Environmental Change Research Centre

Research Report No. 98

Summary of research under Defra contract “Recovery of Acidified Waters in the UK” EPG/1/3/183

Final Report

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June 2004

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ISSN: 1366-7300

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EXECUTIVE SUMMARY

WORK PACKAGE 1: TARGETS FOR RECOVERY

Task 1.1: Reference Sites

- Analogue matching is a palaeolimnological technique that aims to find matches for fossil sediment samples from a set of modern surface sediment samples. Modern analogues were identified that closely matched the pre-disturbance conditions of eight of the UK Acid Waters Monitoring Network (UK AWMN) lakes using diatom- and cladoceran-based analogue matching.

- These analogue sites were assessed in terms of hydrochemistry, aquatic macrophytes and macro-invertebrates as to their suitability for defining wider hydrochemical and biological reference conditions for acidified sites within the UKAWMN. The analogues identified for individual UKAWMN sites show a close degree of similarity in terms of their hydrochemical characteristics, aquatic macrophytes and, to a lesser extent, in the macro-invertebrate fauna.

- The reference conditions of acidified UKAWMN sites are inferred to be less acidic than today and to support a wider range of acid-sensitive aquatic macrophyte and macro-invertebrate taxa than that recorded in the UKAWMN lakes over the period of monitoring since 1988.

Task 1.2: Chemical-biological database and interactive web page

Determination of chemical-biological response curves for national applications

- To improve models of the relationships between the presence of key biological indicator groups and water chemistry, development of the chemical-biological database has continued under this programme. Diatoms and invertebrates have been used because they are key structural components of freshwater ecosystems and are extremely sensitive to changes in acidity.

- These models are essential to predict the probability of occurrence of key taxa under pre-acidified conditions where hindcast water chemistry data are provided by static or dynamic models (i.e. to provide knowledge of likely biological targets for recovery under “reference” conditions) and the probable biological deviation from target conditions (i.e. damage) in future under different emissions reduction scenarios.

- Note that in either case the chemical-biological models can only predict the suitability of chemical conditions for the presence of key taxa and do not account for other important factors such as habitat suitability or presence of biological populations from which dispersion into chemically recovered areas may occur.

- Predictive model development focused on the “alkalinity + xDOC” formulation of ANC using both logistic regression and generalized additive modeling techniques. Response models were fitted to all widespread taxa (38 diatoms, 29 invertebrates) in the database, plus aggregated groups of acid-sensitive diatoms and invertebrates.

- A total of 36 diatoms and 22 invertebrates showed a significant response to ANC, varying from linear/monotonic, Gaussian symmetric unimodal and complex linear or non-symmetric unimodal responses. For all these taxa, it is therefore possible to predict probability of occurrence relative to chemical conditions under past or future conditions suggested by hydrochemical models.

Re-evaluation of critical loads/limits criteria

- Data collated on three themes under the current programme were presented at the DEFRA workshop on 27th February 2004; reconstructions of pre-industrial ANC, evidence for biological responses to ANC values of 0 and 20 μeql^{-1} in current data and current status of UK freshwaters in terms of ANC and critical load exceedance with these two values of ANC_{crit}.

- It was found that ANC values below 20 μeql^{-1} are rare in unimpacted systems, with very few sites showing evidence for pre-industrial values below this limit in dynamic modelling or palaeolimnological reconstruction exercises.

- Monitoring data suggest that ANC = 20 μeql^{-1} may be an important biological recovery threshold, while zero ANC is associated with a high probability of damage.

- Critical loads exceedance maps using both 0 and 20 μeql^{-1} are very consistent in pattern and the higher value of ANC_{crit} does not greatly extend the exceeded areas or numbers of exceeded sites.

- Several options for revision of the critical chemical limit for the UK were considered. The consensus of the workshop was that a general ANC_{crit} value of 20 μeql^{-1} should be applied in the UK, except where site specific modeling data suggest that pre-industrial values may have been lower, in which case 0 μeql^{-1} should be used. These revised criteria were used in the April 2004 freshwater critical load submission to CCE.

WORK PACKAGE 2: ASSESSMENT OF "STOCK AT RISK"

Task 2.1: Regional assessment of lake status

Identification of under-represented regions, updates to FAB mapping dataset and stock at risk assessment

- GIS techniques were used to identify three regions potentially "at risk" from acidification and under-represented in the critical loads database. Sampling programmes were undertaken in these regions, with 21 sites in the Surrey and Sussex Heaths plus 19 in the New Forest, both in southern England, and 30 sites in the Trossachs area of central Scotland.

- In another GIS exercise using digital boundaries for Special Areas of Conservation (SACs), 29 lakes in SACs designated for freshwater features were also randomly selected and sampled.

- For the 2004 CCE call for data, the addition of extra dynamic modeling regional datasets along with the new data collected under this programme resulted in an increased mapping dataset from 1044 Great British sites (lakes and streams) in 2003 to 1595 in 2004. In Northern Ireland the number increased from 119 to 127. 20 subprojects were amalgamated for the UK.

- A screening criterion to remove sites where seasalt contamination may have led to incorrect critical load exceedance calculations was applied beforehand, reducing an original total of 1797 UK sites to 1722 in the submitted dataset.

- The new ANC critical limit of 20 μeql^{-1} agreed at the stakeholder workshop in February 2004, with 0 μeql^{-1} in exceptional cases, was used in FAB applications using a revised version of the model (see Task 1.2 above).

- A preliminary critical loads assessment used deposition datasets for 1970 (worst-case), 1995-97 ("present") and 2010 (NECD – best-case) with the pre-screening database of 1797 sites. Stock at risk was assessed on a regional basis using individual subproject (generally regional) site designations.

- The least impacted groups with the lowest proportion of critical load exceedances included the CLAG seasalts sites in NW Scotland – due primarily to very low deposition, plus the Scottish Random Survey of 1995 and the 10km Grid Survey of Northern Ireland in 2000, in both latter cases because of the inclusion of a large proportion of non-sensitive sites in the survey datasets.

- The greatest proportions of exceeded sites were found in the Pennines, Mournes, WAWS lakes, GANE Snowdonia lakes, Galloway and Southern England.

- In 1970, 15 of the 20 mapping subprojects showed exceedance in more than half of their sites using ANC_{crit} = 20 μeql^{-1}. By 2010, only six groups of sites showed exceedance in more than half of their population. Dramatic improvements in terms of reduced critical load exceedance are therefore apparent for 2010 from the baseline “worst-case” year of 1970.

- At the country-wide scale using ANC_{crit} = 20 μeql^{-1}, exceedances in England are reduced from 267 sites (67%) in 1970 to 173 sites (43%) by 2010. In Scotland, 402 exceedances (43%) decline to 137 (15%); in Wales 269 (78%) declines to 112 (33%) and in Northern Ireland, 26 exceedances (20%) declines to 17 (13%).

- For the UK as a whole, exceedance is reduced from 964 sites (54% of the sampled population) to 439 (24%). Note that these populations of sites are not necessarily representative of the country as a whole (except perhaps in Northern Ireland) as site locations in many datasets are biased towards the most acid-sensitive areas.

- In April 2004, revised deposition datasets for 1995-97, 1998-2000 and 2010 were released by CEH Edinburgh, plus a new dataset for 1999-2001. These datasets were used to recalculate critical load exceedances for the screened mapping dataset of 1722 sites submitted to the CCE mapping programme.

- The new data for 2010 in particular led to some changes in the proportions of exceeded sites. In England, a current (1999-2001) exceedance in 208 sites (53%) is reduced to 186 (47%) by 2010. In Scotland, 244 current exceedances (29%) decline to 182 (21%). In Wales, 176 exceedances (51%) decline to 135 (39%). In Northern Ireland, 20 exceedances (16%) are reduced to 18 (14%).

- In the UK overall, 648 current exceedances (38%) are reduced to 521 (30%) by 2010. This is a larger proportion of exceedances than found in the previous modeling exercise, and this is due primarily to the revised 2010 deposition dataset used.

Acidification in lakes of conservation interest

- Of the 29 conservation sites sampled, 10 exceeded their critical loads in 1970. Six sites are still exceeded at present and are still exceeded by 2010.

- The NECD therefore appears to be of limited success in protecting conservation sites in the UK, with 20% still exceeding critical loads, if it is assumed that the small subset of conservation sites sampled are representative of the whole UK population.

Palaeolimnological study of recovery within a region

- Palaeolimnological studies of the recent sedimentary records of five lakes from the Galloway region of Scotland were undertaken.

- The work demonstrated that four of the five study sites appear to show consistent fluctuations in diatom inferred pH suggesting that the diatoms are responding to some regional forcing factor. None of the studied sites has seen a significant increase in pH over the period studied and that this is inconsistent with the measured hydrochemistry, which does show a consistent and significant increase in pH since the early 1980s.

- Further work is required to understand the reasons for the discrepancy between the measured pH recovery and the lack of response shown in the diatom sediment samples. The effect of climatic fluctuations associated with, for example, the North Atlantic Oscillation, and the observed increases in dissolved organic carbon (See Job 2.1.8 and Figure 2.1.18) may all act to mask diatom recovery and untangling these effects will require a greater understanding of diatom ecology and responses to these other forcing factors.

Palaeolimnological assessment of change in sites of conservation interest

- A total of 42 sites of conservation interest (SACs) were analysed to determine the degree of floristic change between reference conditions and present day in sedimentary diatom assemblages.

- The results of the core top-bottom analysis show that many acid sensitive lakes in designated SCAs have experienced substantial change in their diatom communities over reference conditions. These results indicate that 62 % (26 out of 42 sites) of sites in SACS have undergone substantial change, with a further 28% (12 out of 42 sites) having undergone moderate change. Only 10% of the study sites illustrate only minor or very minor change in their diatom communities over reference conditions.

- The results indicate that a considerable proportion of sites of conservation importance may have been adversely affected by acid deposition and that substantial biological change has taken place.

Monitoring of the Galloway cluster lochs

- Long-term monitoring of the Galloway cluster lochs has now continued for over 25 years, although earlier sampling programmes were irregular.

- The sites show continued recovery from acidification and are at their healthiest in terms of water quality since monitoring began in 1978, with Loch Enoch reaching a mean annual ANC > 0 μeql^{-1} for the first time.

- Nitrate concentrations have remained stable, but the rapid decline in non-marine sulphate since 1994 has leveled off in recent years, with unknown consequences for future recovery.

National scale applications of biological predictive models

- Of the large number of predictive models derived under Task 1.2, four were selected for application to national and regional datasets, to predict the probability of occurrence of the diatom *Achnanthes minutissima*, the mayfly *Baetis* spp., plus the sums of acid sensitive diatom and invertebrate taxa.

- Predictions were based on steady-state ANC for pre-acidification, 1970 and 2010 deposition levels derived using the SSWC model (F-factor predictions).

- Using a probability threshold of 0.3, the likely distribution of the diatom *Achnanthes minutissima* was reduced by more than a third of sampled sites in 1970 relative to pre-industrial times, with only partial recovery by 2010.

- For *Baetis* mayfly species, probable distribution was reduced by around 20% of sampled sites in 1970 but predicted recovery by 2010 is more widespread than for *Achnanthes minutissima*.

- However, using the sums of both acid-sensitive diatom and invertebrate taxa, greater reductions in probable distribution were found for invertebrate groups, while recovery was also slightly less marked by 2010. The same exercise was also carried out for a probability of occurrence of 0.5.

- Taken together, modeling results indicate that 10-20% of sites in the mapping dataset will fail to reach the baseline biological targets by 2010. Water quality will not have improved sufficiently to support acid-sensitive diatom and invertebrate taxa in geologically sensitive parts of the country.

- A schematic, conceptual framework has now been produced linking palaeoecological transfer functions (to hindcast water chemistry from biological sediment records using modern chemical-biological relationships), analogue matching (use of current biological communities in analogue sites that match fossil communities in acidified lakes to indicate restoration targets for impacted sites) and ecological response models (modern chemical-biological relationships used to predict biological response from hindcasts or predictions of chemistry). This framework provides the basis for the assessment of recovery towards biological targets and time to "gap closure" relative to pre-industrial conditions.

Task 2.2: Regional assessment of stream status and risk of episodes

Determination of study catchments and calculation of HRUs

- The PEARLS approach determines empirical relationships between stream water concentrations and catchment characteristics in the form of landscape classes, to simulate acidification in unsurveyed river reaches using simple mixing of drainage from each landscape class.

- Regions selected as having the appropriate data for application of PEARLS were north-west Scotland (relatively unaffected by acid deposition), Galloway and the upper Tywi/Irfon (both with a well known history of acidification) and the Conwy Valley (substantial forestry and acidic headwaters).

- Landscape classes were defined on the basis of soils, geology, land cover and land use. The Skokloster classification was found to be too broad for this purpose.

