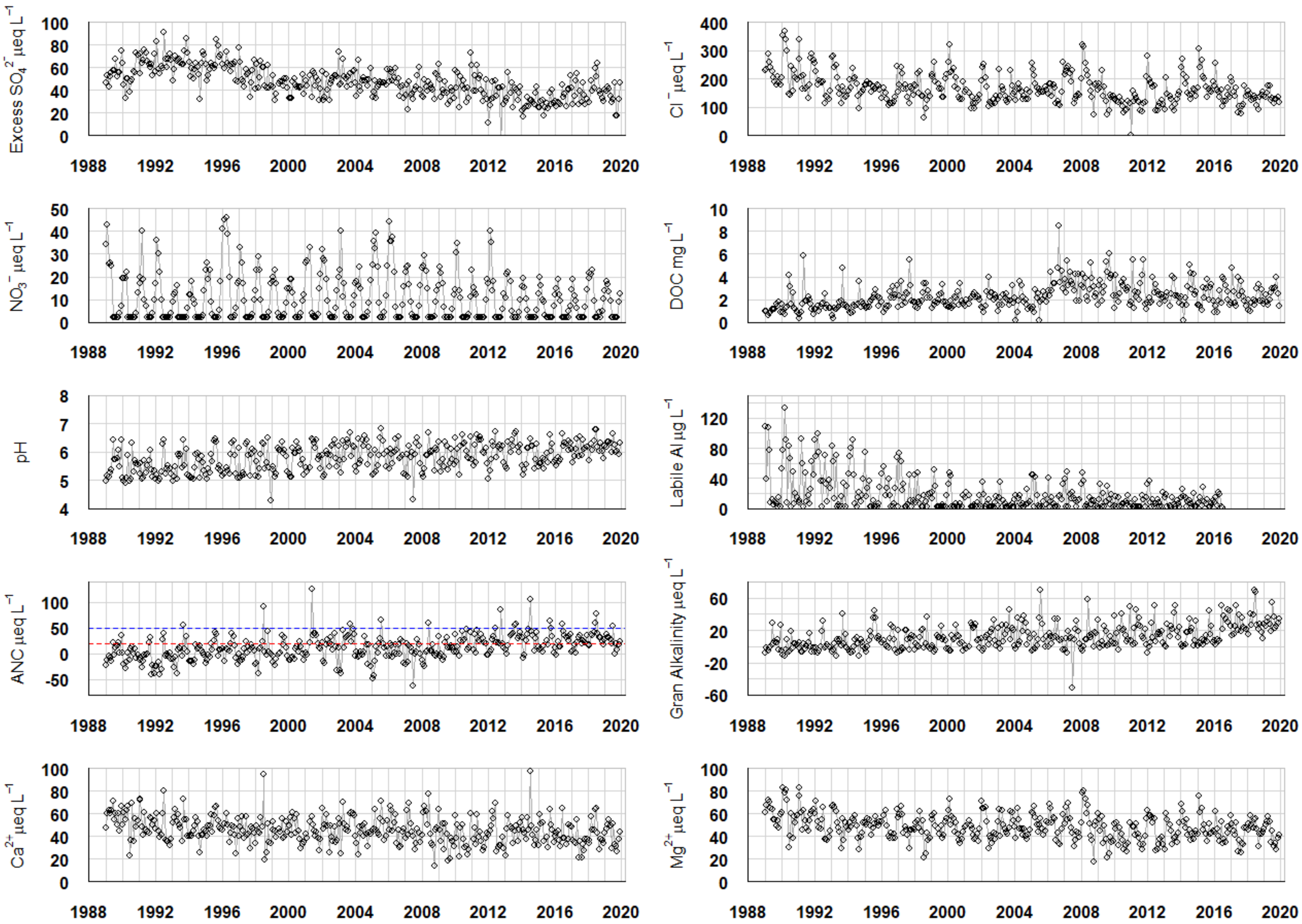


Figure 9.2. Dargall Lane Burn water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

9.2 Dargall Lane Burn: water chemistry trends

Although only 2 km from the Round Loch of Glenhead, and therefore subject to a similar deposition regime, the non-marine sulphate concentration of the Dargall Lane Burn was considerably higher than that for the loch at the onset of monitoring and has fallen at a slower rate. This reflects a significant geological contribution of sulphate, in addition to calcium and magnesium. However, concentrations of non-marine sulphate have still almost halved over the monitoring period.

Throughout the three decades, nitrate concentrations have shown particularly marked seasonal variation - often reaching concentrations of over 30 μeq L^{-1} in the winter months, while falling below levels of detection during the growing season. Since 2012, and roughly coincident with an increase in pH, peak nitrate concentrations have fallen to around 20 μeq L^{-1}, i.e. slightly lower than the median of recent non-marine sulphate concentrations. As with all other sites close to the west coast, chloride concentrations vary substantially, as a consequence of the episodic deposition of sea salt. Unusually for UWMN sites, they have also fallen at a slightly faster rate than non-marine sulphate – the decline driven by a long-term reduction in hydrochloric acid deposition.

The large reduction in the concentration of acid anions has been accompanied by a large reduction in acidity, and particularly in acidity maxima. The latter occur during periods of high discharge, elevated atmospheric inputs of seasalt, and winter release of nitrate. In the early years of monitoring, pH varied from just below 5.0 to just below 6.5, labile aluminium concentrations oscillated from highly toxic concentrations (often above 50 µg L^{-1}) to below limits of detection, while ANC was almost always negative. Since non-marine sulphate concentrations began to decline in around 2006, pH and ANC minima have increased gradually while labile aluminium maxima declined, and in the last 5 years water pH has rarely fallen below 5.5, while ANC has rarely fallen below 0 μeq L^{-1} and remains above 20 μeq L^{-1} in the majority of samples. Also since around 1996, Gran alkalinity has risen from mostly negative to persistently positive levels, indicating the introduction and subsequent increase in bicarbonate.

Concentrations of DOC in the Dargall Lane Burn are low relative to most other UWMN sites but have risen from a median of 1.2 mg L^{-1} in the first five years to 2.0 mg L^{-1} in the last five years.

9.3 Dargall Lane Burn: epilithic diatom community trends

Despite considerable inter-annual fluctuations, the epilithic diatom assemblage at Dargall Lane Burn shows a clear and significant long-term trend in species abundance changes (RDA1, mGLM; Main Report: Table 4.1). The most common diatoms throughout the monitoring period are *Tabellaria flocculosa* (SWAP pH optimum = 5.4) and *Peronia fibula* (optimum = 5.3) (Appendix: Figure 9.3). A marked reduction in the relative abundances of *Eunotia naegelii* (optimum = 5.0) and *Eunotia incisa* (optimum = 5.1) occurred around 1998. *Brachysira vitrea* (optimum = 5.9), an acidification recovery indicator for many acidified sites, shows a clear and significant increase in abundance from 2007.

Overall species turnover is modest at 1.04 SD units, but RDA1 and mGLM, together with the trajectory of PrC scores (Main Report: Figure 4.1), indicate a consistent and significant trend in diatom species changes during the monitoring period. RDA1-pH and trends in DAM scores are also significant, and RDA1-pH/PCA1 is 0.5, indicating that changes is stream-water pH account for the main pattern of variation in the diatom data. Variance partitioning indicates a significant relationship between diatom assemblage change and alkalinity and labile aluminium concentration, but the conditional effects of these variables are not significant, indicating that the trends in the diatom data can be accounted for by the observed increase in streamwater pH alone.

9.4 Dargall Lane Burn: macroinvertebrate community trends

The macroinvertebrate community of the Dargall Lane Burn has undergone substantial change over the monitoring period (Appendix: Figure 9.4) which is consistent with the improvements in water chemistry described above. AWICsp values increased significantly and linearly over the 28 years (Main Report: Figure 5.3 and Table 5.2). Indeed, since 2011 small populations of the acid-sensitive mayflies, Baetidae and Heptageniidae, have established at the site for the first time. Current AWICsp values vary around a mean of circa 4.9, which indicates that there may still be scope for further recovery in the community should chemical trends be sustained.

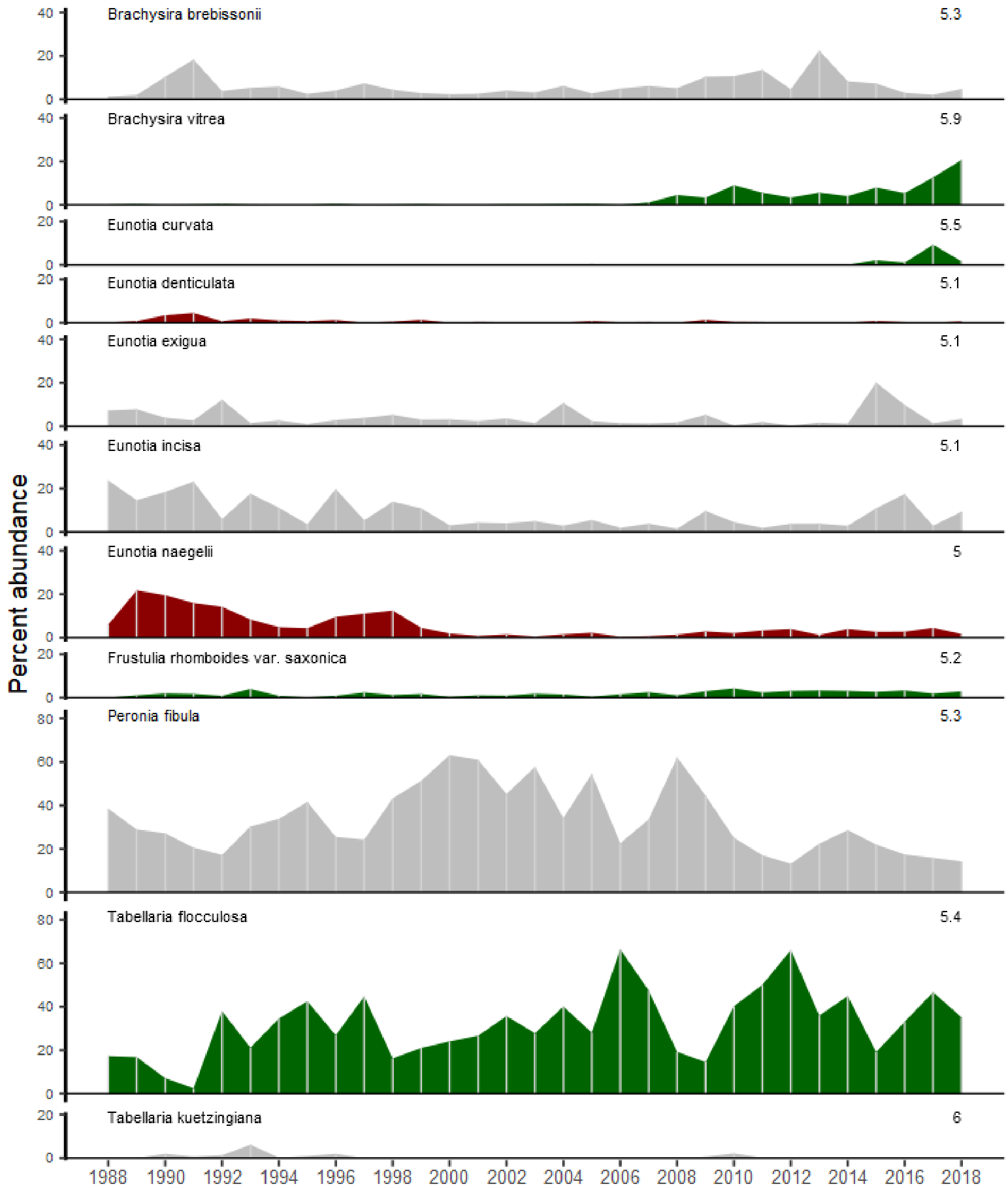


Figure 9.3 Dargall Lane Burn: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

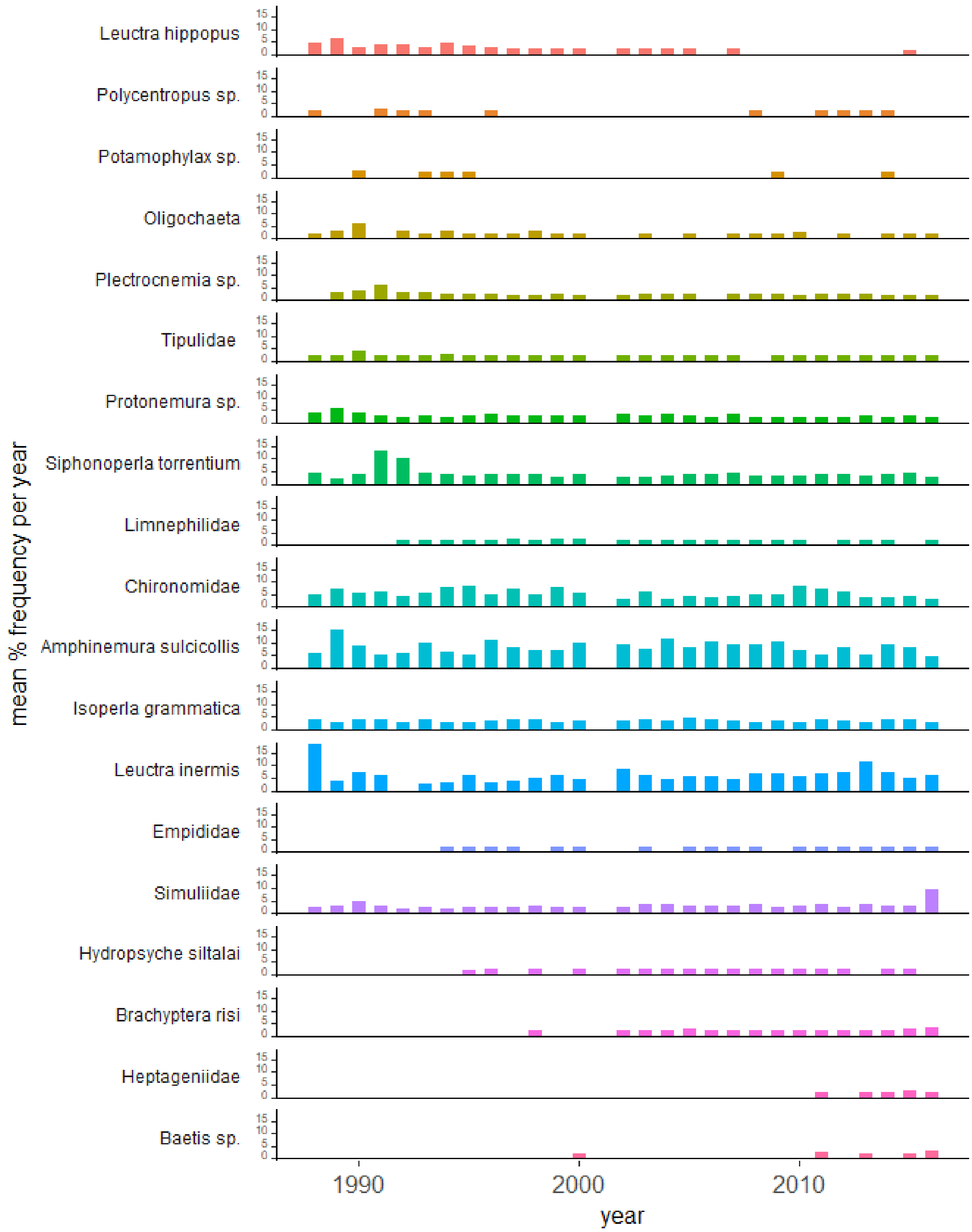


Figure 9.4 Dargall Lane Burn: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

10. Scoat Tarn

10.1 Scoat Tarn site description

Scoat Tarn is one of the highest altitude tarns in the English Lake District. Diatom-based pH reconstruction, using a sediment core taken in 1989, suggests that the site acidified from around pH 5.9 in the early nineteenth century to pH 4.7 in the 1980s (Patrick et al. 1995). There is no evidence of any physical disturbance or changes in grazing regime in the catchment over the past decade. Scoat Tarn is located approximately 6 km north of the more chemically buffered UWMN site Burnmoor Tarn.

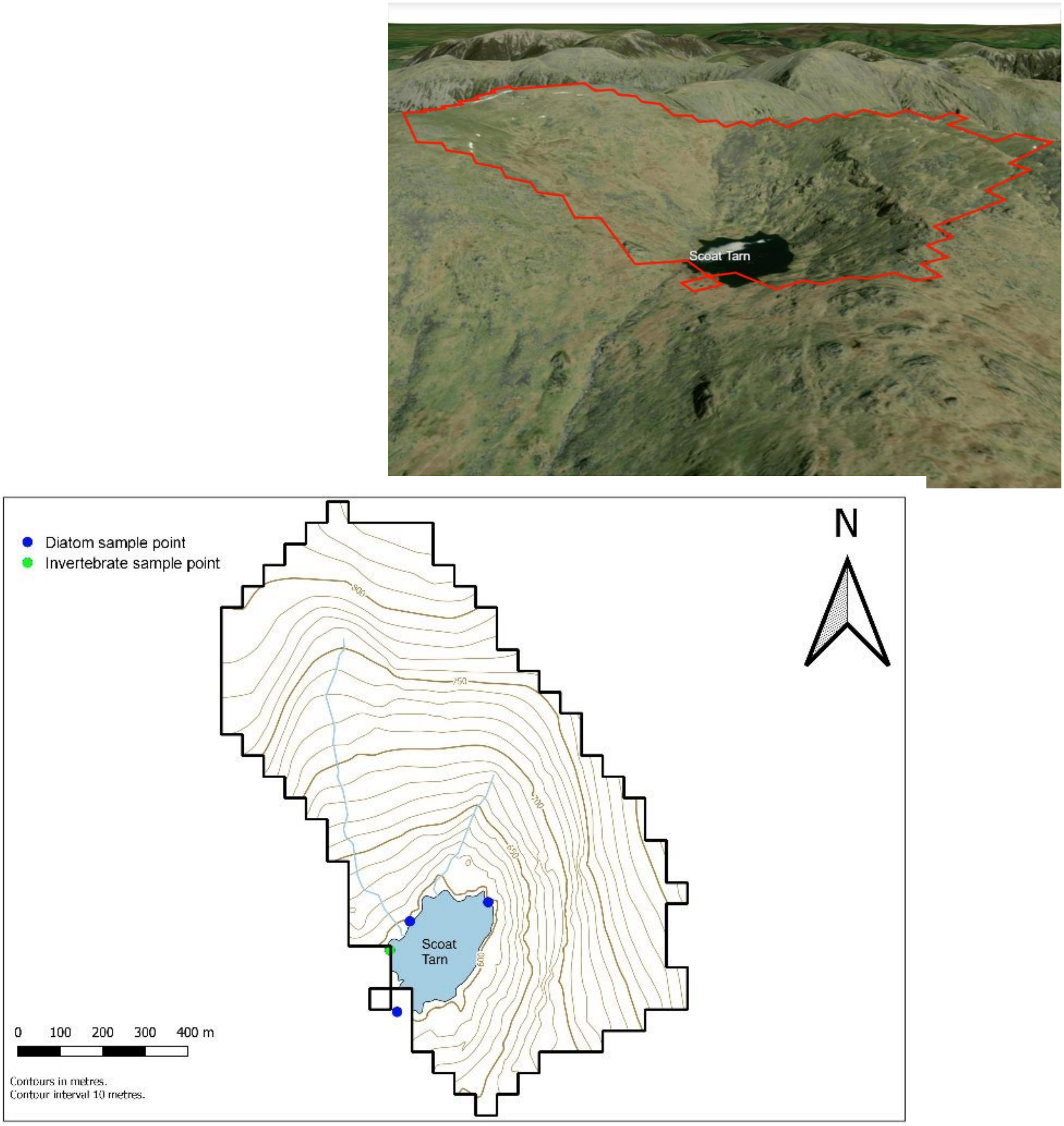


Figure 10.1 Mapped and aerial views of the Scoat Tarn catchment

Table 10.1 Scoat Tarn site characteristics

Maximum altitude	835 m	
Maximum depth	20 m	
Mean depth	10 m	
Volume	4.2 x 10^5 m^3	
Lake area	5.2 ha	
Catchment area	100.2 ha	
Catchment area (excl.lake)	95 ha	
Catchment:Lake ratio	18:2	
Catchment geology	Borrowdale volcanics	
Catchment soils	Shallow peaty rankers	
Catchment vegetation	Moorland	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	41.1	18.7
Non-marine oxidised sulphur	30.5	8.1
Oxidised nitrogen	14.7	10.7
Reduced nitrogen	51.3	22.8

Table 10.2 Scoat Tarn water chemistry characteristics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	63.5	34.6	72.9	44.6	52.1	29.9	-1.04	**
xSO_4^{2-}	µeq l^{-1}	41.7	20.4	53.2	27.4	29.2	12.4	-0.77	**
Cl^-	µeq l^{-1}	207.3	137.1	327.2	207.9	126.9	83.2	-1.15	**
NO^{3-}	µeq l^{-1}	19.1	10.0	42.3	23.2	6.0	5.6	-0.21	**
pH	pH	5.0	5.5	5.2	6.2	4.9	5.0	0.01	**
Alk	µeq l^{-1}	-7.0	8.2	-1.0	37.6	-13.0	3.2	0.46	**
Cond	µS cm^{-1}	35.7	25.4	49.0	35.0	24.0	17.3	-0.26	**
Na^+	µeq l^{-1}	178.4	125.1	265.4	167.9	126.2	87.4	-1.09	**
Ca^{2+}	µeq l^{-1}	36.7	20.2	47.9	49.7	25.4	13.7	-0.40	**
Mg^{2+}	µeq l^{-1}	48.5	34.9	76.5	46.0	29.6	22.8	-0.36	**
K^+	µeq l^{-1}	7.9	5.5	13.0	10.2	2.6	2.9	-0.04	**
Lab Al	µg l^{-1}	97.0	17.5	293.8	46.0	2.0	7.0	-0.35	
DOC	mg l^{-1}	0.5	1.3	1.4	3.4	0.1	0.3	0.02	**
ANC-CB	µeq l^{-1}	-17.0	-0.2	8.2	40.2	-68.5	-21.2	0.48	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

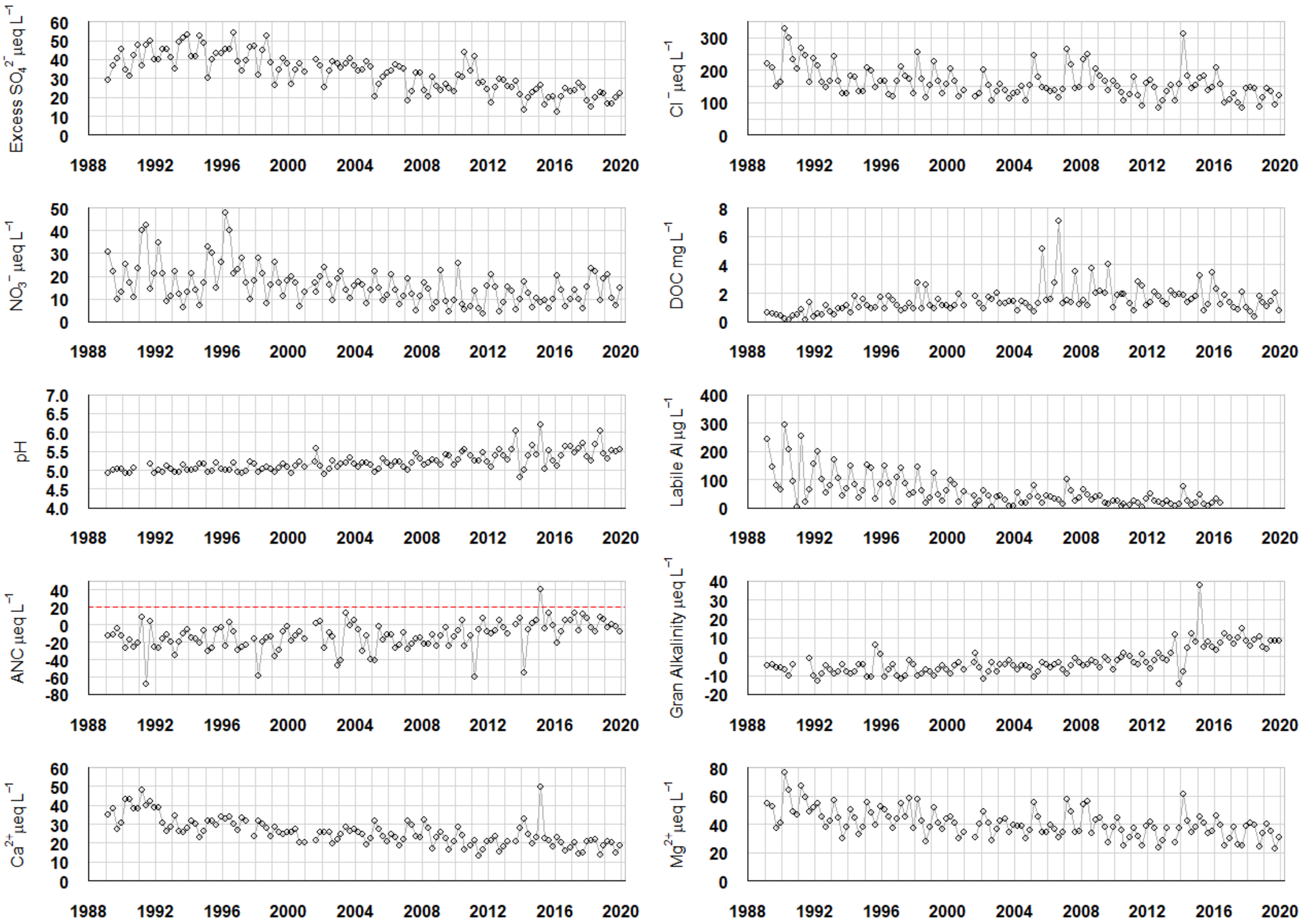


Figure 10.2. Scoat Tarn water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

10.2 Scoat Tarn: water chemistry trends

Water chemistry trends in Scoat Tarn bear some similarity to those in the similarly acidic and acidified Round Loch of Glenhead, some 80 km to the north-west. However, initial sulphur and nitrogen deposition loads, as estimated by CBED, were considerably higher, and have not fallen to the same extent. Consequently non-marine sulphate concentrations have fallen by approximately 50% over the monitoring period, as opposed to over 75% at the Round Loch, and the 2015-2019 median concentration of 20.4 μeq L^{-1} is approximately double that of the Scottish site.

Concentrations of chloride show similar average levels and fluctuations in response to variations in sea salt inputs, and a similar long-term rate of reduction in response to the reduction in hydrochloric acid deposition. In contrast to the Round Loch, however, concentrations of nitrate show a steep decline over time. While nitrate concentrations dip during the growing season, they remain detectable throughout the year. As a consequence of the decline in nitrate, non-marine sulphate remains the dominant acidifying anion.

The most notable chemical response to the early declines in acid deposition was a major reduction in labile aluminium concentration from extremely toxic levels, initially often exceeding 100 μg L^{-1}. By 2016, when aluminium measurements were curtailed, median concentrations had fallen to less than 20 μg L^{-1}. Lake water pH was exceptionally stable in the early years, averaging 5.0, and only began to show an obvious increase from around the turn of the century . By the most recent five-year period, median pH had reached 5.5, and now shows considerably more inter-sample variation. Despite the improvements in these acidity metrics, the decline in acid anions was largely balanced by a decline in base cations until around 2008. Hence ANC remained consistently negative for the first two decades of monitoring. Since 2010, the ANC of an increasing proportion of samples has been slightly positive, although by the end of 2019 the UK critical ANC value of 20 μeq L^{-1} had only been exceeded on one occasion. Thus while recovery from acidification is clearly underway, Scoat Tarn has remained in an acidified condition. The reduction in acid anions and base cations has resulted in a 29% reduction in electrical conductivity, to a 2015-19 median of 25.4 μS cm^{-1}.

Scoat Tarn was an exceptionally clear water lake when monitoring began, with a median DOC concentration of 0.5 mg L^{-1}. The relatively low concentration reflected the absence of peaty soil types and the relatively low temperatures, associated with its high altitude catchment, that restrict the rate of soil organic matter decomposition. As at nearly all UWMN sites, DOC concentrations have climbed progressively over most of the monitoring period as a consequence of the reduction in pollutant deposition, and by 2015-2019 the median had reached 1.3 mg L^{-1}. While this represents an almost trebling of DOC concentration, and by inference water colour, levels remain sufficiently low for most of the lake bed (maximum depth of 20 m) to continue to lie within the theoretical photic zone (Monteith pers. comm).

10.3 Scoat Tarn: epilithic diatom community trends

Scoat Tarn has one of the most diverse epilithic diatom communities across the network (Appendix: Figure 10.3). Overall, it shows some consistent but modest changes (turnover =1.11; Main Report: Table 4.1). The record is dominated by *Eunotia incisa* (SWAP pH optimum = 5.1) with lesser proportions of *Brachysira brebissonii* (optimum = 5.3) and *Achnanthes marginulata* (optimum = 5.2). These taxa remain dominant throughout the monitoring period but there are small and significant changes in other taxa, namely a decline in the acidiobiontic *Tabellaria binalis* (optimum = 4.7) and others with lower pH optima, including *Eunotia exigua* (optimum = 5.1), and a corresponding increase in *Peronia fibula* (optimum = 5.3) and *Tabellaria flocculosa* (optimum = 5.4).

Numerical analysis of the species data demonstrates that the trend in the community-level change is significant (RDA1, mGLM; Main Report: Table 4.1). The trajectory of PrC scores indicate that the trend is gradual and sustained over the whole monitoring period (PrC trajectory; Main Report: Figure 4.1).

Although there is no significant trend in DAM scores, RDA1-pH indicates that the trend in diatom community change is significantly related to pH. The RDA1-pH / PCA1 ratio is 0.73, indicating that changes in lake-water pH account for the dominant pattern of variation in the diatom data. Overall, these results indicate a small but sustained diatom response to the small increase in pH at this site.

10.4 Scoat Tarn: macroinvertebrate community trends

As observed at the even more acidic Loch Grannoch, there was is no distinct signal of biological recovery evident in the macroinvertebrate taxon richness or LAMM diagnostic index data for Scoat Tarn (Main Report: Figures 5.1 & 5.3). Indeed, low values for both metrics persisted up to the current final year of available data (2016). However, there was significant directional change in community composition over the monitoring period, driven mainly by changes to the Corixidae assemblage, the almost complete loss of water beetles and the establishment of Leptophlebiidae mayflies. While the chemistry of Scoat Tarn clearly remains a challenging environment for many species, continued chemical recovery should soon provide conditions for the early phases of recovery in the macroinvertebrate community.

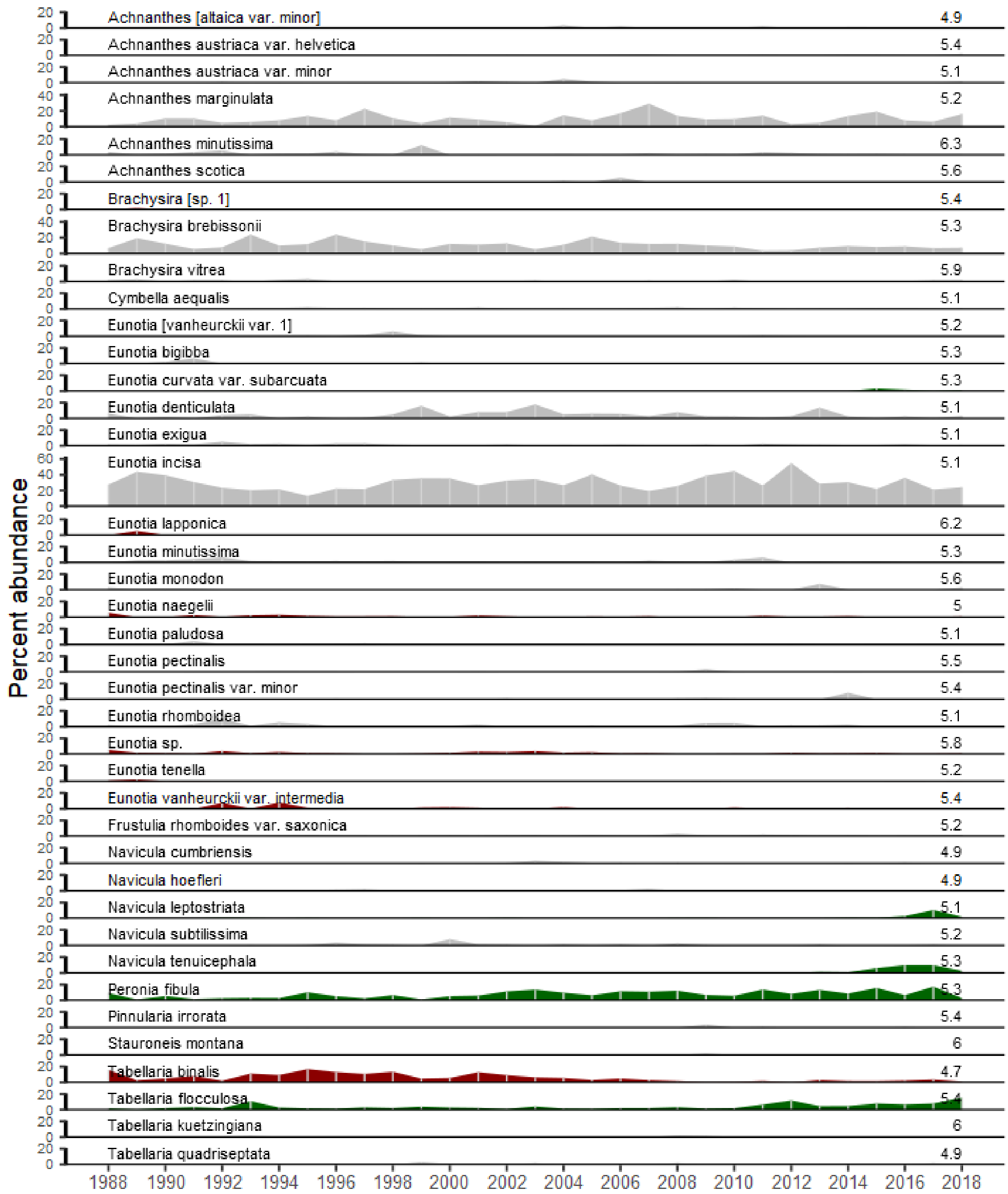


Figure 10.3 Scoat Tarn: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

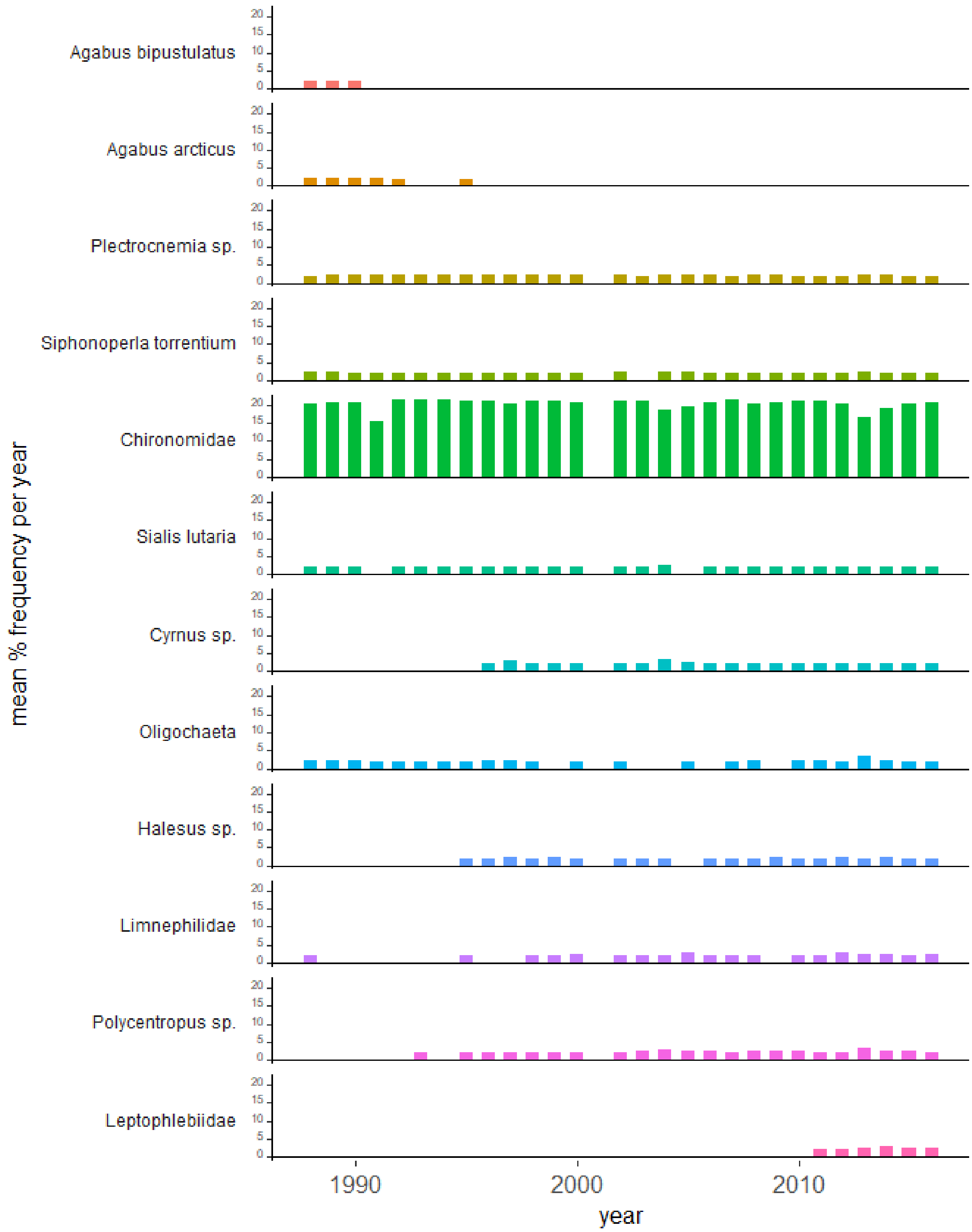
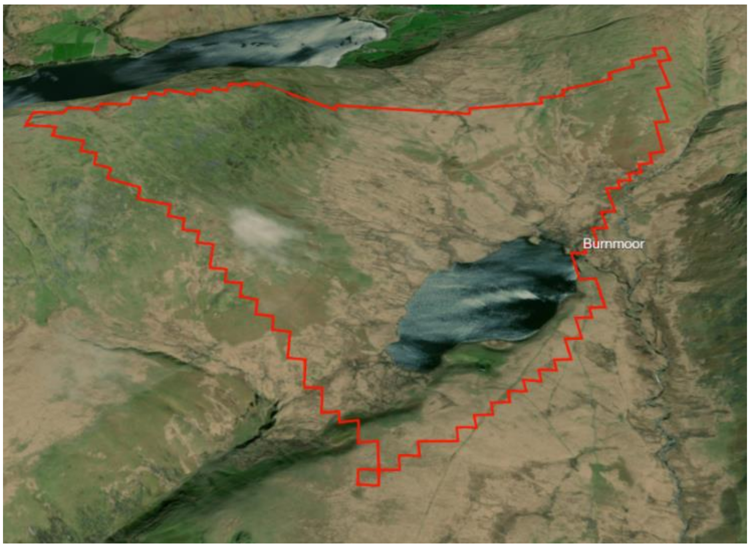