- New sampling subcatchments were selected in each of the key landscape classes within each region, except in the Twyi/Irfon where 20 existing study sites based on moorland or forest catchments were used. The final number of new study subcatchments was 52 in north-west Scotland, 59 in Galloway and 24 in the Conwy.

- Sampling campaigns were designed to obtain high- and low-flow water chemistry. During 2001-2002, the Twyi/Irfon subcatchments were sampled twice, Conwy three times and the two Scottish regions four times.

- Water chemistry was characterized for each landscape class in each region for application of PEARLS. Mixing in the river network is then determined using a topographical network of hydrological response units (HRUs) and river reaches derived from a digital elevation model.

- PEARLS was then used to determine the probability distribution of ANC falling below selected thresholds for each reach of the river networks, and hence the total river length within or below ANC classes, in the Conwy, the Cree (Galloway) and the Tywi/Irfon.

- A key application of the PEARLS approach is then to link it to the dynamic model MAGIC for the prediction of past or future changes in water chemistry across the river network (Task 3.2).

- Invertebrate samples collected at high and low flows were used to explore relationships with measures of episodic water chemistry below.

Characterisation of episodic, circumneutral and acid streams and effects on invertebrate assemblages

- The northwest Highlands and Galloway in the southwest of Scotland, Conwy in north Wales and the Llyn Brianne (Twyi/Irfon) catchment in mid Wales are geologically sensitive to acidification but occupy regions with contrasting deposition. Despite the extensive work on acidification in these regions, data on the effects on invertebrates are scarce. In this section, the potential effects of episodic acidification in these regions was examined.

- We hypothesised from existing data that, if episodic effects are important, invertebrates in streams should reflect high-flow (episodic) chemistry more than base-flow chemistry.

- To test this hypothesis, benthic macroinvertebrate assemblages, base-flow and episode chemistry were determined in 22-25 streams in each target region. Water chemistry for all streams was determined for low- and high-flow between 2001 and 2002 and invertebrates collected by kick sampling during April 2002.

- The streams were grouped by cluster analysis and characterised as acid, episodic or circumneutral. One-way ANOVA ($P<0.05$) and Tukey's pairwise comparisons ($P=0.05$) illustrated corresponding variation between the clusters and high-flow chemistry. Variables varying most between episodic, circumneutral and acid groups were pH, ANC, Al, Ca and DOC at high-flow.

- Variation in invertebrate assemblages between cluster groups were assessed using one-way ANOVA. There was significant ($P<0.05$) variation between groups in the abundances of Plecoptera and Ephemeroptera in both Wales and Scotland, and in the abundance of Trichoptera in Wales.

- In canonical correspondence analysis (CCA), pH, ANC, DOC and Al during episodes all explained significant variation in species composition across the Welsh sites, but at base-flow only Al was significant. Al during high-flow was significant in explaining species variation at the Scottish sites, while only DOC was significant during base-flow.

- Species varying with episode chemistry in both regions were the ephemeropterans *Baetis rhodani* and *Heptagenia lateralis*; the plecopterans *Isoperla grammatica*, *Chloroperla torrentium* and various species of Nemouridae; and the trichopteran *Plectrocnemia conspersa*.

- These data illustrate how acid-base status varies between sites at high-flow, explaining more variation in invertebrate assemblages than low-flow chemistry. However, effects vary across regions with episodic effects in Wales apparently stronger than in Scotland.

Effects of episodes on invertebrate indicator species

- The response of benthic invertebrates to stream recovery from acidification is slow. Acid episodes have been implicated as affecting this response and are being investigated as a factor that might offset recovery. In this section transplantation and intensive quantitative sampling were used to assess episodic effects on an acid-sensitive indicator species in the Llyn Brianne experimental catchment.

- We hypothesised that strong seasonal variation in invertebrate abundance in the episodic streams would indicate possible episodic effects, while experimental transplantations were used to mimic short-term acid episodes directly.

- A set of six streams were sampled over a 20 month period for benthic invertebrates, pH, and conductivity, while temperature was also recorded. In addition base-flow and high-flow chemistry were evaluated for the sites.

- One-way ANOVA ($P<0.05$) illustrated clear variation in pH between streams classified as episodic, acidic and circumneutral. Also, differences in ionic concentrations were observed over different flows and between stream types (episodic, acidic and circumneutral).

- Acid-sensitive mayfly species were found in the circumneutral streams (*Ephemerella ignita*, *Baetis rhodani*, *B. muticus*, *B. vernus*, *Rithrogena semicolorata*, *Ecdyonurus* spp. and *Heptagenia lateralis*), but none occurred in the acidic streams. Only *B. rhodani* occurred in the episodic streams, where densities declined substantially in autumn.

- Transplantation experiments were carried out with *B. rhodani* during base-flow (September 2003) and high-flow (April 2004) between the acidic and circumneutral streams. T-tests determined significant ($P<0.001$) drops in pH, conductivity and temperature during high-flow events, with the exception of conductivity in the acidic streams. One-way ANOVA highlighted significant ($P<0.001$) variation in pH and conductivity between the episodic, acidic and circumneutral streams.

- *Baetis* survival in the control cages during both high- and low-flow was high. T-tests found mortality of *B. rhodani* in the chronic and episodic exposures increased significantly ($P<0.001$) during the high-flow experiment. Mortality was also much higher in the chronic exposure compared to the episodic during high-flow. Two-way ANOVA showed that survival varied significantly ($P<0.05$) between streams at high-flow, with mortality in episodic exposure intermediate between chronic acidity and controls.

- These data confirm that episodic exposure to low pH at high-flow can be detrimental to mayfly survival. Density data, by contrast, were equivocal. Seasonal variations in *B. rhodani* were similar across circumneutral and episodic streams, but only this mayfly species occurred in the latter indicating possible episodic effects on mayfly assemblage composition. Further work is still required on the field effect of acid episodes on species other than *B. rhodani*.

Development of biological 'episode response' model

- Although much evidence indicates that many organisms in acid-sensitive streams are affected by episodic acidification, models that predict the response of stream biota to episodes have proved elusive. This is an important gap that has frustrated attempts to link realistic biological responses to episodic stream chemistry with important hydrochemical models such as PEARLS or MAGIC, described elsewhere in this report.

- Using data from 89 streams in Wales and Scotland, here we evaluate whether high-flow chemistry better predicts invertebrate community composition than base-flow chemistry.

- We reduced invertebrate composition to principal components and then used stepwise multiple regression to model scores on the first (i.e. major) axis of variation using combinations of acid-base determinands derived from either base-flow or high-flow.

- In all cases, regressions were evaluated from i) the fit of the modelled relationships to empirical data and ii) their performance in predicting invertebrate PC scores at independent sites ($n = 22$) reserved from the initial calibration set.

- Invertebrate principal components reflected well known trends in response to acid-base status, illustrating a shift from acid-tolerant to acid-sensitive species on the first axis.

- Regression models using combinations of pH, aluminium, DOC and charge-balance alkalinity always explained 40-60% of the variance in invertebrate score. While determinands measured at high flow on average explained more variance (49-59%) than at low flow (42-57%), differences were modest and in no case statistically significant.

- All models gave invertebrate scores for the 22 test sites that were highly significantly related to observed scores ($r = 0.71$-0.88), although there was a moderate tendency in all cases to underestimate acidification effects at the most acid sites.

- Comparison across determinands illustrated that pH at high flow either alone ($r^2 = 0.58$) or in combination with aluminium ($r^2 = 0.59$) gave the best overall fit to both calibration and test data. Charge-balance ANC performed worst, particularly at low flow ($r^2 = 0.42$).

- Overall, these data indicate that, for the purposes of modelling invertebrate assemblages in acid-sensitive streams, combinations of pH and aluminium at high-flow offer the most accurate outcome. However, base-flow chemistry can offers a valuable approximation to biological effects at more extreme flows, although losses in accuracy will be greatest using base-flow ANC as a sole predictor.

Modelling the chemical signature of episodes and risk to biology from catchment character

- Evidence is increasing that acid episodes might offset the recovery of acid-sensitive invertebrates in previously acidified streams, but factors influencing the character of episodes and their risks to biota are still poorly quantified.

- In this section, we assess variations in the chemical signature of episodic acidification between contrasting stream types (n = 89 streams) in Wales and Scotland that were respectively strongly acidified (pH < 5.0), intermediate (pH 5-5.7) and circumneutral (pH > 5.7) at high flow. All the sites were described elsewhere in the report, and respectively came from the Conwy/Llyn Brianne area in Wales, and the Galloway/NW regions of Scotland.

- Using established methods, we compared variations between these groups in i) the respective percentage contribution by dilution and strong acid anions to episodic acidification at high flow and ii) the percentage contributions of acid anions to total anion concentration during high flow events. We also assessed variations among acid-sensitive invertebrates between these groups.

- ANC in some streams increased at high flow over low flow for the events measured (3/48 in Scotland, 17/45 in Wales) - presumably because of increased base cation release.

- In Wales, contributions to episodic acidification by base cation dilution differed highly significantly ($P < 0.001$) between circumneutral streams (mean = 42%), intermediate (0%) and strongly acidified streams (0%), where strong acid addition was the dominant source of acidification at high flow.

- By contrast, in Scotland, episodic acidification reflected greater contributions by dilution in all stream types (Circumneutral = 58%; Intermediate = 26% and strongly acidified 44%; N.S. at $P < 0.1$). As a result, strong acid additions during high flow events were a much greater source of episodic acidification in Wales than in Scotland, even for strongly acidified and intermediate sites ($P < 0.001$).

- Contributions to anion loading at high flow due to sulphate were significantly greater in Wales (16-24%) than at the Scottish sites (3-5%). Similarly, in Wales (4-7% on average), anion contributions due to nitrate were significantly greater than in Scotland (2-4%). Chloride made up the bulk of the remaining anion loading at high flow, particularly in Scotland.

- The apparent consequences of these chemical effects for invertebrates differed between species. Acid tolerant organisms such as *Chloroperla torrentium* (Plecoptera) and *Plectrocnemia conspersa* (Trichoptera) were at least as abundant in streams that were intermediate or strongly acidified at high flow as they were at circumneutral sites.

- By contrast, acid sensitive species such as *Baetis rhodani* (Ephemeroptera), *Heptagenia lateralis* (Ephemeroptera; Wales only) and *Isoperla grammatica* (Plecoptera; Scotland only) were significantly reduced in abundance or absent at strongly acidified and intermediate sites compared with those that remained circumneutral at high flow ($P = 0.05$-0.001).

- Together, these data indicate that acid anions – and still dominantly sulphate over nitrate – drive episodic acidification more in acid-sensitive areas of Wales than in Galloway and NW Scotland. Nevertheless, strong acid additions still contribute significantly to acid episodes at some episodically acidified sites in all regions, which in turn have markedly different invertebrates than those where pH remains over pH > 5.7 at high flow.

WORK PACKAGE 3: PREDICTING RECOVERY USING DYNAMIC MODELLING

Task 3.1: Recovery in lakes

MAGIC simulations of water chemistry

- Work under this programme represents the most extensive dynamic model assessment of surface waters in the UK, comprising calibrations to 454 sites in eight regions.

- The MAGIC model has been tested against 15 years of observed water chemistry data at seven sites in the UK AWMN. The simulations effectively match both long-term trends and year-to-year variation at most sites.

- A poor match of observed and simulated data in the wider dataset indicates a possible influence of S adsorption/desorption dynamics, variation in annual rainfall inputs and climatic effects.

- Reconstructed ANC concentrations are above zero (except one site which requires further examination) in all regions and are generally above 20 $\mu eq\ l^{-1}$.

- In all regions, acidity peaked in the early 1970s and has decreased significantly to present day in line with observed reductions in S deposition.

- Predictions to 2020 under the emission reductions agreed for the Gothenburg Protocol indicate that surface water acidification will remain a problem at a significant (15-50%) number of sites in the Mournes, the S. Pennines and the Lake District. This indicates that further emission reductions will be required.

- Invoking nitrogen dynamics in the model (at four regions where appropriate soils data were available) causes model predictions of significantly increased NO_3 concentrations and, consequently, decreased ANC by 2050.

- The changes in ANC, however, are not sufficiently large to cause significant changes in the percentage of sites achieving relevant biological thresholds. It must be considered, however, that the increased NO_3 concentration might have an impact with respect to eutrophication.

- With respect to ANC zero, all regions return to their pre-acidification status by 2030 except for the S. Pennines. For ANC 20 $\mu eq\ l^{-1}$ no regions completely return to their pre-acidification status by 2100.

- Set in a European context, the predictions for 2016 (i.e. Water Framework Directive deadline) indicate the acidity problems that persist in the Lake District and S. Pennines are comparable with those predicted to occur in S. Sweden, Slovakia and N. Italy. A more significant problem is predicted to remain in the Mournes, comparable to the prediction for S. Norway.

Linking chemical simulations with biological status

- Regional MAGIC predictions of water chemistry have been linked to biological status using the predictive models developed in Task 1.2, specifically for the sum of acid-sensitive diatoms and invertebrates in six regions; Cairngorms, Galloway, Lake District, Pennines, Dartmoor and Wales.

- Significant biological change from baseline to present is modeled, with great regional variation. The Cairngorms are the least impacted region while in the most impacted Pennines, the probability of occurrence of acid-sensitive species is currently less than 0.5 at more than 40% of sites.

- Most sites in the six regions should achieve a probability of occurrence of at least 0.5 for the sum of acid-sensitive diatoms and invertebrates by 2010. Even in the most impacted Pennines region, this biological target will generally be met by 2010. However, in the Lake District, 20% of sites for invertebrates and 10% for diatoms will not meet this biological target within the next 100 years.

- Using a more stringent biological target of 0.75 probability of occurrence, none of the regions achieve the target entirely by 2010. The greatest biological recovery is predicted for Galloway and Wales. For the Pennines and Lake District, biological targets will still not have been reached in 10-20% of sites by 2100.

Task 3.2: Recovery in streams

Testing the linked PEARLS-MAGIC-biological model in the Conwy region

- All streams in the Conwy are subject to episodic ANC decreases. However, biologically-damaging episodic conditions (ANC < 0 or ANC < 20 μeql^{-1}) are most likely at streams with an already low mean ANC.

- The PEARLS-MAGIC approach provides an effective means by which to simulate present-day and future stream chemistry at the large-catchment scale based on readily available GIS datasets, and a limited programme of targeted sampling. The models allow lengths of chemically damaged stream to be predicted, both at present day and in the past and future.

- For the Conwy above Betws-y-Coed, 27% of stream length is currently predicted to be below an acceptable mean chemical threshold (ANC 20 μeql^{-1}). At high flow, this increases to 46%. Acidification (mean and episodic) is most severe for streams draining peat or conifer forest catchments.

- In 1850, simulated mean ANC was above 40 μeql^{-1} for all landscape types. ANC may have fallen below 20 μeql^{-1} during episodes in the most acid-sensitive landscapes, but probably did not fall below zero. By the 1970 S deposition peak, many streams would have been chronically acidic, with mean ANC < 20 μeql^{-1} and in much of the catchment negative.

- The models predict that some recovery has already occurred; the major acidification problems in the Conwy are now associated with acidic episodes, rather than chronic acidification. Under the Gothenburg Protocol, some further improvement is predicted, but some continued episodic acidification is likely in peat, forest and montane areas of the catchment.

- For the first time, PEARLS-MAGIC ANC simulations have been used to predict changes in biological status at the catchment scale. This represents an important step towards a full linked chemical-biological model, in which the dynamics of biological recovery may be linked to spatial and temporal patterns of chemical change.

Task 3.3: Model uncertainty

Transfer functions for hindcasting ANC from sediment core diatoms

- While previous transfer functions have been developed to predict pH from lake sediment diatoms, the MAGIC model more reliably hindcasts ANC.

- The European Diatom Database (EDDI) created under an EU-funded project was used to develop a new transfer function using diatom data plus alkalinity and DOC to derive ANC. 163 samples from all the main softwater areas of the UK in both acidified and relatively pristine areas had sufficient data to be used in this exercise.

- Canonical correspondence analysis and Monte Carlo permutation tests were used to ascertain the relationship between ANC and diatom distributions independent of pH effects. While only a small proportion of variance is explained by these two parameters, it is highly significant, and both explain unique components of the diatom data.

- A predictive ANC transfer function was developed using weighted-averaging with classical deshrinking, and its performance assessed by comparison with model predicted ANC for training set lakes. Internal cross-validation was also carried out using a bootstrap technique.

- Compared with other transfer functions the ANC model is relatively weak, accounting for only 49% of variation in the training set ANC compared with 80% for a pH transfer function developed using the same dataset.

Comparison of MAGIC, F-factor and diatom inference models with instrumental data

- For a comparison of techniques, seven AWMN sites were selected with both sediment core data and MAGIC hindcasts. It has to be assumed that the training dataset fully encompasses the chemical and biological conditions represented by the fossil assemblages, i.e. contains analogues for the fossil assemblages.

- Only Round Loch of Glenhead was found to have close analogues for the whole sediment sequence. Other sites (Loch Grannoch, Llyn Llagi, Scoat Tarn, Lochnagar and Loch Tinker) have close modern analogues but not for the whole core, while Blue Lough lacks good analogues for its whole history due to the presence of a diatom species not represented in the training set.

- Despite these “no-analogue” problems, both diatom and MAGIC predictions agree well with measured ANC at four sites (Llyn Llagi, Round Loch, Scoat Tarn and Lochnagar).

- For 1850, diatom and MAGIC pH hindcasts agree well at Llyn Llagi, Loch Grannoch and Loch Tinker. At Lochnagar, Round Loch and Scoat Tarn, MAGIC pH hindcasts are higher than diatom-based reconstructions by c.0.5 pH units. MAGIC ANC hindcasts are similarly higher than diatom-based reconstructions at all sites except Loch Tinker and Llyn Llagi.

- A wider dataset was used to compare ANC hindcasts based on MAGIC, diatoms and the F-factor (SSWC) model. There is considerable discrepancy between the three methods, with a systematic bias in the methods towards higher ANC predictions in the diatom, F-factor and MAGIC models respectively.

- Multiple linear regression of site variables against differences in ANC hindcasts between models found only one significant relationship, in the difference between diatom and MAGIC ANC values and site alkalinity. MAGIC baseline ANC values are increasingly high compared with diatom-based ANC values in the more sensitive, acidified sites with very low current alkalinities. The reasons for these systematic differences are currently unknown.

WORK PACKAGE 4: METAL DEPOSITION AND CYCLING AT LOCHNAGAR

- At end of 2003, up to 7 years of high quality data had been collected for trace metals in a range of ecological compartments at Lochnagar, including bulk deposition, lake waters, terrestrial and aquatic plants, aquatic invertebrate fauna and sediment traps.

- Few of the potential trends identified at the end of the previous CLAM project have been shown to continue whilst most have been shown to be short-term phenomena emphasising the need for long-term monitoring data prior to any attempt at statistical interpretation.

- With this in mind, recent lake water and deposition data lead to an ambiguity in trends. In particular, 2003 is seen to be unusually high for most metals, except Hg. Although these high fluxes are not due to unusually high rainfall, it is likely that this is an anomaly. The declining trend in Hg is observed over a period of years and is more likely to be "real".

- Similarly, Pb in both lake water and bulk deposition appears to have been increasing over a number of years, although this is in contrast to most biota Pb data which appear to show declines over the monitoring period.

- The lack of clear trends is probably a result of two factors; first, the short lifetime of the monitoring period and second, current low levels of metal emission and deposition following decades of considerable decline. Long-term monitoring will resolve both of these issues.

- Intra-annual methyl Hg data are beginning to show intriguing temporal trends with elevated levels in winter deposition. The reason for this is unclear and this pattern is not known to be observed elsewhere.

- Nickel levels have been below detection limit for a number of parameters over the period of the project, although they have been seen to increase slightly over the last year in deposition and lake water. However, Ni levels remain detectable in sediment trap data. This situation will remain under review as long periods of below detection limit values are of limited use.

- Whilst the Lochnagar data are valuable and continuing this monitoring remains a priority, their usefulness and our confidence in observed trends would be increased by the introduction of monitoring at other sites. It is hoped that the move of the trace metal monitoring at Lochnagar to the UK AWMN will allow this expansion to occur.

POLICY RELEVANCE AND IMPLICATIONS

WORK PACKAGE 1: TARGETS FOR RECOVERY

The major focus of WP1 was the development of methods for identifying appropriate recovery targets, through the use of palaeolimnological "analogue matching" techniques and the derivation of dose-response functions using national datasets to link chemical and biological targets.

It was demonstrated that the analogue matching technique may successfully be used to reconstruct reference conditions (in both hydrochemistry and biology) for acidified sites and hence to provide appropriate chemical and biological targets for recovery. The achievement of "good ecological status" under the requirements of the Water Framework Directive may therefore be assessed in terms of progress in recovery towards these reference conditions.

The chemical-biological dose-response functions (response curves) further developed within this Work Package have a two-fold role in policy formulation at the national and international scales.

i) Critical loads

Critical loads of acidity provide the scientific data input into international-scale integrated assessment modelling runs for the optimization of emissions reductions policies negotiated under the CLRTAP.

Response curves underpin the choice of an appropriate value of ANC_{crit} in critical loads models to provide a required level of protection to target organisms of interest (e.g. brown trout, macroinvertebrate communities). Work carried out under the Freshwater Umbrella programme in the UK further provides for the choice of the most appropriate ANC_{crit} value on a national or regional scale without undue reliance on dose-response functions derived in other parts of Europe (notably Scandinavia). The choice of ANC_{crit} can therefore be better justified to stakeholders within the UK.

ii) Linking chemical and biological recovery

While chemical recovery of acidified waters may quickly follow emissions reductions in a region, there may be hysteresis in biological recovery due to different rates of dispersion and colonization of locally extinct organisms from less impacted areas, or the persistence of acid episodes. Response curves provide a measure of the chemical suitability of a site to facilitate biological recovery, even where biological recovery may not yet have occurred due to these other confounding factors.

Furthermore, the MAGIC model most often used to hindcast pre-acidification conditions or predict future conditions under changing deposition levels (generally in terms of recovery) provides modelled chemistry (ANC or pH) only. Response-curves are therefore required to link chemical predictions with predictions of (potential) biological status (see below).

Work completed under this Task fed directly into the Critical Loads Workshop in February 2004 at which it was agreed to change the value of ANC_{crit} used in UK model applications from 0 μeql^{-1} to 20 μeql^{-1}. The direct policy implication is that more stringent emission reductions will be required to achieve non-exceedance of critical loads at some sites.

WORK PACKAGE 2: ASSESSMENT OF "STOCK AT RISK"

Given the non-statistical nature of the existing critical loads database and the mixture of standing and running waters, the focus of this work package was the more detailed assessment of "stock at risk" from acidification for lakes and the development of separate methods for assessing damage to stream networks. Further work on the acidification threat to lakes of conservation interest was also included.

<u>Lakes and conservation sites</u>

The regional assessment of lake status and expansion of the mapping dataset has provided much improved regional coverage of critical loads data to give a better picture of damage (exceedance) and recovery on a regional lake population basis than was available from the previous grid-based dataset.

The success of previous emission reduction measures in reducing the extent of critical load exceedance from a "worst-case" baseline of 1970 is well illustrated but the regions still heavily impacted are also identified, allowing future work to focus more on facilitating recovery in these areas. Great improvements in monitored water quality in the Galloway cluster are evident, but the potential future effects of nitrate are still uncertain. Furthermore, in order to assess the biological implications of modelled future recovery in water chemistry, better understanding of other confounding factors is required, including climatic effects and increases in DOC.

"Good ecological status" in terms of diatom and invertebrate communities will not be achievable at up to 20% of sites by 2010 because of insufficient recovery in water chemistry. While more stringent emission reductions may be required, a conceptual framework now exists for the assessment of recovery towards biological targets and a possible "gap closure" approach to achieving "good ecological status".

Further emissions reductions beyond those required under the NECD will be required if all UK waters of conservation interest are to be protected. Critical loads exceedance indicates that "good ecological status" is unlikely to be maintained or achieved in the long-term at 20% of conservation sites under the NECD.

If reference conditions are taken as a guideline target of "good ecological status" then most conservation sites fail to meet this target at present. Acid deposition may have been a major driver of observed changes in the past but other forcing factors may also have been important. A greater understanding of the interactions between these forcing factors is required to inform policy decisions on measures to achieve "good ecological status" or some other measure of recovery.

Rivers and streams

The PEARLS approach is shown here to provide a feasible means of assessing the extent of acidification and recovery across whole river networks and hence a method for assessing the overall effects of emissions reductions for given proportions of stream or river habitat in a region. As with the critical loads approach for lakes, critical values of ANC for selected organisms can be compared with ANC distributions across stream networks to assess chemical suitability for biological recovery.

There are regional differences in both the episodicity of streams in terms of measures of acidity and in the strength of episodic effects, as inferred from variation in invertebrate assemblages. Acid episodes have also been experimentally shown here to affect the survival of certain mayfly species, notably *B. rhodani*, but effects on densities and on other species are equivocal.

The importance of acid episodes in determining the biological status of a stream suggests a requirement for sampling during short duration episodes which may not be logistically feasible. Work done here indicates that base-flow chemistry can, however, provide a valuable approximation to biological effects under acid episodes at higher flows, with pH and aluminium providing better results than ANC alone, which may aid in the design of monitoring programmes.