Figure 10.4 Scoat Tarn: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

11. Burnmoor Tarn

11.1 Burnmoor Tarn site description

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



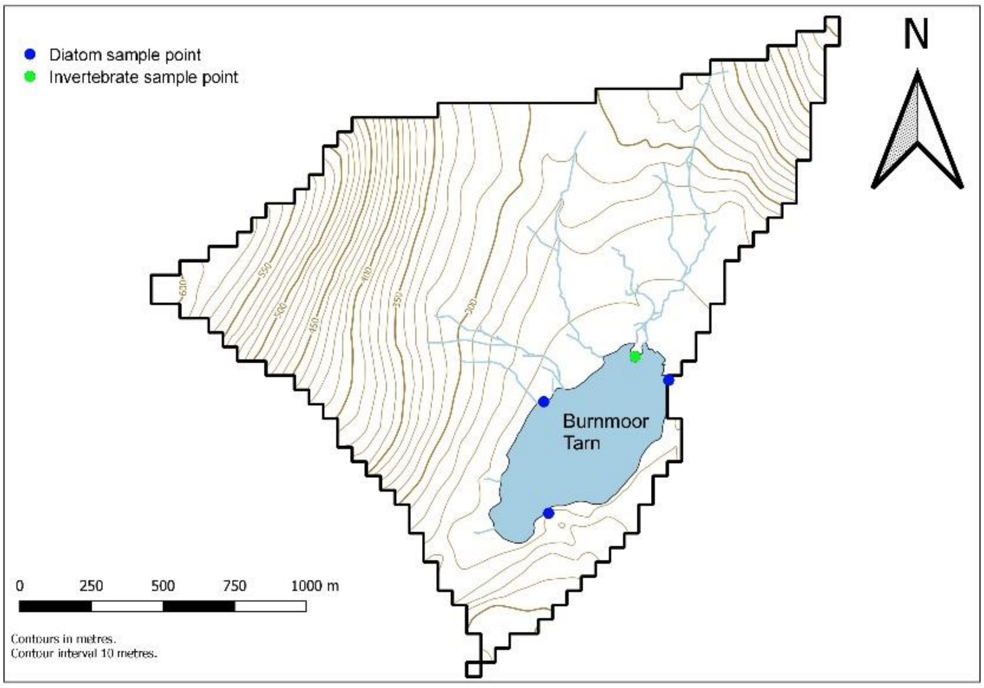


Figure 11.1 Mapped and aerial views of the Burnmoor Tarn catchment

Table 11.1 Burnmoor Tarn site characteristics

Grid Reference	NY 184044	
Lake altitude	252 m	
Maximum altitude	605 m	
Maximum depth	13 m	
Mean depth	5.1 m	
Volume	8.9 x 10^5 m^3	
Lake area	24 ha	
Catchment area	250 ha	
Catchment area (excl.lake)	226 ha	
Catchment:Lake ratio	9:4	
Catchment geology	Andesite lava and granite	
Catchment soils	Podsols shallow peat, rankers	
Catchment vegetation	Moorland – 100%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	27.7	10.7
Non-marine oxidised sulphur	21.2	4.7
Oxidised nitrogen	9.2	6.2
Reduced nitrogen	32.3	15.0

Table 11.2 Burnmoor Tarn water chemistry statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	81.2	45.5	118.7	52.4	64.6	33.9	-1.24	**
xSO_4^{2-}	µeq l^{-1}	57.1	28.9	102.3	38.6	38.5	15.9	-1.01	**
Cl^-	µeq l^{-1}	229.9	146.0	287.7	214.7	158.0	113.1	-1.69	**
NO^{3-}	µeq l^{-1}	5.4	5.8	12.9	19.5	2.1	2.1	0.00	
pH	pH	6.6	6.6	7.0	6.9	4.4	5.2	0.00	
Alk	µeq l^{-1}	50.0	71.0	75.0	111.2	-44.0	2.4	0.47	**
Cond	µS cm^{-1}	44.6	32.5	53.9	39.0	34.0	28.3	-0.25	**
Na^+	µeq l^{-1}	211.0	147.7	243.6	183.6	156.6	121.4	-1.22	**
Ca^{2+}	µeq l^{-1}	96.1	69.4	118.3	90.8	44.4	25.2	-0.55	**
Mg^{2+}	µeq l^{-1}	65.8	51.0	79.0	64.8	42.8	45.2	-0.28	**
K^+	µeq l^{-1}	8.4	6.3	15.3	13.4	2.6	3.5	-0.04	**
Lab Al	µg l^{-1}	2.0	2.0	14.0	2.0	2.0	1.0	0.00	
DOC	mg l^{-1}	1.5	2.8	4.7	4.9	0.9	0.8	0.03	**
ANC-CB	µeq l^{-1}	58.0	72.3	94.5	124.6	-12.8	-10.2	0.77	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

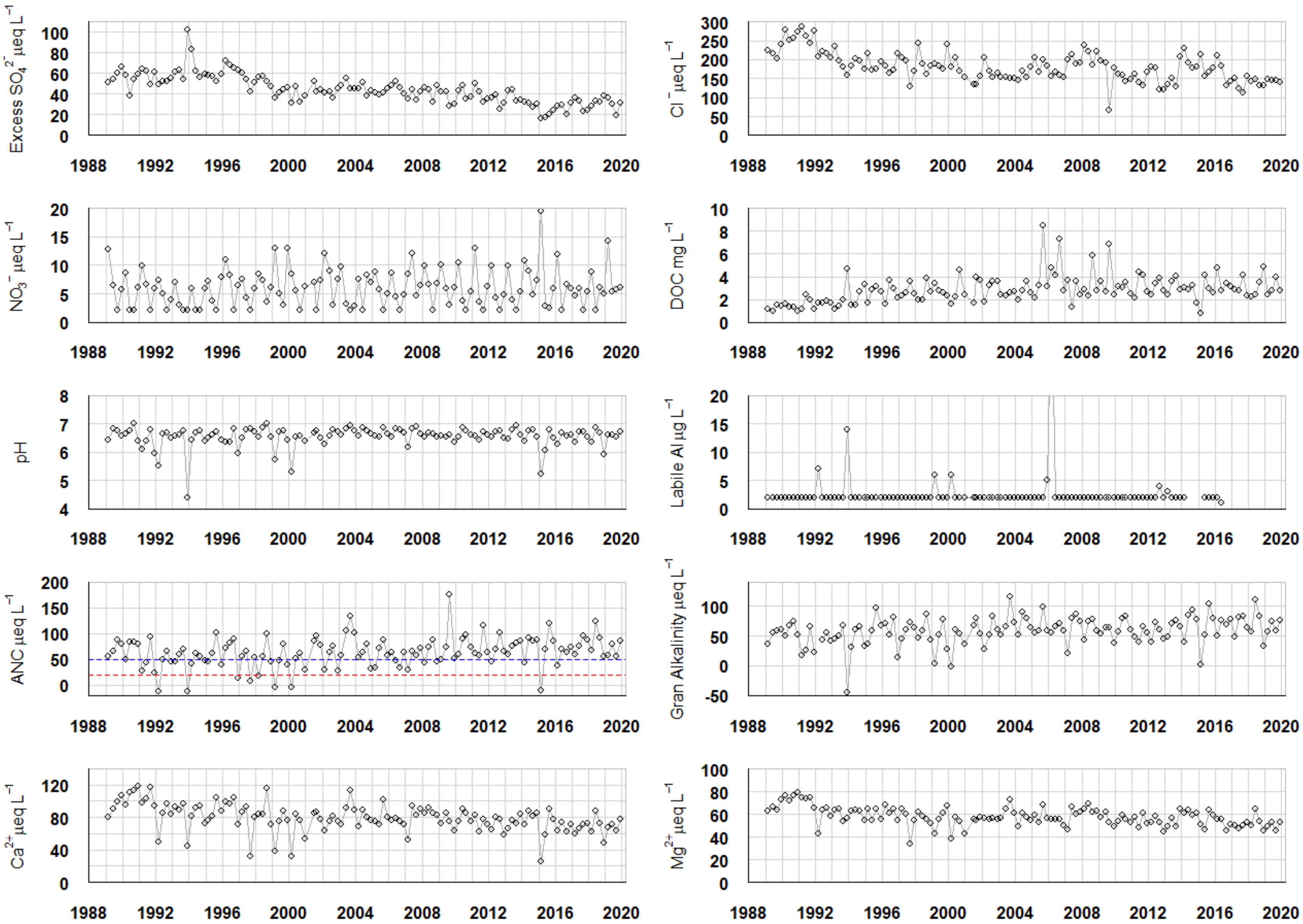


Figure 11.2 Burnmoor Tarn water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

11.2 Burnmoor Tarn: water chemistry trends

While the CBED model suggests that sulphur and nitrogen deposition rates to Burnmoor Tarn have been considerably less than to the neighbouring, higher altitude and wetter, Scoat Tarn, the long-term reductions in non-marine sulphate and chloride concentrations in Burnmoor Tarn have occurred at a slightly faster rate. Current concentrations of non-marine sulphate remain around 1.4 times higher than in Scoat Tarn.

Nitrate concentrations have been considerably lower in Burnmoor Tarn than Scoat Tarn, and also show clearer seasonality, with levels falling below limits of detection during the growing season. This could reflect higher biological demand for reactive nitrogen by terrestrial and aquatic (both vegetation and soil microbial) elements of a more productive landscape and lake. Unlike Scoat Tarn, nitrate concentrations have not changed significantly over the monitoring period.

Burnmoor Tarn has been largely protected from acidification by calcite in the catchment's glacial till. Weathering of the latter explains the higher concentrations of calcium in Burnmoor Tarn, relative to its neighbour, and Gran Alkalinity values that initially averaged 50 µeq L^{-1} and have increased significantly over time. With the exception of the increase in DOC (see below) this is the only clear chemical response to the large reduction in acid deposition, but the increase in bicarbonate concentration could still be biologically significant for aquatic plants that have a preference for bicarbonate over CO_2 as a carbon source for photosynthesis. Acid Neutralising Capacity occasionally dropped below the UK critical limit of 20 µeq L^{-1} over the first decade of monitoring, but more recently values below 50 µeq L^{-1} have become rare. Unsurprisingly, therefore, pH values have remained stable, rarely registering less than pH 6.2.

Concentrations of DOC have increased in response to reductions in deposition at a similar rate, proportionally, to the more acidified lakes and streams on the network, i.e. almost doubling, from 1.5 to 2.8 mg L^{-1}, between the first and most recent five-year period. Despite the associated increase in water colour, recent DOC levels are still low enough for most of the lake bed to normally lie within the theoretical photic zone.

11.3 Burnmoor Tarn: epilithic diatom community trends

Unsurprisingly, given the modest chemical response described above, the overall turnover in the epilithic diatom assemblages is low (0.8), although there are some consistent but modest changes in species abundance during the monitoring period (Appendix: Figure 11.4). Overall, the community is dominated by the acid-sensitive taxa *Achnanthes minutissima* (SWAP pH optima = 6.3), *Brachysira vitrea* (optimum = 5.9), and lesser numbers of *Cymbella microcephela* (optimum = 6.3). The proportional abundances of these species have remained relatively constant across the whole monitoring period. Several minor species, including *Frustulia rhomboides* var. *saxonica* (optimum = 5.2), *Nitzschia perminuta* (optimum = 5.7) and *Tabellaria flocculosa* (optimum = 5.4), show significant and gradual decline while *Cymbella cesatii* (optimum = 6.4) shows a corresponding significant increase.

The RDA1 and mGLM community-level trend tests give conflicting results (the test based on RDA is not significant but that based on mGLM is; Main Report: Table 4.1) and the trajectory of PrC scores reveals a complex non-linear pattern of change (Main Report: Figure 4.1). There is no significant relationship between diatom community change and lake-water chemistry, although there is a significant but weak trend in DAM scores (Main Report: Table 4.1 & Figure 4.2), driven by the increase in *C. cesatii* (optimum = 6.4). While the changes in DAM scores and species optima are indicative of a subtle response to increasing pH, the water chemistry data does not support this. It is therefore more likely that these trends represent a response to an increase in bicarbonate alkalinity, and/or dissolved organic matter during the monitoring period.

11.4 Burnmoor Tarn: macroinvertebrate community trends

The macroinvertebrate assemblage of Burnmoor Tarn features a range of abundant acid-sensitive taxa such as the bivalve *Pisidium*, the aquatic amphipod *Gammarus lacustris*, the mayfly *Caenis*, and the caddisflies *Mystacides* and *Tinodes waeneri* (Appendix: Figure 11.4). Despite little evidence for acidification, the LAMM diagnostic index at the onset of monitoring was about 85% of a typical score for non-acidified lakes of similar typology. It then increased by a further 10% or so over the first 15 years (Main Report: Figure 5.3). Interestingly, rarefied taxon richness declined over time at Burnmoor Tarn. This trend was driven mainly by some erratic inter-annual variation in the first five years of monitoring; since about 1995 taxon richness has been stable. There has not been any significant directional change in community composition at the site (Main Report: Figure 5.2 and Table 5.3).

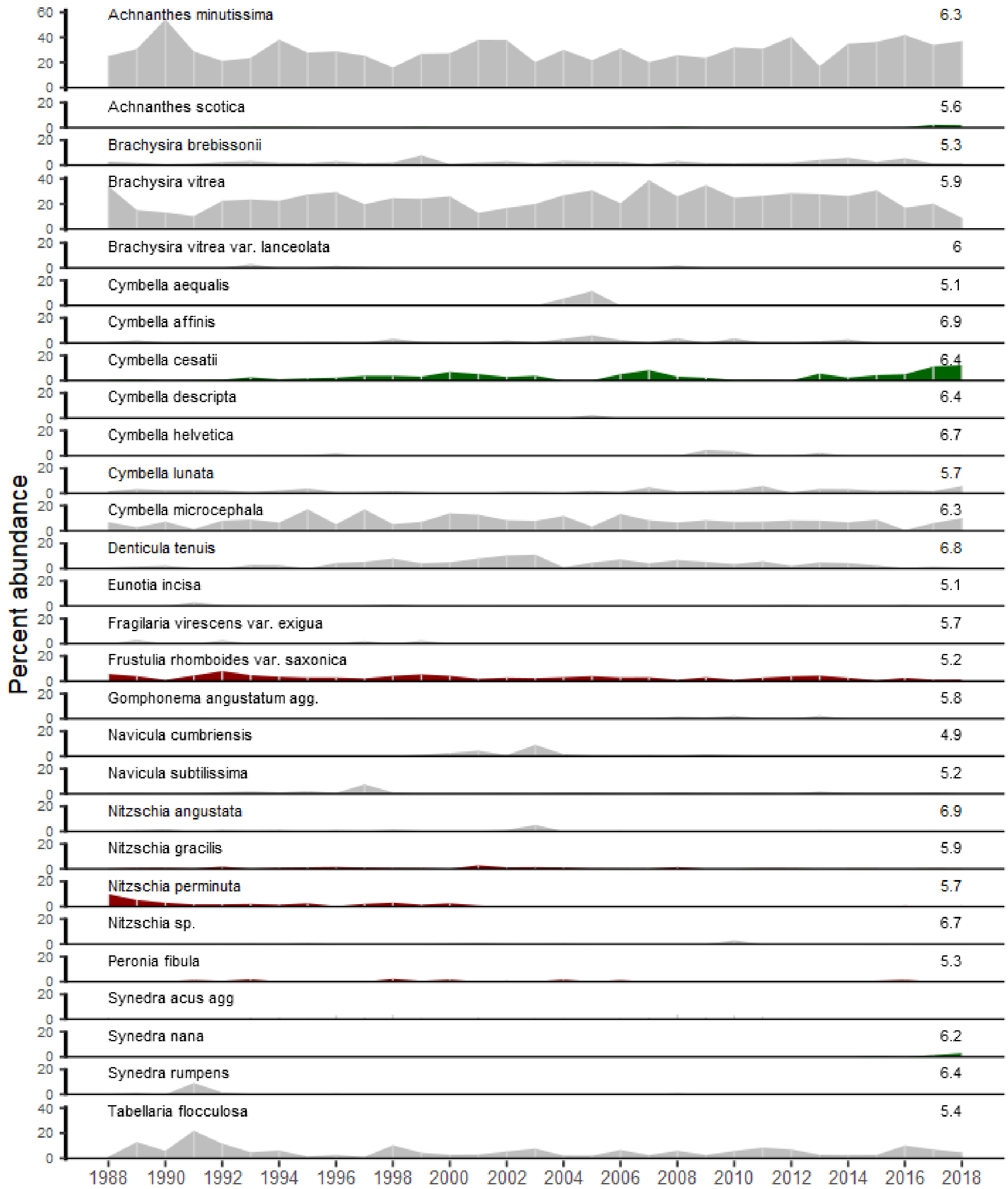


Figure 11.3 Burnmoor Tarn: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

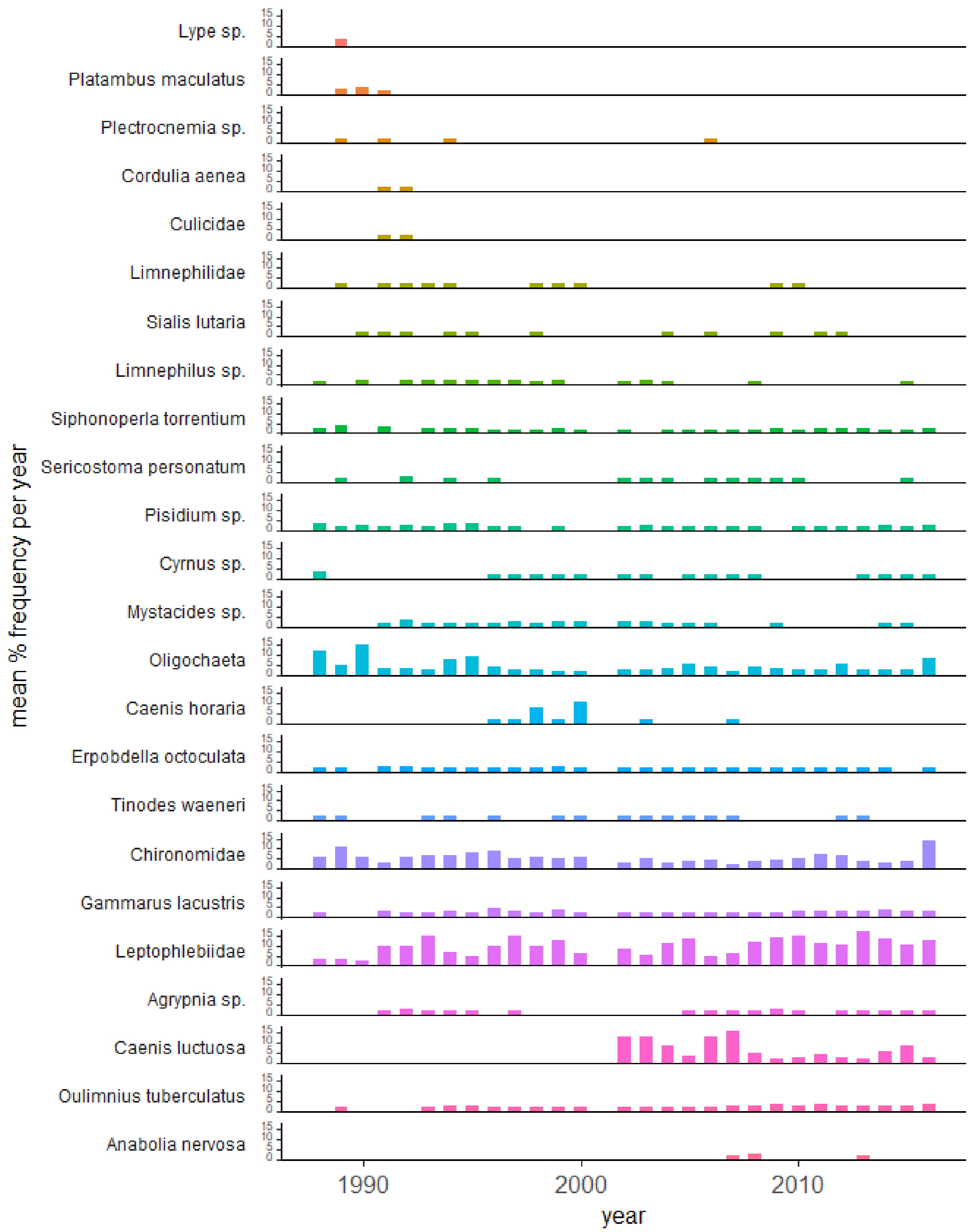


Figure 11.4 Burnmoor Tarn: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

12. River Etherow

12.1 River Etherow site description

The River Etherow flows into the Woodhead reservoir to the east of Manchester in the southern Pennines. This severely deposition-impacted site has been subject to considerable hydrochemical and hydrobiological research (e.g. Say et al., 1981; Harding et al., 1981; Evans & Jenkins, 2000) and detailed studies of catchment nitrogen dynamics under the Defra Freshwater Umbrella project. It is likely that the water chemistry of the River Etherow is occasionally influenced by road-salt, blown or washed in from the nearby A628 trunk road. As a source of drinking water containing relatively high, and increasing, levels of dissolved organic carbon (DOC), the chemistry record is of particular interest to water companies dependent on upland catchments across the south Pennines region. A consortium comprising United Utilities, Yorkshire Water and Severn Trent Water, managed by the Peak District National Park Authority, have been supporting the UWMN chemical analysis of this site since 2016.

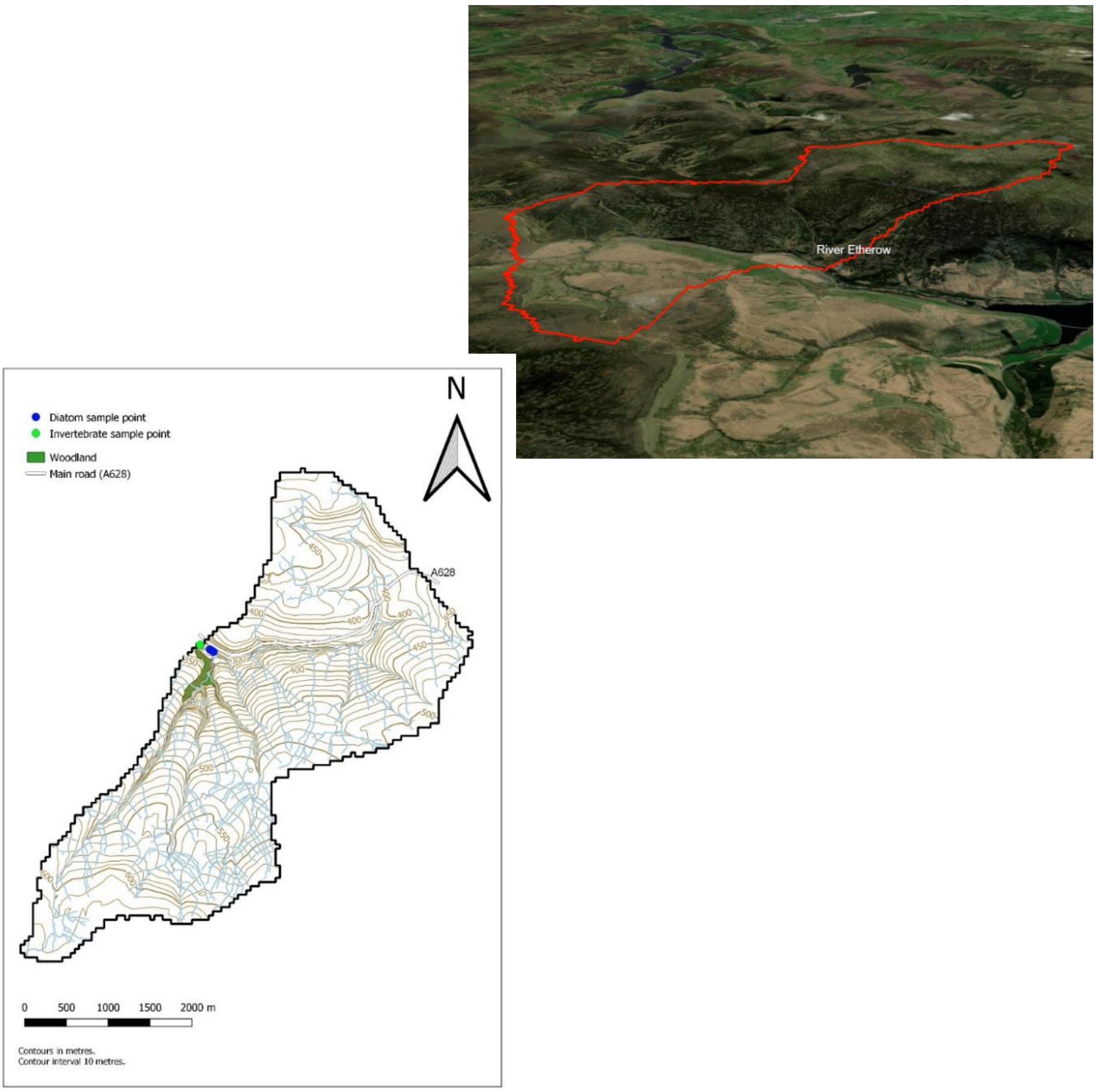


Figure 12.1 Mapped and aerial views of the River Etherow catchment

Table 12.1 River Etherow site statistics

Grid Reference	SK 116996	
Catchment area	1300 ha	
Minimum catchment altitude	280 m	
Maximum catchment altitude	633 m	
Catchment geology	Millstone grit	
Catchment soils	Peaty podsols, blanket peat	
Catchment vegetation	moorland	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	48.5	10.2
Non-marine oxidised sulphur	45.1	7.1
Oxidised nitrogen	15.8	9.3
Reduced nitrogen	49.8	19.9

Table 12.2 River Etherow water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	285.4	145.6	408.3	218.1	237.5	34.9	-5.41	**
xSO_4^{2-}	µeq l^{-1}	252.0	122.2	373.0	193.2	211.4	13.6	-5.00	**
Cl^-	µeq l^{-1}	304.7	214.8	643.2	406.2	205.9	98.7	-3.48	**
NO^{3-}	µeq l^{-1}	47.0	29.6	74.3	53.9	7.1	2.1	-0.79	**
pH	pH	5.5	6.2	7.2	7.3	3.9	4.2	0.02	**
Alk	µeq l^{-1}	1.0	62.2	150.0	275.8	-163.0	-72.8	2.33	**
Cond	µS cm^{-1}	81.0	62.8	137.7	82.6	32.8	37.8	-0.78	**
Na^+	µeq l^{-1}	295.8	236.2	526.4	343.2	213.2	99.2	-2.33	**
Ca^{2+}	µeq l^{-1}	181.1	130.7	349.3	223.1	103.8	59.4	-1.62	**
Mg^{2+}	µeq l^{-1}	175.2	125.0	289.6	210.6	102.0	48.1	-1.73	**
K^+	µeq l^{-1}	20.2	15.4	31.2	25.3	11.0	6.8	-0.15	**
Lab Al	µg l^{-1}	23.5	8.0	279.0	131.0	2.0	1.0	-0.04	
DOC	mg l^{-1}	3.7	9.6	14.1	37.0	0.3	2.8	0.16	**
ANC-CB	µeq l^{-1}	15.2	108.1	344.8	487.2	-194.6	1.5	3.06	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

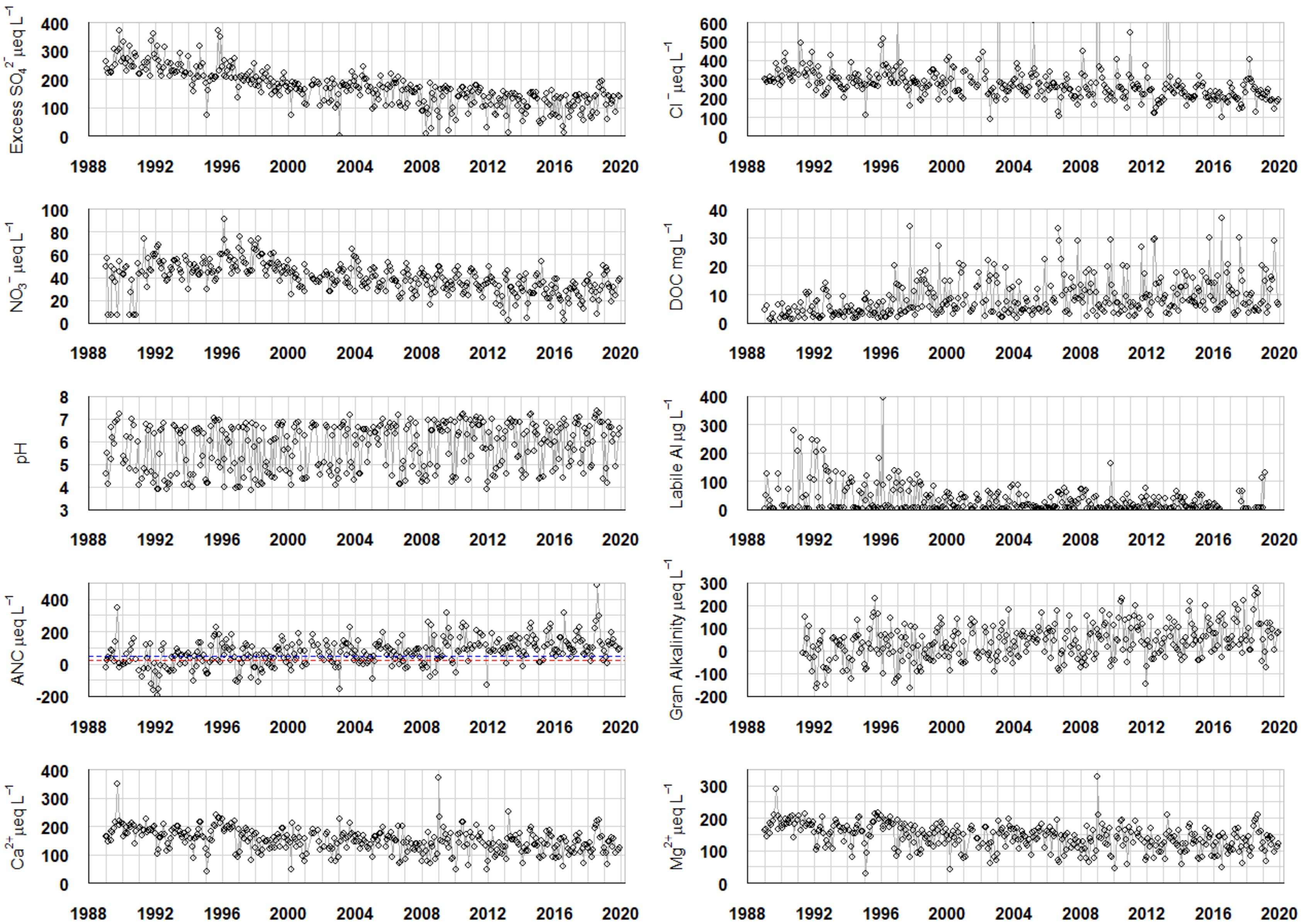


Figure 12.2 River Etherow water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

12.2 River Etherow: water chemistry trends

Surrounded by urban and industrial areas that once supported several of the UK's largest coal burning power stations, the catchment of the River Etherow has historically received much higher levels of acid deposition than any other site on the UWMN. Non-marine sulphate concentrations at the onset of monitoring averaged more than 250 µeq L^{-1}, and have since fallen more rapidly than at any other site on the network as emissions from these sources have been reduced and in several cases eliminated. Despite the large reduction, however, the median non-marine sulphate concentration for the 2015-2019 period was still 122 µeq L^{-1}, i.e. considerably higher than for any other UWMN site, even during the early years of monitoring. The anoxic peaty soils of the River Etherow catchment have retained a substantial quantity of anthropogenically-derived (legacy) sulphur. Much of this is held in the form of insoluble sulphides, but lowering of the water table during drier spells leads to oxidation to soluble sulphates and subsequent release to runoff when the soils rewet. Occasional peaks in non-marine sulphate concentrations following spells of drier weather are therefore likely to continue to edge downwards for some time, while concentrations following wetter periods are beginning to approach the very low levels now recorded at the majority of other sites.

The River Etherow catchment is sufficiently distant from the west coast for sea salt deposition to have had a relatively small influence on its chemistry. This helps to bring out the clear downward trend in chloride concentration (in terms of equivalence, around 70% of that for non-marine sulphate) which has been driven by a long-term reduction in hydrochloric acid deposition. Nitrate concentration has also fallen in a roughly linear manner. Throughout the record it has shown some seasonality, with the highest concentrations occurring during the winter months when catchment uptake is lowest. For most of the time, nitrate concentrations during the growing season have remained high but since 2013 are occasionally dipping below the limit of detection. This indicates that the nitrogen saturation status of the site is moving from one of year-round leaching to seasonal leaching only – an important milestone in the wider recovery process.

The very large reductions in acid anion concentrations have been accompanied by major reductions in water acidity, but trends are complicated by the fact that the chemistry of the River Etherow during drier weather is dominated by strongly buffered ground-water, as indicated by high concentrations of calcium and magnesium at low flows. Hence water pH during periods of low flow has remained largely above pH 6.5 throughout the last three decades, while ANC has remained substantially above 50 µeq L^{-1}, and labile aluminium concentration below the limit of detection. Conversely, during the first decade of monitoring, river water pH during high flow conditions occasionally dropped below pH 4.0, while labile aluminium concentrations were mostly at highly toxic levels (often above 100 µg L^{-1}) and ANC was normally exceptionally negative. Over time, the acidity of these extremely acidic events has lessened, so that over the last decade, pH has mostly ranged between 4.5 and 5.0, ANC is almost always above 20 µeq L^{-1}, and labile aluminium concentrations (up until measurements were discontinued in 2016) were falling below the limit of detection with increasing frequency.

On average, concentrations of DOC are high relative to most other UWMNN sites, reflecting the influence of the peat dominated catchment. Concentrations have increased dramatically over the monitoring period, and particularly during high flows in late summer to early autumn, while the median concentration has almost trebled. The trend has been driven largely by an increase in the solubility of soil organic matter, in turn resulting from a deposition-driven reduction in soil water ionic strength. Although streamwater pH of the River Etherow still falls well below pH 4.5 during high flows, the increasing contribution to acidity over time from organic acids (as indicated by DOC) relative to that from "mineral acids" (derived from atmospheric pollutants) results in more of the aluminium in runoff being in a relatively biologically benign organically bound, rather than labile, phase.

12.3 River Etherow: epilithic diatom community trends

Inter-annual variability in the epilithic diatom community of the River Etherow is greater than in any other site on the Network, reflecting the highly variable chemistry discussed above. The first part of the record, from 1988 to around 2005, is characterised by alternating dominance of the acidophilous/acidobiontic species *Eunotia exigua* (SWAP pH optimum = 5.1) and the acid-sensitive taxon *Achnanthes minutissima* (optimum = 6.3), and lesser numbers of *Eunotia rhomboidea* (optimum = 5.1) and *Brachysira vitrea* (optimum = 5.9). This likely reflects the dominant flow conditions in the days leading up to sampling, with the more acid-loving species dominating the biofilm during the more acidic conditions occurring during periods of high discharge.

Since 2000 the assemblage has become more stable with a progressive and significant increase in the more acid-sensitive species *Achnanthes saxonica* (SWAP pH optimum = 5.7) and lesser numbers of *Gomphonema angustatum* (optimum = 5.8) (Appendix: Figure 12.3). Numerical analysis of the species data demonstrates a significant community-level trend (RDA1, mGLM; Main Report: Table 4.1). This site shows the largest species turnover of all the network sites but the trajectory of PrC scores suggest that most of this change happened in the early part of the record and that since 2008 diatom community composition has been relatively stable (Main Report: Figure 4.1).

DAM scores also show substantial inter-annual variability, and although there is a shift to higher scores in the later part of the record the overall trend is not significant (Main Report: Figure 4.2 & Table 4.1). RDA-chemistry tests indicate a significant relationship between diatom assemblage changes and stream-water chemistry but the RDA1-pH / PCA1 ratio is only 0.29. Monthly water sampling is probably insufficient to fully capture the short-term hydrologically driven chemical variability influencing the assemblage structure at the time of biological sampling. Nevertheless, the epilithic diatom record provides clear evidence of a slight reduction in this magnitude of this chemical episodicity, and, in the later part of the record, a biological response to falling acidity levels.

12.4 River Etherow: macroinvertebrate community trends

The macroinvertebrate community of the River Etherow has undergone substantial changes over the monitoring period that are consistent (Appendix: Figure 12.4) with the improvements in water chemistry described above. The site shows a significant increase in taxon richness, directional change in community composition and a striking linear increase in AWICsp scores from around 3.5 in the late 1980s to values varying around 5.3 by 2016 – i.e., similar to levels seen at control streams earlier in the monitoring period (Figure 5.3 and Table 5.2). The macroinvertebrate community was dominated initially by acid-tolerant stoneflies and caddisflies, but as chemical conditions have improved, moderately tolerant stoneflies (*Brachyptera risi*), Dytiscid predatory diving beetles (*Oreodytes* and *Agabus*) and Elmid water beetles (*Elmis* and *Limnius*) have appeared, followed in the 2010s by moderately acid-sensitive Elmid riffle beetles (*Esolus*), the mayfly family Heptageniidae and the stonefly *Perlodes microcephalus*. There is, as yet, no indication of a plateauing in the recovery trend, and there remains the potential for taxa from acid-sensitive groups such as gastropod Mollusca and amphipod crustaceans to colonise if environmental conditions continue to improve.