As well as regional variations in the importance of acid episodes within streams as a confounding factor in biological recovery, there are also regional differences in the drivers of episodic acidification between anthropogenic and other sources of acidity. In policy terms this suggests that measures to reduce acid deposition are likely to be more successful in some areas (e.g. Wales) than others (e.g. Scotland) in reducing the confounding effects of acid episodes on recovery from acidification.

WORK PACKAGE 3: PREDICTING RECOVERY USING DYNAMIC MODELLING

The MAGIC model is still a key tool for the determination of pre-industrial chemical conditions used in recovery targets and also for the prediction of future responses to reduced emissions, i.e. for predicting rates of chemical recovery. In this work package, MAGIC applications have been further developed and expanded to the new regional lakes datasets and linked to chemical-biological models for the prediction of biological recovery.

MAGIC hindcasts show that an ANC_{crit} value of 20 μeql^{-1} is defensible in the great majority of UK freshwater sites since pre-industrial ANC would have been greater than this threshold value. This work largely underpinned the move to the higher ANC_{crit} value from the previous zero ANC value in national critical loads submissions to the international mapping and integrated assessment modelling programme under the CLRTAP.

MAGIC also shows that timescales to achieve the higher ANC value are much greater than for zero ANC, with direct implications for assessments of the success of emissions reductions over the next 10-20 years. If the achievement of "good ecological status" is assumed to require a return to critical ANC values, then no regions of the UK will meet this requirement in all water bodies even by the year 2100.

In policy terms, achieving reductions in sulphur emissions remains the key factor in facilitating freshwater recovery in the next 10-20 years, but the future role of nitrate saturation and leaching remains uncertain, with the possibility of a future decline in ANC by 2050 in some regions, preventing or reversing recovery from acidification.

Linked chemical-biological dynamic modelling shows significant biological change to the present from pre-industrial conditions, supporting the conclusions of similar work using SSWC hindcasts.

In response to present and future emissions reductions, MAGIC predicts an increase in probability of occurrence for key biological groups by 2010 in most regions, but the degree of recovery measured as a proportion of sites meeting a selected probability of occurrence is highly dependent on the probability threshold chosen. For informing policy decisions, great care must therefore be taken to select realistic "probability of occurrence" targets on a regional basis, perhaps using reconstructed water chemistry as a basis.

In linked PEARLS-MAGIC simulations, a tool is now available for the prediction of biological change across river networks, which also differentiates between episodically and chronically acidic stretches. The linked model further assists in the characterisation of catchments with physical attributes most likely to lead to acid episodes and thus in the identification of areas where episode-related hysteresis in biological recovery following emissions reductions may be most severe.

While critical loads and dynamic models generally use ANC as the critical chemical parameter, pH is shown here to be a more powerful predictor of diatom distributions than ANC. Hence there is an additional source of uncertainty introduced into predictions or hindcasts of biological status using ANC from static or dynamic models rather than pH.

Furthermore, while diatom, static and dynamic model hindcasts of pH and ANC are generally in broad agreement, there are some systematic differences between approaches that are not yet fully understood. Further work on the reasons for these differences would improve our confidence in model predictions.

WORK PACKAGE 4: METAL DEPOSITION AND CYCLING AT LOCHNAGAR

The monitoring of trace metals (including mercury and methyl mercury (MeHg)) in a range of ecological compartments at Lochnagar has produced a unique high quality dataset. However, as with the early years of the UK AWMN the observed trends over this seven year period emphasises the need for long-term monitoring. Only now are trends beginning to emerge with which we have any confidence. The value of such work is in its longevity and its value increases the longer that monitoring can continue. To this end, the move of the metals monitoring work to the auspices of the AWMN is seen as a positive one and it is important that monitoring is secured to continue into the future.

However, whilst the investment in the monitoring at Lochnagar is starting to show real value, there is no comparable work being undertaken anywhere else in the UK. Therefore, we are uncertain whether the trends starting to emerge at Lochnagar are typical of the UK uplands or are unique to the site. Further, there is generally a lack of Hg and MeHg data, especially with respect to biota, for the UK. It is, therefore, essential that this monitoring programme is expanded to other upland lake sites across the UK and we would recommend that this includes at least one site in each of England, Wales, N.Ireland and a 'control' site in north-west Scotland. This 'proto-network' of sites would allow national trends to be observed and further increase the value of the work currently ongoing at Lochnagar.

Finally, whilst there are limited metals (especially Hg) data for UK upland freshwaters, there are almost none for persistent organic pollutants (POPs). It would be highly valuable to start monitoring for POPs in a similar way to trace metals i.e. in a range of ecological compartments. As with metals, a pilot study could be initiated at Lochnagar with expansion after a period of time once the essential determinands and key compartments have been identified. This would complement the current monitoring under the AWMN.

Task 1.1: Reference Sites

Jobs 1.1.1 and 1.1.2: Defining reference conditions for acidified waters using a modern analogue approach

Abstract

Analogue matching is a palaeolimnological technique that aims to find matches for fossil sediment samples from a set of modern surface sediment samples. Modern analogues were identified that closely matched the pre-disturbance conditions of eight of the UK Acid Waters Monitoring Network (AWMN) lakes using diatom- and cladoceran-based analogue matching. These analogue sites were assessed in terms of hydrochemistry, aquatic macrophytes and macroinvertebrates as to their suitability for defining wider hydrochemical and biological reference conditions for acidified sites within the AWMN. The analogues identified for individual AWMN sites show a close degree of similarity in terms of their hydrochemical characteristics, aquatic macrophytes and, to a lesser extent, macro-invertebrate fauna. The reference conditions of acidified AWMN sites are inferred to be less acidic than today and to support a wider range of acid-sensitive aquatic macrophyte and macro-invertebrate taxa than that recorded in the AWMN lakes over the period of monitoring since 1988.

1 Introduction

The acidification of sensitive surface waters through the deposition of strong acids has had serious impacts on the biological communities they support (e.g. Battarbee and Charles, 1986; Charles and Whitehead, 1986; Muniz, 1991; Henriksen et al., 1992). Using palaeolimnological techniques the cause of this acidification has been shown to be the emissions of oxides of sulphur and nitrogen from industrial and other sources (e.g. Flower and Battarbee, 1983; Battarbee et al., 1985; Battarbee and Charles, 1986; Battarbee, 1990). As a result of these and other findings, emission reduction protocols have been adopted across Europe and North America to control the emissions of these compounds, such as the Oslo and Gothenburg protocols. These have led to the dramatic reduction in the levels of sulphur deposition throughout Europe and beyond (NEGTAP, 2001).

As a result much of the focus of the work within the study of lake acidification has shifted towards monitoring acidified systems for signs of recovery from acidification (e.g. Monteith and Evans, 2000). Evaluating progress towards pre-disturbance conditions is an important component of any monitoring programme designed to detect recovery in that system. To evaluate recovery a target community or state is required with which to compare present conditions (Bradshaw, 1984; Battarbee, 1997, 1999). Ideally, this target should reflect the community composition of the lake prior to the onset of acidification, which in the UK would be the community composition of the lake in *c.* 1850 AD or before. However, the majority of acidified lakes are found in remote locations and few, if any, have records of their biological communities for this period.

In addition to the progress made in reducing the levels of acid deposition, the European Council Water Framework Directive (WFD; European Union, 2000) and the US Clean Water Act (Barbour et al., 2000) require that reference conditions be defined for different lake types based on biological, hydromorphological and physico-chemical elements of the water so that the current status of fresh waters can be assessed relative to a baseline state (Moss et al., 1997; Battarbee, 1999). The historical record of past environments, as recorded in lake sediments, is perhaps the only record of past community composition available for use in setting biologically-based targets for recovery from acidification (Battarbee, 1999). Yet, here the record is limited to those organisms that leave identifiable remains in the sediments of lakes (e.g. Smol et al., 2001a,b). These include diatoms (Battarbee et al., 2001), single-celled siliceous algae, Cladocera (Korhola and Rautio, 2001), a group of microscopic crustacea, and chironomids (Walker, 2001), non-biting midges.

The use of palaeolimnology is stated in the WFD as one method by which reference conditions may be defined (European Union, 2000). One palaeolimnological approach is that of Bennion et al. (2004), who used TWINSPAN (Hill, 1979) to classify the pre-disturbance floras of 26 Scottish lochs. This allowed characterisation of the reference condition diatom floras for different lake types, while diatom-total phosphorus (TP) transfer functions applied to sediment cores from the 26 lochs were used to determine reference condition TP concentrations. An alternative approach is the use of a technique called analogue matching.

Analogue matching makes use of the historical record of community composition recorded in lake sediments. This is compared with the contemporary record found in the surface sediments of a range of modern reference lakes (Overpeck et al., 1985; Flower et al., 1997). By using a number of slices from different levels of a sediment core, corresponding to different periods in the history of the lake, it is possible to identify a series of ecological states ranging from the most highly impacted to reference conditions. These states may be used as restoration targets were total restoration is not achievable or prohibitively costly. It is assumed that those samples selected from the modern lakes as being the most similar to the fossil sample will also have a similar community composition in those species that do not leave reliable or interpretable records in lake sediments—a shortcoming of the more direct approach of Bennion et al. (2004).

The analogue approach has mainly been used by pollen analysts where fossil pollen spectra retrieved from lake or bog archives were compared to modern pollen spectra taken from a range of habitat types (e.g. Guiot et al., 1989; Fauquette et al., 1998; Peyron et al., 1998). By identifying that modern assemblage which is most similar to each of the fossil assemblages it is possible to infer the environmental conditions in the past from those of the lakes today where the modern assemblage was sampled. As such, analogue matching is also a well established technique used in palaeoenvironmental reconstruction (e.g. Overpeck et al., 1985).

Flower et al. (1997) extended the use of analogue matching, using the technique to identify restoration targets for two acidified lakes, Loch Dee (DEE) and the Round Loch of Glenhead (RLGH). Sub-fossil remains of diatoms were used to match fossil samples from these two lakes with surface samples taken from 194 sites from across Northern Europe. Their work demonstrated that close modern analogues could be identified for the reference conditions of the two study sites using diatom assemblages (Flower et al., 1997).

Some of the close modern analogues identified by Flower et al. (1997), however, had excessive lake water calcium concentrations when compared to the present day hydrochemistry of DEE and RLGH, placing their true value as reference sites in some doubt, especially if comparisons with the wider fauna and flora of the analogues were made (Flower et al., 1997).

An alternative approach has been developed by Simpson (2004, and in prep) that builds on the work of Flower et al. (1997), but which uses a matching process based on diatom and cladoceran remains. In this paper we use this new approach to identify modern analogues that can be used as reference conditions for the lakes in the Acid Waters Monitoring Network (AWMN). We then compare a range of selected acid-sensitive aquatic macrophyte and macro-invertebrate taxa to define reference conditions for the AWMN lake sites and to assess how well the analogue matching approach performs in defining these conditions.

2 Methods

2.1 Modern training set and study sites

Analogue matching using sub-fossil remains of diatoms and cladocerans from lake sediment samples is described in detail in Simpson (2004, and in prep), and was used to identify close modern analogues for ten of the lake sites in the AWMN from a modern training set of 83 acid sensitive lakes from Wales and Scotland, UK. Analogue matching was not performed for Loch Grannoch, Galloway, Scotland, because no core material from the pre-acidification period was available for analysis.

Briefly, the training set is based on the UK sites included in the SWAP calibration set (Stevenson et al., 1995). Additional sites were added to the training set from an assessment of acidification in lochs from northwest Scotland (Allott et al., 1995), a study on the effects of recent water quality changes on populations of the black throated diver (Allott and Rose, 1994) and a lake classification project in Wales (Allott and Monteith, 1999). A few remaining sites were included from unpublished work (ECRC, unpublished data). A total of 163 lakes were included in the diatom training set. A subset of these lakes was analysed for cladoceran remains where sufficient material was available in the surface sediment sample. 83 lakes were subsequently included in the combined diatom and cladoceran training set used in this paper.

The cladoceran remains were enumerated from the dried surface sediment samples using a standard deflocculation of the sediment in hot 10% potassium hydroxide (KOH) followed by washing on a 37 μm mesh sieve and subsequent mounting of a known amount of the residue on to microscope slides (Korhola and Rautio, 2001). The remains were identified using standard reference works (Frey, 1959, 1960, 1962a,b; Goulden and Frey, 1963; Flößner, 1972). 200 remains from each sample were enumerated and identified to at least species level. The taxonomy follows that of Flößner (1972).

2.2 Analogue matching

The degree of similarity (or dissimilarity) in the diatom and cladoceran communities between each fossil sample from the AWMN lakes and every sample in the modern training set was then calculated using the chord distance (CD) (Overpeck et al., 1985; Gavin et al., 2003; Wahl, 2004):

$$d_{ij} = \sqrt{\sum_{k=1}^{m} \left(y_{ik}^{0.5} - y_{jk}^{0.5} \right)^2},$$

where the CD between the i^{th} and j^{th}samples (d_{ij}) is the square root of the sum of the squared differences between the square root of the proportion of taxon k in samples i and j.

The CD is known as a signal to noise coefficient (sensu. Overpeck et al., 1985), and attempts to emphasise the signal or pattern in the data at the expense of the noise or random variation in species abundances. Prentice (1980) and Overpeck et al. (1985) have shown thoeretically that signal to noise coefficients have desirable properties for determining ecological resemblance amongst samples and that these performed better than other types of coefficients in their tests at distinguishing between similar and non-similar samples. More recently, these findings have been confirmed, in a statistical sense, through the use of receiver operating characteristic curves (Gavin et al., 2003).

Having determined the CD between each fossil sample and every sample in the modern training set, those lakes in the training set that are sufficiently similar to the fossil sample are selected as close modern analogues. Close modern analogues are those samples in the modern training set that have a CD less than or equal to a critical value. This critical value can be determined (i) from the distribution of all CDs between samples in the modern training set, (ii) *a priori* using expert judgement, (iii) by means of a permutation test or (iv) from a distribution of random, approximately normally distributed deviates (see Simpson, 2004, for more details).

For this study we determined a critical value for the CD by method (iv), randomly generating $\frac{1}{2}n(n-1)$ approximately normally distributed deviates (n = number of sites in the modern training set), which range from the lower to the upper limits of the chord distance (0 and 2). It is assumed that the frequency with which we expect to find that any two samples are similar will be relatively low within a random sample of a population of lakes. Taking the extreme 5^{th} percentile of the distribution of randomly generated distances as the critical value of the chord distance gives a rough approximation of the degree of similarity required for any two sites to be considered similar. Using this method, a critical CD of 0.476 was identified.

The past hydrochemistry of the fossil samples can be inferred from the selected analogues by taking the (weighted-)average of the values for all analogues for each determinand as those of the past hydrochemistry of the reference condition (ter Braak, 1995). If used, the weights are the inverse of the CD value for each analogue.

2.3 Contemporary hydrochemical and biological sampling of modern analogues

Following analogue matching to identify close modern analogues for the pre-acidification condition of AWMN lakes, the selected sites were sampled quarterly for hydrochemistry for one year to provide autumn, winter, spring and summer samples. A full suite of base cation, acid anion and nutrient chemistry determinands was analysed on the collected samples as were measures of total organic carbon and labile and non-labile aluminium concentrations following standard AWMN techniques (Patrick et al., 1991). A list of the sampled lakes and their codes (as used in the text) is shown in Table 1, and Figure 1 shows a map of the UK displaying the locations of the analogue sites. For logistical reasons, LAI, GRUA and TEAN were not sampled as part of this work.

Macro-invertebrates were sampled from the littoral area of each modern analogue following techniques similar to those used by the AWMN (Monteith and Evans, this issue). One minute kick/sweep samples were collected in April 2002 from five littoral locations for each of the close modern analogues and with the exception of Chironomidae, Oligochaeta, Sphaeriidae and Hydracarina were identified to species level where possible.

Sampling of the aquatic macrophytes was also performed using standard AWMN techniques, employing a combination of an inshore lake survey, 2-4 trawl surveys using a grapnel and 3 transect surveys per lake (Patrick et al., 1991). The relative abundances of individual macrophyte taxa were determined from a combination of these sampling methods and expressed using the DAFOR scale (Kent and Coker, 1992).

2.4 Numerical analysis

In order to compare how similar the modern analogues for each AWMN site are in terms of their aquatic macrophyte flora and macro-invertebrate fauna the data for the two biological groups were transformed into presence-absence values and the between-site dissimilarity was determined using the Jaccard index:

$$d_{ij} = \sqrt{1 - \left(\frac{a}{a+b+c}\right)},$$

where the similarity has been transformed to a distance by taking the square root of 1 minus the Jaccard index. The Jaccard index between sites i and j is effectively the number of species present in both i and j (a) divided by a plus the number of species that occur only in i (b) or only in j (c) (Legendre and Legendre, 1998). The transformation to presence-absence data was used to focus the analysis of the analogue sites on the criterion of whether sites have different species compositions rather than on the differences between sites in the relative or absolute abundances of individual taxa.

To display the between-analogue dissimilarity matrices a non-metric multidimensional scaling (NMDS) of the two matrices was performed. NMDS is a multivariate technique that aims to map a k-dimensional distance matrix on to a low dimensional ordination space that preserves the ordering of relationships among the samples in the original matrix (Legendre and Legendre, 1998). Ordination plots of the first two dimensions of the NMDS analyses were subsequently produced.

An alternative way of assessing the analogue sites is to determine whether there is concordance between the aquatic macrophyte and macro-invertebrate assemblages of the different sites. For analogue matching to be a valid analysis, it must be demonstrated that sites with similar diatom and cladoceran assemblages also have similar aquatic macrophyte and macro-invertebrate assemblages. Analysis of the raw Jaccard dissimilarity matrices calculated above and the subsequent analysis of these matrices by NMDS is one way of assessing the degree of concordance between the aquatic macrophyte and macro-invertebrate assemblages. An alternative way of addressing this question would be to demonstrate statistically whether the two configurations of sites in the NMDS plots for the aquatic macrophyte and macroinvertebrates were similar to one another. This can be achieved using a Procrustes analysis (Gower, 1971; Mardia et al., 1979) and an appropriate permutation test (Peres-Neto and Jackson, 2001).

Procrustes analysis (Gower, 1971; Mardia et al., 1979) is an ordination technique that aims to find a compromise ordination for two data matrices (usually ordination configurations such as those produced by NMDS for example) by minimising the sum of squared distances between corresponding samples of the two data matrices (Legendre and Legendre, 1998). The statistical significance of the correlation between the two data matrices was assessed using the PROTEST permutation method of Peres-Neto and Jackson (2001) with 1000 permutations.

The analogue matching and other statistical analyses were produced using the R computer software (R Development Core Team, 2004). NMDS was performed using the MASS package for R (Venables and Ripley, 2002), using the random start function of Oksanen (2004). The Procrustes analysis and permutation test were implemented using functions in the vegan package (Oksanen, 2004). For the comparison of the aquatic macrophyte and macro-invertebrate data sets the data matrices were reduced in size by deleting those taxa present in fewer than five samples. This was done to reduce the noise, the effect of rare or uncommon taxa, in the small analogue data set of just 19 sites and to reduce the difference in the numbers of taxa in the aquatic macrophyte and the macro-invertebrate data sets.

3 Results

3.1 Analogue matching

From the 83 lake training set close modern analogues were identified for eight out of the ten AWMN lake sites studied (Table 2). No close analogues were identified for Burnmoor Tarn and Loch Chon, and Loch Grannoch was not included in this analysis (see Methods). The pre-acidification diatom and cladoceran assemblages of Llyn Cwm Mynach (MYN), the Round Loch of Glenhead (RLGH) and Loch Tinker (TINK) were well represented in the training set, with 10, 9 and 7 close modern analogues respectively being identified. Between one and three close modern analogues were identified from the training set for the pre-acidification period of the remaining five sites (Loch Coire nan Arr (ARR), Lochnagar (NAGA), Blue Lough (BLU), Scoat Tarn (SCOATT) and Llyn Llagi (LAG)).

Three close modern analogues were identified for the pre-acidification sample from ARR. The closest analogue for ARR was a modern surface sediment sample from the same lake (ARR, CD = 0.43), which suggests that present-day conditions are similar to those prevailing in the early 1800's. ARR was also a close modern analogue for two other AWMN lakes; LAG and MYN.

Llyn Cwellyn (CWEL) in North Wales and Loch nan Eion (LNEI) in North West Scotland were the two other close modern analogues for ARR with CDs to the fossil sample of 0.461 and 0.463 respectively. The closely matched diatom and cladoceran assemblages of ARR, CWEL and LNEI were characterised by the planktonic cladocerans *Bosmina coregoni* and *B. longispina*, the chydorid cladoceran *Chydorus piger*, and the diatom taxa *Achnanthes minutissima*, *Brachysira vitrea* and *Tabellaria flocculosa* var. *flocculosa*. The analogue inferred hydrochemistry for ARR (Table 3) showed good agreement with the measured mean hydrochemistry for the loch, again suggesting that hydrochemically the loch has changed little over the industrial period. *Myriophyllum alterniflorum*, *Nitella* sp. and *Callitriche hamulata* were present in ARR in both 1988 and 1999, with *Subularia aquatica* also being found in 1999. Two of the three analogues contained *M. alterniflorum* and *Nitella* sp. , whilst all three contained *C. hamulata* and *S. aquatica* (Table 4).

A single close modern analogue was identified for the pre-acidification sample from BLU; Loch Dubh Cadhafuaraich (CADH, CD = 0.453) in northern Scotland. Acid tolerant diatoms *Eunotia incisa*, *Frustulia rhomboides* var. *saxonica* and *Cymbella perpusilla* were the most common taxa in this sample, whilst the acidobiontic (acid loving, pH optima ≤ 5.5) taxon *Tabellaria quadriseptata* was absent from CADH and only present at low abundances (less than 2%) in the pre-acidification sample from Blue Lough. The analogue inferred hydrochemistry for Blue Lough (Table 3) suggested that the reference conditions for the lough were less acidic (pH 5.14) than present day (mean pH 4.69) and had considerably lower labile aluminium concentrations of 3.5 μg l^{-1} compared to a mean of 286.9 μg l^{-1}. The aquatic macrophyte *M. alterniflorum* was the only acid sensitive species found during the macrophyte survey (Table 4) and *Lymnaea peregra* was the sole selected acid sensitive macro-invertebrate present in CADH (Table 5). None of the selected acid sensitive aquatic macrophyte or macro-invertebrate taxa were present during the periods 1988-90 and 2000-2002 in BLU.

ARR was the sole close modern analogue identified for LAG (CD = 0.456). The analogue inferred hydrochemistry of the reference condition sample for LAG suggests the site was less acidic (pH 6.3) and had lower labile aluminium (2.0 μg l^{-1}) and higher alkalinity (20.5 μeq l^{-1}) concentrations than currently observed in the lake (1988-1998 mean pH 5.34, labile aluminium 39.7 μg l^{-1} and alkalinity 5.6 μeq l^{-1}). *M. alterniflorum*, *Nitella* sp. , *C. hamulata* and *S. aquatica* were all found in the macrophyte survey of ARR, as was the macro-invertebrate *Pisidium* sp.

Ten close modern analogues were selected from the training set for the pre-industrial reference condition sample of MYN. As with the previous AWMN sites, the analogue inferred hydrochemistry for MYN suggested a reference condition less acid than the present day with much reduced labile aluminium and higher alkalinity concentrations (Table 3). *M. alterniflorum* currently inhabits MYN and was present in all ten of the analogue sites, with *Nitella* sp. being present in nine analogues, *C. hamulata* and *Chara* sp. in three analogues, *S. aquatica* in six analogues and *Eleogiton fluitans* in four. It is interesting to note that *Nitella* sp. was recorded in 1988 in MYN but has not been recorded recently suggesting that this taxon has been lost from the system, possibly the result of further acidification early in the monitoring period (Monteith and Evans, 2000). *Pisidium* sp. was present in all but one of the analogues for MYN whilst *Baetis* sp. and *L. peregra* were found in four and five of the analogues respectively.

Loch Toll an Lochain (LOCH, CD = 0.447) and Llyn Clyd (CLYD, CD = 0.47) were the two sites identified as close modern analogues for the pre-acidification period in NAGA. The diatom *Achnanthes scotica* was particularly important in characterising the pre-acidification period of NAGA representing almost 11% of the diatom assemblage in the sample. This taxon was quite rare in the training set and this was reflected in the low number of analogues for this site. *S. aquatica* was present in both LOCH and CLYD, with the latter analogue also supporting *M. alterniflorum*, *Nitella* sp., and *C. hamulata* (Table 4). Similarly, *Pisidium* sp. was present in both the analogues, with *L. peregra* also being found in CLYD (Table 5).