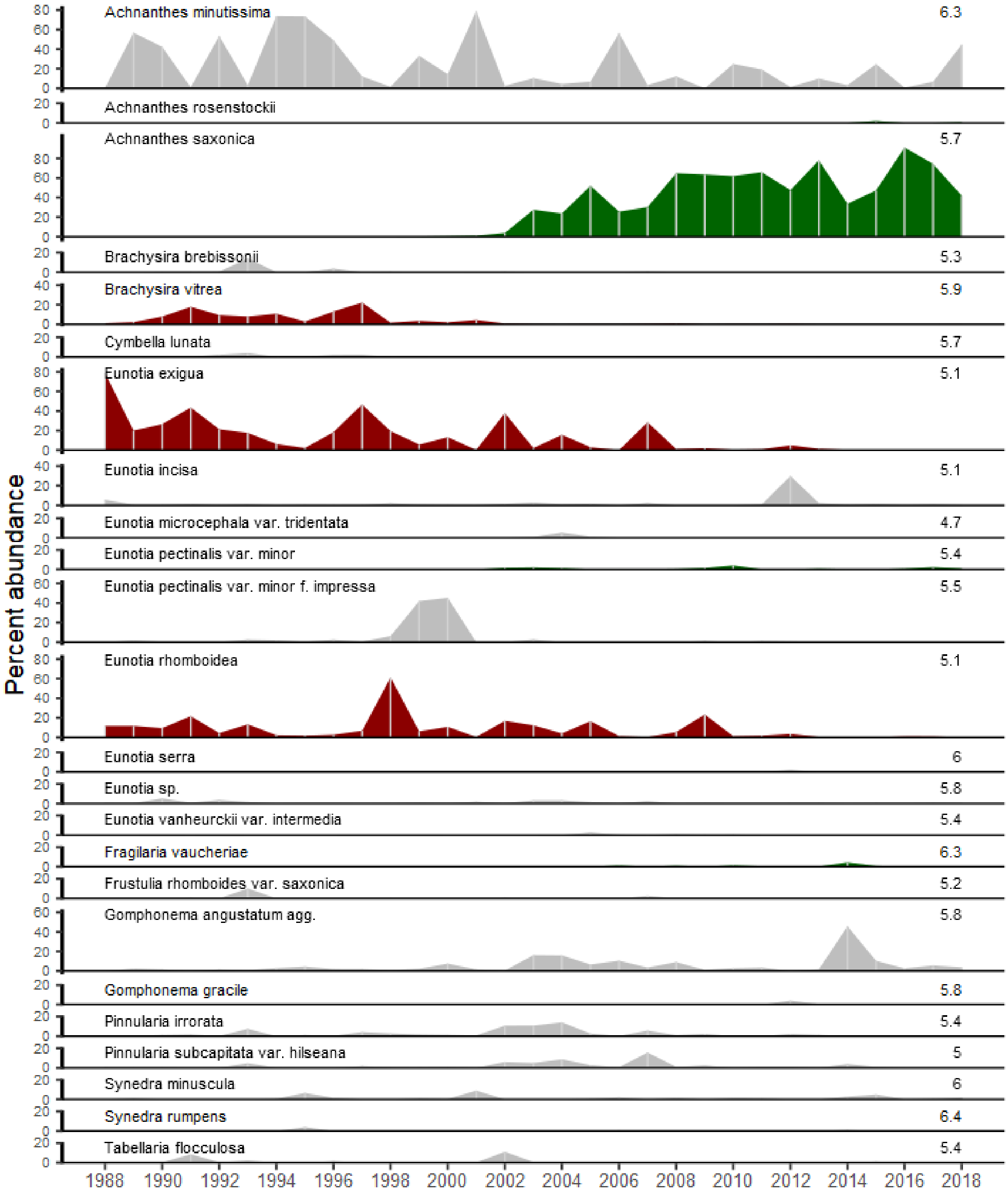


Figure 12.3 River Etherow: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

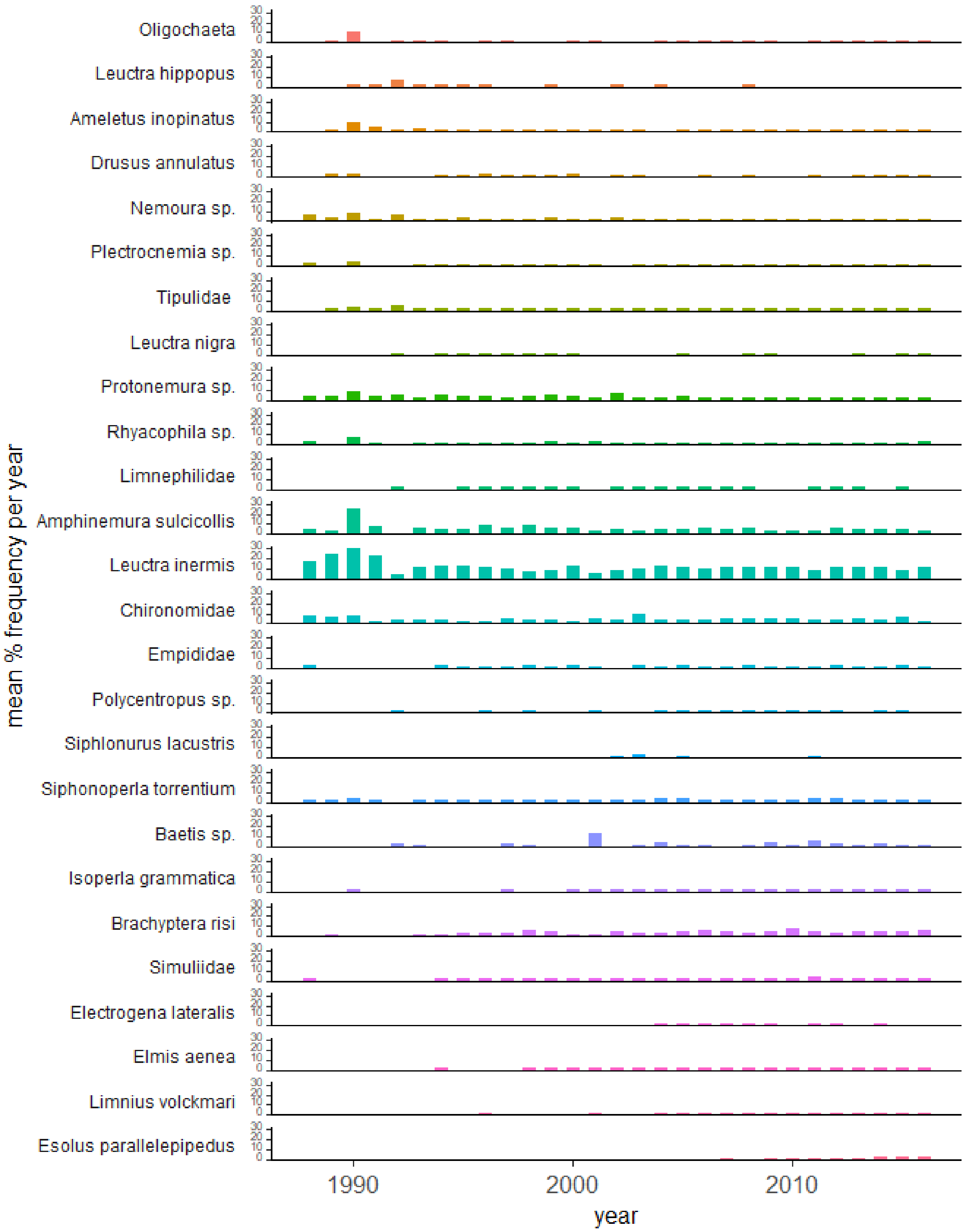
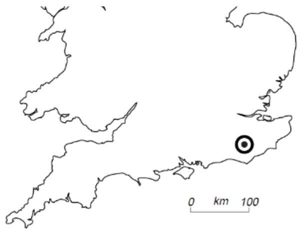


Figure 12.4 River Etherow: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 0.5% of the assemblage in any year.

13. Old Lodge

13.1 Old Lodge site description



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

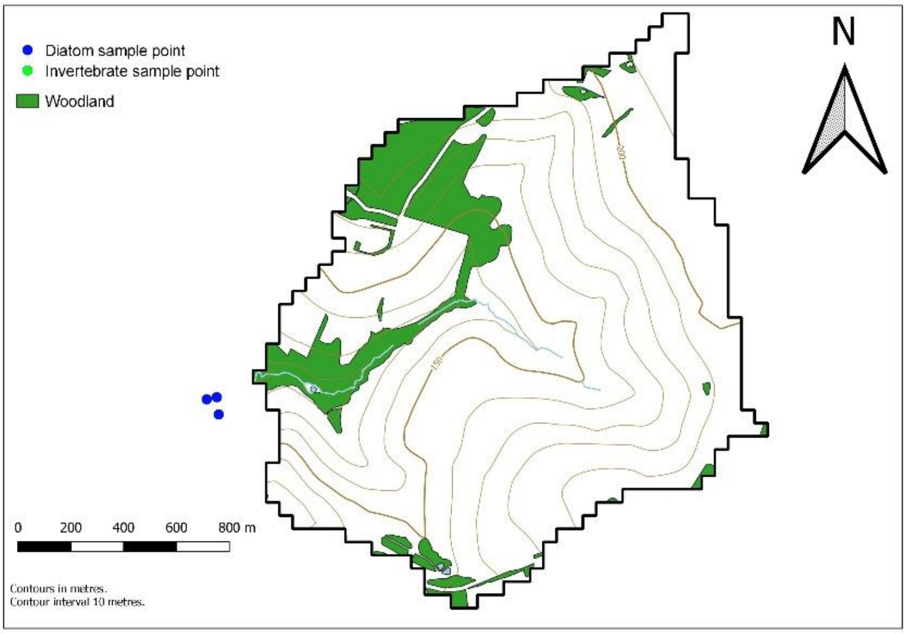


Figure 13.1 Mapped and aerial views of the Old Lodge catchment

Table 13.1 Old Lodge site characteristics

Grid Reference	TQ 456294	
Catchment area	240 ha	
Minimum catchment altitude	94 m	
Maximum catchment altitude	198 m	
Catchment geology	Ashdown sands	
Catchment soils	Podsols	
Catchment vegetation	Heathland 70% Deciduous woodland 15% Conifers 15%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	17.3	4.8
Non-marine oxidised sulphur	13.4	2.3
Oxidised nitrogen	6.8	5.3
Reduced nitrogen	18.8	11.4

Table 13.2 Old Lodge water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	277.0	119.4	818.6	236.2	77.1	36.8	-4.49	**
xSO_4^{2-}	µeq l^{-1}	222.8	71.7	732.1	186.1	5.8	-47.8	-4.57	**
Cl^-	µeq l^{-1}	603.7	503.9	1038.1	919.6	347.0	316.0	-1.24	*
NO^{3-}	µeq l^{-1}	5.0	6.8	18.0	36.4	2.1	2.1	0.00	
pH	pH	4.6	5.8	4.8	7.7	4.4	4.9	0.04	**
Alk	µeq l^{-1}	-32.0	35.8	-19.0	100.2	-54.0	9.0	2.15	**
Cond	µS cm^{-1}	107.5	90.7	201.6	128.2	71.1	61.6	-0.43	**
Na^+	µeq l^{-1}	469.8	427.2	813.5	626.4	287.1	273.6	-0.72	*
Ca^{2+}	µeq l^{-1}	154.7	166.2	353.8	250.0	96.8	88.3	0.33	
Mg^{2+}	µeq l^{-1}	145.6	120.9	347.1	206.5	87.2	73.1	-0.73	**
K^+	µeq l^{-1}	20.7	26.1	55.5	72.4	6.6	8.6	0.18	**
Lab Al	µg l^{-1}	217.5	17.0	530.5	96.0	22.4	5.0	-0.82	
DOC	mg l^{-1}	3.3	9.3	9.2	44.3	0.2	3.0	0.20	**
ANC-CB	µeq l^{-1}	-55.0	75.5	4.5	237.9	-322.6	-27.7	3.94	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

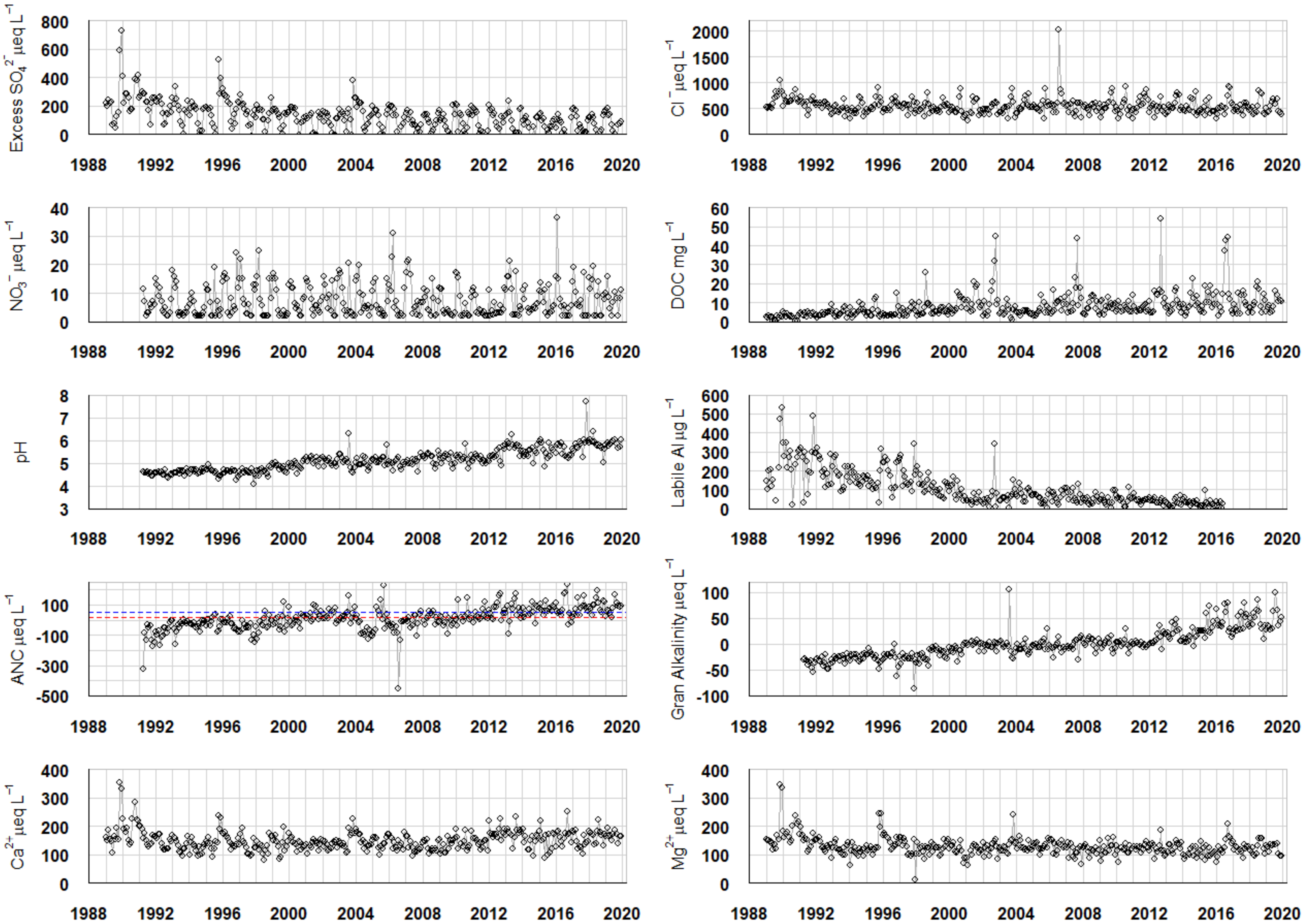


Figure 13.2. Old Lodge water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

13.2 Old Lodge: water chemistry trends

Despite being situated in a region of relatively low deposition, runoff from Old Lodge is almost an order of magnitude lower than for some westerly UWMN sites and historically this resulted in much higher concentrations of atmospheric contaminants, and hence more acidic water. Non-marine sulphate concentrations are comparable only with the River Etherow, and have fallen at a similar rate over the three decades of monitoring, i.e. from a median of 222.8 to 71.7 µeq L^{-1} between the initial and most recent five-year periods. Unusually for UWMN sites, non-marine sulphate concentrations show strong cyclicity, most likely due to strong seasonal fluctuations in the water table and associated fluctuations in redox status, and since around 1994 have often been at undetectably low levels in the summer months before returning to substantial concentrations once the catchment has rewetted in the autumn and winter.

In contrast, chloride concentrations, although also high and oscillating on a seasonal basis, have been relatively stable over time, indicating a much lower contribution from hydrochloric acid deposition in comparison to sites further north. Nitrate concentrations show a regular seasonal cycle, are not detectable during much of the growing season, and have not changed significantly over time.

In response to the large reduction in non-marine sulphate particularly, the acidity of the Old Lodge stream water has declined spectacularly over the monitoring period. Between the first and most recent five year periods, water pH increased from a median of 4.6 to 5.8, median labile aluminium concentrations dropped from 218 to less than 20 µg L^{-1}, Gran Alkalinity rose from -32.0 to 35.8 µeq L^{-1}, and ANC increased from -55.0 to 75.5 µeq L^{-1}. Unlike the River Etherow, the Old Lodge stream shows relatively little chemical dependence on flow, so the changes in acidity-related variables are strongly linear, with relatively little between-sample variation, and from around 2013 ANC has rarely dipped below 20 µeq L^{-1}. In addition to the major reduction in acidity, concentrations of DOC almost trebled over the thirty years – a direct consequence of the effect of the decline in ion deposition on the solubility of soil organic matter in the catchment.

13.3 Old Lodge: epilithic diatom community trends

In common with the other more acidic streams on the Network, the epilithic diatom assemblage of the Old Lodge stream shows clear, consistent changes in species abundances throughout the monitoring period. In the early years the assemblages were usually dominated by the acidophilous/acidobiontic species *Eunotia exigua* (SWAP pH optimum = 5.1). However, since around 2000, frequencies of this species and other low-pH taxa such as *Eunotia incisa* (optimum = 5.1) have declined, while the acid sensitive taxon *Achnanthes minutissima* (optimum = 6.3) has increased, along with *Achnanthes saxonica* (optimum = 5.7). The community has become more diverse with the appearance of a number of taxa with higher pH optima, including *Gomphonema angustatum* agg. (optimum = 5.8) and *Surirella roba* (optimum = 6.3).

Diatom species turnover is moderate (1.3; Main Report: Table 4.1) and the trajectory of PrC scores (Main Report: Figure 4.1) indicates that a consistent and increasing trend in diatom species changes occurred after 1995, i.e. around the time streamwater pH began to increase. RDA and mGLM trend analysis for the whole monitoring period indicates that the floristic change trend is significant (Main Report: Table 4.1). RDA – chemistry analysis indicates a significant diatom response to measured stream-water pH, while the RDA1-pH / PCA ratio of 0.75 indicates that the pH-related trend accounts for the main pattern of variation in the diatom data. The trajectory of DAM scores also shows a significant and consistent trend from the mid- to late-1990s (Main Report: Figure 4.2). Variance partitioning indicates a significant relationship between diatom assemblage change and alkalinity and DOC, but the conditional effect of these variables is not significant, indicating that the trends in the diatom data can be accounted for by the observe increase in stream water pH alone.

13.4 Old Lodge: macroinvertebrate community trends

In the early years of monitoring, Old Lodge was characterised by a relatively simple macroinvertebrate community, indicative of highly acidic conditions, and was dominated by the acid-tolerant stoneflies (*Nemoura*, *Leuctra nigra*) and *Plectrocnemia* caddisflies, midges (Chironomidae) and blackfly (Simuliidae) (Appendix: Figure 13.4). Unusually, the stream also supported a sparse population of the bivalve mollusc *Pisidium* and the amphipod crustacean *Niphargus aquilex*, the latter associated with subterranean freshwater habitats but often found in spring-fed streams. Over the following 28 years of gradual chemical improvement the site has experienced strong biological recovery in taxon richness, with almost twice as many taxa recorded recently in comparison with the late 1980s. Unsurprisingly, given the above observations, there has also been significant directional change in the macroinvertebrate assemblage over that time (Main Report: Table 5.3) driven by accrual of new colonisers and changes in the relative abundance of already established taxa. Changes in the macroinvertebrate community indicate that there has been some recovery from acidification but, after 28 years AWICsp values are still averaging < 4 implying that the stream fauna is still impacted to a substantial extent by acid stress. Promisingly, over the last three years of monitoring small numbers of more acid-sensitive taxa, such as the gastropods *Potamopyrgus antipodarum* and Lymnaeidae, and the crustaceans *Proasellus meridianus* and *Crangonyx,* have been recorded.

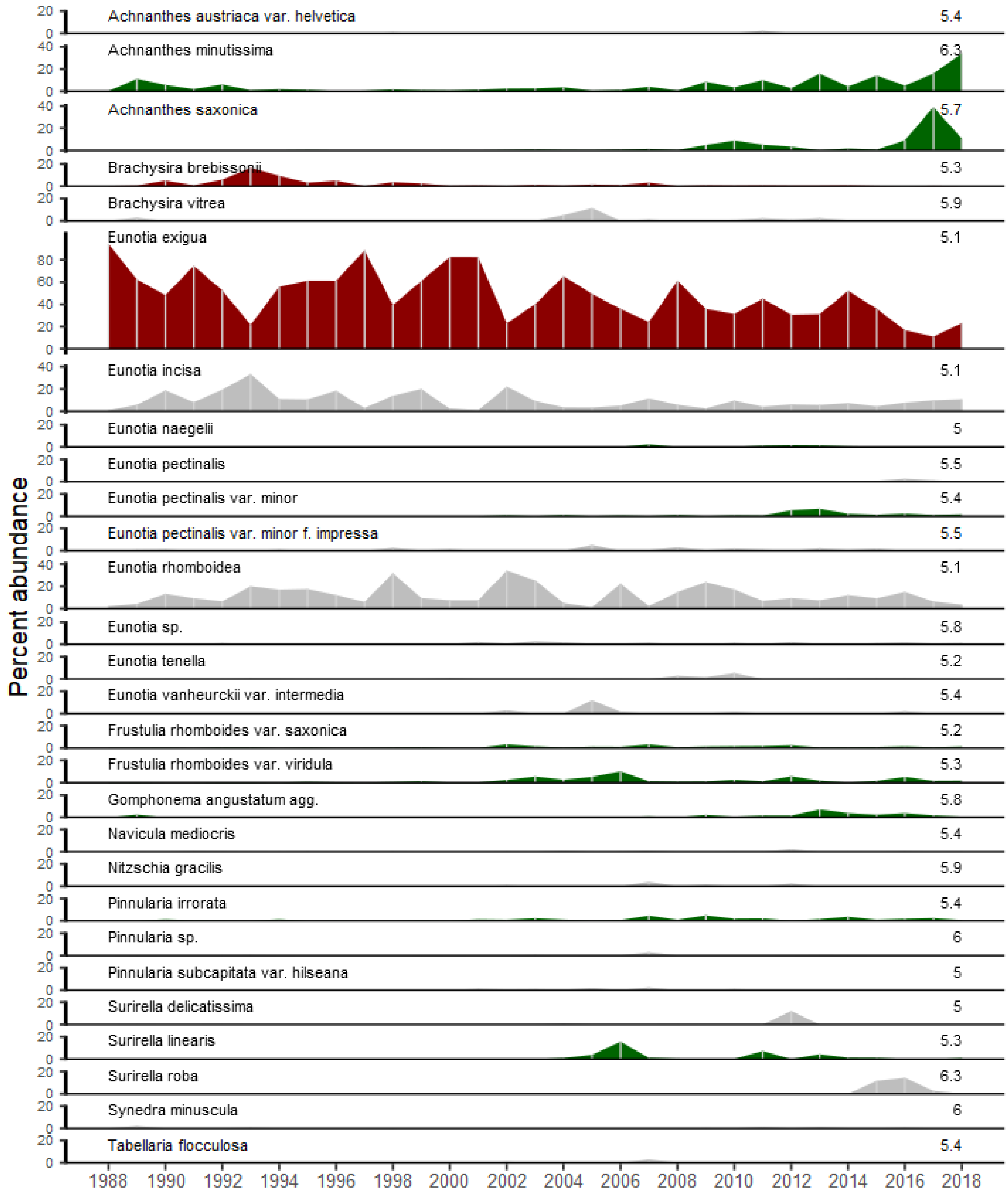


Figure 13.3 Old Lodge: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

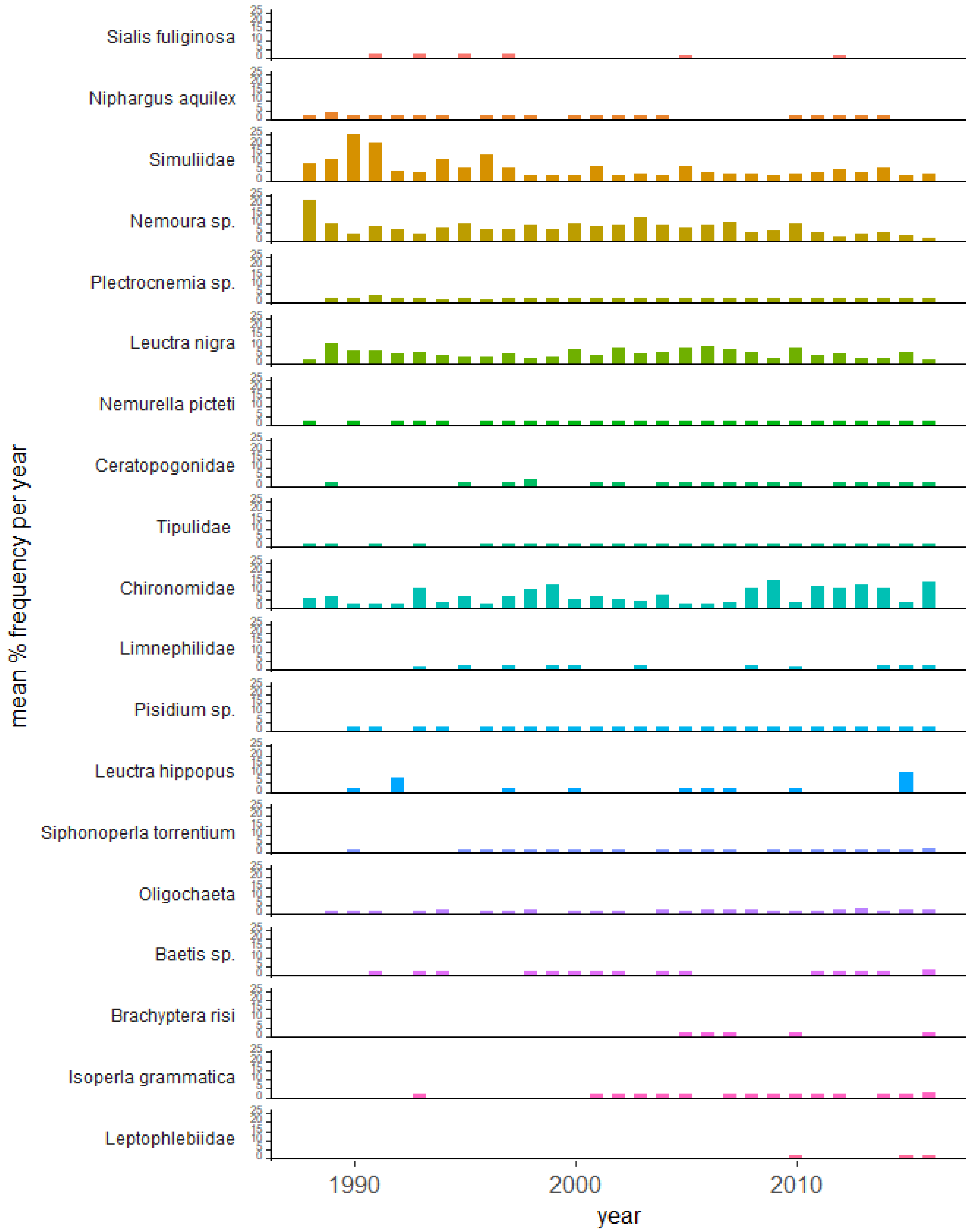


Figure 13.4 Old Lodge: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 0.5% of the assemblage in any year.

14. Narrator Brook

14.1 Narrator Brook site description

Narrator Brook drains moorland overlying granite and feeds the Burrator Reservoir in the Dartmoor National Park in southwest England. The chemistry sampling location was moved upstream in 1991 following some felling of trees in the lower part of the catchment. There is no indication of significant physical disturbance or changes in land use within the catchment since the monitoring site was moved.

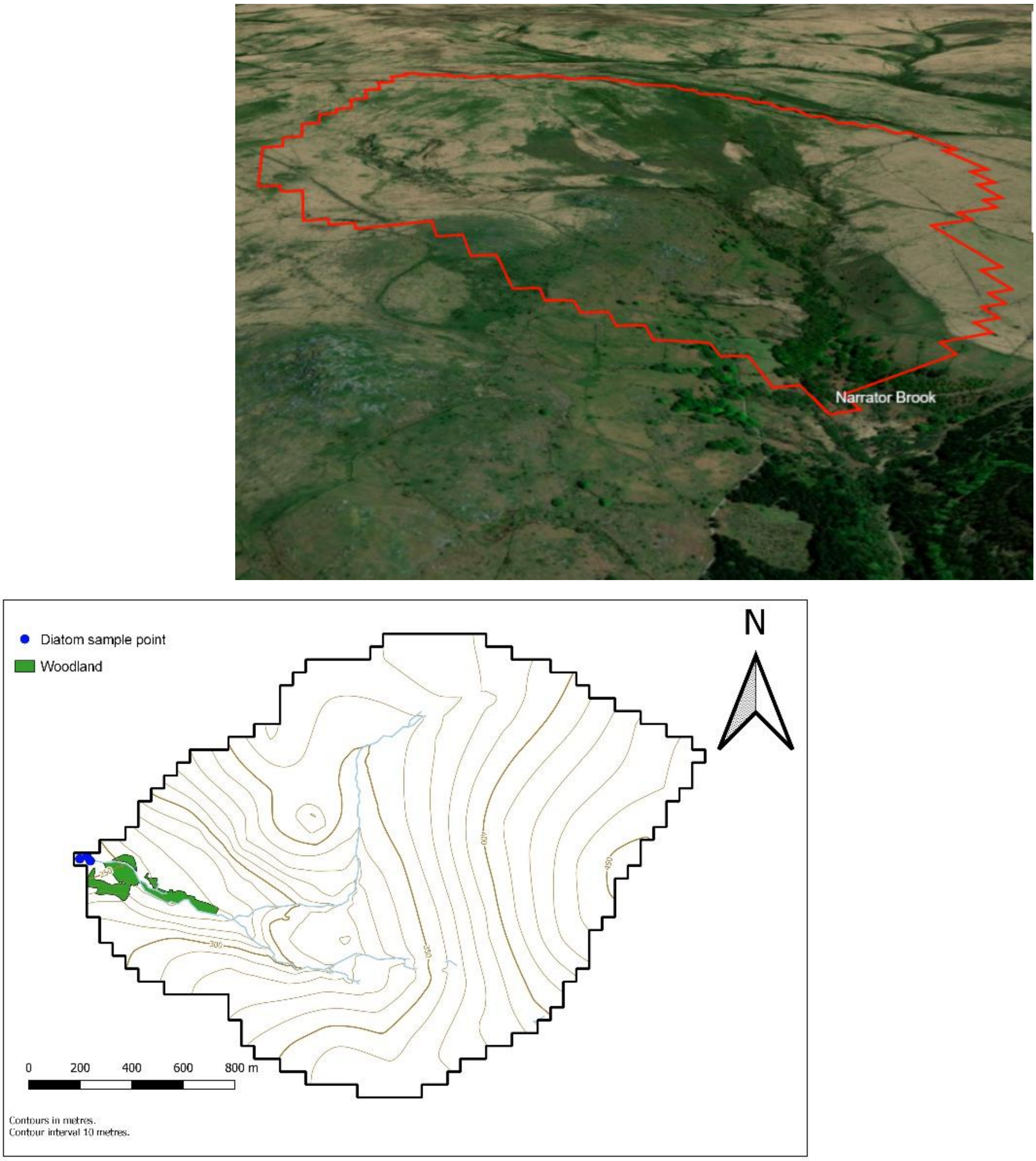


Figure 14.1 Mapped and aerial views of the Narrator Brook catchment

Table 14.1 Narrator Brook site characteristics

Grid Reference	SX 568692	
Catchment area	253 ha	
Minimum catchment altitude	225 m	
Maximum catchment altitude	456 m	
Catchment geology	Granite	
Catchment soils	Iron pan stagnopodsols, brown podsols	
Catchment vegetation	Moorland/acid grassland 98% Deciduous woodland 15%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	20.7	10.9
Non-marine oxidised sulphur	11.6	3.9
Oxidised nitrogen	6.6	5.8
Reduced nitrogen	9.0	12.6

Table 14.2 Narrator Brook water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope year^{-1}	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	70.8	63.1	79.2	75.0	64.6	31.2	-0.23	**
xSO_4^{2-}	µeq l^{-1}	41.5	38.7	56.3	49.8	34.1	9.0	-0.15	**
Cl^-	µeq l^{-1}	282.1	237.5	344.2	270.8	220.0	160.8	-1.30	**
NO^{3-}	µeq l^{-1}	5.3	7.9	10.5	17.4	2.7	2.1	0.07	**
pH	pH	5.7	6.1	6.0	6.4	5.1	5.3	0.01	**
Alk	µeq l^{-1}	12.0	39.2	21.0	64.8	-5.0	15.7	0.56	**
Cond	µS cm^{-1}	48.4	42.8	50.2	48.1	40.6	28.3	0.24	*
Na^+	µeq l^{-1}	256.7	230.6	269.7	278.8	208.8	161.0	-0.68	**
Ca^{2+}	µeq l^{-1}	33.9	32.6	42.9	40.7	25.9	25.0	-0.03	**
Mg^{2+}	µeq l^{-1}	65.8	62.7	69.9	80.1	47.7	48.9	0.00	
K^+	µeq l^{-1}	21.0	19.9	25.1	33.8	16.4	10.5	0.06	**
Lab Al	µg l^{-1}	16.0	8.0	52.0	32.0	2.5	2.0	-0.10	
DOC	mg l^{-1}	1.0	1.6	5.5	8.5	0.3	0.7	0.01	**
ANC-CB	µeq l^{-1}	15.3	38.1	42.2	82.0	-51.3	10.6	0.54	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

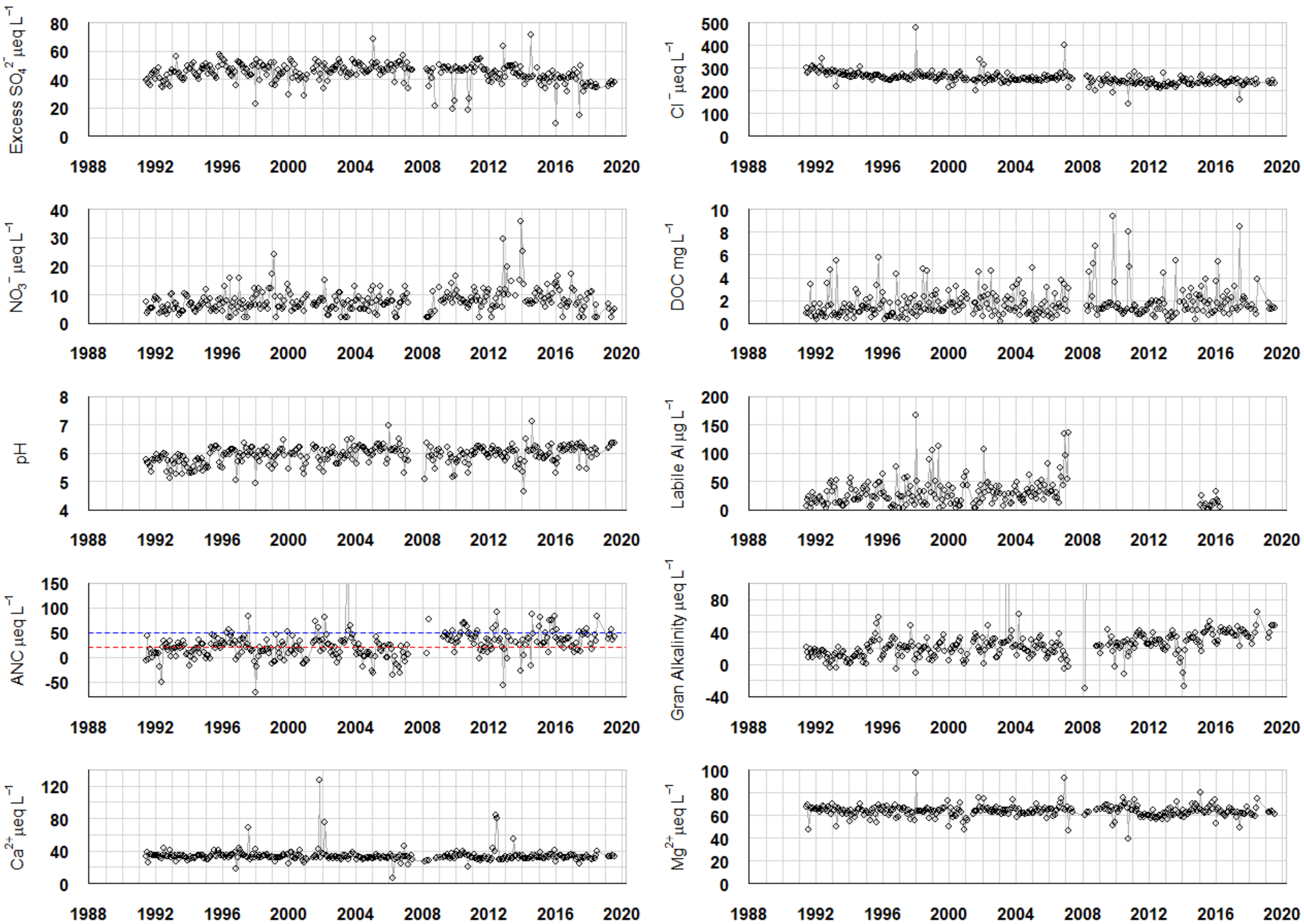


Figure 14.2 Narrator Brook water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

14.2 Narrator Brook: water chemistry trends

The patterns of change in the water chemistry of Narrator Brook are unusual for the network. Most notably, non-marine sulphate concentration underwent a slight increase over the first 15 years or so of monitoring, before falling again - resulting in a significant, but overall only slight, decline over the three decades. The CBED estimates for non-marine sulphur and nitrogen deposition at the onset of monitoring, and the rate of change over time, are very similar to those for Loch Coire nan Arr, i.e. one of the low deposition "control" sites in northern Scotland. However, initial concentrations of non-marine sulphate were three times those of the control site, suggesting that the site is likely to have a significant geological source of sulphur.

The most striking change in the concentration of an acid anion at Narrator Brook was an early fall in chloride, from around 300 µeq L^{-1} in 1992, to a median of 238 µeq L^{-1} during the last five years of monitoring. This appears due to a reduction in hydrochloric acid deposition in the 1990s and early 2000s. Curiously for a UWMN site so close to the coast, chloride concentrations are very stable in comparison to the highly variable concentrations seen in most sites with westerly locations. This may be partly a consequence of the vulnerability of the catchment to multiple sea salt deposition trajectories, with storm tracks from any direction other than easterly likely to make contributions to the marine ion deposition load. Groundwater may also provide a significant damping effect on water chemistry, as similarly stable concentrations are also observed for calcium and magnesium. In contrast, nitrate concentrations are highly variable, almost always above limits of detection and, unusually for the network, show a very slight but significant increase over the full monitoring period.