Nine close modern analogues were identified for RLGH. The analogue inferred chemistry (Table 3) indicates that prior to acidification RLGH was a typical acid sensitive, upland, brown water loch, and suggests that the loch has acidified from an inferred pH of 5.83 to a present day mean pH of 4.9. Labile aluminium concentrations have increased markedly from an inferred value of 5.44 μg l^{-1} to a current mean of 60.2 μg l^{-1} and alkalinity has declined from over 20 μeq l^{-1} to a present day mean alkalinity of -12.2 μeq l^{-1}. The aquatic macrophyte and macro-invertebrate surveys of the analogue sites suggest that the reference conditions of RLGH were characterised by the presence of a number of acid sensitive species, including *M. alterniflorum* (present in 7 of 8 analogues), *Nitella* sp. (5 analogues), *C. hamulata* (4 analogues), *S. aquatica* (6 analogues), *E. fluitans* (3 analogues). *Pisidium* sp. was found in all ten analogues, whilst *Baetis* sp., *L. hirtum* and *L. peregra* were present in four, one and five of the analogues respectively.

The pre-acidification sample from SCOATT contained a high abundance of *Cyclotella* [*kuetzingiana*] agg. (*ca.* 25%). This taxon was also highly abundant in the identified close modern analogue, Llyn Edno (EDNO, CD = 0.398), as was the planktonic cladoceran *B. coregoni* and the chydorids *Acroperus harpae*, *Alonella nana* and *Alonella excisa*, which were present in similar percentages in the SCOATT sample. The analogue inferred chemistry suggested that the chemical reference conditions for SCOATT were only slightly less acidic than today (analogue inferred pH = 5.15), with zero alkalinity and moderately high labile aluminium concentrations (54.5 μg l^{-1}). Of the selected acid sensitive aquatic macrophyte taxa only *S. aquatica* was found in EDNO and none of the macro-invertebrate species were present.

Seven close modern analogues were identified for the reference state of TINK. As was the case for ARR, a surface sediment sample from TINK was identified as the closest modern analogue in the training set (CD = 0.3683), suggesting that the diatom and Cladocera reference conditions for TINK are not too dissimilar from the present day. The analogue inferred pH was, however, lower than the present day (Table 3), driven by three of the close analogues, Loch na h'Achlaise (ACH, pH = 5.24, CD = 0.3849), Lochan Fhionnlaidh (FHIO, pH = 4.97, CD = 0.3898) and Loch Gruagaich (GRUA, pH = 5.16, CD = 0.4605).

The main diatoms in the fossil sample from TINK were acid sensitive taxa, such as *B. vitrea* and *Fragilaria virescens*, and acidophilous taxa, such as *Frustulia rhomboides* var. *saxonica* and *E. incisa*. These same species were also the dominant taxa in the close modern analogues. *B. longispina* was present at high abundances in both the sample from TINK and the close modern analogues. The pre-acidification period in TINK was characterised by a lower diversity of chydorid cladocerans than those of the analogue sites. However, the main chydorid species (*A. excisa*, *A. harpae*, *C. piger* and *Alona affinis*) were similar. The aquatic macrophyte surveys of the analogue sites suggests that *M. alterniflorum* would still have been present in the pre-acidification period of TINK and that other acid sensitive taxa, such as *S. aquatica*, *Nitella* sp. and *Chara* sp., were also potentially present. *Pisidium* sp. was found in three of the analogue sites with *L. peregra* and *Baetis* sp. each being found in a single analogue.

3.2 Comparison of aquatic macrophyte and macro-invertebrate assemblages

The Jaccard distance matrices show that the individual sets of samples selected for each AWMN lake were somewhat dissimilar in terms of their aquatic macrophyte and macro-invertebrate assemblages. This is not unexpected in a small data set with many species (19 samples and 31 taxa), where there will be a high degree of noise. In general the aquatic macrophyte assemblages were more similar between analogues for the same AWMN lake than the corresponding macro-invertebrate assemblages.

The Jaccard distance matrices are illustrated graphically in Figure 2 using NMDS of the original distance matrices. In these plots, sites that are similar to each other are placed close together and those sites that are dissimilar to one another are positioned further apart. In general, the analogues for MYN (LOSG, DUBH, TINK, FEOI, NEUN, ARR and CLAI) were located closely together on the NMDS plot of the aquatic macrophyte data (Figure 2a). The same can be said for those analogues for RLGH (LNEI, DUBH, CLAI, LACH, DOI, HIR, CHAM and ARR) and TINK (TINK, ACH, LOSG, FHIO and NEUN). The two analogues that stand apart from the other sites in Figure 2a were CLYD and LOCH, two high altitude sites that are both analogues for Lochnagar, another high altitude site.

For the macroinvertebrates, the patterns were less clear in the NMDS plot (Figure 2b). The analogues for MYN were located close together in the centre of the plot with the exception of TINK and ARR, which were positioned towards the top left of the diagram. The analogues for RLGH were also located closely together in the ordination, again with the exception of ARR and, to a lesser extent, HIR. The analogues for TINK were, however, located across the entire ordination and illustrate little similarity in terms of their macro-invertebrate fauna.

The results of the Procrustes analysis are shown in a Procrustean superimposition plot (Figure 3, Peres-Neto and Jackson, 2001). Points represent the NMDS sample positions using the aquatic macrophyte data and the ends of the arrows are the NMDS positions of the samples using the macro-invertebrate data. The majority of the samples were located in similar positions in both sets with the exception of TINK, ARR, FHIO, ACH, CADH and LOCH, as indicated by the length of the arrow in the plot. The first impression is that the two configurations are somewhat similar but that there are a number of departures from this pattern, suggesting that there is only loose concordance between the aquatic macrophyte and macro-invertebrate data sets. The results of the PROTEST permutation test, however, indicate that there is a particularly strong correlation between the two configurations (correlation = 0.5717, P value = 0.001).

4 Discussion

4.1 Analogue matching

Of the ten AWMN lakes to which the analogue matching procedure was applied, eight had close modern analogues for diatoms and Cladocera in the training set. In general the hydrochemical reference conditions indicated by the analogues, for those AWMN lakes that have acidified, are less acidic than the present day conditions in these lakes with concomitantly lower labile aluminium concentrations and higher alkalinity. Exceptions to this are ARR and TINK, where a surface sample from these two sites is the closest analogue for the pre-industrial period. This suggests that for these two AWMN lakes little acidification and/or sufficient recovery has taken place as the diatom and cladoceran communities are today much the same as they were prior to the start of the industrial revolution.

The result for ARR is not unexpected as Patrick et al. (1995) and Monteith and Evans (2000) suggest that, contrary to earlier evidence (Flower et al., 1993), ARR is in fact only slightly acidified. The changes seen in this loch are more likely to be related to natural responses to changes in the prevailing climate in the North West of Scotland over the last 70 years or so (Monteith pers. comm.). A recent study by Rose and Rippey (2002) further indicates that ARR is one of the least polluted lakes in the UK, with low levels of spheroidal carbonaceous particles, PAHs and PCBs recorded in the post 1800 AD sediment record of the loch.

The result for TINK, on the other hand, is more difficult to understand. Palaeolimnological analysis of the site suggests that TINK acidified to a minimum pH of 5.13 at the start of the 20th Century and that since this period pH has increased markedly to the present day 1988-1998 mean pH of 6.13 (Patrick et al., 1995). This evidence and the similarity of the surface sediment sample to the pre-acidification sample would indicate an unlikely scenario that during a period of increasing emissions of sulphur dioxide Loch Tinker was recovering from previous acidification. The results, however, do suggest that today TINK is very similar to its reference condition and the diatom inferred pH for this period (pH 6.5) is in close agreement with the present day mean pH (Patrick et al., 1995).

The analogues for this site suggest, however, a much lower pH (5.45) for the reference condition than indicated by the diatom inferred pH, driven by particularly low pH values for three of the analogues (see Results and Table 3). It is interesting that there is such a wide range of pH values for the analogues for TINK (range 4.97–5.79) when, with the exception of GRUA, all the close modern analogues have relatively low chord distances to the pre-disturbance sample (CD range 0.368–0.417). Given that the surface sediment sample for Loch Tinker is the closest analogue for the reference conditions of TINK it would make little sense to interpret the close modern analogues for this site any further.

Table 3 demonstrates that other hydrochemical properties of the analogue sites, particularly the Ca^{2+} and total organic carbon (TOC) concentration, and conductivity are very similar to those of the respective AWMN lake today. This suggests that hydrochemically the selected lakes are good analogues for the reference conditions of the various AWMN lakes. Although not presented here, there is also good agreement between the sets of close modern analogues and the associated AWMN lake in terms of the major ions. This is encouraging as it suggests that the diatoms and Cladocera are reflecting the wider hydrochemical conditions of the lakes, where in a previous study, using diatom-based analogues only (Flower et al., 1997), the selected analogues were found to have excessive calcium concentrations compared with the pre-disturbance samples. As such the results suggest that making wider floristic and faunistic comparisons between the reference conditions and the close modern analogues is appropriate.

4.2 No-analogue sites

The diatom and cladoceran assemblages of the reference condition samples of Burnmoor Tarn (BURNMT) and Loch Chon (CHON) do not have any close analogues within the modern training set. This can be related to the uniqueness of the diatom and cladoceran assemblages in the samples from these two sites.

The pre-acidification sediment sample from BURNMT contains a high abundance of the acid sensitive diatom *A. minutissima*, which represents over 20% of the total assemblage. *A. minutissima* is found in many of the training set lakes but rarely at such high abundances. The planktonic diatom *Cyclotella comensis* is the dominant taxon in the reference condition sample of Burnmoor Tarn but in the training set relatively few planktonic taxa are found, especially at such high abundances. The main planktonic taxon in the training set is *Cyclotella* [*kuetzingiana*] agg., an aggregate taxon containing both the nominate and its varieties as specified in the SWAP taxonomic guide (Stevenson et al., 1995). The high abundance of this taxon in the training set is in part, therefore, an artefact of the taxonomic harmonisation using the SWAP taxonomy rules. BURMNT is also a naturally alkaline system with a mean pH (1988-1998) of 6.48 and is well buffered against acid deposition (mean Ca^{2+} concentration 1988-1998 of 89 μeq l^{-1}). Lakes of this type are under represented in the training set. We would expect the diatom and cladoceran assemblage of a surface sediment sample from this site to be a close analogue for the reference conditions, however, insufficient material was available for cladoceran analysis and therefore BURNMT is not present in the modern training set.

The cladoceran fauna of the pre-acidification sample from CHON is likewise relatively unique when compared to the training set assemblages. The sample contains no remains of the planktonic species *Bosmina coregoni*—the dominant Bosminid is *Bosmina longispina*—and has a rich chydorid cladoceran community (15 species), including a number of large bodied, macrophyte associated taxa, such as *Graptoleberis testudinaria*, *Eurycercus lamellatus* and *Sida crystallina*. In the training set, only eight lakes contain no remains of *B. coregoni* and those lakes are not as rich in chydorid cladocerans as the pre-acidification sample from CHON. Unlike BURNMT, the hydrochemistry of CHON is typical of that associated with acid-sensitive, upland lakes in the UK, being mildly acidic (1988-1998 mean pH of 5.6) with low alkalinity (1988-1999 mean of 10 μeq l^{-1}). However, physically it is relatively large and deep and the only dimictic lake in the AWMN. Absence of close modern analogues may therefore result from an under-representation in the training set of lakes with similar physical properties.

Clearly one criticism of the modern training set used here is that it is relatively small in comparison to the diatom training set used by Flower et al. (1997), which contained 194 sites from the UK, the NW of Ireland, Norway and Sweden. During the creation of the modern training set a decision was made to select only samples from the UK in order to minimise biogeographical differences between analogues when comparisons to the wider biological groups were made (Simpson, 2004). One consequence of the reduced size of the training set used in this study is that there are no identifiable close modern analogues for two, and few close analogues for a further four, of the AWMN lakes. This has consequences for the wider application of the technique to other sites in the UK. Improving the coverage of the training set would have the effect of reducing edge effects from the analogue analysis (ter Braak, 1995), where two similar sites will potentially be positioned far apart in multivariate space in at least one dimension. This is one area where the utility of the approach could be greatly enhanced.

4.3 Aquatic macrophytes and macroinvertebrates

The results of the aquatic macrophyte and macro-invertebrate surveys are difficult to interpret. The work presented here has concentrated on the presence or absence of selected acid sensitive taxa in the reference conditions of the AWMN lakes (Tables 4 and 5) as well as the full range of taxa found in these sites (Figures 2 and 3). In the case of the aquatic macrophytes, the selected analogues suggest that the reference conditions for the relevant AWMN lakes contained at least one acid sensitive aquatic macrophyte species where none were found during the first year of monitoring on the network (Table 4).

The results for MYN and RLGH in particular demonstrate the utility of the approach. Two and no acid sensitive aquatic macrophyte species were present at the start of monitoring in 1988 in MYN and RLGH, respectively. The close modern analogues indicate that the reference conditions for these two sites potentially contained a much more diverse flora containing a number of the selected acid sensitive taxa.

M. alterniflorum in particular is present in all the analogues for MYN and all but one of the analogues for RLGH. Other elodeid species, such as *Nitella* sp., *C. hamulata* and *Chara* sp., are also found in many of the analogues for these two sites. These species, which derive their inorganic carbon from the water column are often absent from acid sites with pH below 5.5 (Maessen et al., 1992; Arts, 2002), where bicarbonate in the water is absent or limited and the dominant form of inorganic carbon is free CO_2 at low concentrations (Wetzel, 1983; Wetzel et al., 1985). In such environments these acid sensitive taxa are unable to establish themselves and isoetid forms that derive inorganic carbon from sedimentary sources tend to dominate. Monteith et al. (this issue) describe the first detection of *M. alterniflorum* at this site in 2003 and attribute this to a sufficient recovery in alkalinity. The return of this species is entirely consistent with the results of the analogue matching.

The presence of these elodeid forms in the reference conditions of many of the AWMN lakes is particularly important. The between-analogue distances based on the aquatic macrophyte data suggest that the sets of analogues are not particularly similar in terms of their aquatic macrophyte flora. In some sites

M. alterniflorum may be present with *C. hamulata*, whilst in others *M. alterniflorum* is present with *Nitella* sp. It is possible that the main criteria illustrated in the chosen analogues is the presence of a diverse aquatic macrophyte flora consisting of more than just low growing isoetid forms rather than being dependent upon specific individual taxa. Elodeid species, such as *M. alterniflorum* and *C. hamulata*, rise up through the water column of the littoral zone of lakes, structuring the water column into a greater diversity of habitat types than is present in sites with acid tolerant, low growing isoetid taxa. This increased heterogeneity in habitat availability is subsequently reflected in the zooplankton and macro-invertebrate communties supported by such lakes.

Similar patterns are found in the results for the macroinvertebrates though here the results are less clear. The reference conditions of many AWMN lakes are characterised by the presence of one or more acid-sensitive species, in particular *Pisidium* sp. and *L. peregra* with the particularly sensitive *Baetis* sp. and *L. hirtum* being found occasionally. This is not unexpected as many of the AWMN site are naturally acidic, upland systems.

4.4 Lake management and reference conditions

Reference conditions for various lake types are being produced following recent legislation in order to assess deviations from reference conditions in polluted surface waters. The analogue matching procedure, as outlined in this paper, can be used to define these reference conditions and proper interpretation of the results will be of particular importance to lake managers.

We can perhaps be confident about these inferences where there is consistency in the inferences from the modern analogues. For example *M. alterniflorum* is found in all the analogues identified for Loch Tinker and Llyn Cwm Mynach, and as such there can be a high degree of confidence that *M. alterniflorum* was present in these two sites prior to acidification. The situation is much less clear where there is inconsistency. *Chara* sp. was found in one third of the analogues for Llyn Cwm Mynach, for example, so it is difficult to determine whether this taxon should be included in the definition of the reference conditions for this lake. Clearly, the greater the proportion of analogues that contain a particular taxon the greater the certainty that can probably be attached to its use in defining the reference conditions.

It is unclear how one might resolve this situation and provide more conclusive evidence of the presence or absence of a particular taxon prior to disturbance. For *Nitella* sp. and *Chara* sp. it may be possible to confirm the presence of either of these two taxa prior to disturbance as they are well recorded in lake sediments (Carvalho et al., 2001). It is not possible to confirm their absence as the sampling effort can never be sufficient to rule out finding remains of a taxon if more sediment material were analysed.

It is worth reiterating an observation made above, that the diatom and Cladocera communities of the analogues may be reflecting the presence or absence of particular functional groups of aquatic macrophytes (Willby et al., 2000). Broadening the focus in this way should improve consistency and may be of greater practical value to lake managers.

4.5 Uncertainties

Aquatic ecosystems are also exposed to a wide variety of impacts and confounding factors such as global climate change (Skjelkvåle and Wright, 1998), landscape change or physical manipulation, and other pollutants such as toxic metals (e.g. Rose and Rippey, 2002). This might undermine the utility of the analogue approach if present day environments are perturbed into states not previously encountered (Skjelkvåle and Wright, 1998).

It is also important to consider whether any suitable modern analogues exist within the same biogeographical region as the impacted lakes. Where these confounding factors are likely to have an impact upon disturbed sites into the future it may be necessary to re-evaluate the applicability of using modern analogue-derived reference conditions as targets for future recovery or restoration.

5 Conclusions

Analogue matching using diatom and cladoceran sub-fossil remains is a useful tool for defining reference conditions for lakes. The approach is numerically simple to apply to biological data and, where a sufficiently wide-ranging modern training set is available, can produce ecologically plausible results. As with other palaeolimnological techniques, analogue matching need not be restricted to just one or two proxies and the approach might benefit when applied in a multi-indicator study. The use of additional proxies in the matching procedure should act to filter the potential analogues for unsuitable sites according to the dominant environmental sensitivities of these biological groups.

For those sites that have undergone change the modern analogues that define their reference conditions contain a number of acid sensitive aquatic macrophyte and macro-invertebrate taxa that are currently absent. The reference conditions for most sites suggest that more diverse aquatic macrophyte and macro-invertebrate communities were once supported by many AWMN lakes prior to their acidification. Such information is potentially highly informative to the assessment of the current status of biological recovery of these systems (e.g. Monteith et al., this issue). Further work is required, however, to extend the modern training set and to develop training sets for different lake types if the analogue matching approach is to be used more widely.

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Figure 1: Map showing the locations of the 22 sites identified as close modern analogues for AWMN lake sites

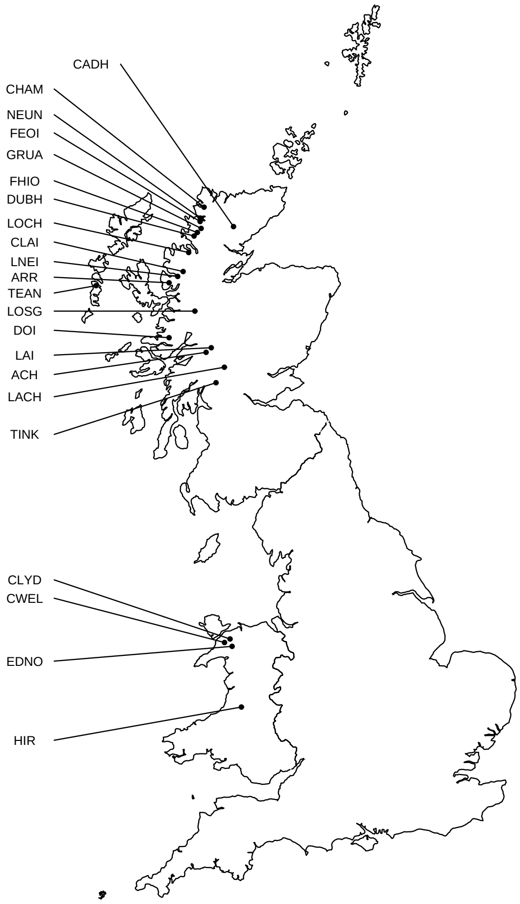

Figure 2: NMDS ordination plots of the presence-absence values of the analogue sites for a) the aquatic macrophytes and b) macroinvertebrates

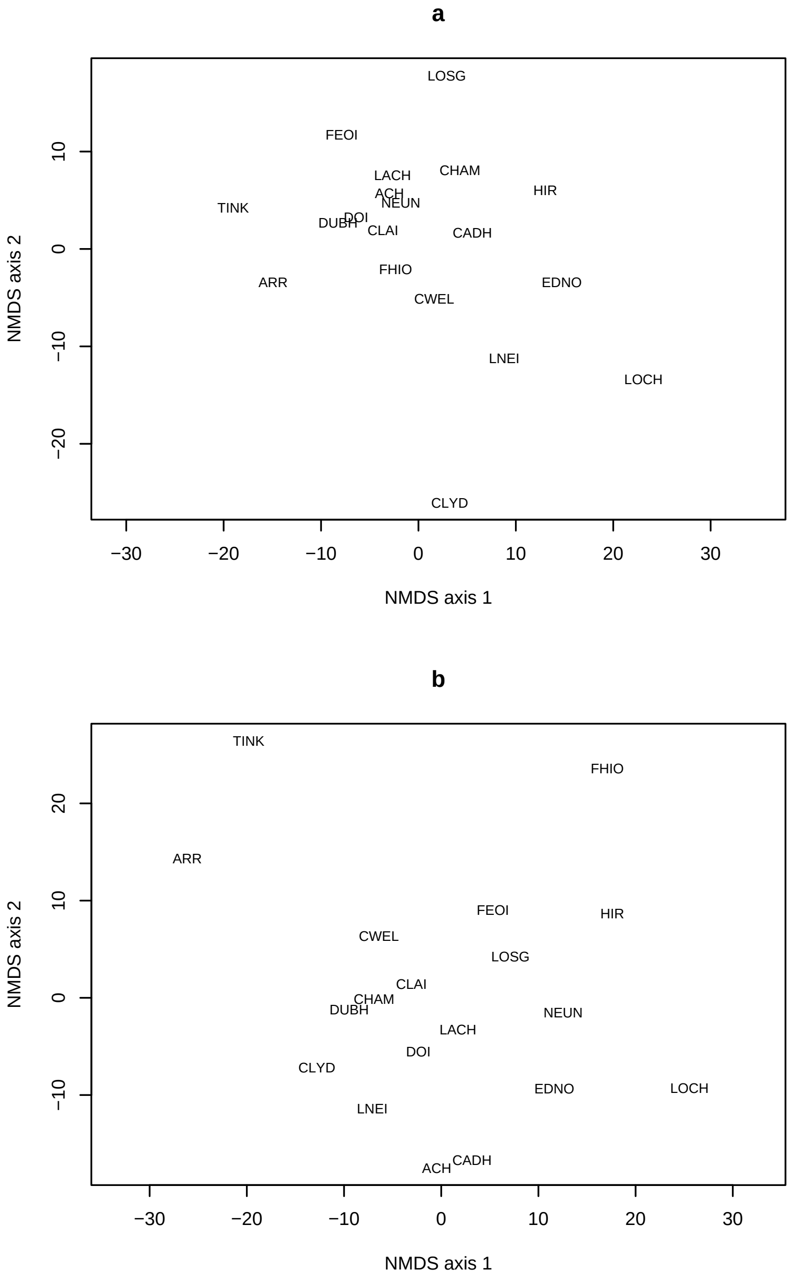

Figure 3: Procrustes superimposition plot showing the results of the Procrustes analysis of the aquatic macrophyte and macro-invertebrate data for the selected analogues sites. Points represent the NMDS sample positions using the aquatic macrophyte data and the ends of the arrows are the NMDS positions of the samples using the macro-invertebrate data.

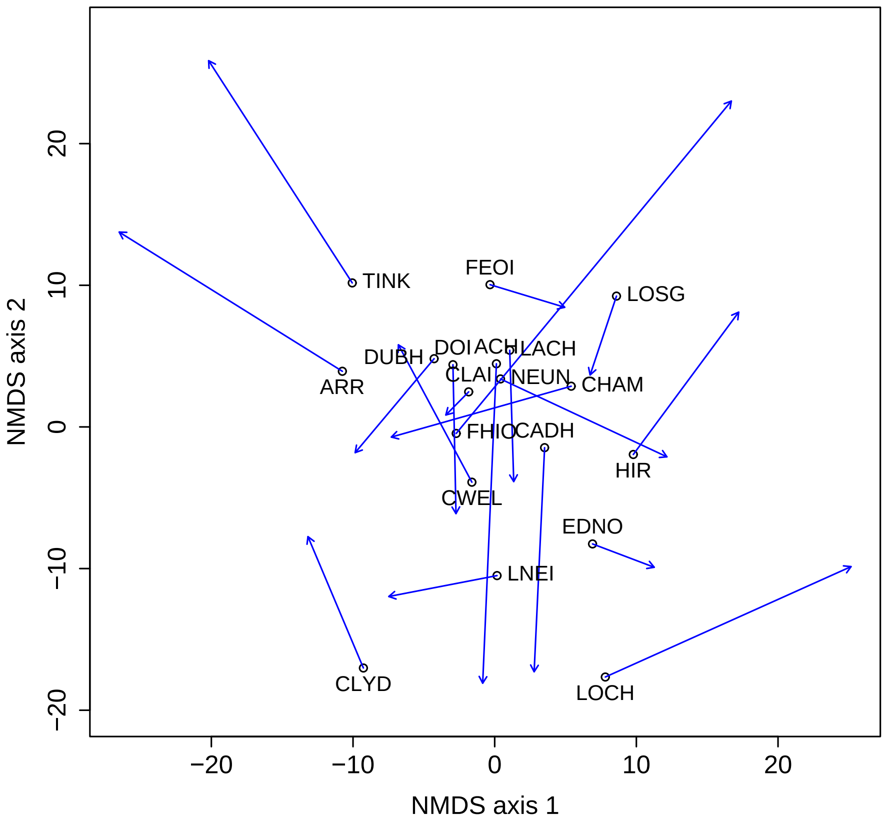

Table 1: Site codes, names and grid references of the 22 sites identified as close modern analogues for AWMN lake sites. LAI, GRUA and TEAN were not included in the contemporary surveys of aquatic macrophytes and macroinvertebrates for logistical reasons (see Methods)