The large early change in chloride provides the clearest explanation for an early increase in pH, with the median increasing from 5.7 (1992-993) to 6.1 by the most recent five-year period. Most of the pH rise had occurred by 2000, but ANC, that averaged around 15 µg L^{-1} at the onset of monitoring, shows a later rise (around 2010), after a two year gap in regular monitoring. Over the most recent five year period ANC has averaged 38 µg L^{-1}, with very few samples registering below the UK ANC_{crit} value of 20 µeq L^{-1}. Unlike the northern control sites, the water chemistry of Narrator Brook was sufficiently acidic in the early years of monitoring for moderate levels of labile aluminium concentration, with values occasionally exceeding a highly toxic 100 µg L^{-1}. Unfortunately, aluminium measurements for this site largely ceased in 2007, but a short period of renewed monitoring in 2015 suggest that concentrations have since dropped to near-detection levels.

Dissolved Organic Carbon concentrations in Narrator Brook have mostly been very low, but are highly variable, and in common with the other sites on the network show a significant increase over time that again reflects a reduction in pollutant deposition.

14.3 Narrator Brook: epilithic diatom community trends

The epilithic diatom flora of Narrator Brook is dominated by the acid-sensitive *Achnanthes minutissima* (SWAP pH optimum = 6.3) but showed considerable interannual variation, with *Fragilaria vaucheriae* (optimum = 6.3)*, Surirella linearis* (optimum = 5.3) and *Eunotia vanheurkii* var. *intermedia* (optimum = 5.4) also abundant in some years.

Numerical analysis of the species data indicates a significant community-level trend (RDA1 but not mGLM; Main Report: Table 4.1) although the trajectory of PrC scores (Main Report: Figure 4.1) suggests a complex pattern of community change with a consistent increasing trend since 2000 only. While the timing of this inflection is broadly consistent with a delayed reduction in non-marine sulphate at this site, there is no significant trend in DAM scores. Although the RDA-pH test indicates a significant response to measured stream-water pH, the effect size is small, indicating that the response to changing acidity is not the main pattern of variation in these data. Overall, the diatom communities at this site exhibit considerable variability and species changes that have only a weak relationship to trends in the measured chemistry.

14.4 Narrator Brook: macroinvertebrate community trends

This Dartmoor stream supports a diverse macroinvertebrate community (Appendix: Figure X.4). Over the first 15 years of monitoring, taxonomic richness increased by about 40% and has thereafter remained relatively level. The rate of increase in richness is comparable only with Old Lodge, although Narrator Brook was considerably more diverse than Old Lodge in its early highly acidic phase. The significant temporal trend in variation in community composition (Main Report: Figure 5.2 and Table 5.3) was driven by the changing relative abundances of Elmidae (riffle beetles), the caddisfly families Limnephilidae and Philopotamidae, the establishment of new taxa such as the diving beetle *Oreodytes sanmarkii*, the moss beetle genus *Hydraena*, and the mayfly genus *Ecdyonurus,* and the loss of what were initially common taxa such as the caddis species *Plectrocnemia* and *Wormaldia*. Together, these shifts caused the already relatively high AWICsp values to rise by a small but significant amount over the first 10 years of monitoring. AWICsp scores have remained stable around 5.8 from 2000 to 2016 indicating little to no continuing stress from acidification at this site.

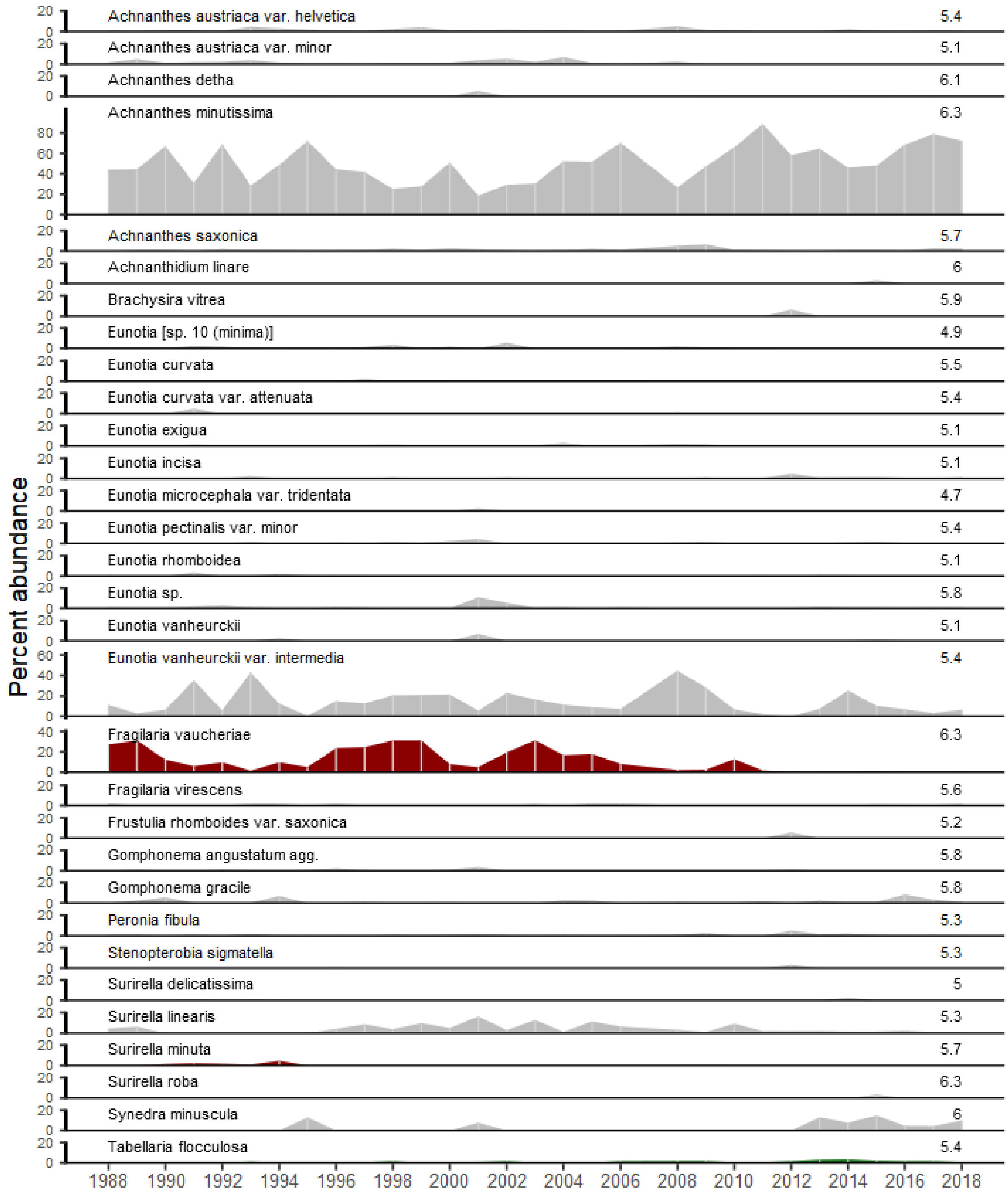


Figure 14.3 Narrator Brook: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

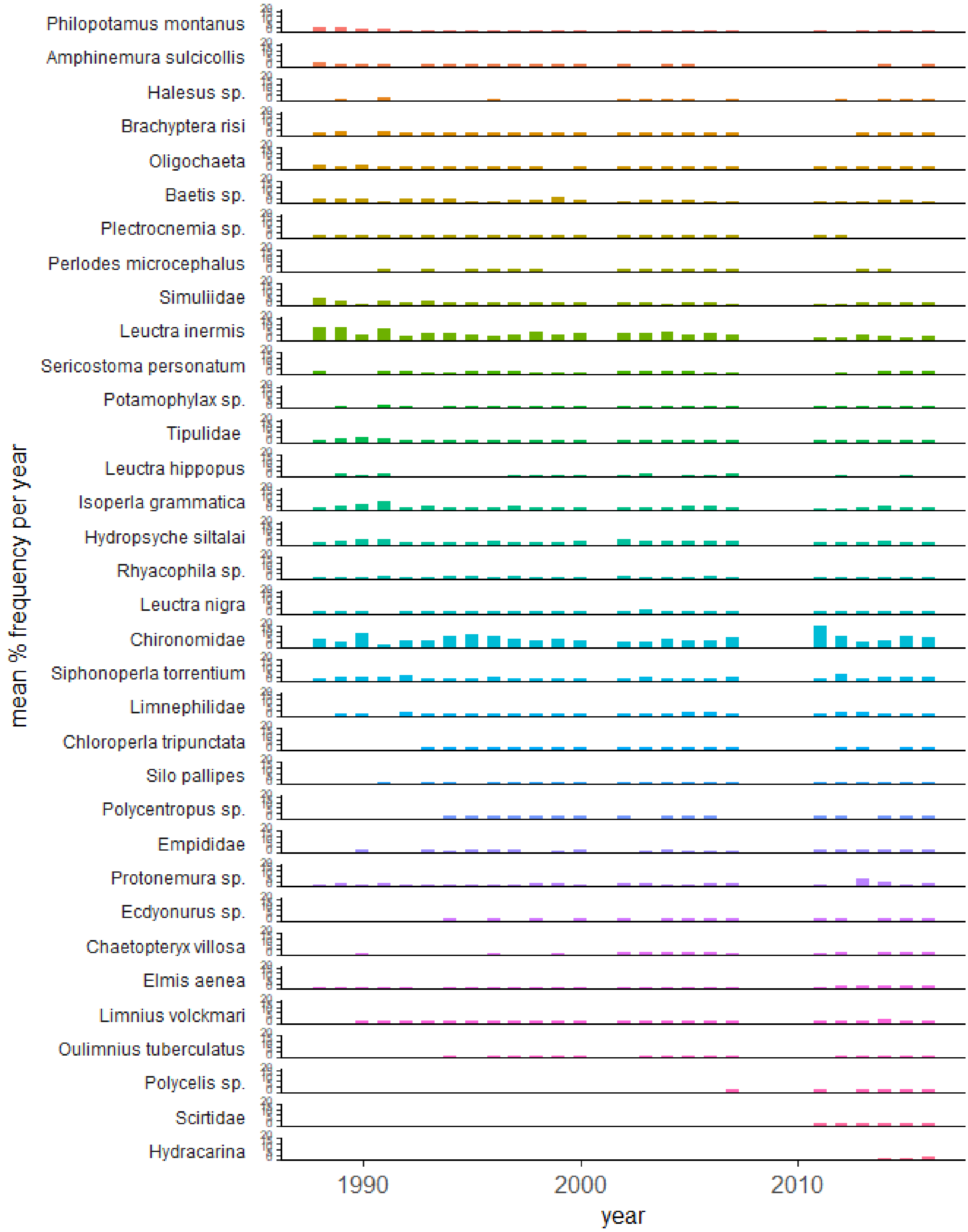


Figure 14.4 Narrator Brook: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

15. Llyn Llagi

15.1 Llyn Llagi site description

Llyn Llagi lies at an altitude of 380 m in the Snowdonia National Park, and is fed by a second water body, Llyn yr Adar. Changes in the fossil diatom assemblage of a sediment core from the site indicate that the lake acidified progressively from the mid-nineteenth century (diatom inferred pH 6.0) to around pH 4.6 by the mid-1980s (Patrick et al., 1995). The uppermost levels of the sediment core suggested a slight improvement (i.e. recovery) in the diatom flora from this time to the top of the core (1990), indicating therefore that some chemical recovery was already underway when monitoring began in 1988. There has been no physical disturbance or change in the land management regime (low intensity sheep grazing) in the catchment over the last decade.

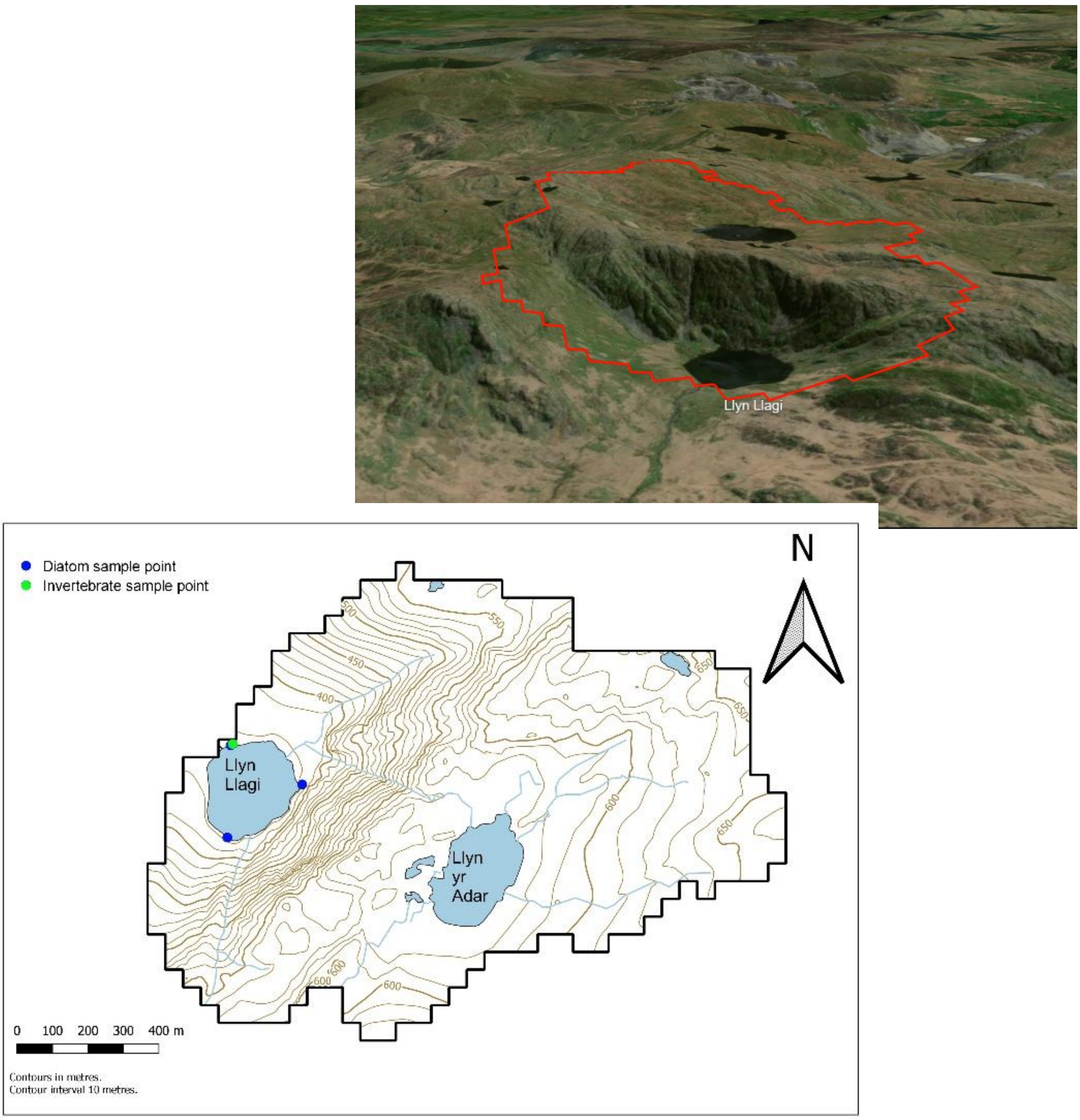


Figure 15.1 Mapped and aerial views of the Llyn Llagi catchment

Table 15.1 Llyn Llagi site characteristics

Grid Reference	SH 649483	
Lake altitude	380 m	
Maximum altitude	680 m	
Maximum depth	16.5 m	
Mean depth	5.8 m	
Volume	3.3×10^5 m^3	
Lake area	5.67 ha	
Catchment area	1401.3 ha	
Catchment area (excl.lake)	157 ha	
Catchment:Lake ratio	27:7	
Catchment geology	Ordivcian slates and shales, dolerite and volcanic intrusions	
Catchment soils	Stagnopodsols, stagnohumic gleys, blanket peat	
Catchment vegetation	Moorland	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	29.7	11.2
Non-marine oxidised sulphur	19.7	4.5
Oxidised nitrogen	9.5	5.2
Reduced nitrogen	37.9	13.0

Table 15.2 Llyn Llagi water chemistry statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope year^{-1}**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	64.6	28.4	79.2	43.7	50.0	13.4	-1.13	**
xSO_4^{2-}	µeq l^{-1}	40.5	11.7	60.9	19.6	22.8	-1.4	-1.00	**
Cl^-	µeq l^{-1}	228.5	146.7	378.0	434.4	121.3	65.2	-0.78	**
NO^{3-}	µeq l^{-1}	7.1	4.1	38.6	10.9	2.1	2.1	0.00	
pH	pH	5.2	5.8	6.3	6.1	4.8	5.0	0.01	**
Alk	µeq l^{-1}	-0.3	23.5	35.2	43.8	-14.3	-9.1	0.54	**
Cond	µS cm^{-1}	35.0	27.7	58.0	67.8	24.0	15.5	0.00	*
Na^+	µeq l^{-1}	191.4	141.8	291.5	340.2	126.2	86.1	-0.60	**
Ca^{2+}	µeq l^{-1}	52.4	37.9	93.8	56.4	38.4	27.8	-0.33	**
Mg^{2+}	µeq l^{-1}	50.2	36.9	74.9	81.4	34.5	23.4	-0.19	**
K^+	µeq l^{-1}	2.6	3.7	6.6	9.3	2.6	1.5	0.03	*
Lab Al	µg l^{-1}	25.0	5.5	159.0	15.0	2.5	3.0	-0.10	
DOC	mg l^{-1}	2.1	3.9	3.7	6.1	0.1	1.9	0.03	**
ANC-CB	µeq l^{-1}	5.5	37.8	31.8	69.7	-19.1	-14.9	0.70	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

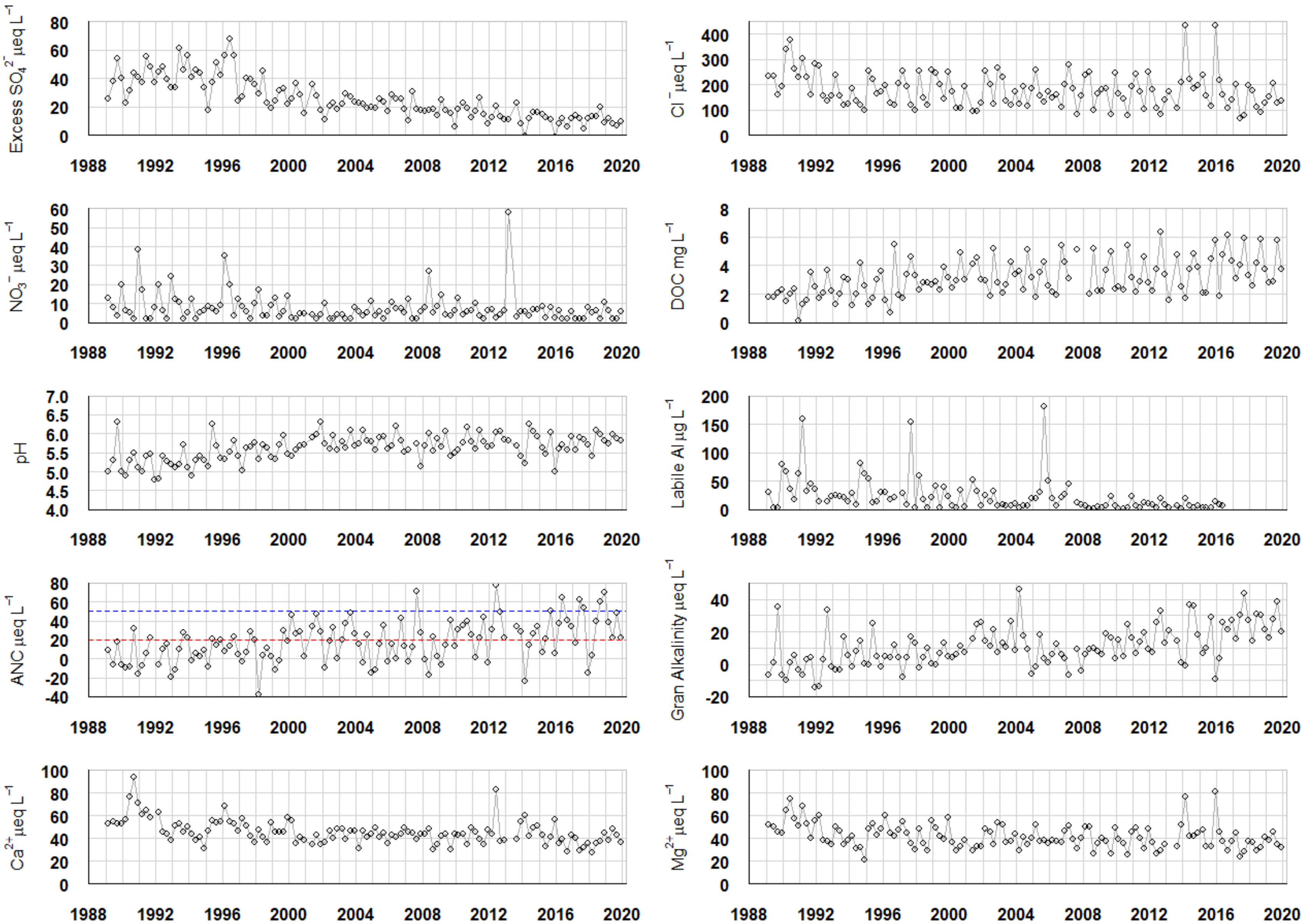


Figure 15.2 Llyn Llagi water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

15.2 Llyn Llagi: water chemistry trends

According to CBED estimates, deposition loads of non-marine sulphur and nitrogen to the Llyn Llagi catchment were similar to those experienced at moorland sites in Galloway and the English Lake District at the onset of monitoring and have since fallen at a similar rate. Consequently non-marine sulphate concentrations in Llyn Llagi have fallen by over 70% between the first and most recent five year periods. Chloride concentrations have oscillated substantially, emphasising the strong influence of sea salt deposition to the catchment, and have fallen in the longer term (at a slightly slower rate than non-marine sulphate) as a consequence of the long-term reduction in hydrochloric acid deposition. Nitrate concentrations were relatively low, but mostly above the limit of detection, in the early years of monitoring, but have declined over time and, over the last five years, have frequently been undetectable.

In comparison with other UWMN lakes with similar catchments and deposition histories, i.e. the Round Loch of Glenhead and Scoat Tarn, divalent base cation concentrations in Llyn Llagi have always been relatively high, and at the onset of monitoring median Gran alkalinity was approximately zero - as opposed to significantly negative at the other two sites. Despite initially acidic conditions, therefore, the greater chemical buffering offered by the soils and underlying geology have enabled a particularly striking rebound in acidity as the acid deposition load lessened. Most of this chemical recovery occurred within the first 15 years of monitoring. In the first five-year period, median lake water pH was 5.2, ANC of the majority of samples registered below 20 µeq L^{-1} and was frequently negative, and labile aluminium concentrations, while generally low, occasionally exceeded 50 µg L^{-1}. Since 2008, pH has averaged around 5.8, ANC of the majority of samples has exceeded 20 µeq L^{-1} and has rarely been negative, and by 2016 labile aluminium concentrations had fallen to close to or below the limit of detection. Despite these substantial improvements, the acid-base chemistry of Llyn Llagi remains vulnerable to major seasalt deposition events. For example, a major deposition episode in December 2015 was sufficient to drive pH below 5.0, one of the most acidic samples ever recorded for the site.

Over the monitoring period DOC concentrations have approximately doubled, a result of the increasing solubility of soil organic matter as pollutant deposition to the catchment has fallen. The change in water colour associated with a change in median DOC concentration between the first and most recent five-year period of 2.1 to 3.9 mg L-1, is estimated to have halved the photic depth of the lake, from 13.5 to 7.3 m, so that aquatic photosynthesis is theoretically no longer viable over approximately 30% of the lake bed (Monteith pers. comm).

15.3 Llyn Llagi: epilithic diatom community trends

The epilithic diatom assemblage of Llyn Llagi is relatively diverse and has exhibited considerable turnover (1.78; Main Report: Table 4.1) over the period of monitoring. During the first 5 years the assemblages were dominated by the acidobiontic species *Tabellaria quadriseptata* (SWAP pH optimum = 4.9), *Eunotia incisa* (optimum = 5.1) and *T. flocculosa* (optimum = 5.4) (Appendix: Figure 15.3). *Tabellaria quadriseptata* ceased to be detected after 1995, while proportions of *Brachysira brebissonii* (optimum = 5.3), *Nitzschia perminuta* (optimum = 5.7) and *Brachysira vitrea* (optimum = 5.9) increased. The latter taxon has remained dominant from around 2005 when it was joined by low proportions of *Cymbella lunata* (optimum = 5.7). The acid-sensitive taxon *Achnanthes minutissima* has been present in small proportions from 2011.

RDA trend analysis for the whole monitoring period indicates that the community-wide trend is significant (RDA1, mGLM; Main Report: Table 4.1) although the trajectory of the PrC scores (Main Report: Figure 4.1) suggest that the main period of species turnover was from 1988 to 2008 and since then there has been little change in the diatom flora. RDA1-pH also indicates a significant relationship with pH, and the RDA1-pH / PCA1 ratio suggests that the relationship with changes in measured lake-water pH accounts for the dominant pattern of variation in the diatom data. The trend in the DAM score is relatively large and significant (Main Report: Table 4.1) but the trajectory also suggests the species response to changing pH has levelled off since the early 2000s, which is consistent with the trend in measured pH.

Overall, there is strong evidence that diatom epilithon at this site has tracked the measured increase in pH for the early part of the record, but that lake-water pH and the diatom assemblages have remained relatively unchanged since the early 2000s.

15.4 Llyn Llagi: macroinvertebrate community trends

During the first 15 years of monitoring at Llyn Llagi there was considerable change in macroinvertebrate richness and assemblage composition (Appendix: Figure 15.3). A number of new taxa established populations at the site including the freshwater bivalve mollusc *Pisidium*, the stonefly *Siphonoperla torrentium*, and the caddisflies *Mystacides*, *Oxyethira*, and *Tinodes waeneri*. Thereafter, richness has remained relatively stable and the temporal trend in community change has weakened. Over the monitoring period these changes have indicated a small but significant trend in recovery, although by 2016, LAMM values were still at only about 70% of what would be expected for non-acidified lakes of comparable typology (Main Report: Figure 5.3). It is worth noting that in the last 3 years the acid-sensitive gastropod mollusc *Bathyomphalus contortus* has been consistently recorded in samples, which may suggest that another phase of biological recovery is now taking place.

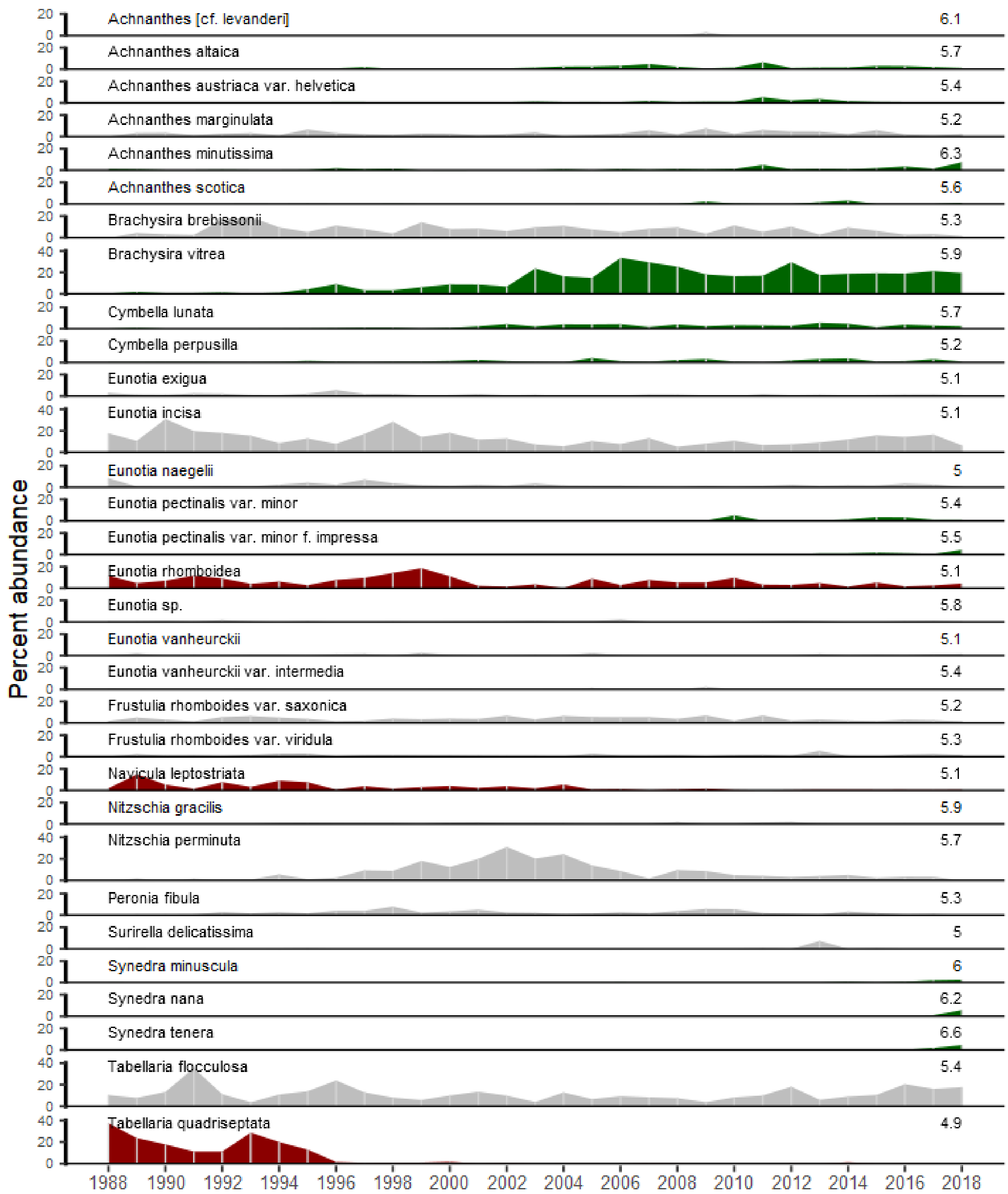


Figure 15.3 Llyn Llagi: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

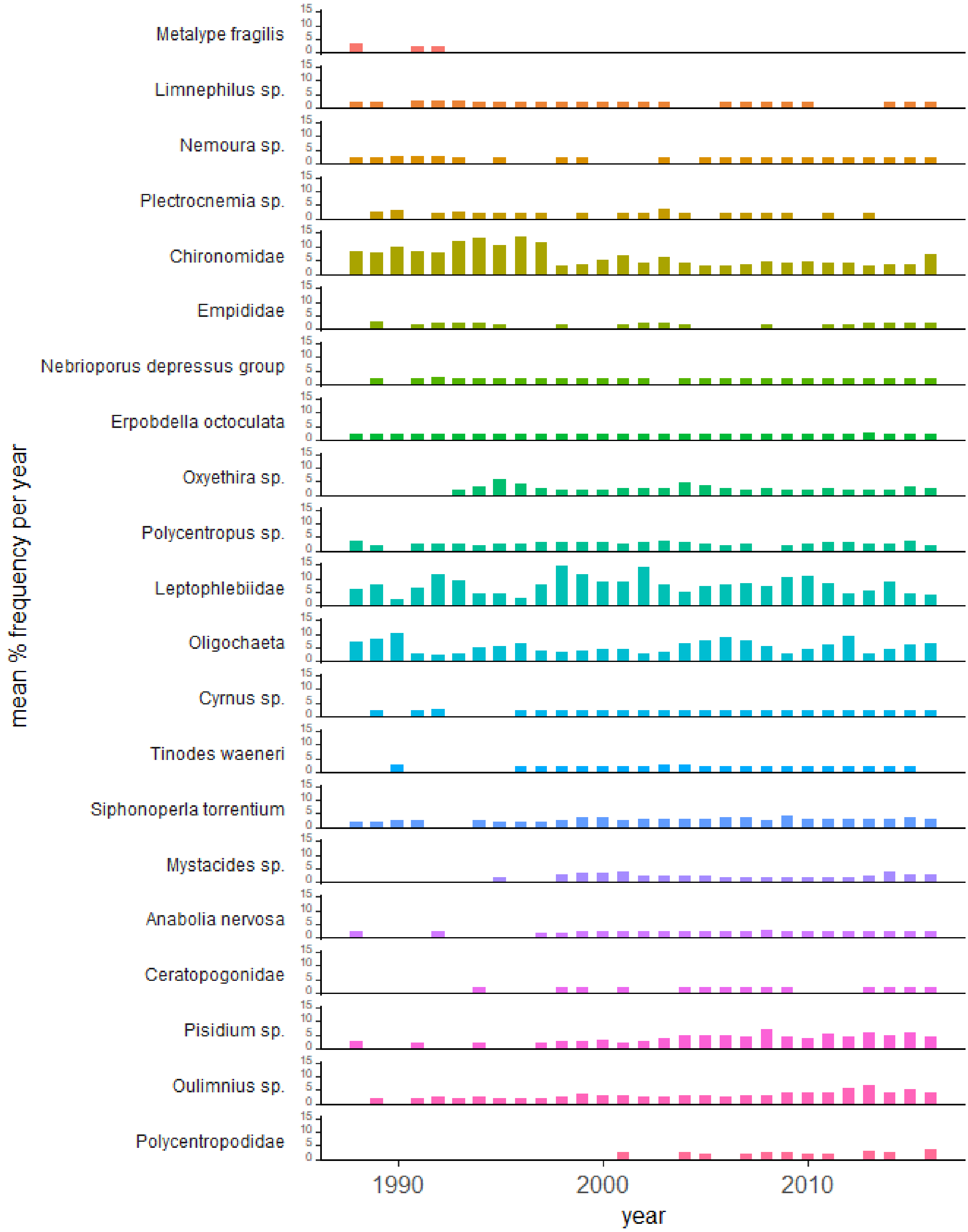
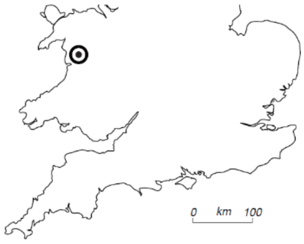


Figure 15.4 Llyn Llagi: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

16. Llyn Cwm Mynach



16.1 Llyn Cwm Mynach site description

The catchment of Llyn Cwm Mynach, in the Rhinog mountains of north Wales, includes a substantial proportion of mature forest. Palaeoecological analysis showed that Llyn Cwm Mynach acidified relatively recently, with pH declining from 5.8 at the turn of the century to 5.4 by the onset of the monitoring period. A considerable amount of felling of conifers has been carried out over the past decade. Throughout the monitoring period the main lake basin has been affected by the blue-green alga *Plectonema* which has blanketed large areas and out-competed submerged vascular aquatic macrophytes, resulting in significant amounts of dead plant material accumulating in the littoral strand-line. The Llyn Cwm Mynach catchment forms part of Blaen Cwm Mynach Forest, which was privately owned until its recent purchase by the Woodland Trust. The Trust aims to gradually transform the present conifer forest to predominantly native broadleaf woodland. This will take many decades and in the interim, some of the conifer crop will be converted to continuous cover stands. There is also likely to be a lowering of the tree line with conversion back to former heathland. The proportion of conifer forest is expected to be reduced from 53% in the 1980s to 30% by 2050. In 2018, a small makeshift wooden dam on the lake outflow was lost, resulting in a drop in water level of a few tends of centimetres.

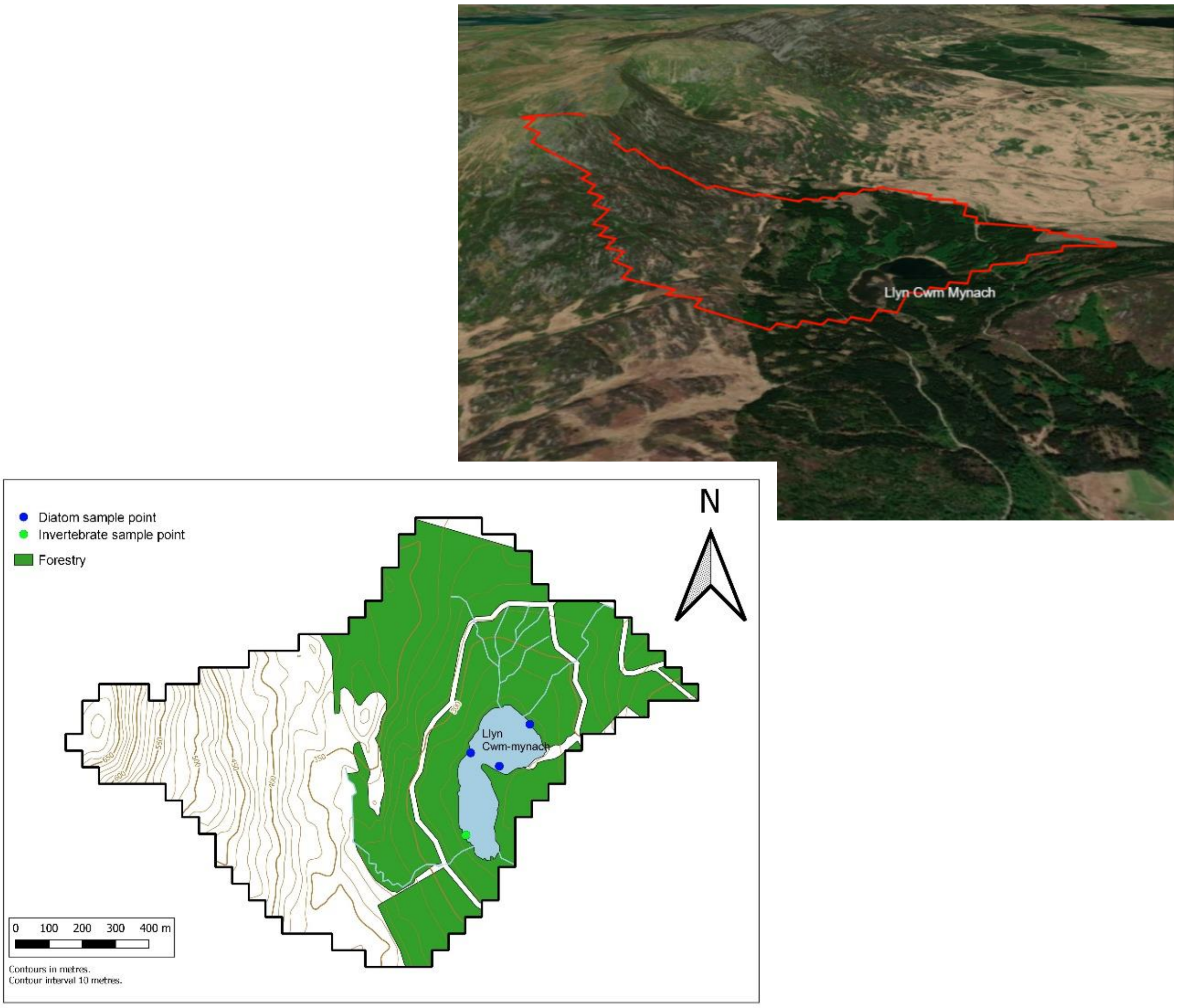


Figure 16.1 Mapped and aerial views of the Llyn Cwm Mynach catchment

Table 16.1 Llyn Cwm Mynach site characteristics

Grid Reference	SH 678238	
Lake altitude	285 m	
Maximum altitude	680 m	
Maximum depth	11.0 m	
Mean depth	0.9 m	
Volume	5 x 10^4 m^3	
Lake area	5.9 ha	
Catchment area	159 ha	
Catchment area (excl.lake)	153 ha	
Catchment:Lake ratio	11:3	
Catchment geology	Cambrian sedimentary	
Catchment soils	Blanket peats, acid rankers	
Catchment vegetation	Conifers – 55%, Moorland – 45%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	26.2	9.3
Non-marine oxidised sulphur	18.1	3.9
Oxidised nitrogen	9.1	5.8
Reduced nitrogen	34.7	13.0

Table 16.2 Llyn Cwm Mynach water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	87.5	57.4	154.1	154.3	68.7	22.1	-0.98	**
xSO_4^{2-}	µeq l^{-1}	51.4	21.9	110.7	127.8	33.3	14.6	-0.88	**
Cl^-	µeq l^{-1}	334.3	264.3	519.1	485.2	143.9	71.7	0.03	
NO^{3-}	µeq l^{-1}	7.9	10.8	30.7	50.5	2.1	2.1	0.06	*
pH	pH	5.3	5.4	6.3	6.5	4.7	4.8	-0.02	
Alk	µeq l^{-1}	2.8	3.0	35.2	66.0	-21.0	-102.0	0.16	
Cond	µS cm^{-1}	48.5	46.3	72.0	77.4	33.0	20.1	0.21	
Na^+	µeq l^{-1}	278.4	270.1	404.6	421.1	174.0	94.0	0.19	
Ca^{2+}	µeq l^{-1}	76.6	60.1	127.7	97.3	37.4	19.0	-0.14	*
Mg^{2+}	µeq l^{-1}	67.5	64.9	96.2	96.2	41.1	22.8	0.10	
K^+	µeq l^{-1}	2.6	7.1	7.4	12.1	2.6	1.9	0.08	**
Lab Al	µg l^{-1}	38.0	24.0	291.0	59.0	2.5	1.0	-0.10	
DOC	mg l^{-1}	2.2	3.5	10.7	10.1	0.1	0.8	0.02	**
ANC-CB	µeq l^{-1}	4.4	47.0	35.6	121.1	-45.2	-49.9	0.86	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

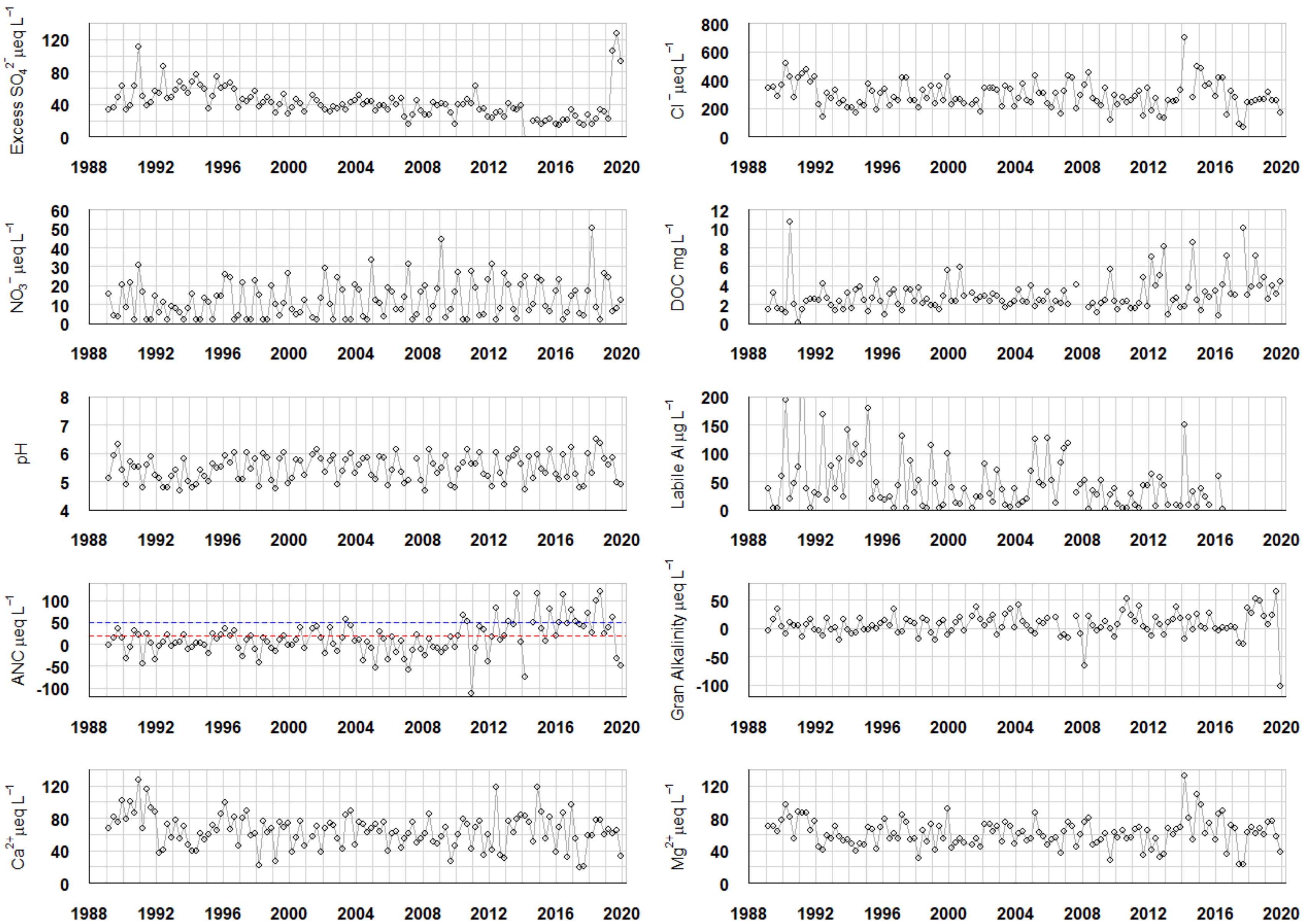


Figure 16.2 Llyn Cwm Mynach water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

16.2 Llyn Cwm Mynach: water chemistry trends

Despite the forested catchment, the CBED estimates of non-marine sulphur and nitrogen deposition loadings at this site are similar to those for the moorland site Llagi Llagi, 25 km to the north, and have declined at a similar rate over the monitoring period. Lake water non-marine sulphate concentrations also show a generally similar rate of decline to Llyn Llagi, although over the last five years median concentrations have been approximately double (21.9 µeq L^{-1}) that of the Snowdonian site. Uniquely for the UWMN, non-marine sulphate concentrations increased sharply in 2019. This is likely to be a side effect of major recent felling activity within the catchment, and the related soil disturbance that may have led to the oxidation of legacy sulphur stored as sulphides. Alternatively, it may be due to a recent small reduction in the water level (of circa 0.5 m) following the loss of a small wooden construction that spanned the outflow. Although probably a short-term pulse disturbance, therefore, the recent surge in sulphate highlights the potential for actions within catchments to have a significant impact on acid-base chemistry despite the considerable reduction in the deposition load.

Soil disturbance may also account for the absence of a significant trend in chloride concentration - in contrast to most other UWMN sites. Although the pattern of inter-sample variation in chloride concentration is similar to Llyn Llagi, unusually high concentrations were recorded between 2014 and 2016, and these have countered the expected response to falling levels of hydrochloric acid deposition seen at the majority of UWMN sites. Typically for UWMN sites with partially forested catchments, nitrate concentrations are relatively high over the winter months, but are often below limits of detection during the growing season, resulting in a pronounced seasonal cycle. Nitrate concentrations have increased slightly but significantly over the three decades, and this is again most likely linked to forestry activity within the catchment.

In comparison with several other UWMN lakes, the chemistry of Llyn Cym Mynach was relatively well buffered at the onset of monitoring, as evidenced by the calcium and magnesium concentrations and fractionally positive median Gran alkalinity and ANC values over the first five years. Furthermore, the net reduction in acid anion concentrations has been relatively modest, and because of these two factors changes in acidity have not been as pronounced as at most other acid-sensitive sites. There was, however, a substantial drop in labile aluminium maxima over the first 15 years of monitoring, while median pH increased from 5.3 to 5.4 between the first and most recent five-year periods. A more substantial rise in ANC since 2010 seems to be related to an increase in DOC over the same period, and this may in turn again be linked to recent forest disturbance and felling. Over the full monitoring period, the rise in DOC, from first to most recent five year medians of 2.2 to 3.5 mg L^{-1}, is modest compared to most other sites.

16.3 Llyn Cwym Mynach: epilithic diatom community trends

The epilithic diatom flora of this lake is relatively diverse and has shown considerable inter-annual variability and some sustained change over the monitoring period. Most noticeably there was a gradual replacement of *Eunotia rhomboidea* (SWAP pH optimum = 5.1) and *Eunotia vanheurkii* var. 1 (optimum = 5.1) by a range of generally slightly less acid indicating species in the early part of the record. Initially, these included *Brachysira brebissonii* (optimum = 5.3), *Eunotia denticulata* (optimum = 5.2) and *Navicula tenuicephala* (optimum = 5.3). After 1993, other taxa became more abundant, including *Brachysira vitrea* (optimum = 5.9) and *N. leptostriata* (optimum = 5.1). *Brachysira brebissonii* became more abundant after 2000 and was joined by increases in *Frustulia rhomboides* var. *saxonica* (optimum = 5.2) and the acidiobiontic taxon *Tabellaria binalis* (optimum = 4.7) and small numbers of *Cymbella aequalis* (optimum = 5.1) and *Brachysira serians* (optimum = 4.8).

Numerical analysis of the species data indicates that these community-level changes are significant (RDA1, mGLM; Main Report: Table 4.1). Species turnover is moderate (1.17) and the trajectory of PrC scores suggests that most of the turnover occurred in the first 20 years of monitoring with little change since 2010 (Main Report: Figure 4.1). Community-level changes are not significantly related to monitored lake-water pH (RDA1-pH; Main Report: Table 4.1) or other chemistry variable (Figure 3) and there is no significant trend in DAM scores over the monitoring period (Main Report: Table 4.1 & Figure 4.2).

Overall, the trends in epilithic diatoms, while significant, are small and cannot be linked to changes in acidity or other chemistry variables, at least as expressed as seasonal mean values. Llyn Cwm Mynach is a forested site and it is possible they are responses to changes in substrate availability and forest management actions.

16.4 Llyn Cwym Mynach: macroinvertebrate community trends

The macroinvertebrate taxonomic richness of Llyn Cwm Mynach declined over the first decades of monitoring, during which the assemblage became increasingly dominated by Chironomidae (non-biting midge larvae) at the expense of groups such as caddisflies, dragonflies, and some stonefly and bug species (Appendix: Figure 16.4). Community composition changed most markedly between 1988 and 2000. Over that period, Leptophlebiidae mayflies and the caddisflies *Plectrocnemia*, *Polycentropus* and *Anabolia nervosa* decreased in relative abundance, while other taxa became established, such as the dragonfly *Cordulia aenea*, and the caddisfly *Holocentropus*. After 2000, directional community change was less evident but additional taxa continued to be recorded for the first time, e.g. the dragonfly *Libellula quadrimaculata,* and bugs *Gerris* and *Notonecta*. Collectively these shifts in assemblage composition reflect a modest biological recovery from acidification, with the recovery taking place mostly between 1988 and 2000 but with a suggestion that a second phase of recovery is now underway. LAMM scores are now about 75% of that expected for a lake of comparable typology unimpacted by acidification (Main Report: Figure 5.3).

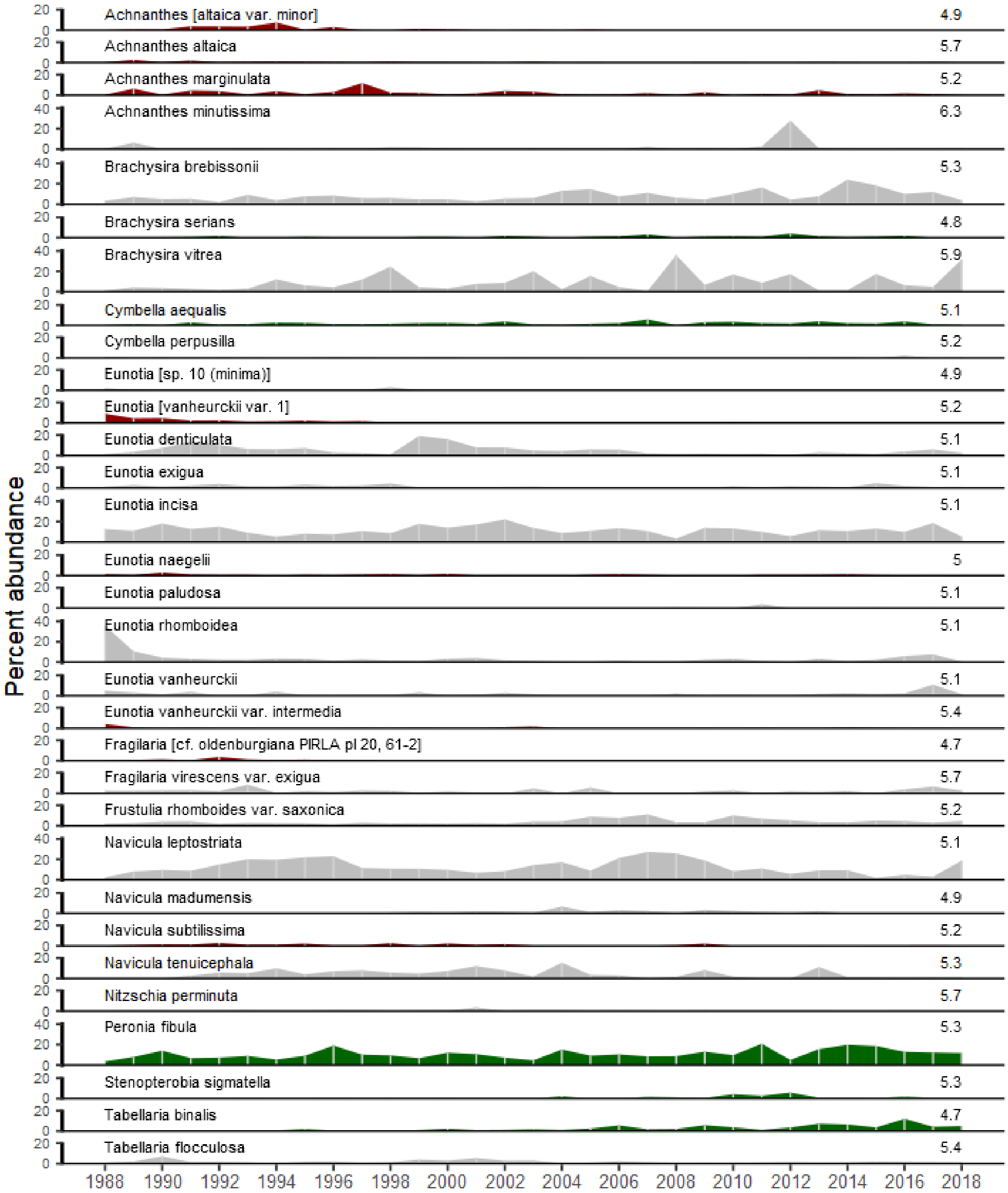


Figure 16.3 Llyn Cwm Mynach: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

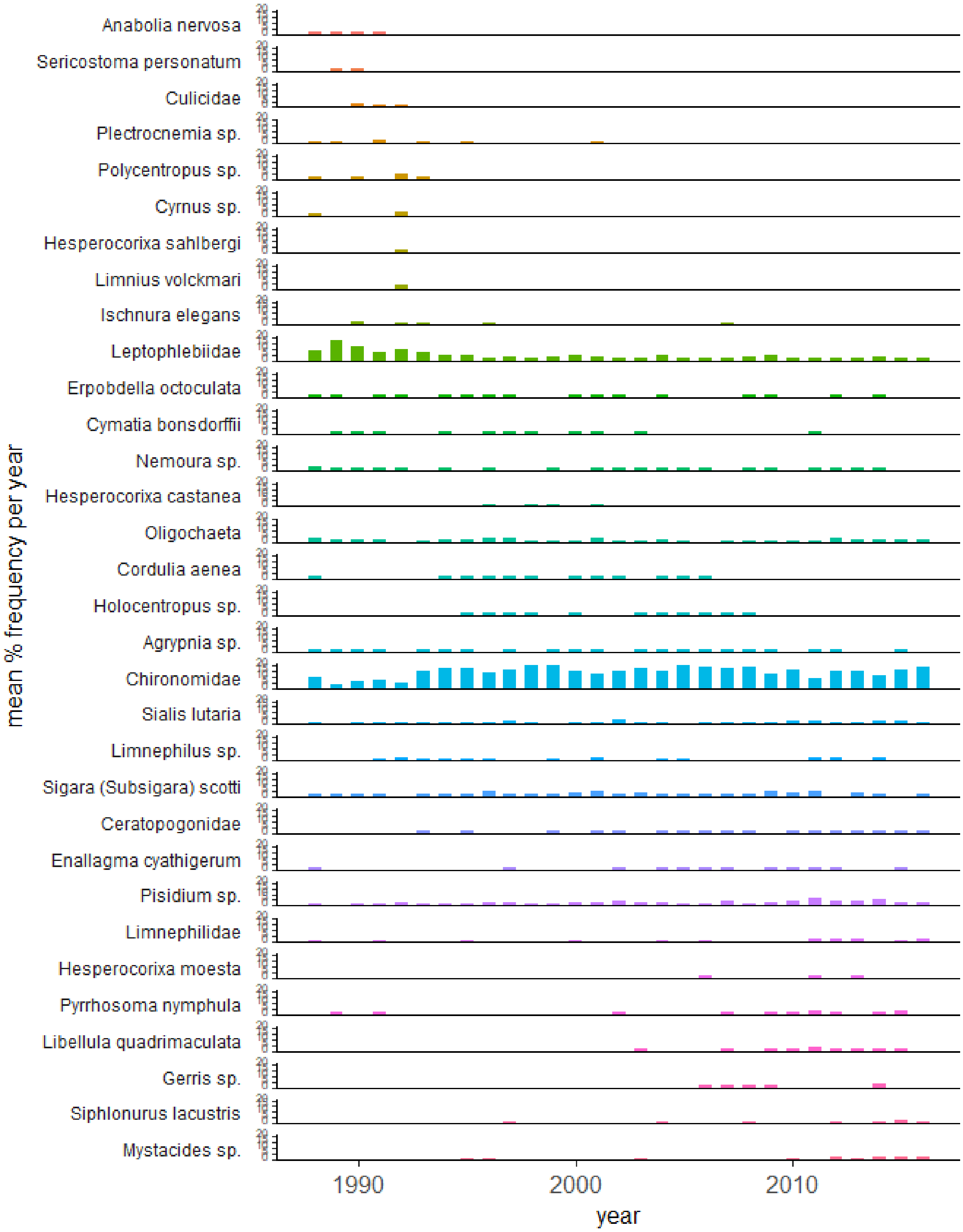
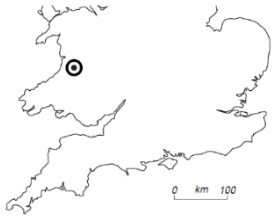


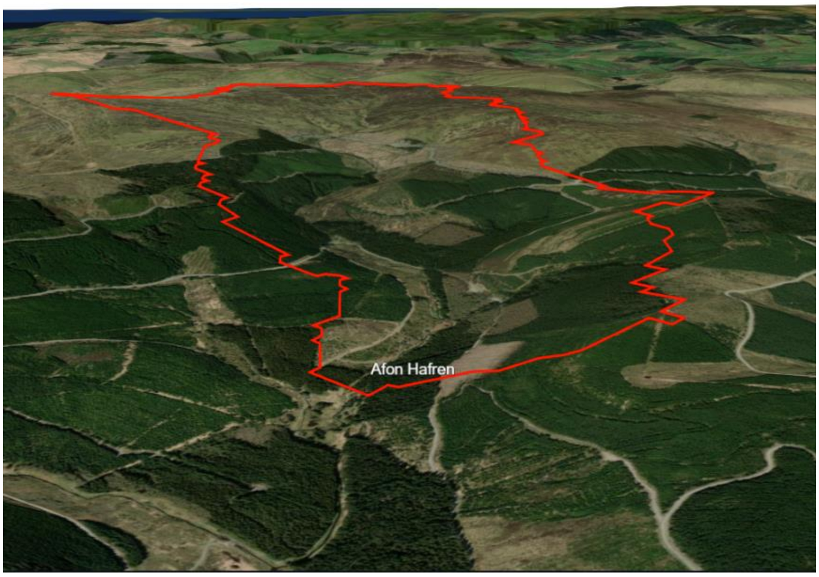
Figure 16.4 Llyn Cwm Mynach: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

17. Afon Hafren



17.1 Afon Hafren site description

The hydrology and ecology of the Afon Hafren, a forested headwater of the River Severn at Plynlimon, has received considerable scientific attention since the early 1980s due to its inclusion in Plynlimon catchment studies (e.g. Neal et al. 1997, Gee & Smith, 1997). The Hafren Forest lies within Natural Resources Wales's Coed y Gororau Forest District and the design plan aims for a progressive reduction in the proportion of conifer cover over time - from 49% in the 1980s to 32% by 2050. This will be accompanied by the establishment of 100-150 m wide native riparian woodland buffer zones along the two main watercourses.



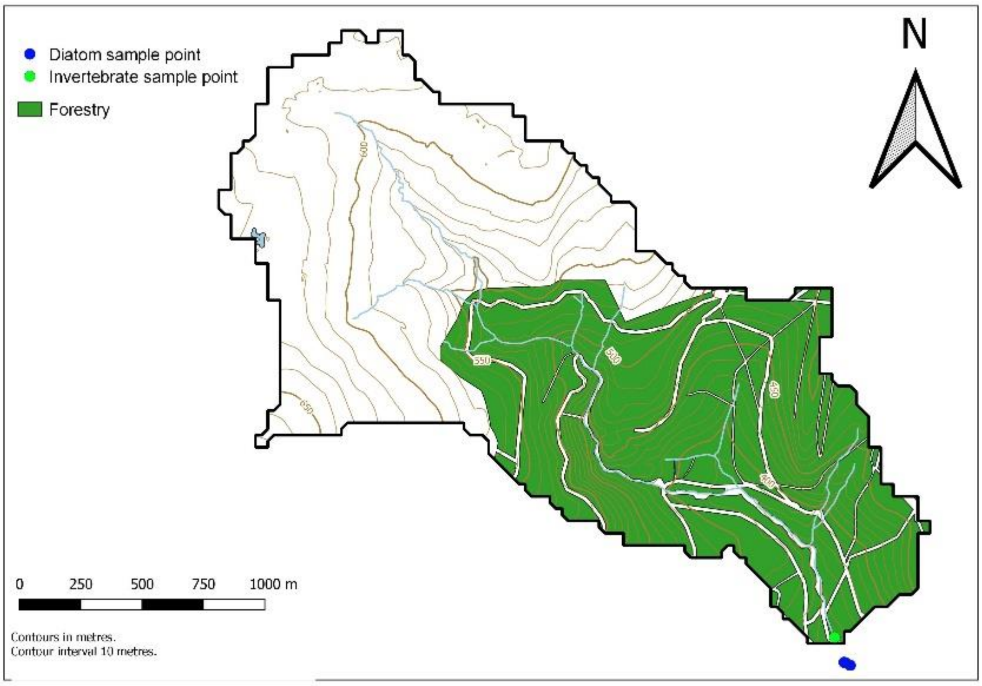


Figure 17.1 Mapped and aerial views of the Afon Hafren catchment

Table 17.1 Afon Hafren site characteristics

Grid Reference	SH 844876	
Catchment area	358 ha	
Minimum catchment altitude	355 m	
Maximum catchment altitude	690 m	
Catchment geology	Ordovician and Silurian sedimentary	
Catchment soils	Podsols and organic peats	
Catchment vegetation	Conifers 50%, Moorland 50%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	42.1	18.2
Non-marine oxidised sulphur	29.9	7.2
Oxidised nitrogen	18.4	9.9
Reduced nitrogen	44.9	21.8

Table 17.2 Afon Hafren water chemistry statistics

Determinand	**Units**	**Median (1989 – 1993)**	**Median (2015 - 2019)**	**Max (1989 – 1993)**	**Max (2015 - 2019)**	**Min (1989 – 1993)**	**Min (2015 - 2019)**	**Slope $year^{-1}$**	**Significance *p < 0.05 **p< 0.001**
SO_4^{2-}	µeq l^{-1}	79.2	54.9	139.6	73.1	64.6	36.9	-1.04	**
xSO_4^{2-}	µeq l^{-1}	56.3	36.4	113.5	55.7	35.2	19.1	-0.87	**
Cl^-	µeq l^{-1}	211.6	174.6	318.8	296.2	152.3	115.7	-1.49	**
NO^{3-}	µeq l^{-1}	19.6	9.5	51.4	23.9	3.6	2.1	-0.36	**
pH	pH	5.2	5.7	6.6	6.7	4.3	4.7	0.02	**
Alk	µeq l^{-1}	-0.3	17.2	60.9	68.0	-42.6	-23.0	0.62	**
Cond	µS cm^{-1}	39.0	34.6	112.0	54.6	31.0	26.6	-0.08	*
Na^+	µeq l^{-1}	195.8	170.3	252.3	225.8	161.0	124.0	-0.97	**
Ca^{2+}	µeq l^{-1}	46.9	35.4	102.3	56.4	7.0	19.2	-0.40	**
Mg^{2+}	µeq l^{-1}	65.8	59.2	88.0	74.0	41.1	37.7	-0.27	**
K^+	µeq l^{-1}	2.6	4.1	15.3	8.4	2.6	0.6	0.04	**
Lab Al	µg l^{-1}	80.0	50.0	366.0	143.0	2.5	4.0	-0.24	
DOC	mg l^{-1}	1.3	3.1	8.1	8.7	0.1	0.3	0.05	**
ANC-CB	µeq l^{-1}	-7.4	25.0	44.5	91.2	-65.4	-41.8	1.52	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

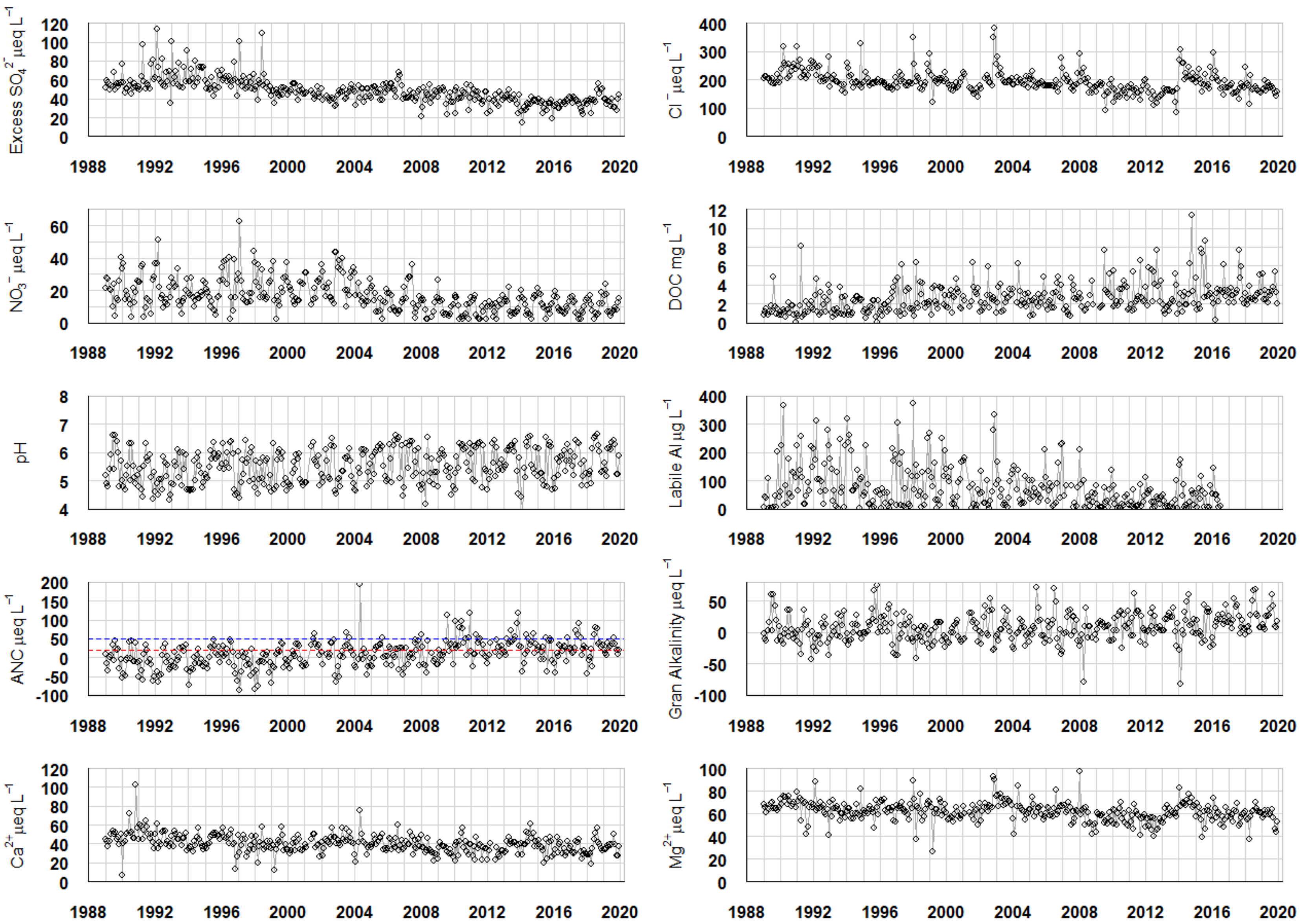


Figure 17.2 Afon Hafren water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

17.2 Afon Hafren: water chemistry trends

CBED estimates of non-marine sulphur and nitrogen deposition to the Afon Hafren catchment for the early years of monitoring were slightly higher than those for the neighbouring Afon Gwy – reflecting the enhanced pollutant interception provided by the Hafren forest canopy. This discrepancy is also apparent in the slightly higher initial non-marine sulphate concentrations and a faster rate of decline in the Afon Hafren over the full monitoring period.

Over the first 20 years of monitoring, concentrations of nitrate in the Afon Hafren were substantially higher than for the Afon Gwy and, in contrast to the moorland site, demonstrated year round nitrate leaching – indicative of nitrogen saturated catchment soils. By around 2008, however, peak nitrate concentrations had fallen by approximately 50%, and since then nitrate leaching has become seasonal, with concentrations approaching the limit of detection during the summer months. As a consequence, both seasonal patterns and absolute concentrations of nitrate in the two streams have become quite similar in the last decade. It is not yet clear to what extent the change in nitrate dynamics in the Afon Hafren is due to the reduction in the nitrogen deposition load, as opposed to increased uptake by vegetation and soil biota as its more heavily acidified soils recover from acidification.

Chloride concentrations show substantial short-term variability, reflecting variable marine ion inputs, and a particularly strong long-term decline (approximately 50% greater than for non-marine sulphate in terms of equivalence) in response to a reduction in hydrochloric acid deposition. The rate of reduction in chloride is approximately double that for the Afon Gwy, a further demonstration of the importance of canopy interception of pollutants. The greater rate of decline in ion deposition has also led to a greater rate of increase in the solubility of soil organic matter and hence a more rapid increase in Dissolved Organic Carbon concentrations, which have more than doubled over the thirty years.

The Afon Hafren has remained strongly acidic at higher flows, but significantly buffered by more alkaline groundwater during drier periods. Accordingly, pH ranged from less than 4.5 to over 6.0 in the early years of monitoring, while labile aluminium concentrations often reached levels highly toxic to acid-sensitive biota. Labile aluminium concentrations regularly exceeded 200 µg L^{-1} during spates while falling below the detection limit during low flows. Over time, pH has increased progressively at both low and high flows, with the median increasing from pH 5.2 and 5.7 between the first and most recent five-year periods. Labile aluminium concentrations at high flows fell sharply over the first 20 years, before appearing to stabilise. By 2016, when measurements were discontinued, labile aluminium concentrations were averaging around 50 µg L^{-1}, with peak values occasionally exceeding 100 µg L^{-1}. These levels are still likely to be toxic to some aquatic species. Given continued reductions in acid anion concentrations since then, it is likely that short-term peak labile aluminium concentrations have continued to fall, and therefore that chemical conditions are continuing to improve from an ecological standpoint up to the present day. Over the full monitoring period, ANC has shifted from being predominantly strongly negative (median -7.4 µeq L^{-1}), and rarely exceeding 20 µeq L^{-1} in the early years, to a median of 25 µeq L^{-1} between 2015 and 2019. Nevertheless, sea salt deposition events and high flows can still result in strongly negative levels of ANC on occasions, and this is likely to continue to pose some limitations on biological recovery.

17.3 Afon Hafren: epilithic diatom community trends

This stream has relatively low diversity, and for the first 15 or so years of monitoring was dominated by a single acidophilous/acidobiontic species, *Eunotia exigua* (SWAP pH optimum = 5.1), with lesser numbers of *Achnanthes austriaca* var. *minor* (1988-1994) and *Eunotia vanheurckii* var. *intermedia* (1988-2004) (Appendix: Figure 17.3). After 2004, the stream underwent a significant decline in *Eunotia exigua*, the appearance and then rise in *Tabellaria flocculosa* (optimum = 5.4) and an increase in overall diversity driven by the appearance of a number of higher pH optimum taxa including *Synedra miniscula* (optimum = 6.0), *Gomphonema angustatum* agg. (optimum = 5.8) and *Fragilaria virescens* var. *exigua* (optimum = 5.8). Overall turnover is relatively large (1.6; Main Report: Table 4.1) and the trajectory of PrC scores suggests that this turnover has been continuous and sustained over the whole period of monitoring (Main Report: Table 4.1). The community-level trend in turnover is significant (RDA1, mGLM1; Main Report: Table 4.1) but this could not be significantly related to the small but significant increase in monitored pH (RDA1-pH). There is a significant trend in DAM scores overall (Table 1) but scores only began increasing from around 2000 (Main Report: Figure 4.2). The RDAs with other chemistry variables suggest a significant relationship between diatom assemblage change and DOC (Main Report: Figure 4.3).

Overall, the changes in epilithic diatom communities since 2000 are consistent with a gradual improvement in pH, but changes in the earlier part of the record may be confounded by DOC or other chemistry variables.

17.4 Afon Hafren: macroinvertebrate community trends

Improvements in the water chemistry of the Afon Hafren have been accompanied by evidence for partial recovery in the macroinvertebrate community, as evidenced by moderate but significant increases in taxon richness and AWICsp scores over the 28 years (Main Report: Figures 5.1 & 5.3). The water beetle and mayfly fauna have become more diverse, with acid-sensitive riffle beetles *Limnius volckmari* and the more acid-tolerant Leptophlebiidae mayfly beginning to occur from the mid-1990s (Appendix: Figure 17.4). From about 2008 onwards, additional acid sensitive taxa became established, such as the mayfly *Baetis* and the riffle beetle *Elmis aenea*. There is a diverse assemblage of stoneflies at the site, most of which are tolerant of acid conditions. However, the relative abundance of the more sensitive species stonefly species *Isoperla grammatica* has increased over time. As water chemistry continues to improve there is scope for further recovery in the macroinvertebrate population at this site.

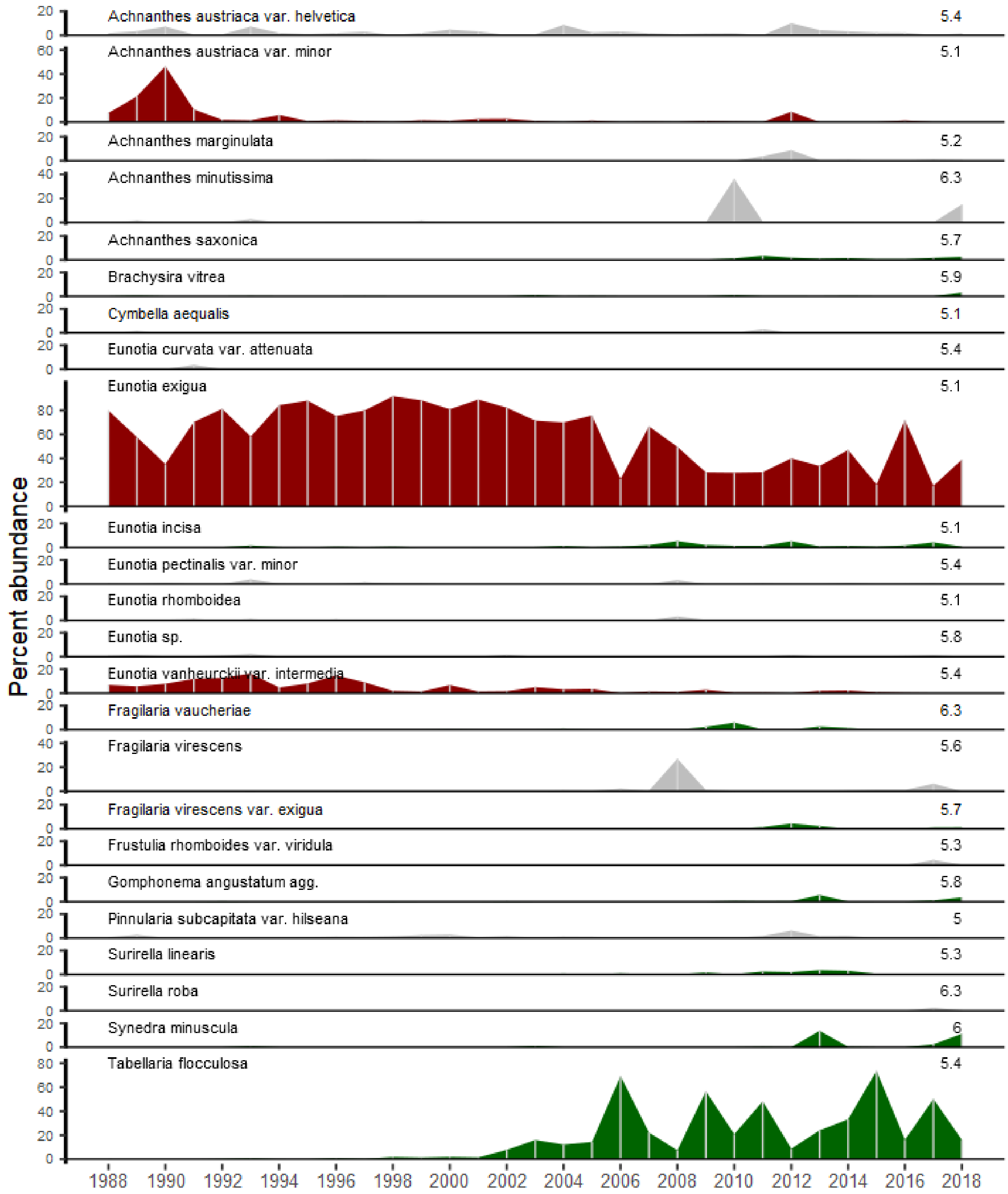


Figure 17.3 Afon Hafren: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

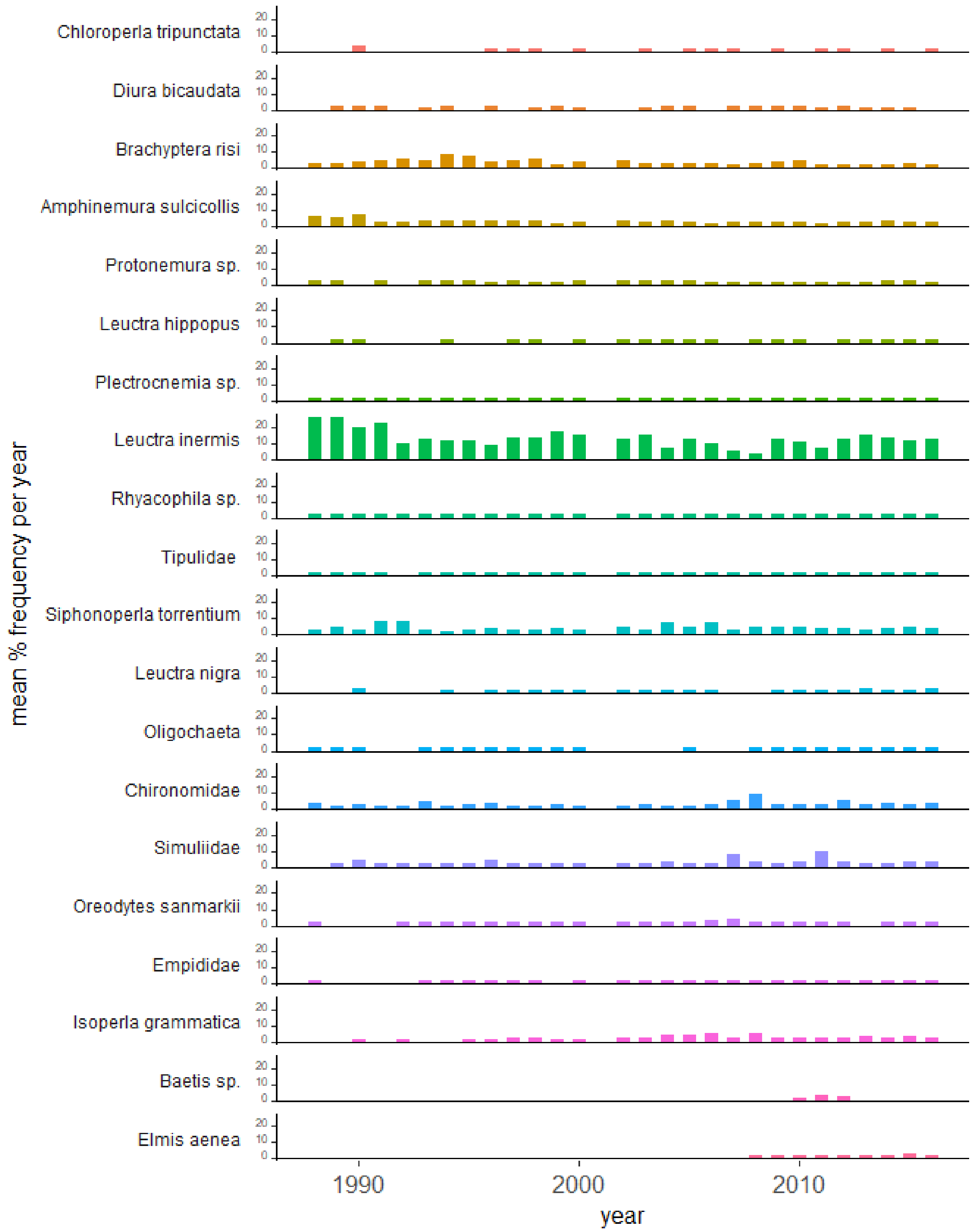
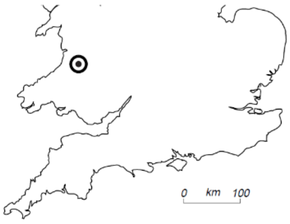


Figure 17.4 Afon Hafren: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

18. Afon Gwy



18.1 Afon Gwy site description

Monitoring of the moorland Afon Gwy within the UWMN began in 1991, although like the neighbouring site, the Afon Hafren, longer chemical time series records exist due to its inclusion in the Plynlimon catchment studies which commenced in 1983. The two sites provide an excellent forested/control pair to examine evidence for the impact of forest management. There is no evidence of disturbance within the catchment of the Afon Gwy since the onset of monitoring.

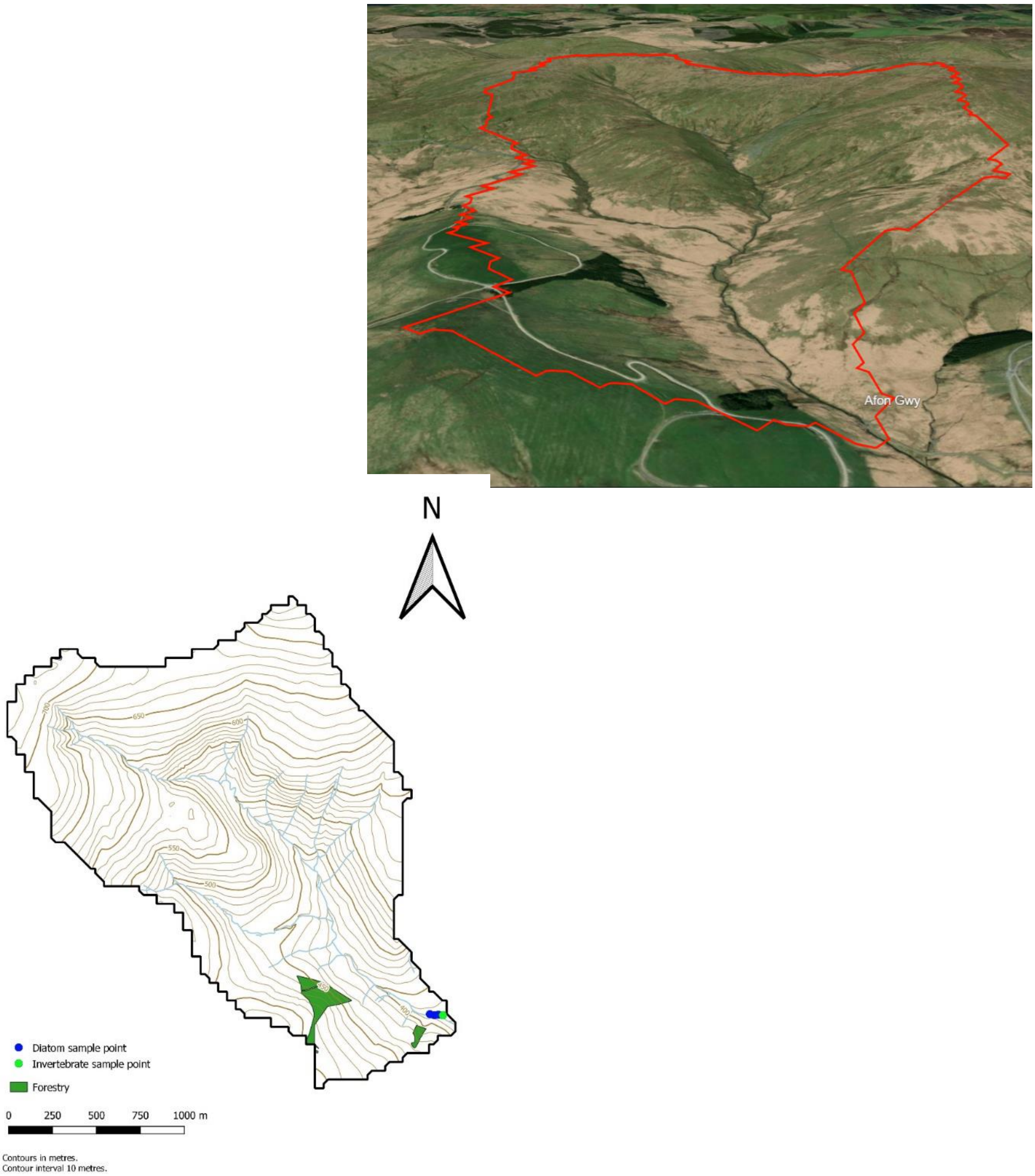


Figure 18.1 Mapped and aerial views of the Afon Gwy catchment

Table 18.1 Afon Gwy site characteristics

Grid Reference	SN 842854	
Catchment area	389 ha	
Minimum catchment altitude	440 m	
Maximum catchment altitude	730 m	
Catchment geology	Lower Palaeozoic sedimentary	
Catchment soils	Peats, peaty podsols	
Catchment vegetation	Moorland 96%, Conifer plantation 4%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	38.5	16.8
Non-marine oxidised sulphur	27.0	6.5
Oxidised nitrogen	13.2	7.9
Reduced nitrogen	34.1	19.2

Table 18.2 Afon Gwy water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	$\mu eq\ l^{-1}$	64.6	43.6	97.9	101.9	47.9	24.3	-0.79	**
xSO_4^{2-}	$\mu eq\ l^{-1}$	47.3	27.3	75.0	88.8	32.4	5.3	-0.69	**
Cl^-	$\mu eq\ l^{-1}$	163.6	139.2	220.0	318.8	104.4	90.0	-0.78	**
NO^{3-}	$\mu eq\ l^{-1}$	3.6	5.1	53.6	34.7	2.1	2.1	0.00	
pH	pH	5.4	5.8	6.4	6.7	4.5	5.0	0.02	**
Alk	$\mu eq\ l^{-1}$	7.2	23.5	42.3	86.6	-19.5	-6.3	0.64	**
Cond	$\mu S\ cm^{-1}$	29.0	29.1	44.1	55.1	20.0	20.0	0.13	**
Na^+	$\mu eq\ l^{-1}$	147.9	137.9	195.8	237.1	113.1	98.7	-0.39	**
Ca^{2+}	$\mu eq\ l^{-1}$	40.4	34.2	63.4	61.4	19.5	17.7	-0.07	*
Mg^{2+}	$\mu eq\ l^{-1}$	53.5	50.5	75.7	83.1	28.0	28.7	-0.12	
K^+	$\mu eq\ l^{-1}$	2.6	2.9	16.4	10.7	2.6	0.3	0.00	
Lab Al	$\mu g\ l^{-1}$	43.0	26.0	198.0	94.0	2.5	2.0	-0.11	
DOC	$mg\ l^{-1}$	1.8	2.6	6.3	7.0	0.1	0.3	0.03	**
ANC-CB	$\mu eq\ l^{-1}$	2.7	25.0	44.3	88.2	-45.5	-4.6	1.07	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

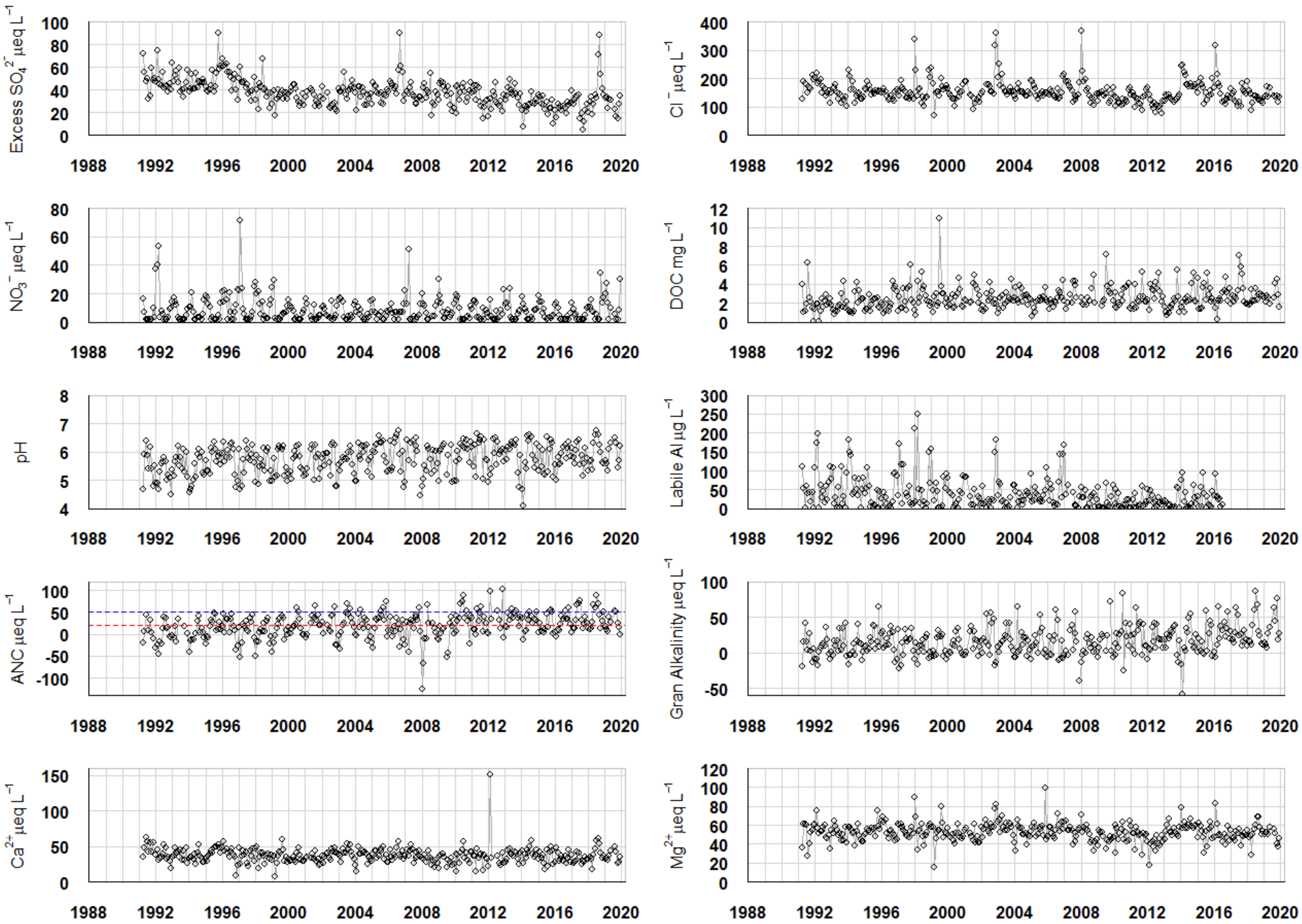


Figure 18.2 Afon Gwy water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

18.2 Afon Gwy: water chemistry trends

The Afon Gwy was less acidic than the neighbouring forested Afon Hafren at the onset of monitoring, but has undergone similar chemical change over the last three decades as a consequence of the similar deposition and meteorological environment. Concentrations of non-marine sulphate and chloride in Afon Gwy streamwater were around 80% of the forested site at the onset of monitoring, and non-marine sulphate has fallen at approximately 80% of the rate observed in the Afon Hafren, while chloride concentrations have fallen by around half of the Afon Hafren rate.

One of the main contrasts with the chemistry of the Afon Hafren has been Afon Gwy's nitrate leaching pattern, which has always been seasonal as opposed to year round. Peak concentrations occur during the winter, but have rarely exceeded 20 µeq L^{-1}, and unlike the Afon Hafren, concentrations in the Afon Gwy do not show a long-term decline.

In common with the Afon Hafren, the acid chemistry of streamwater at low flows has always been well buffered by groundwater, but the associated pH maxima have still risen over time, from just over pH 6.0 to slightly above pH 6.5. The reduction in the acidity of acid episodes associated with high flows and/or sea salt deposition events has been particularly striking. Over the full monitoring period, pH minima have risen from around pH 4.5 to over 5.0. In the early years, these acidic events frequently resulted in highly toxic labile aluminium concentrations of over 100 µg L^{-1} and ANC values as low as -50 µeq L^{-1}. By 2016, when labile aluminium measurements ceased, concentrations rarely exceeded 50 µg $L^{-1}$and in the most recent years ANC has been almost invariably positive, with most samples above the UK ANC_{crit} level of 20 µeq L^{-1}.

Concentrations of DOC have increased from the first to most recent five year medians of 1.8 to 2.6 mg L^{-1}. The slower rate of increase relative to the Afon Hafren is again likely to reflect the more gradual reduction in pollutant deposition to this non-forested catchment.

18.3 Afon Gwy: epilithic diatom community trends

The epilithic diatom community of this stream has a number of similarities with the nearby Afon Hafren. It has relatively low diversity and is dominated throughout by the acidophilous /acidobiontic species *Eunotia exigua* (SWAP pH optimum = 5.1) (Appendix: Figure 18.3). However, abundances exhibit a statistically significant decline from around 2000, with a corresponding significant increase in *Tabellaria flocculosa* (optimum = 5.4) and lesser numbers of *Brachysira vitrea* (optimum 5.9). Synedra miniscula (optimum = 6.0) forms a significant part of the community for the first time in 2018.

Overall turnover, at 0.8, is much lower that at Afon Hafren (1.8), due to the low diversity and dominance throughout by *E. exigua*. However, the trends in turnover are significant (RDA1, mGLM; Main Report: Table 4.1) and the trajectory of PrC scores suggest that change has been sustained over the whole monitoring period (Main Report: Figure 4.1). Like Afon Hafren, these changes cannot be statistically related to monitored pH, at least not when expressed as seasonal mean pH, but there is a significant trend in DAM scores (Report: Table 4.1) that is again sustained over the whole monitoring period (Figure 2). RDAs with other chemistry variables suggest a significant relationship between diatom assemblage change and alkalinity and labile aluminium (Main Report: Figure 4.3). As with Afon Hafren, the change in epilithic diatom communities in Afon Gwy is consistent with the gradual increase in pH recorded in the monitored stream-water chemistry, and it is likely that some of these changes will be confounded with other chemistry variables.

18.4 Afon Gwy: macroinvertebrate community trends

The macroinvertebrate community of the Afon Gwy (Appendix: Figure 18.4) underwent significant directional change in assemblage composition over the monitoring period, although there was no evidence for any change in rarefied taxon richness (Main Report: Figure 5.1). The change in community composition has been driven more by increases in the relative abundance of the numerically dominant stoneflies *Isoperla grammatica*, *Leuctra inermis*, *Leuctra hippopus* and *Siphonoperla torrentium*. As was seen at Afon Hafren, there was a modest but significant increase in AWICsp over the 25 years of monitoring (Main Report: Figure 5.3 and Table 5.2). Indications of a biological recovery from acid stress come from the appearance of acid-sensitive riffle beetles (*Limnius volckmari*, *Esolus parallelepipedus and Elmis aenea*) from the mid-1990s, along with sporadic occurrences of *Baetis* and *Hydropsyche siltalai* in the 2010s. Many of the acid-tolerant stoneflies and caddisflies persist and continue to dominate the community numerically.

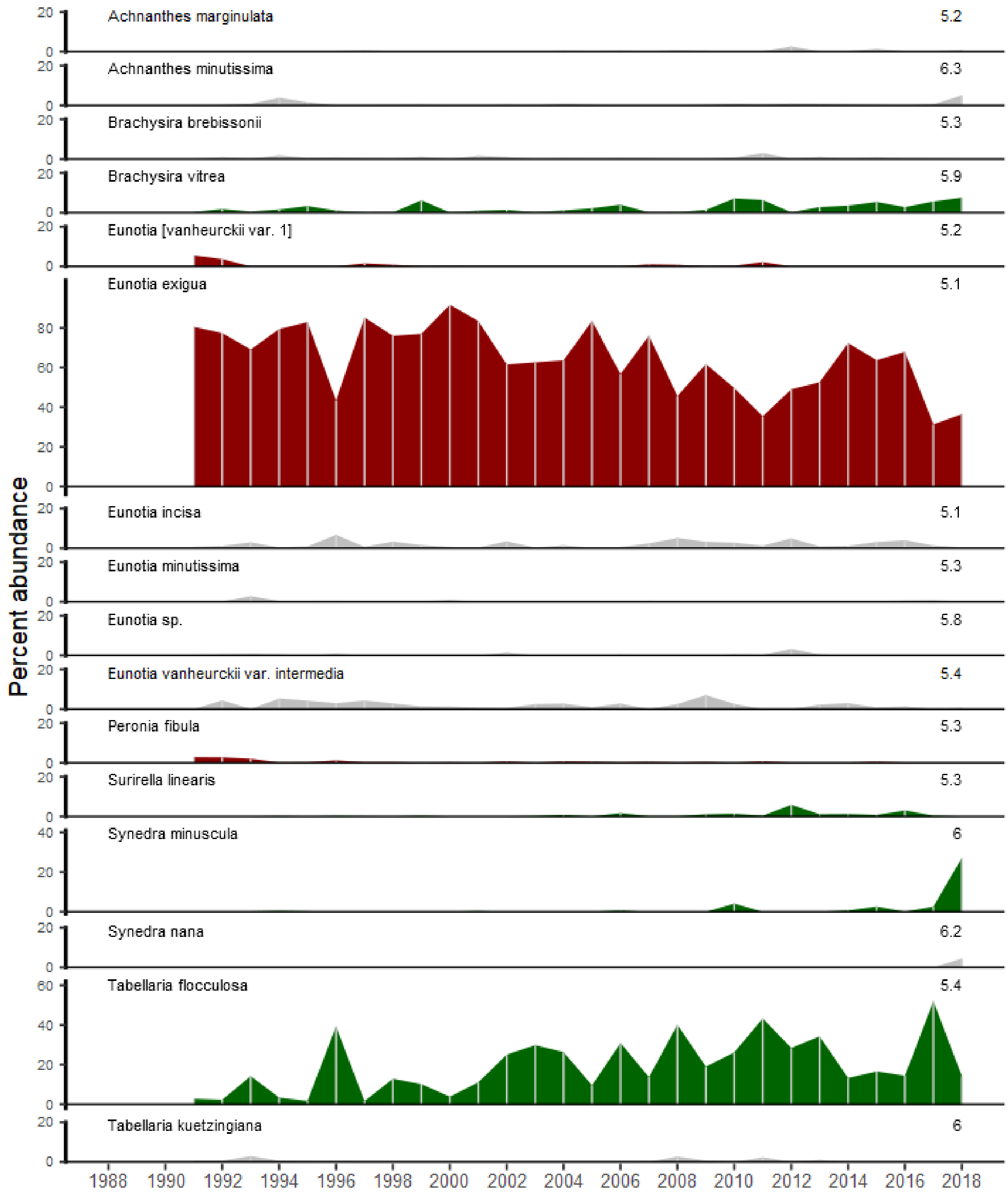


Figure 18.3 Afon Gwy: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

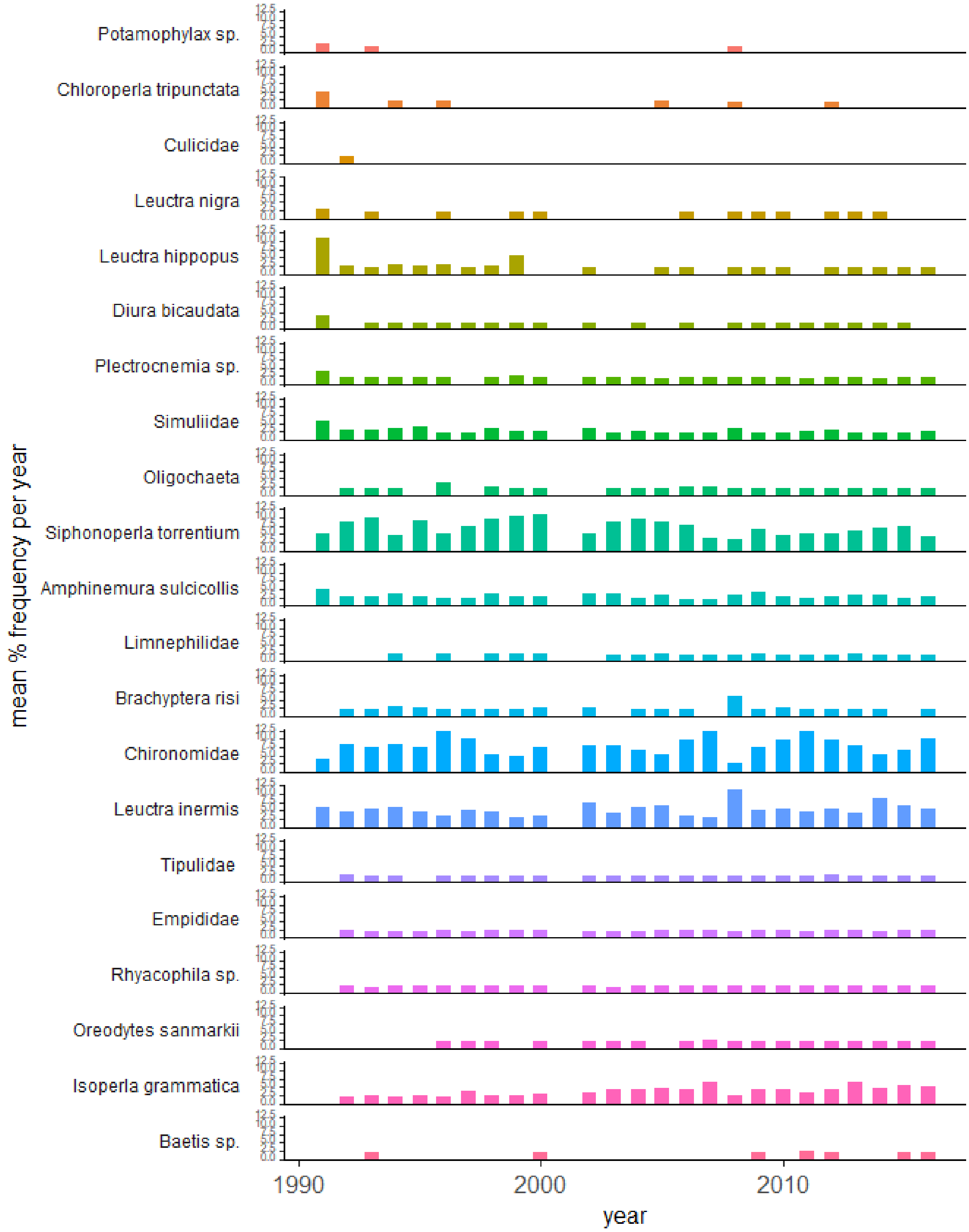
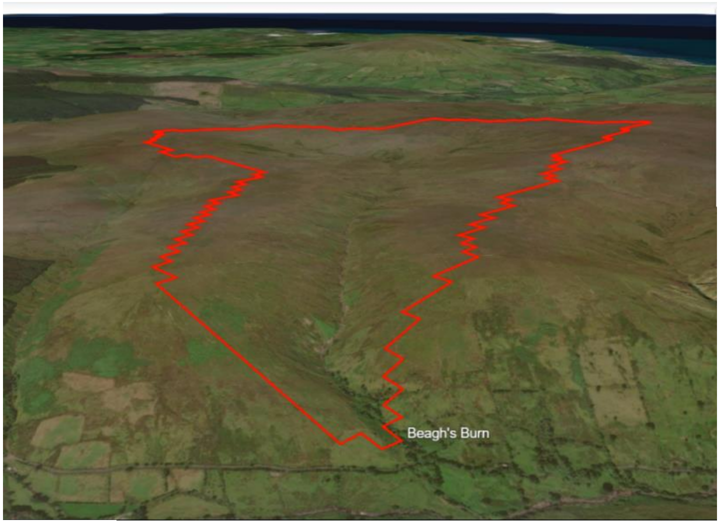


Figure 18.4 Afon Gwy: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

19. Beagh's Burn

19.1 Site description

The Beagh's Burn sampling site drains a small peatland catchment in the Glens of Antrim in north-east Northern Ireland, used for upland grazing of sheep. The site was subject to a major storm event in 1991 that resulted in a redistribution of the boulder-dominated stream bed. Recent work carried out by a local farm, involving improvements to a wall and sheep pen, are all beneath the water sample point and biological survey stretches. There is no evidence of any physical disturbance within the catchment over the survey period.



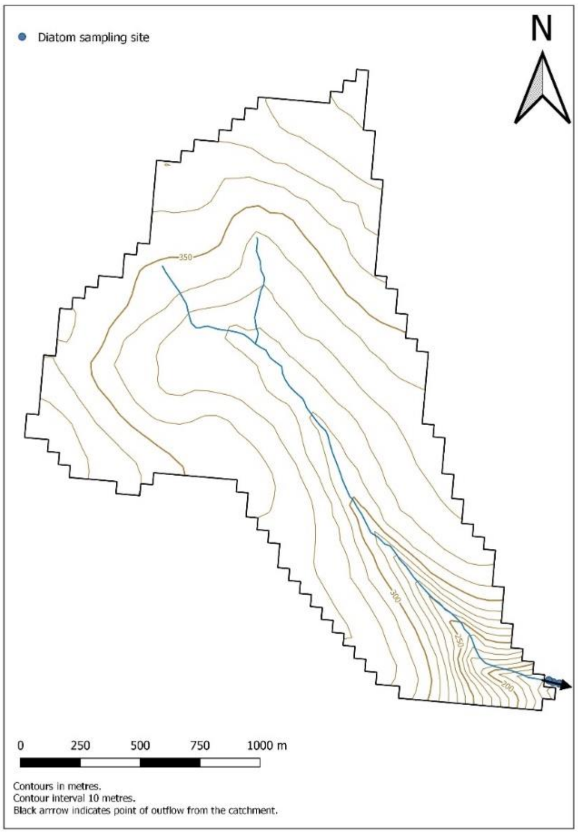


Figure 18.1 Mapped and aerial views of the Beagh's Burn catchment

Table 19.1 Beagh's Burn site characteristics

Grid Reference	D 173297	
Catchment area	303 ha	
Minimum catchment altitude	150 m	
Maximum catchment altitude	397 m	
Catchment geology	Schists	
Catchment soils	Blanket peats	
Catchment vegetation	Moorland >99%, Deciduous trees <1%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	22.3	7.7
Non-marine oxidised sulphur	17.1	2.1
Oxidised nitrogen	5.9	2.6
Reduced nitrogen	24.4	12.1

Table 19.2 Beagh's Burn water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope year^{-1}	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	65.6	28.1	252.0	148.7	27.1	9.6	-1.19	**
xSO_4^{2-}	µeq l^{-1}	25.1	-0.1	216.6	122.2	0.3	-12.9	-0.76	**
Cl^-	µeq l^{-1}	330.1	255.5	617.8	510.7	194.6	150.1	-2.67	**
NO^{3-}	µeq l^{-1}	2.1	2.1	14.0	337.9	2.1	2.1	0.00	
pH	pH	5.8	5.9	7.0	7.0	4.4	4.3	0.00	
Alk	µeq l^{-1}	29.0	40.0	240.0	266.0	-49.0	-159.4	0.22	
Cond	µS cm^{-1}	57.5	48.1	88.0	92.6	39.0	33.9	-0.32	**
Na^+	µeq l^{-1}	302.3	245.1	443.7	381.5	204.5	181.0	-2.09	**
Ca^{2+}	µeq l^{-1}	104.3	85.3	214.6	202.6	35.4	32.6	-0.44	**
Mg^{2+}	µeq l^{-1}	110.2	89.8	178.5	159.6	53.5	46.3	-0.73	**
K^+	µeq l^{-1}	11.4	6.3	23.0	21.0	2.6	1.4	-0.09	**
Lab Al	µg l^{-1}	6.0	9.0	60.0	22.0	2.0	2.0	0.00	
DOC	mg l^{-1}	8.5	14.0	18.9	29.9	3.1	3.6	0.15	**
ANC-CB	µeq l^{-1}	92.3	134.3	351.5	370.9	-34.0	-80.0	0.75	

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

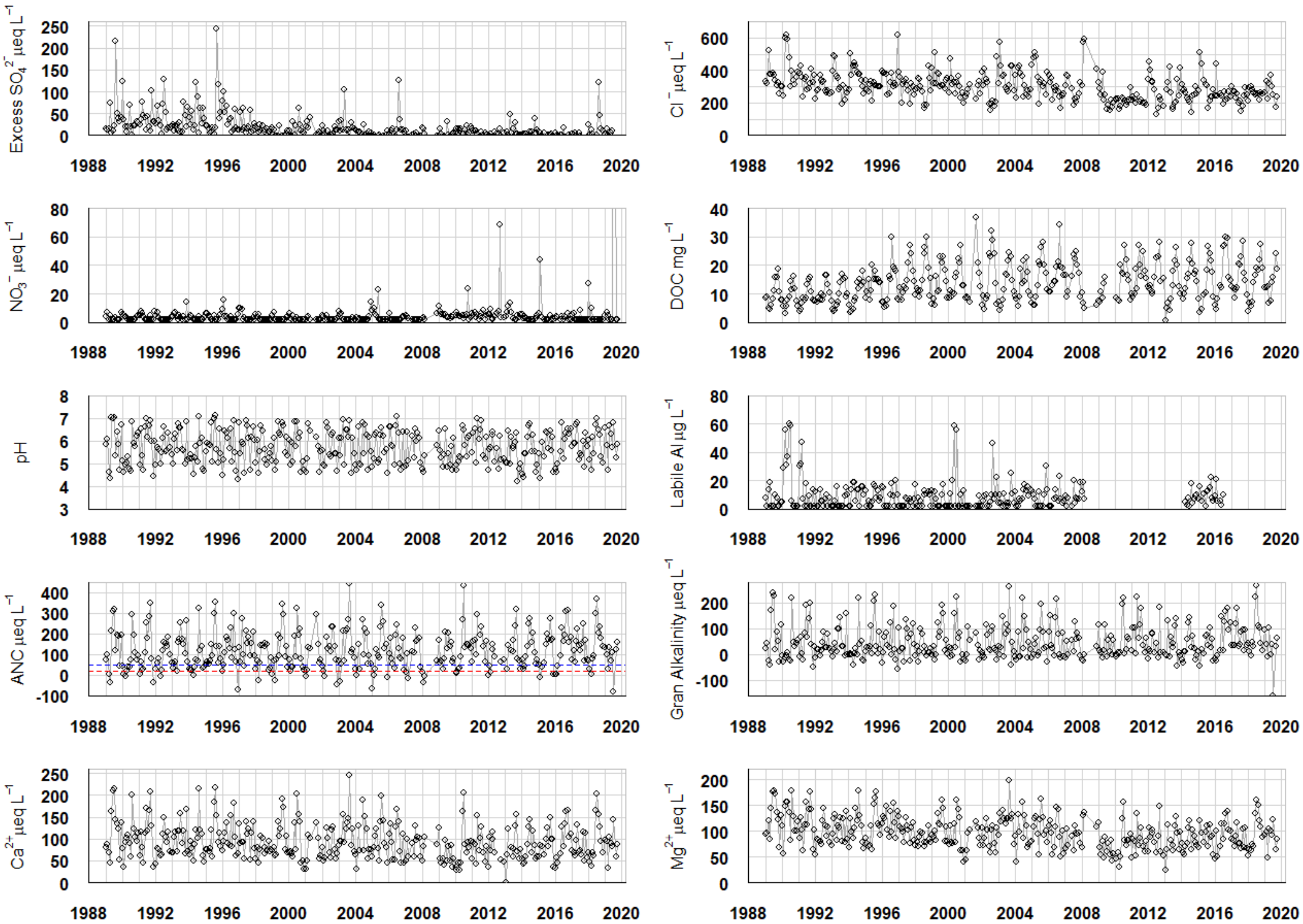


Figure 19.2 Beagh's Burn water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

19.2 Beagh's Burn: water chemistry trends

At the onset of monitoring, CBED deposition estimates indicate that the Beagh's Burn catchment was receiving significantly higher levels of sulphur and nitrogen deposition than the low deposition "control" site Coneyglen Burn, 55 km to the south-west. However, rates of deposition have also fallen more sharply, and by 2017 had become very similar in magnitude to the site in the Sperrin hills. This is reflected in a very sharp decline in non-marine sulphate concentration over the first 10 years of monitoring, after which levels have often been below the limit of detection, and continuously low concentrations of nitrate. The most marked change in acid deposition has been the reduction in hydrochloric acid deposition, as indicated by a large long-term reduction in chloride concentration, despite sea salt inputs at this coastal site dominating short-term variation.

The water chemistry of Beagh's Burn has always been highly dependent on flow, and the seasonally variable contribution of organic acids generated by its peat-dominated catchment. In the first few years of monitoring, stream water pH at high flows occasionally fell below pH 4.5. However, due to the extent to which organic (as opposed to mineral) acidity contributed to these acid episodes, concentrations of labile aluminium have never reached the potentially toxic levels experienced in the more acidic sites with lower DOC concentrations elsewhere on the network. At low flows pH has always plateaued at around pH 7.0, indicating significant buffering from groundwater sources, and peak levels have not changed over time. Acid Neutralising Capacity has always oscillated wildly and has not changed significantly over time, although the occurrence of occasional negative ANC values has become much less frequent during the last 15 years.

Higher atmospheric inputs of sulphur and hydrochloric acid in the early years account for the suppression of DOC over this period, since when concentrations have approximately doubled and, more recently, stabilised.

19.3 Beagh's Burn: epilithic diatom community trends

The epilithic diatom flora of this stream is relatively diverse and exhibits some overall significant trends but with considerable inter-annual variation. *Pinnularia subcapitata* var. *hilseana* (optimum = 5) and *Eunotia exigua* (optimum = 5.1) are present in fluctuating numbers throughout (Appendix: Figure 19.3). The early part of the record is also characterised by *Achnanthes minutissma* (optimum 6.3) and several *Eunotia* species. *Gomphonema angustatum* agg. and *Synedra miniscula* (optimum 6.0) are common in some years between the late 1990s and 2010. Finally, Achnanthes saxonica (optimum 5.7) shows a significant increasing trend from 2000 increases and replaces *A. minutissima* around 2005.

Overall turnover is relatively high (1.5) and significance tests (RDA1, mGLM; Main Report: Table 4.1) indicate that the community-level species trends are significant. However, the RDA1/PCA1 ratio is only 0.51, suggesting that the other factors, including inter-annual variation, explain similar amounts of variance to the turnover trend. The trajectory of PrC scores reflect the considerable inter-annual variation and show no obvious trend (Main Report: Figure 4.1). Changes in diatom community composition are not significantly related to monitored pH or other chemistry variables (Main Report: Table 4.1, Main Report: Figure 4.3), at least expressed as when chemistry is represented as seasonal means, and there is no significant trend in DAM scores, which again reflect the high inter-annual variability in community composition (Main Report: Figure 4.2).

Overall, this stream shows considerable inter-annual variation in the diatom flora, superimposed on a significant change in community structure over the monitoring period. There is no significant trend in measured stream water pH, and no evidence from the diatom data that the observed species changes are a response to changing acidity. However, it is likely that the major species fluctuations observed in the record are, at least in part, explained by extreme hydrological episodes that will often be missed in the monthly chemistry sampling and any analysis based on seasonal mean data.

19.4 Beagh's Burn: macroinvertebrate community trends

The macroinvertebrate community of Beagh's Burn has remained relatively species poor over time, but there is evidence of a directional shift in the assemblage, driven mainly by changes seen after the four-year hiatus in sampling that occurred between 2008-2011 (Appendix: Figure 19.4). A number of newly recorded taxa appeared after 2011, including two *Leuctra* (stonefly) species, two flatworm taxa, and Scirtidae water beetles. The relative abundance of the numerically dominant blackfly larva, Simuliidae, decreased between the two periods. The AWICsp metric provides no evidence for a monotonic biological recovery trend (Main Report: Figure 5.3 and Table 5.2), although scores increased slightly up to about 2001 before declining again. The peak in AWICsp scores midway through the time series corresponds with the temporary appearance of moderately acid-sensitive *Silo pallipes*, *Sericostoma personatum* and *Hydropsyche* caddisflies at the site, which were not recorded again after 2007. The stream community remains indicative of a system moderately influenced by acidity, and while there seems little potential for further significant chemical recovery, the extent to which this is due to naturally- (i.e. organic) as opposed to pollutant-derived acidity has yet to be clarified.

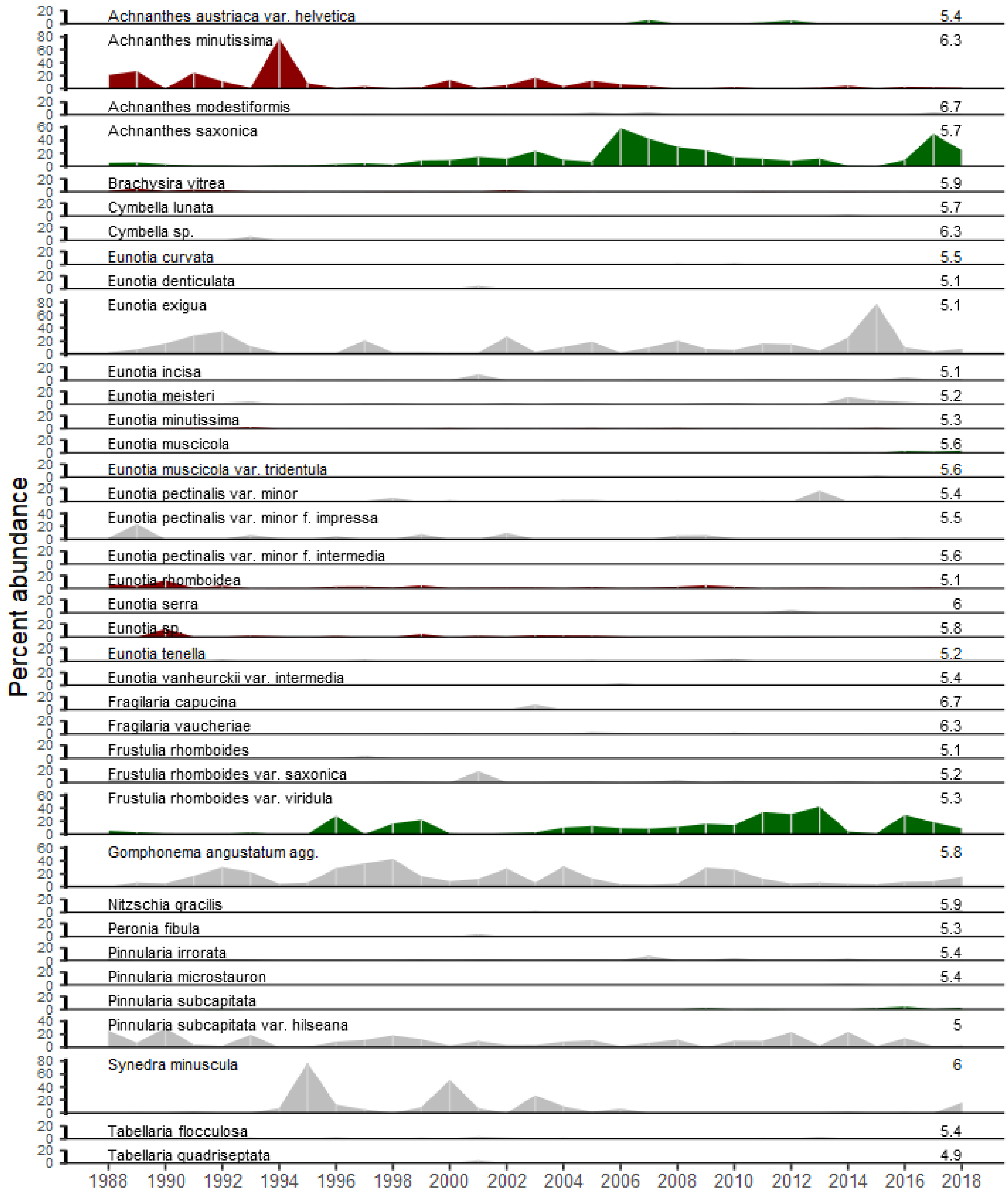


Figure 19.3 Beagh's Burn: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

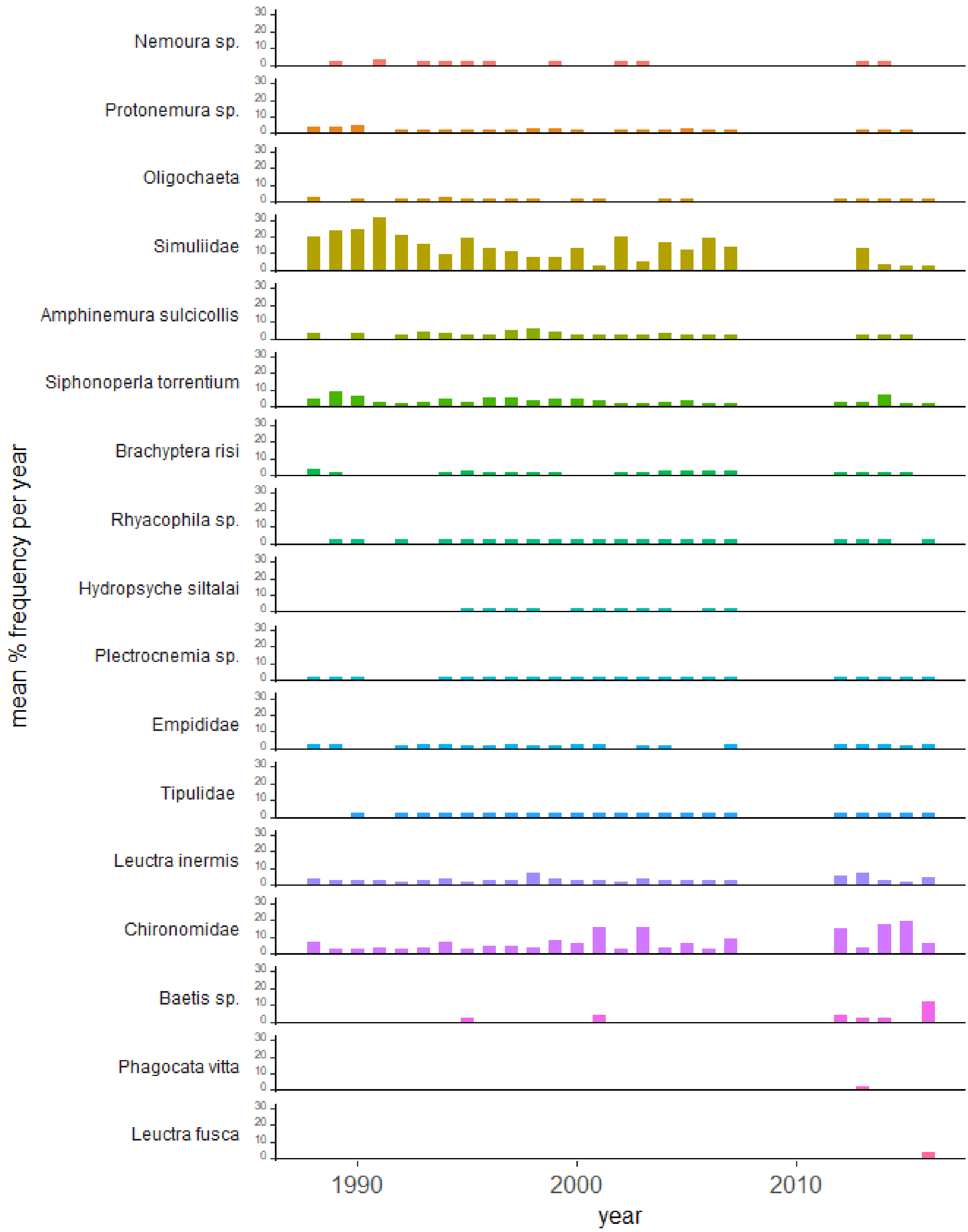


Figure 19.4 Beagh's Burn: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

20. Bencrom River

20.1 Bencrom River site description

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

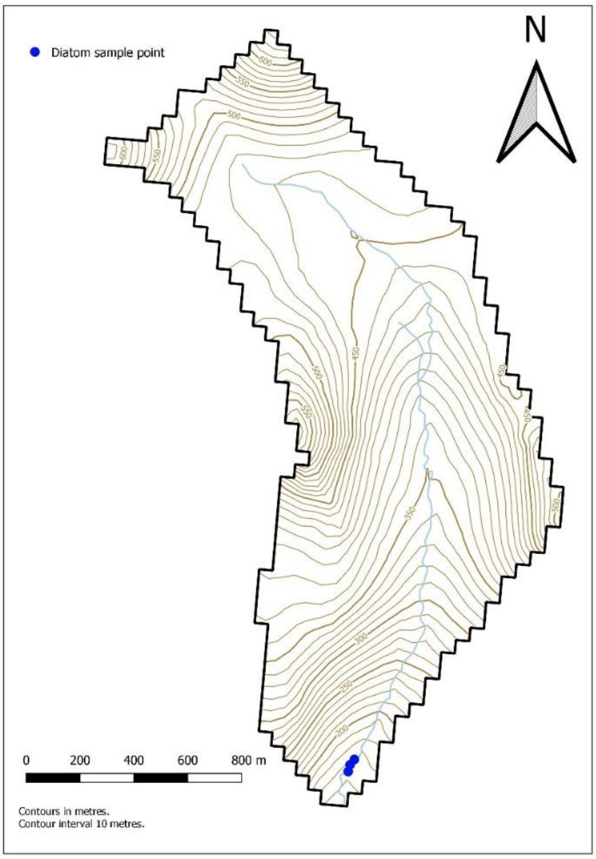


Figure 20.1 Mapped and aerial views of the Bencrom River catchment

Table 19.1 Bencrom River site characteristics

Grid Reference	J 304250	
Catchment area	216 ha	
Minimum catchment altitude	140 m	
Maximum catchment altitude	700 m	
Catchment geology	Granite	
Catchment soils	Blanket peat	
Catchment vegetation	Moorland	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	20.3	9.2
Non-marine oxidised sulphur	15.1	2.9
Oxidised nitrogen	7.1	3.7
Reduced nitrogen	25.0	17.5

Table 19.2 Bencrom River water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	94.8	50.8	145.8	68.7	56.2	16.5	-1.69	**
xSO_4^{2-}	µeq l^{-1}	66.9	29.2	121.5	45.7	28.7	-9.5	-1.52	**
Cl^-	µeq l^{-1}	256.7	210.6	327.2	378.0	138.2	148.1	-1.70	**
NO^{3-}	µeq l^{-1}	22.0	25.6	62.9	57.5	6.0	12.2	-0.03	
pH	pH	5.2	6.1	6.1	6.7	4.4	4.9	0.02	**
Alk	µeq l^{-1}	-2.5	29.8	19.0	91.4	-45.0	0.0	0.99	**
Cond	µS cm^{-1}	49.0	41.9	68.0	64.3	36.0	30.6	-0.29	**
Na^+	µeq l^{-1}	265.4	229.6	317.6	296.7	178.4	170.5	-1.24	**
Ca^{2+}	µeq l^{-1}	52.1	61.4	81.3	86.3	29.4	31.3	-0.25	**
Mg^{2+}	µeq l^{-1}	58.0	48.9	125.0	87.2	36.2	38.1	-0.46	**
K^+	µeq l^{-1}	12.1	10.1	18.4	15.9	6.6	7.5	-0.04	**
Lab Al	µg l^{-1}	117.5	75.0	276.0	125.0	2.0	28.0	-0.28	**
DOC	mg l^{-1}	3.0	3.4	10.0	9.3	1.3	1.1	0.01	
ANC-CB	µeq l^{-1}	15.0	47.9	120.2	103.4	-47.5	-17.6	1.42	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

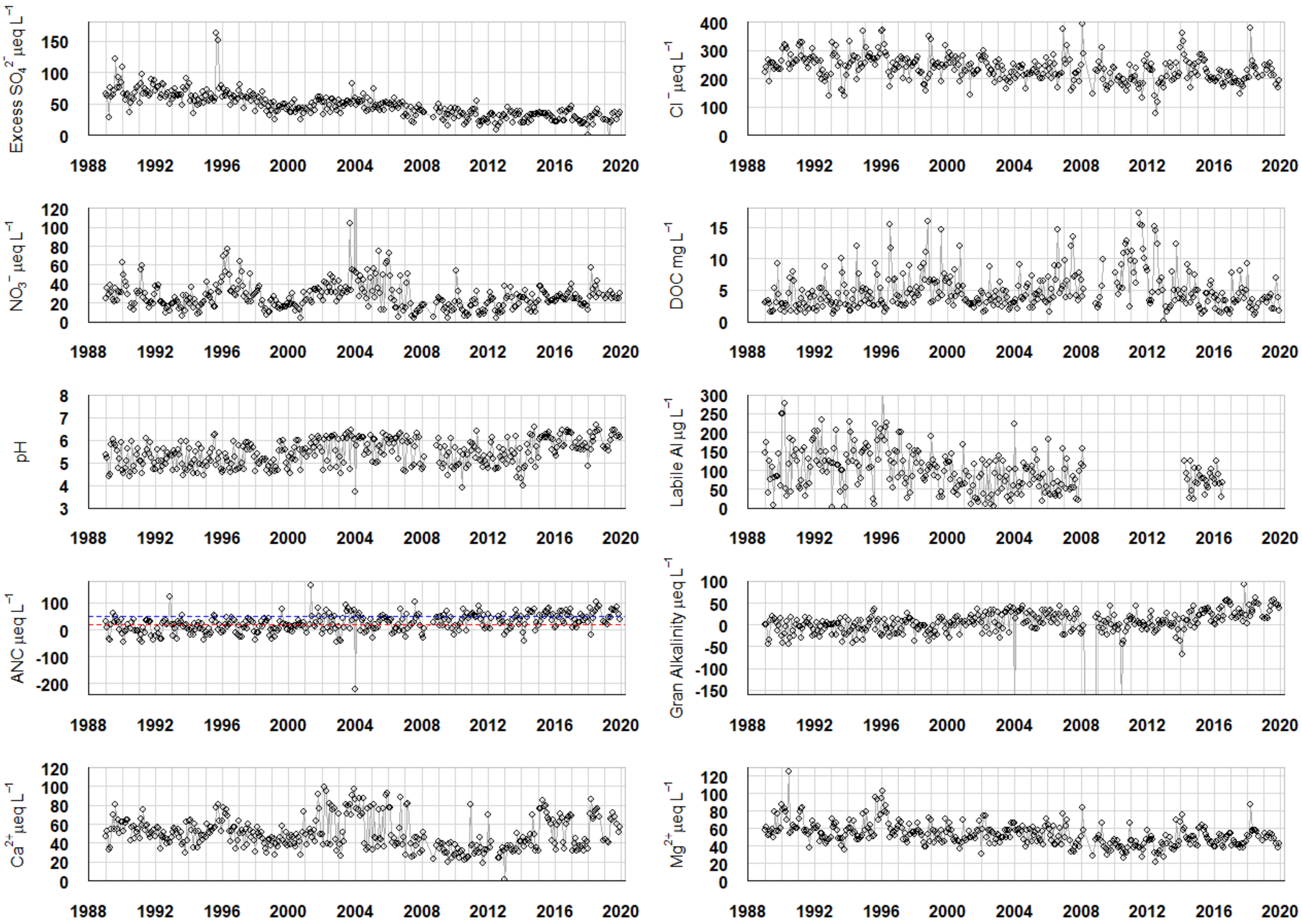


Figure 20.2. Bencrom River water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

20.2 Bencrom River: water chemistry trends

According to CBED estimates, the Bencrom River catchment received slightly lower amounts of sulphur and nitrogen deposition than Beagh's Burn (100 km to the north) historically, but has not experienced as much of a reduction in deposition over time. However, Bencrom River streamwater concentrations of non-marine sulphate in the early years of monitoring were approximately three times those of both Northern Irish stream sites to the north, and while they have fallen more rapidly over the monitoring period, remain at relatively high levels in comparison with the majority of UWMN sites. Chloride concentrations have fallen at a similar rate to non-marine sulphate (in terms of equivalence), again emphasising the importance of hydrochloric acid deposition in the acidification/recovery story.

Bencrom River also receives significant contributions to acidity from nitrate. Nitrate leaching has occurred throughout the year for most of the monitoring period, indicative of a nitrogen saturated catchment, although there was a period between around 2006 and 2013 when it temporarily became more seasonal. In recent years concentrations have remained mostly between 20-30 µeq L^{-1}, and have been making a similar contribution to acidity as non-marine sulphate.

As a consequence of lower geological weathering rates, indicated by calcium and magnesium concentrations that are around half of those of the Northern Irish stream sites to the north, and rates of acid deposition that may have been underestimated by CBED, Bencrom River water chemistry has been much more acidic throughout most of the monitoring period. Over the first decade of monitoring, streamwater pH regularly fell below pH 4.5 while labile aluminium concentrations often exceeded 150 µg L^{-1}, potentially highly toxic conditions for a range of aquatic biota. Streamwater pH was significantly higher during low flows, but rarely reached pH 6.0. There was then a strange hiatus in the water chemistry record between 2002 and 2007 that has never been fully explained but could be due to shifts in hydrology, during which calcium and nitrate concentrations almost doubled, and the majority of samples had a pH of around 6.0. Calcium concentrations subsequently fell to much lower levels, before reviving again in around 2015, and over the last 5 years streamwater pH has rarely fallen below pH 5.5. Unfortunately, recording of labile aluminium concentrations largely ceased beyond 2008, although they were found to still occasionally exceed 100 µg L^{-1} during a brief resumption of measurements between 2014-16. Over the full monitoring period, ANC increased from predominantly negative values during the first decade of monitoring, to predominantly positive levels from 2010 onwards, and over the last five years has remained mostly above the UK ANC_{crit} of 20 µeq L^{-1}. Concentrations of DOC have fluctuated substantially throughout the monitoring period, but still show an overall tendency to increase over time.

20.3 Bencrom River: epilithic diatom community trends

The epilithic diatom flora of this stream has relatively low diversity and has been dominated by *Eunotia naegelii* (optimum = 5.0) with lesser numbers of *Brachysira brebissonii* (optimum = 5.3), *Frustulia rhomboides* var. *saxonica* (optimum = 5.2), and *Tabellaria flocculosa* (optimum 5.4) throughout (Appendix: Figure 20.3). Overall species turnover is low (0.75; Main Report: Table 4.1) but trends in individual taxa and at the community level (RDA1, mGLM; Main Report: Table 4.1) are significant, with *Eunotia naegelii* declining slightly since the early 2000s and a corresponding rise in *Frustulia rhomboides* var. *saxonica* and, since 2010, a rise in *Tabellaria flocculosa.* The acidiobiontic taxon *Tabellaria quadriceptata* (optimum = 4.9) is present at the start of the record but shows significant decline to very low numbers after 1994. *Brachysira vitrea* (optimum = 5.9) also appears consistently in the record after the early 2000s.

Numerical analyses indicate there is a significant trend in the community level species changes (RDA1, mGLM; Main Report: Table 4.1), that is significantly related to changes in monitored pH (RDA1-pH), but not other chemistry variables (Main Report: Figure 4.3). However, while significant, the overall response of the diatom communities to changing pH is small: The RDA1-pH / PCA1 ratio is only 0.3, suggesting that diatom change associated with pH is not the main pattern of variation in the data, and although there is a significant trend in DAM scores the overall effects size (DAM-slope; Main Report: Table 4.1) is small. Overall, the diatom changes in this stream are consistent with the small increase in monitored pH and show a small but significant species response to increasing pH.

20.4 Bencrom River: macroinvertebrate community trends

The community of Bencrom River is dominated by Chironomidae (non-biting midges), Simuliidae (blackfly), acid-tolerant stoneflies and caddisflies and moderately acid-sensitive riffle beetles (Appendix: Figure 20.4). Despite the chemical recovery evident in Bencrom River, there is no evidence of biological recovery response linked to these improvements in acid chemistry. Taxon richness has increased slightly over time, but not AWICsp scores (Main Report: Figure 5.3 and Table 5.2), and there is no indication of significant directional change in the assemblage.

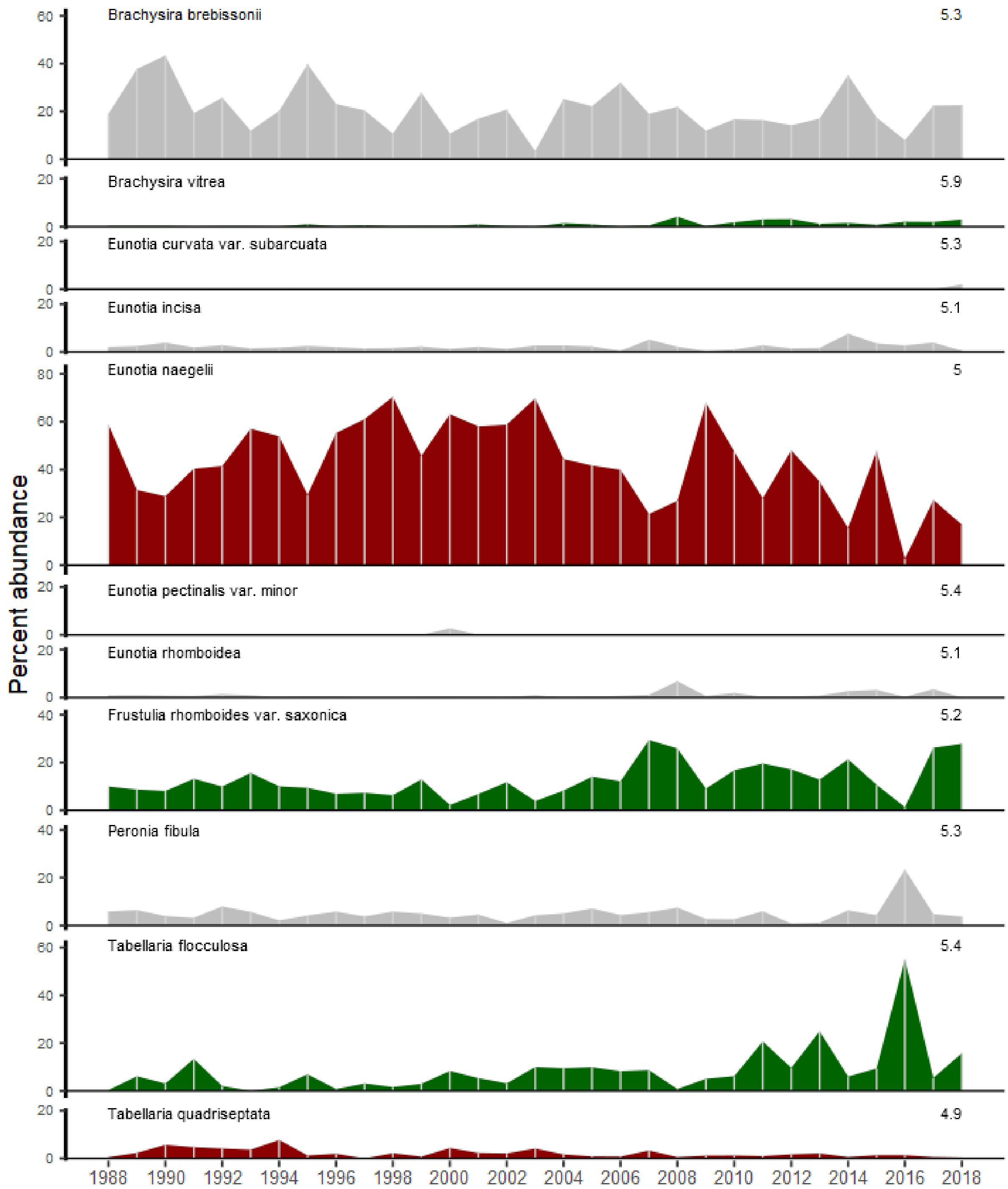


Figure 20.3 Bencrom River: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

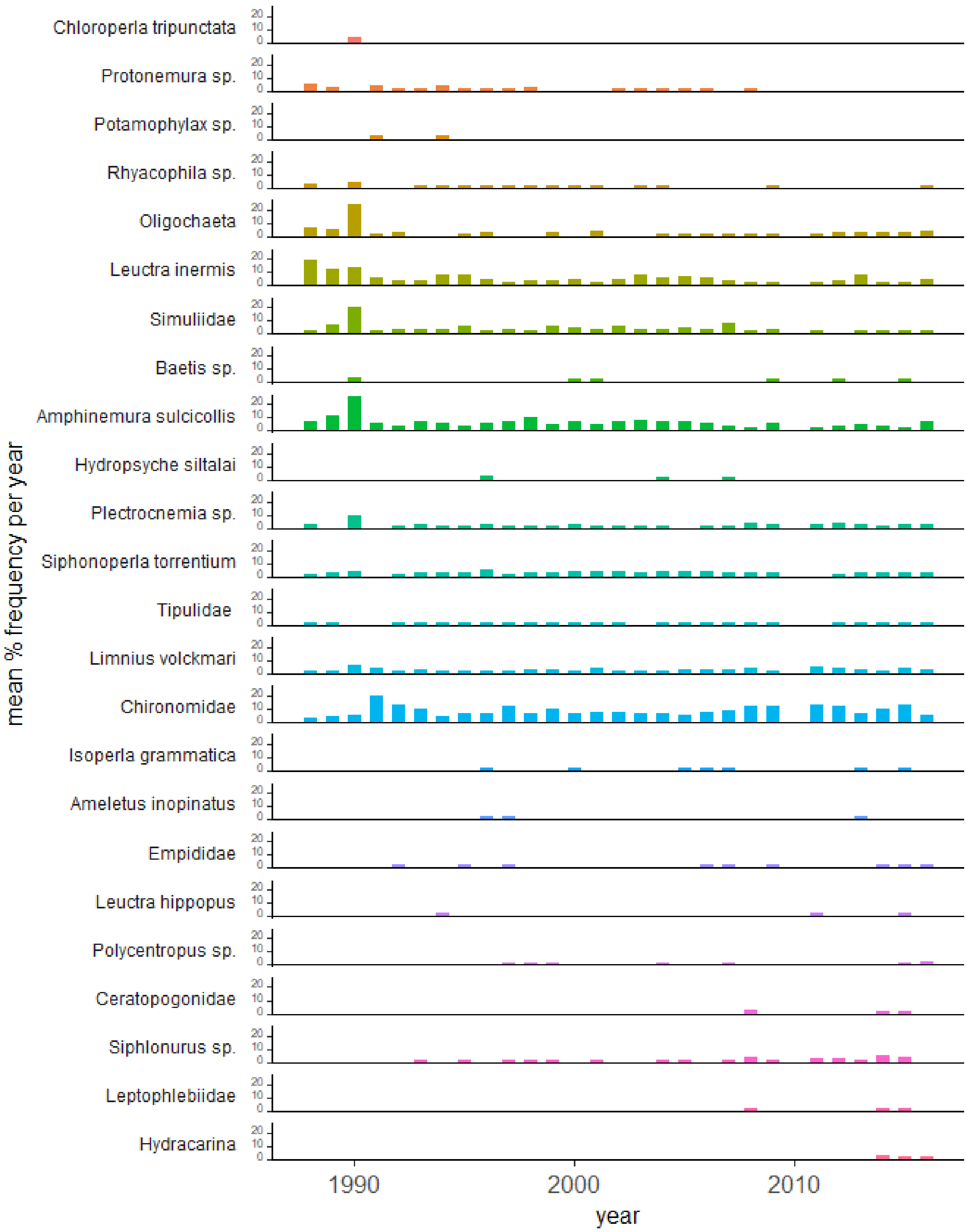


Figure 20.4 Bencrom River: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

21. Blue Lough

21.1 Site description

Blue Lough is the smallest lake on UWMN by volume and surface area. It lies in a col between the Silent Valley and the Annalong Valley in the Mourne Mountains, southeastern Northern Ireland. Diatom based pH reconstruction of a sediment core taken in 1992 suggest it is naturally acidic (acidic conditions extending back at least to the mid-nineteenth century - represented by the base of the core), but acidified further (i.e. pH 4.8 to 4.4) during the 20th century (Patrick et al. 1995). The peats in the catchment were subject to a wildfire in 2011 that had a major impact on the lough's water chemistry (Evans et al., 2016).

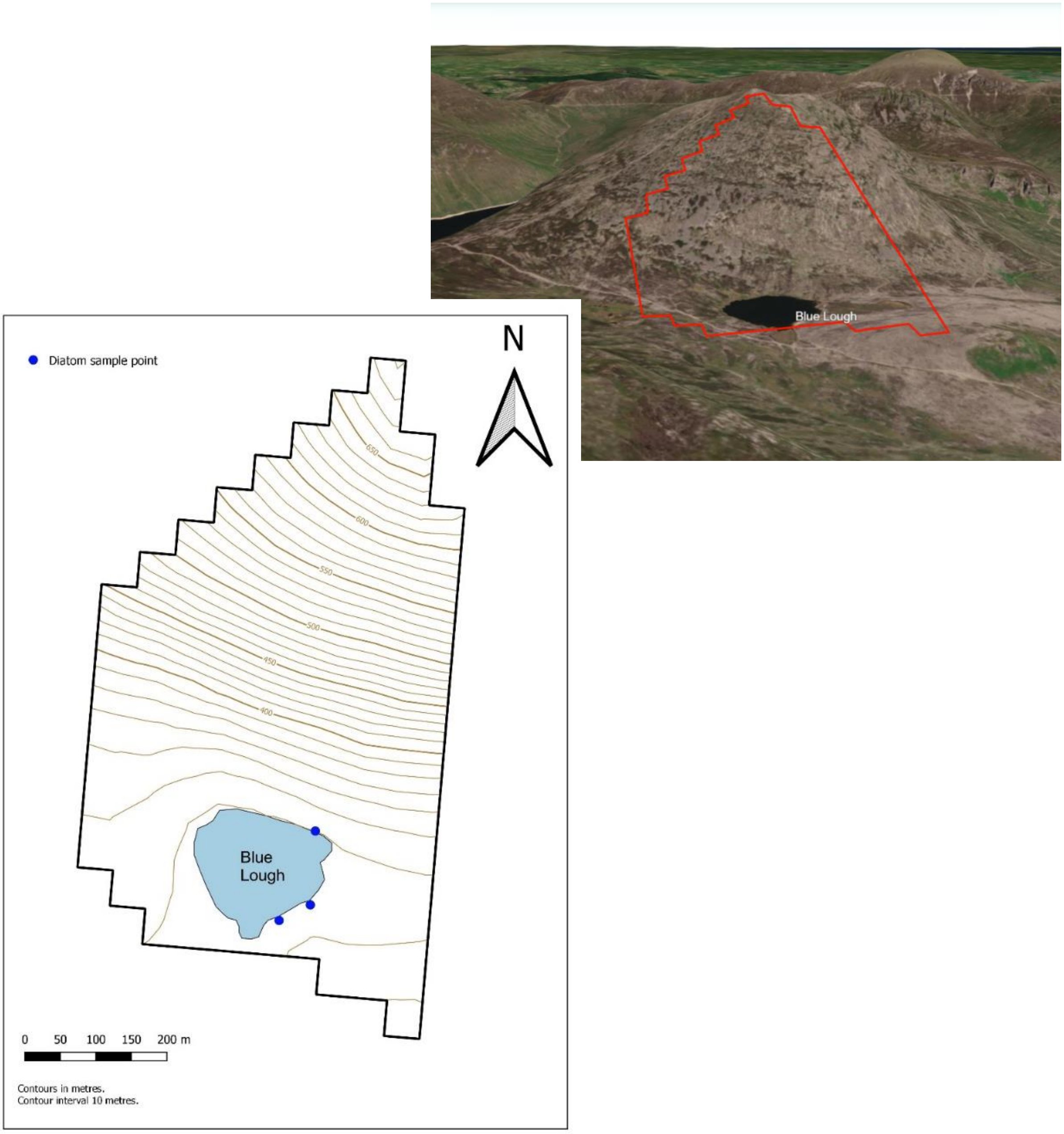


Figure 21.1 Mapped and aerial views of the Blue Lough catchment

Table 21.1 Blue Lough site characteristics

Grid Reference	J 327252	
Lake altitude	340 m	
Maximum altitude	700 m	
Maximum depth	5.0 m	
Mean depth	1.7 m	
Volume	3.6 x 10^4 m^3	
Lake area	2.1 ha	
Catchment area	50 ha	
Catchment area (excl.lake)	47.9 ha	
Catchment:Lake ratio	19:9	
Catchment geology	Granite	
Catchment soils	Blanket peats	
Catchment vegetation	Moorland	
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	22.2	9.5
Non-marine oxidised sulphur	16.1	3.0
Oxidised nitrogen	7.9	3.8
Reduced nitrogen	27.6	17.4

Table 21.2 Blue Lough water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	100.0	38.4	118.7	56.6	70.8	30.2	-1.85	**
xSO_4^{2-}	µeq l^{-1}	69.7	17.3	87.2	27.8	43.8	11.6	-1.60	**
Cl^-	µeq l^{-1}	259.5	215.2	378.0	277.6	180.5	144.7	-1.70	**
NO^{3-}	µeq l^{-1}	22.0	22.5	47.9	54.8	10.0	10.9	0.00	
pH	pH	4.7	5.0	4.8	5.5	4.5	4.8	0.01	**
Alk	µeq l^{-1}	-24.0	-0.8	-19.0	14.2	-33.0	-13.8	0.61	**
Cond	µS cm^{-1}	54.0	40.6	73.0	52.1	36.0	28.7	-0.37	**
Na^+	µeq l^{-1}	239.3	197.9	313.2	252.5	195.8	159.2	-1.59	**
Ca^{2+}	µeq l^{-1}	33.9	23.9	97.8	60.0	27.4	14.8	-0.31	**
Mg^{2+}	µeq l^{-1}	57.6	39.8	82.3	66.1	37.0	25.4	-0.40	**
K^+	µeq l^{-1}	11.8	8.7	16.1	12.5	8.4	5.5	-0.06	*
Lab Al	µg l^{-1}	326.0	162.0	421.0	206.0	191.0	115.0	-0.65	
DOC	mg l^{-1}	3.0	4.4	4.9	7.9	2.3	2.5	0.02	**
ANC-CB	µeq l^{-1}	-29.8	-2.1	32.5	25.7	-49.8	-22.4	0.70	**

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

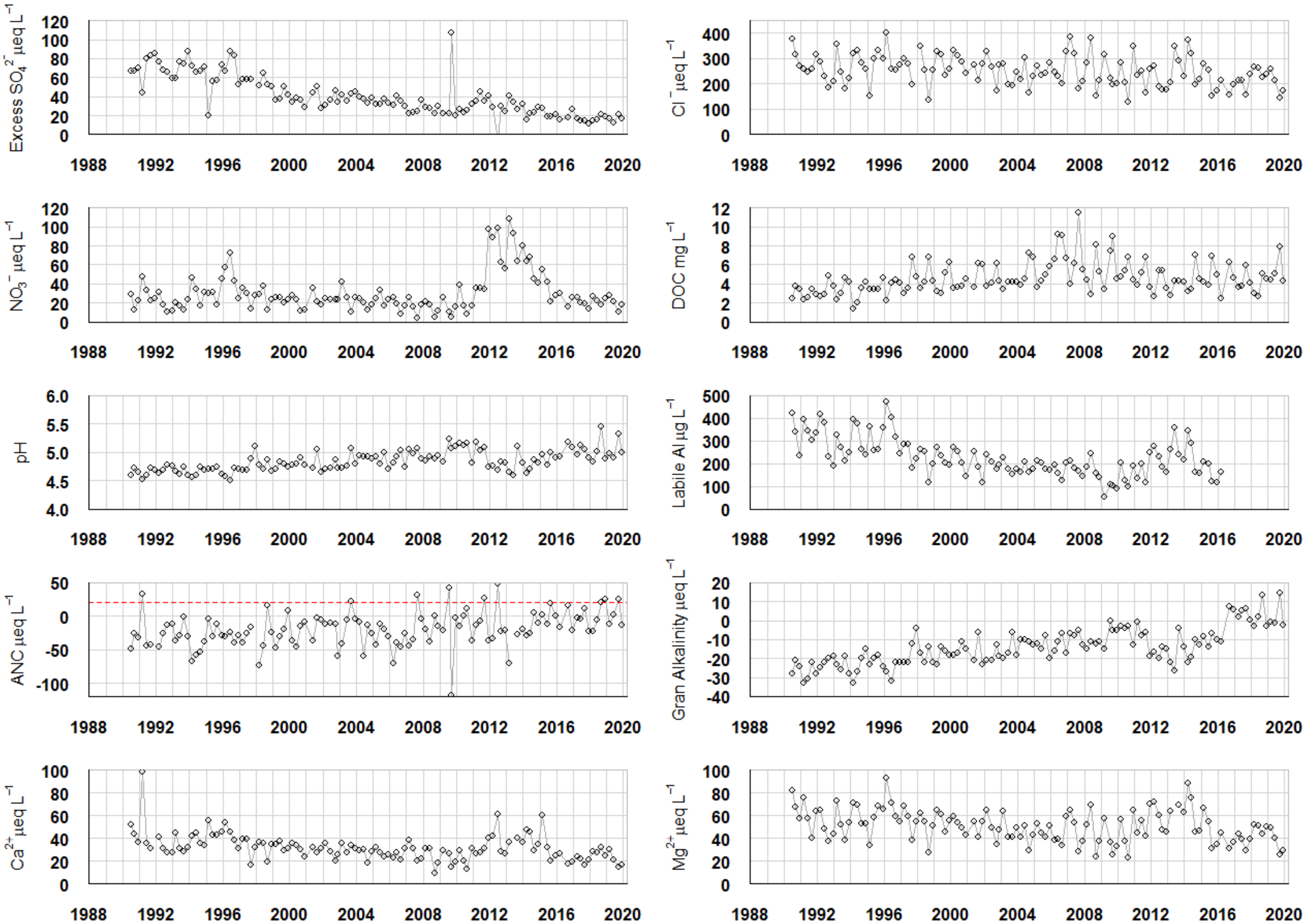


Figure 21.2 Blue Lough water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

21.2 Blue Lough: water chemistry trends

The water chemistry of Blue Lough is indicative of a naturally acidic site that has been further acidified by atmospheric deposition. CBED estimates of non-marine sulphur and nitrogen deposition are unsurprisingly very similar to those for the neighbouring Bencrom River. Lake water concentrations of non-marine sulphate and nitrate are also very similar, again suggesting, therefore, that the historical deposition estimates may be a little too low. Concentrations of non-marine sulphate in Blue Lough have fallen by a factor of four over the monitoring period, and rates of change in non-marine sulphate and chloride, when expressed in terms of equivalence, are very similar. Nitrate concentrations have remained elevated throughout the year and are thus indicative of a nitrogen-saturated catchment. They have largely remained stable (although see text on moorland fire impacts below) so that current contributions to water acidity are commensurate with those from non-marine sulphate.

Throughout the last three decades, Blue Lough has exhibited higher concentrations of labile aluminium concentration and lower pH than any other site on the UWMN. Over the first decade of monitoring labile aluminium concentrations rarely fell below 200 $\mu g\ L^{-1}$ and lake water pH rarely rose above pH 4.8, while ANC was almost always negative and mostly less than -20 $\mu eq\ L^{-1}$. Despite the initially high acid anion concentrations, calcium concentrations were very low, reflecting the very limited buffering potential of the catchment. Despite these exceptionally acidic starting conditions, the acidity of the site has responded to the major fall in acid deposition over the monitoring period. For most of that time, water pH has been rising almost linearly, and by the most recent five year period had a median of pH 5.0. Labile aluminium concentrations have fallen dramatically although, when measurements ceased in 2016, still regularly exceeded 200 $\mu g\ L^{-1}$ and are therefore likely to have continued to present highly toxic conditions to a range of potential invertebrate colonists. Levels of ANC have increased, but the median for the most recent 5 year period was still only -2.1 $\mu eq\ L^{-1}$, and the UK ANC_{crit} level of 20 $\mu eq\ L^{-1}$ has only been reached very occasionally. Dissolved Organic Carbon concentrations were relatively low at the onset of monitoring, but have risen by approximately 50% over the three decades.

Uniquely for the UWMN, the catchment of Blue Lough was heavily affected by a moorland fire in 2011, and this had a profound impact on water chemistry and acidity. Burning of the peat resulted in the mineralization of a significant amount of soil-stored nitrogen and suphur, leading to an approximately four-fold increase in nitrate concentration, and a smaller increase in non-marine sulphate. As a consequence, pH levels, that had reached an average of around 5.2, were driven down again to values between pH 4.6 and 4.8, while labile aluminium concentrations almost doubled. It took approximately 5 years for the water chemistry of the Lough to return to the recovery trajectory observed before the fire.

21.3 Blue Lough: epilithic diatom community trends

The epilithic diatom data at this site is dominated by two taxa: the acidibiontic *Tabellaria quadrisepta* (SWAP pH optimum = 4.9) and *Brachysira brebissonii* (optimum = 5.3), with lesser numbers of the acidobiontic *Tabellaria binalis* (optimum = 4.7), and acidophilous *Eunotia incisa* (optimum = 5.1) (Appendix: Figure X.3). The record shows a very clear trend, with the two *Tabellaria* species gradually declining over the monitoring period and *Brachysira brebissonii*, and *Eunotia incisa*, along with other acidiphilous taxa including *Peronia fibula* (optimum = 5.3), *Tabellaria flocculosa* (optimum = 5.4) all showing a significant increase in abundance. Alongside the increase in these acidophilous taxa there are several species indicative of high acidity that have also appeared and increased since 2000 (e.g. *Navicula subtilissima* and *Semiorbis. Hemicyclus*, optima 5.2, 4.8 respectively).

Overall species turnover is moderate (1.4; Main Report: Table 4.1) and significant (RDA1, mGLM) species changes are related to changes in monitored pH (RDA1-pH) with a small, additional response to changes in Gran alkalinity, which is perhaps acting as a surrogate to labile aluminium (Main Report: Figure 4.3). The RDA1-pH / PCA1 ratio is 0.5, suggesting that diatom change associated with pH is the main pattern of variation in the data, and there is a significant trend in DAM scores, although the overall effects size (DAM-slope; Main Report: Table 4.1) is moderate. Trajectories of PRC and DAM scores suggest that the response to changing pH has been consistent and sustained over the whole monitoring period, and there is little indication of a response to the depression in acidity following and after the moorland fire in 2011.

Overall the epilithic diatoms in this lake indicate a slight decline in acidity as the classic acidification indicators *T. quadrisepta* and *T. binalis* have both decreased in abundance. However, several other species *(N. subtilissima* and *S. hemicyclus)* are also indicative of high acidity. These show small increases during the latter years of monitoring and may indicate different sources of acidity.

21.4 Blue Lough: macroinvertebrate community trends

Blue Lough is an extremely acidic lake, and despite the clear improvements in water chemistry the lake waters still present an extremely challenging environment for macroinvertebrate life. As such Blue Lough is the most species-poor lake in the Network and there has been no significant change in rarefied richness or directional change in community composition over the monitoring period. The relatively simple assemblage is dominated by Oligochaeta (aquatic worms), Chironomidae (non-biting midges), individuals of the mayfly family Leptophlebiidae, the tube making caddis *Polycentropus* and water boatmen Corixidae (Appendix: Figure 21.4). There is evidence from the LAMM scores for a minor biological response to chemical improvements, with much of the improvement taking place over the first 10-15 years. In five of the first six years the returned LAMM score was 2, the minimum possible score. After 1993, scores improved slightly and remained variable from year to year, but without a further consistent recovery trend (Main Report: Figure 5.3). When there are so few scoring taxa contributing to the LAMM score, the returned value becomes vulnerable to relatively large shifts as a result of sporadic occurrences of individuals, e.g. in 1994 a single Empididae individual caused the score to more than double from the previous year.

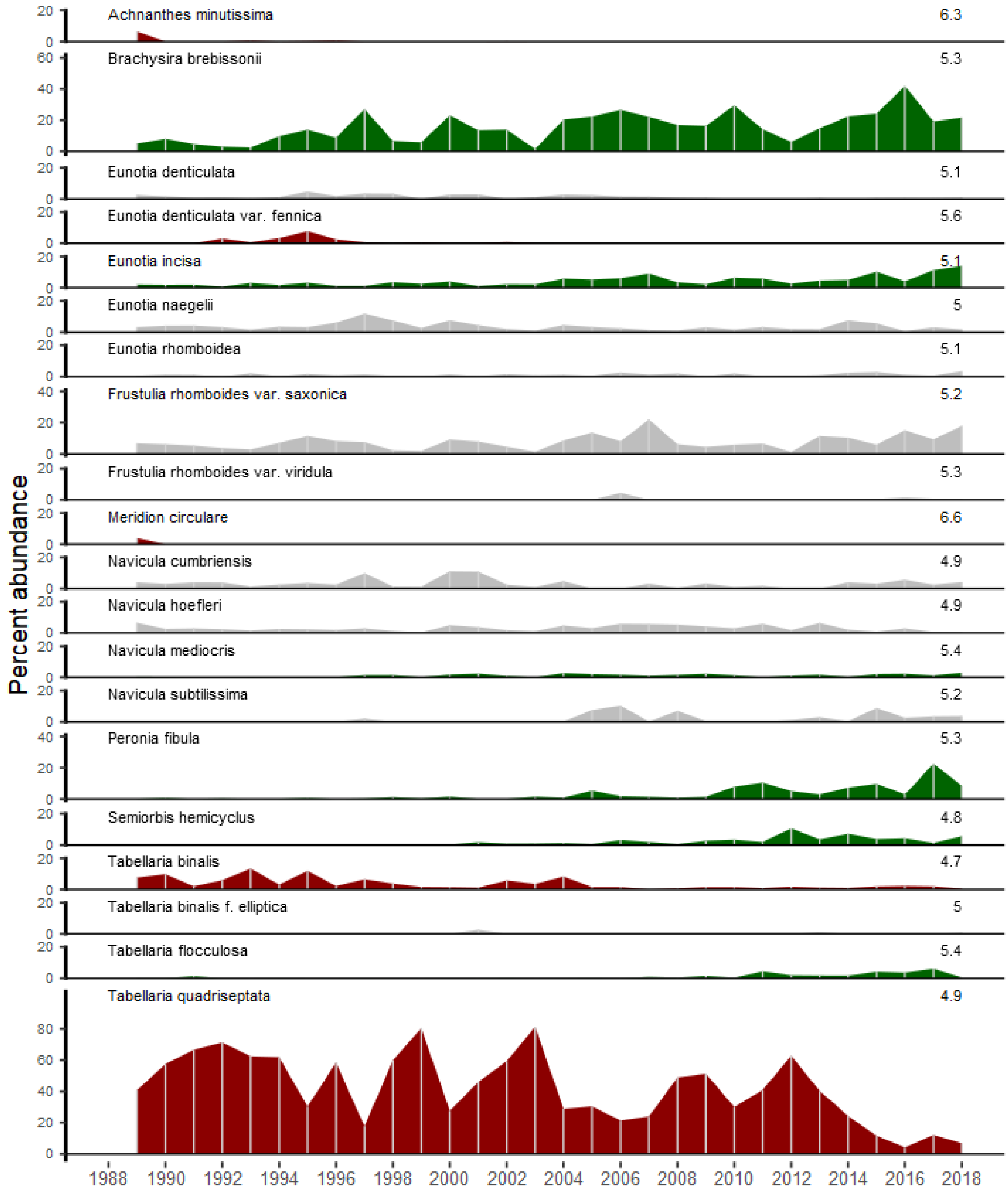


Figure 21.3 Blue Lough: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

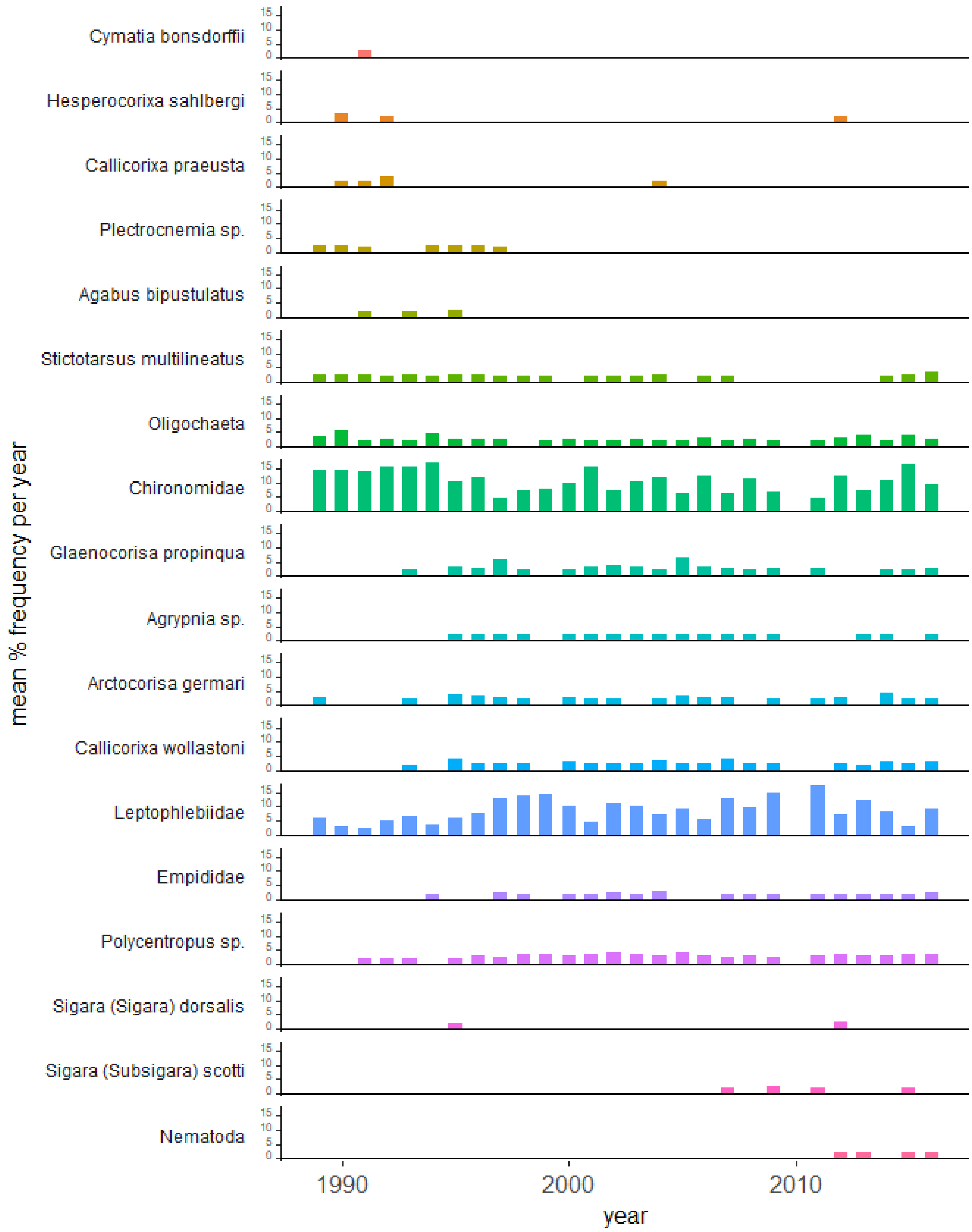
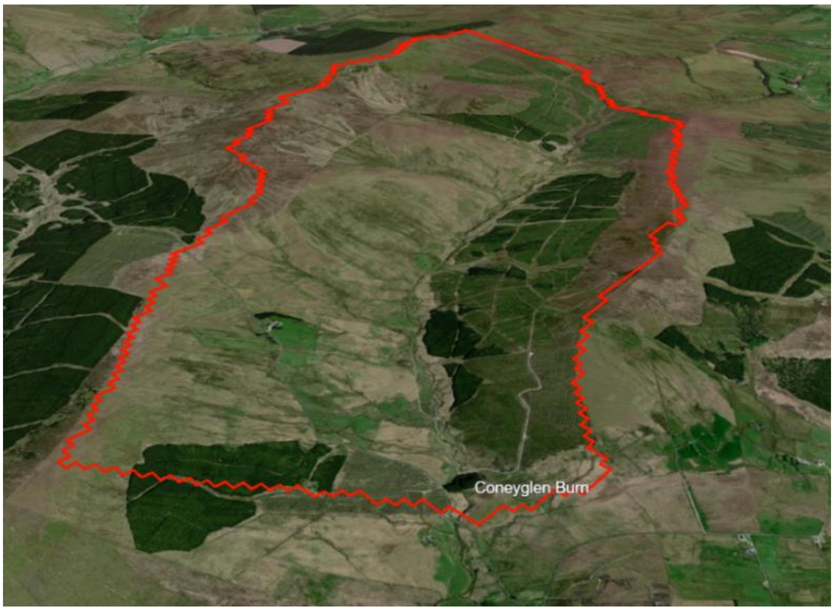


Figure 21.4 Blue Lough: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

22. Coneyglen Burn

22.1 Coneyglen Burn site description

Coneyglen Burn, in the Sperrin Hills of Northern Ireland, drains a large area of moorland, and is flanked by a relatively small area of coniferous forestry immediately upstream of the sampling stretches. The lower stretches of the catchment were under coniferous forestry at the onset of monitoring, but a larger part of the catchment was planted with trees in the early 2000s. In contrast to the sites in the Mourne Mountains, 90 km to the south east, Coneyglen Burn is one of the least deposition-impacted sites on the UWMN.



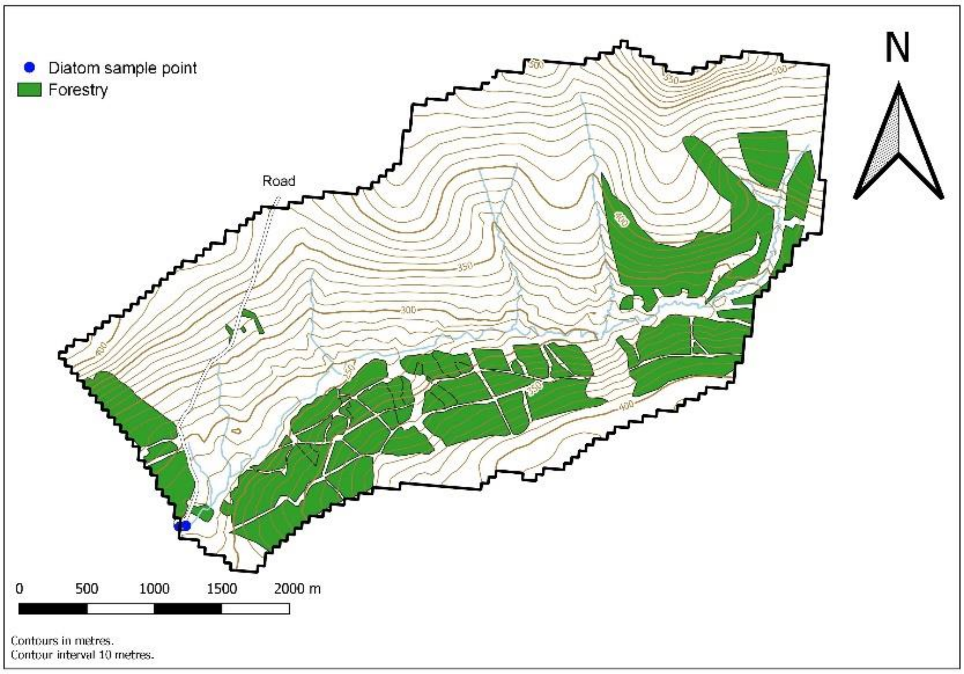


Figure 2.1 Mapped and aerial views of the Coneyglen Burn catchment

Table 22.1 Coneyglen Burn site characteristics

Grid Reference	H 641884	
Catchment area	1311 ha	
Minimum catchment altitude	230 m	
Maximum catchment altitude	562 m	
Catchment geology	schists	
Catchment soils	Blanket peat	
Catchment vegetation	Moorland 76%, Conifers 24%	
Mean annual runoff (precipitation – evaporation)		
	CBED estimated deposition (kg S or N ha^{-1})	
	1990	**2017**
Total oxidised sulphur	17.7	7.2
Non-marine oxidised sulphur	12.4	2.0
Oxidised nitrogen	4.5	2.4
Reduced nitrogen	17.1	12.0

Table 22.2 Coneyglen Burn water chemistry statistics

Determinand	Units	Median (1989 – 1993)	Median (2015 - 2019)	Max (1989 – 1993)	Max (2015 - 2019)	Min (1989 – 1993)	Min (2015 - 2019)	Slope $year^{-1}$	Significance *p < 0.05 **p< 0.001
SO_4^{2-}	µeq l^{-1}	50.0	28.6	120.8	68.5	20.8	12.1	-0.74	**
xSO_4^{2-}	µeq l^{-1}	20.9	6.5	86.5	42.8	-0.5	-9.4	-0.51	**
Cl^-	µeq l^{-1}	245.4	207.8	496.5	429.8	158.0	46.6	-1.31	**
NO^{3-}	µeq l^{-1}	2.1	2.1	5.0	32.5	2.1	2.1	0.00	**
pH	pH	6.7	6.6	7.4	7.4	4.6	4.8	0.00	
Alk	µeq l^{-1}	168.0	131.5	448.0	518.0	-26.0	-15.4	0.58	
Cond	µS cm^{-1}	55.0	49.5	78.0	87.0	35.0	31.2	-0.09	*
Na^+	µeq l^{-1}	239.3	216.6	374.1	370.1	182.7	160.5	-0.71	**
Ca^{2+}	µeq l^{-1}	154.7	124.8	294.4	354.8	26.9	46.6	-0.30	
Mg^{2+}	µeq l^{-1}	127.5	94.6	201.5	193.3	55.1	47.0	-0.36	**
K^+	µeq l^{-1}	8.9	7.4	15.6	37.8	5.4	0.6	-0.04	**
Lab Al	µg l^{-1}	2.0	8.0	28.0	23.0	2.0	1.0	0.00	
DOC	mg l^{-1}	5.6	9.7	17.0	30.4	1.7	3.5	0.05	**
ANC-CB	µeq l^{-1}	190.3	211.8	476.4	505.2	-23.1	3.5	1.28	

Alk = Gran alkalinity; Cond = Electrical conductivity (25 °C); Lab Al = labile aluminium concentration; DOC = Dissolved Organic Carbon; ANC-CB = Acid Neutralising Capacity (determined by charge balance)

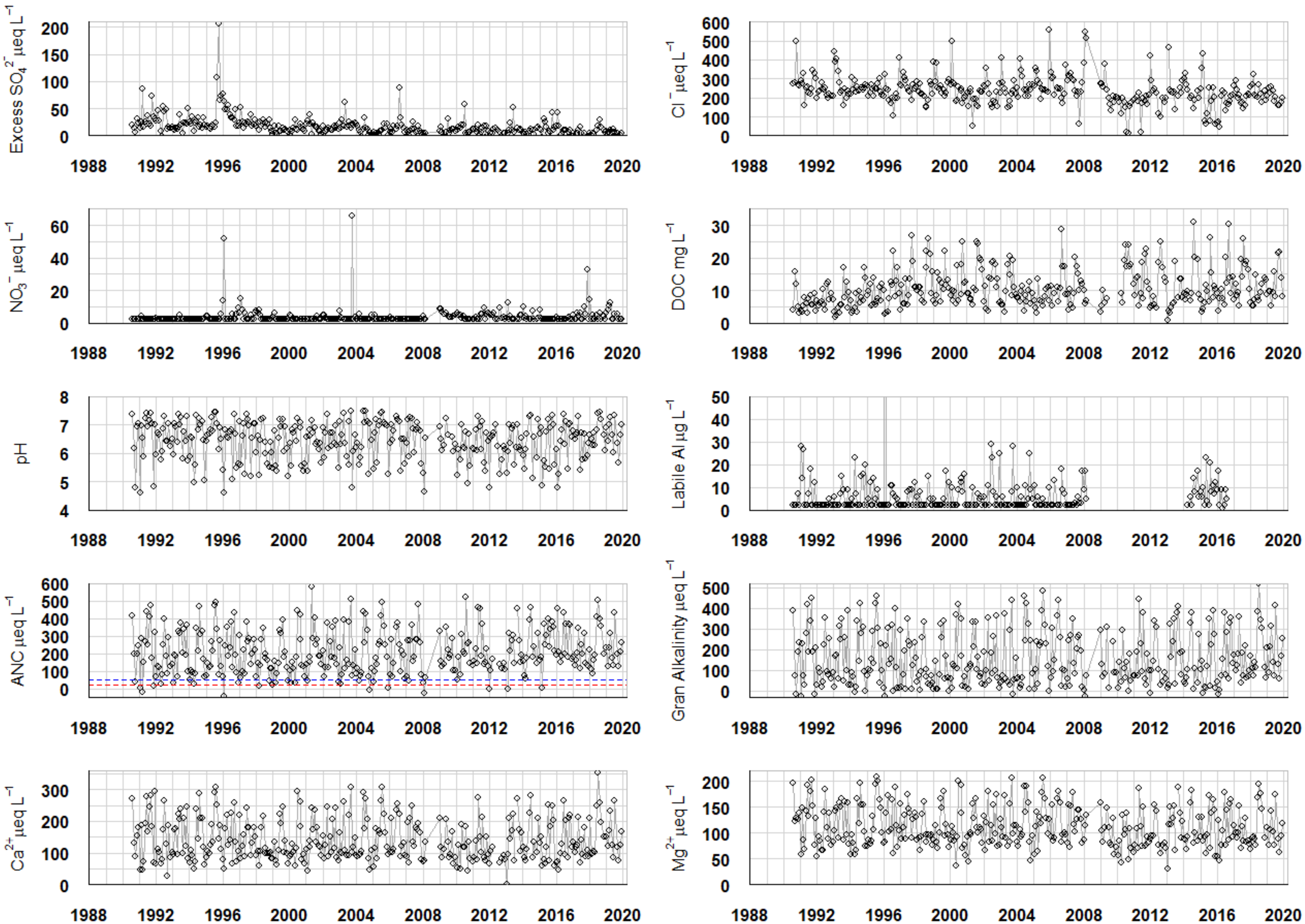


Figure 22.2 Coneyglen Burn water chemistry time series for key determinands. Red dotted line represents the UK critical Acid Neutralising Capacity limit of 20 µeq L^{-1}; blue dotted line is set to a higher limit of 50 µeq L^{-1}.

22.2 Coneyglen Burn: water chemistry trends

Coneyglen Burn is considered a “control” site on the UWMN, both because it received very low levels of acid deposition historically relative to most other sites, and because its water chemistry is relatively well buffered by the underlying geology. Despite this, CBED modelling suggests it has experienced substantial reductions in both sulphur and nitrogen deposition over the monitoring period. The streamwater is further protected from deposition effects by the catchment’s peaty soils that retain much of the deposited sulphur in the form of insoluble sulphides. Non-marine sulphate concentrations are therefore often below levels of detection, and while they become more evident following periods of drought (and consequent oxidation of sulphides), such as in the autumn of 1995, there is also evidence for maximum concentrations (following periods of drought) to have fallen over time. When expressed in terms of equivalence, chloride concentrations have fallen at almost three times the rate reduction in non-marine sulphate, a consequence of the reduction in hydrochloric acid deposition, and therefore represents the main driver of the overall decline in acid inputs. Nitrate concentrations have mostly been below limits of detection, and although trend analysis suggests a slight positive trend, the change is essentially negligible.

Although the water chemistry of Coneyglen Burn is highly dependent on flow conditions and inputs of dissolved organic matter (that peak in late summer), streamwater pH only very rarely drops below pH 5.0 and mostly ranges between pH 5.2 and 7.4, while ANC levels only very rarely drop below 0 µeq L^{-1} and mostly range from above 20 to 500 µeq L^{-1}. Labile aluminium concentrations rarely exceeded 20 µg L^{-1}, at least up to the point that regular measurements ceased in 2008, and are therefore likely to have been biologically benign throughout the monitoring period. Concentrations of calcium and magnesium are high relative to all other sites on the network, while the median Gran alkalinity level has remained above 100 µeq L^{-1}. The extent of the geological buffering has prevented any significant change in pH, labile aluminium or ANC, despite modest reductions in acid anion inputs.

The Coneyglen Burn streamwater had one of the highest concentrations of DOC at the onset of monitoring. Despite the lack of evidence for a change in acidity status, DOC concentrations have almost doubled (from a median of 5.6 to 9.7 mg L^{-1}) over the monitoring period as a consequence of the increasing solubility of soil organic matter as atmospheric inputs of ions have declined.

22.3 Coneyglen Burn: epilithic diatom community trends

Coneyglen Burn has a relatively diverse epilithic diatom flora that exhibits considerable inter-annual variability. *Achnanthes minutissima*, *Synedra menuscula* and *Gomphonema angustatum* were the most common taxa during most years although their frequencies varied quite strongly (Appendix: Figure X.3). The relative abundance of *A. minutissima and S. minuscula* declined after the mid-2000s, with *Eunotia tridentula* var. *perminuta*, *Achnanthes detha* and *Cymbella lunata* increasing after this time.

Overall turnover is moderate (1.4; Main Report: Table 4.1) but a community-level trend in diatom composition is not significant (RDA1, mGLM). While there is no significant trend in the measured stream-water pH, the inter-annual variation in pH does account for a statistically significant fraction of variation in the diatom data (RDA1-pH; Main Report: Table 4.1). However, the effect size (RDA1-pH/PCA1) is only 0.35, indicating that this accounts for only a minor pattern of variation in the diatom data. There is a slight but significant negative trend in the DAM scores, indicative of increasing acidity (Main Report: Figure 4.2). In this respect it is interesting to note the water chemical evidence of a slight long-term reduction in median pH (Main Report: Figure 3.18), which most likely results from the increase in organic acids over a period when the reduction in acid deposition has been very modest. However, there is considerable variability in the scores and the resulting trends should be treated with caution.

The epilithic diatom data therefore show strong inter-annual variability reflecting comparable variability in water chemistry data. The diatom changes, though quite marked, do not constitute a significant trend change and there is no indication of any positive response to reductions in acid deposition.

22.4 Coneyglen Burn: macroinvertebrate community trends

While there has been no significant change in the rarefied macroinvertebrate taxon richness of Coneyglen Burn, there was a moderate amount of turnover and directional community change over the 27 years of monitoring (Main Report: Figure 5.2 and Table 5.3). These changes are driven mainly by shifts in the relative abundance of the stoneflies *Isoperla grammatica* (declining) and *Leuctra inermis* (increasing)*,* Chironomidae (non-biting midge larvae; increasing*)*, as well as the absence of three stonefly taxa (*Brachyptera risi*, *Protonemura*, and *Amphinemura sulcicollis*) for eight years after 2002. There were also indications of a drop in the average acid-sensitivity of the macroinvertebrate community over the 2011-2015 period of monitoring, when moderately acid-sensitive riffle beetles and caddis flies were lost, and the acid-tolerant stonefly taxa *Nemoura* and *Leuctra hippopus* appeared, but the 2016 sample included various acid-sensitive taxa again (*Limnius volckmari*, *Elmis aenea*, *Hydropsyche pellucidula*). Overall, therefore, the macroinvertebrate assemblage is indicative of chemically dynamic site, but provides little indication of long-term change associated with recovery from acidification.

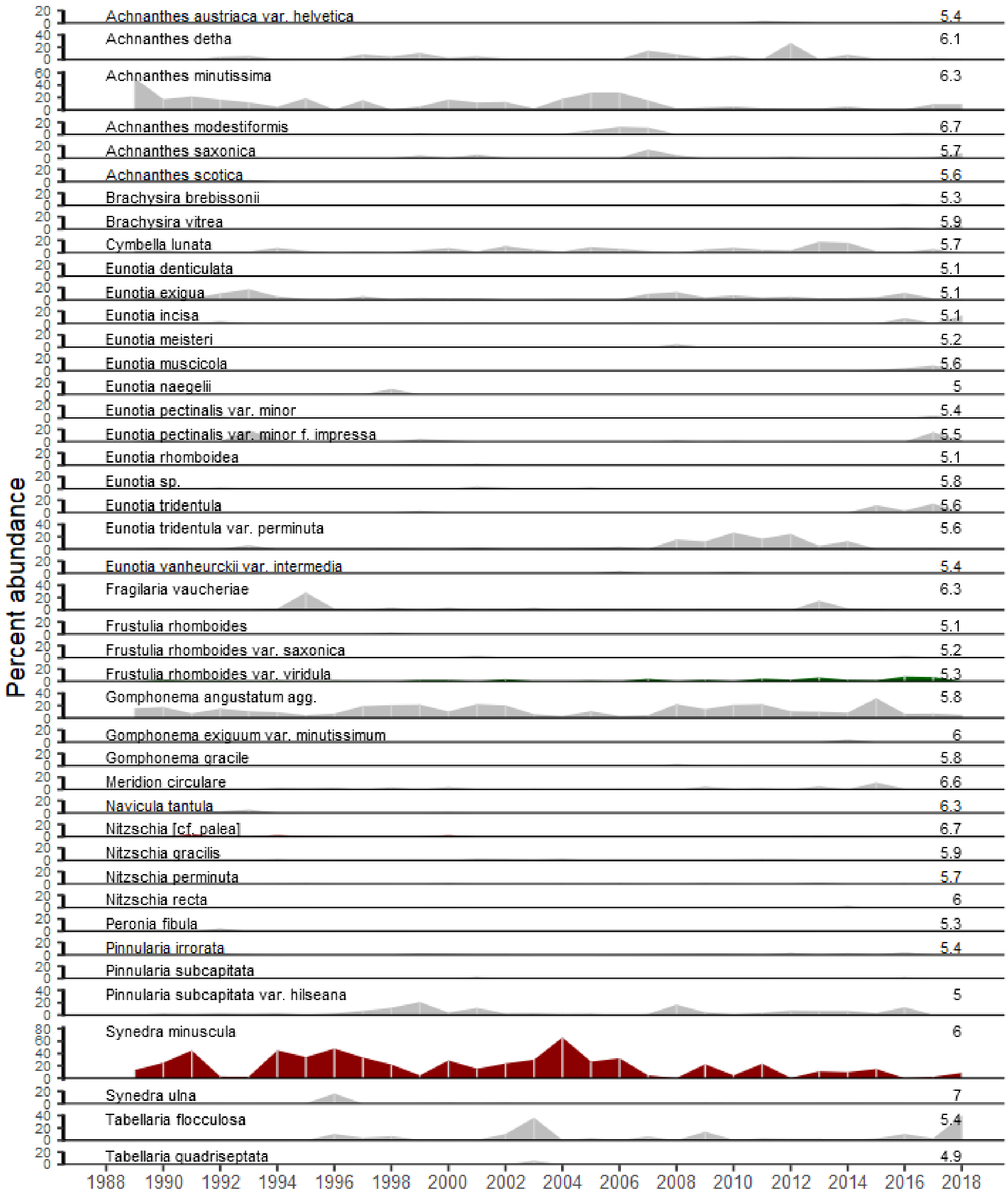


Figure 22.3 Coneyglen Burn: Annual mean relative abundance of epilithic diatom taxa. Species shaded red and green show significant reductions or increases over time respectively. Numbers to the right represent the pH optima of each species.

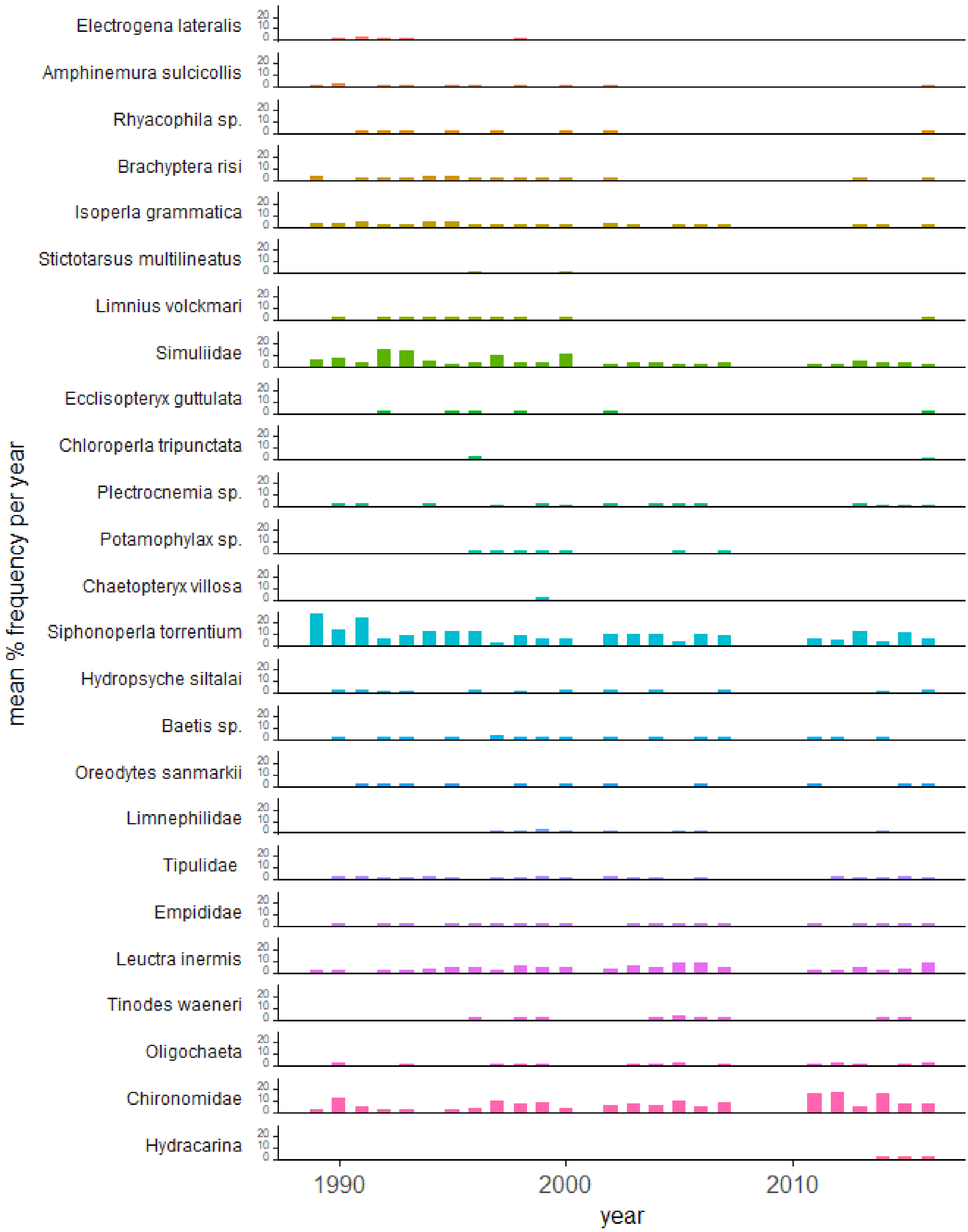


Figure 22.4 Coneyglen Burn: Annual mean relative abundance of aquatic macroinvertebrate taxa. Taxa are ranked in order of when during the monitoring period they have the greatest relative abundance. Includes all taxa comprising at least 1% of the assemblage in any year.

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