Code	Name	Easting	Northing
ACH	Loch na h'Achlaise	231000	748000
ARR	Loch Coire nan Arr	180800	842200
CADH	Loch Dubh Cadhafuaraich	268200	918300
CHAM	Loch a Cham Alltain	228300	944600
CLAI	Loch Clair	199900	857400
CLYD	Llyn Clyd	263500	359700
CWEL	Llyn Cwellyn	256000	354900
DOI	Loch Doilet	180800	767800
DUBH	Lochan an Dubha	214700	905500
EDNO	Llyn Edno	266300	349700
FEOI	Lochan Feoir	222900	925200
FHIO	Lochan Fhionnlaidh	219100	910300
GRUA	Loch na Gruagaich	224300	915800
HIR	Llyn Hir	278900	267500
LACH	Lochan Lairig Cheile	255800	727800
LAI	Loch Laidon	238000	754200
LNEI	Loch Nan Eion	192500	850800
LOCH	Loch Toll an Lochain	207400	883200
LOSG	Loch Bad an Losguiun	215800	803800
NEUN	Loch na Eun	223200	929800
TEAN	Loch Teanga	81800	838300
TINK	Loch Tinker	244500	706800

Table 2: Number of close modern analogues selected from the modern training set for the AWMN lake sites. The numbers of analogues contain the sites GRUA, LAI and TEAN which were not included in the contemporary surveys of aquatic macrophytes and macroinvertebrates for logistical reasons (see Methods)

Code	AWMN lake	No. of close analogues
ARR	Loch Coire nan Arr	3
BLU	Blue Lough	1
BURNMT	Burnmoor Tarn	0
CHON	Loch Chon	0
LAG	Llyn Llagi	1
MYN	Llyn Cwm Mynach	10
NAGA	Lochnagar	2
RLGH	Round Loch of Glenhead	9
SCOATT	Scoat Tarn	1
TINK	Loch Tinker	7

Table 3: 1988–1998 mean (M) measured hydrochemistry and associated standard deviations (SD), and analogue inferred (I) hydrochemical characteristics of the AWMN lakes and their respective close modern analogues (LabAl—Labile Aluminium; EqAlk—equivalent alkalinity; Cond—conductivity; Ca—Calcium; TOC—Total Organic Carbon)

Code		pH	LabAl μg l^{-1}	EqAlk μeq l^{-1}	Cond μS cm^{-1}	Ca μeql^{-1}	TOC mg l^{-1}
	M	6.39	3.1	37.8	39.2	42.5	2.2
ARR	SD	0.3	1.23	20.3	13.21	11.32	1.2
	I	6.13	1.35	39.91	30.94	56.48	2.29
	M	4.69	286.9	-22.8	55.9	40.0	3.5
BLU	SD	0.11	80.72	5.98	9.28	13.55	1.16
	I	5.14	3.5	-2.0	52.0	49.0	5.35
	M	5.34	39.7	5.6	31.2	52.5	2.4
LAG	SD	0.34	35.11	10.6	9.52	11.71	1.07
	I	6.3	2.0	49.06	39.17	43.33	2.17
	M	5.37	65.2	4.6	46.0	70.0	2.6
MYN	SD	0.42	23.0	5.16	6.27	4.71	0.79
	I	5.79	3.89	20.5	43.45	60.94	3.85
	M	5.33	22.5	0.6	21.8	29.0	1.1
NAGA	SD	0.19	28.65	4.73	4.75	5.03	0.61
	I	6.07	3.55	24.42	31.96	38.66	0.77
	M	4.90	60.2	-12.2	36.7	33.0	3.0
RLGH	SD	0.12	23.0	5.16	6.27	4.71	0.79
	I	5.83	5.44	23.04	44.03	56.33	3.18
	M	4.99	108.9	-8.4	35.1	32.5	0.9
SCOATT	SD	0.09	67.57	3.77	6.27	5.85	0.59
	I	5.15	54.5	0.00	28.67	38.07	1.43
	M	6.13	3.3	37.6	31.4	85.0	4.7
TINK	SD	0.31	2.16	23.62	7.62	20.0	1.87
	I	5.45	3.58	5.93	38.31	41.75	3.64

Table 4: Presence-absence data for selected acid-sensitive aquatic macrophyte taxa for AWMN lake sites and their close modern analogues (+ signifies presence and − absence). The data for the AWMN sites is from the routine monitoring survey for the indicated year.

AWMN site	**Analogue / Year**	***M. alterniflorum***	***Nitella* sp.**	***C. hamulata***	***Chara* sp.**	***S. aquatica***	***E. fluitans***
Loch Coire nan Arr	1988	+	+	+	−	−	−
	1999	+	+	+	−	+	−
	ARR	+	+	+	−	+	−
	CWEL	+	+	+	−	+	−
	LNEI	−	−	+	−	+	−
Blue Lough	1989	−	−	−	−	−	−
	2001	−	−	−	−	−	−
	2003	−	−	−	−	−	−
	CADH	+	−	−	−	−	−
Llyn Llagi	1988	+	−	−	−	−	−
	2001	+	−	+	−	−	−
	2003	+	−	+	−	+	−
	ARR	+	+	+	−	+	−
Llyn Cwm Mynach	1988	+	+	−	−	−	−
	2001	+	−	−	−	−	−
	2003	+	−	−	−	−	−
	LOSG	+	−	−	+	+	−
	DUBH	+	+	−	−	−	+
	TINK	+	+	+	−	−	−
	FEOI	+	+	−	+	−	+
	NEUN	+	+	−	+	+	+
	ARR	+	+	+	−	+	−
	CLAI	+	+	+	−	+	+
	ACH	+	+	−	−	+	−
	LACH	+	+	−	−	+	−

AWMN site	**Analogue / Year**	***M. alterniflorum***	***Nitella* sp.**	***C. hamulata***	***Chara* sp.**	***S. aquatica***	***E. fluitans***
Lochnagar	1988	−	−	−	−	−	−
	2001	−	−	−	−	−	−
	2003	−	−	−	−	−	−
	LOCH	−	−	−	−	+	−
	CLYD	+	+	+	−	+	−
Round Loch of Glenhead	1988	−	−	−	−	−	−
	2001	−	−	−	−	−	−
	2003	+	−	−	−	−	−
	LNEI	−	−	+	−	+	−
	DUBH	+	+	−	−	−	+
	CLAI	+	+	+	−	+	+
	LACH	+	+	−	−	+	−
	DOI	+	−	+	−	−	+
	HIR	+	−	−	−	+	−
	CHAM	+	+	−	−	+	−
	ARR	+	+	+	−	+	−
Scoat Tarn	1988	−	−	−	−	−	−
	2001	−	−	−	−	−	−
	2003	−	−	−	−	−	−
	EDNO	−	−	−	−	+	−
Loch Tinker	1988	+	+	+	−	−	−
	2001	+	+	+	−	−	−
	2003	+	+	+	−	−	−
	TINK	+	+	+	−	−	−
	ACH	+	+	−	−	+	−
	LOSG	+	−	−	+	+	−
	FHIO	+	−	−	−	−	−
	NEUN	+	+	−	+	+	+

Table 5: Presence-absence data for selected acid-sensitive macro-invertebrate taxa for AWMN lake sites and their close modern analogues (+ signifies presence and − absence). The data for the AWMN sites is from the routine monitoring survey for the indicated year

AWMN site	**Analogue / Year**	***Baetis* sp.**	***L. hirtum***	***L. peregra***	***Pisidium* sp.**
Loch Coire nan Arr	1988-90	−	−	+	+
	2000-2002	−	−	−	+
	ARR	−	−	−	+
	CWEL	+	+	−	+
	LNEI	−	−	+	−
Blue Lough	1988-90	−	−	−	−
	2000-2002	−	−	−	−
	CADH	−	−	+	−
Llyn Llagi	1988-90	−	−	−	+
	2000-2002	−	−	−	+
	ARR	−	−	−	+
Llyn Cwm Mynach	1988-90	−	−	−	+
	2000-2002	−	−	−	+
	LOSG	−	−	+	+
	DUBH	+	−	+	+
	TINK	−	−	−	+
	FEOI	−	−	+	+
	NEUN	+	−	−	+
	ARR	−	−	−	+
	CLAI	+	−	+	+
	ACH	−	−	−	−
	LACH	+	−	+	+

AWMN site	**Analogue / Year**	***Baetis* sp.**	***L. hirtum***	***L. peregra***	***Pisidium* sp.**
Lochnagar	1988-90	−	−	−	−
	2000-2002	−	−	−	−
	LOCH	−	−	−	+
	CLYD	−	−	+	+
Round Loch of Glenhead	1988-90	−	−	−	−
	2000-2002	−	−	+	+
	LNEI	−	−	+	+
	DUBH	+	−	+	+
	CLAI	+	−	+	+
	LACH	+	−	+	+
	DOI	+	+	−	+
	HIR	−	−	−	+
	CHAM	−	−	+	+
	ARR	−	−	−	+
Scoat Tarn	1988-90	−	−	−	−
	2000-2002	−	−	−	−
	EDNO	−	−	−	−
Loch Tinker	1988-90	−	−	−	+
	2000-2002	−	−	−	+
	TINK	−	−	−	+
	ACH	−	−	−	−
	LOSG	−	−	+	+
	FHIO	−	−	−	−
	NEUN	+	−	−	+

Job 1.1.3: Examine the full range of biological remains in pre-acidification sediments of key sites

The aim of this Job was to determine whether the palaeolimnological record contained in lake sediments could be used to define biological reference conditions – the state of a lake prior to recent anthropogenic disturbance, in this case, the effects of acid deposition. This work stemmed from the study and application of the analogue matching approach to defining reference conditions in the previous CLAM contract (Curtis and Simpson 2001), where close analogues were identified for ten of the UK Acid Waters Monitoring Network (UKAWMN) lakes. Task 1.1 Jobs 1 and 2, above, have proceeded to analyse the selected modern analogues for a range of biological groups that do not leave reliable or complete sedimentary records. Biological surveys are time consuming to undertake, especially at remote sites. An alternative way that reference conditions might be defined is to utilise as much of the sedimentary record as is possible, and to enumerate sedimentary remains for as wide a set of biological groups as possible.

During April 2002, key UKAWMN and Galloway lakes were cored as part of the fieldwork campaign to survey the modern analogue sites in Jobs 1.1.1 and 1.1.2. These cores where then subjected to a thorough and rigorous laboratory analysis on separate fractions of the retrieved samples for a full range of biological proxies. Samples were analysed using a variety of techniques to extract so called macro-fossil material from sieved sediment samples. It was apparent that the cores, which were taken from the deepest area of the lake where accumulating sediments were known to be found, contained few if any additional remains over the standard diatom and cladoceran remains that had already been sampled as part of the previous CLAM contract and which were used to select the modern analogue sites.

To investigate whether the lack of suitable remains was related to the small sample sizes initially analysed, a number of the cores were re-examined by bulking a 5cm section of each core and homogenising the sediment sample before the laboratory sieving was repeated on these much larger samples. Each bulked sample was again analysed for biological remains using standard microscopy techniques. Again no identifiable biological remains could be retrieved from these sediment samples, except for cladoceran remains, which as mentioned above, had already been analysed using more traditional techniques as part of the CLAM project.

As a result of these findings it must be concluded that, with the exception of diatom and cladoceran remains, little useful and reliable information can be extracted from open water cores taken in the deepest area of a lake basin. This is most likely related to problems of transportation of macrofossil remains from the main areas of production in the littoral areas of lakes into the profundal zone where the most reliable sedimentary records are found.

A parallel study investigating the application of palaeolimnological techniques for use in defining reference conditions ina range of lake types produced similar results to these findings on the open water cores that were sampled (Bennion et al 2004a).

Marginal cores may provide a more informative sedimentary record of macrofossil remains as cores taken from these locations will be close to the sources of production of the macrofossil remains. But analysis of marginal cores is particularly difficult without good stratigraphic dating to constrain the interpretation, as currents and mixing of lake water, which act to concentrate deposited remains in the deeper sediments for lighter remains, can also lead to variable deposition of sediments in these marginal areas or the loss of sections of the stratigraphy through erosion. A further complication arises because the most reliable records of diatom and cladoceran remains are known to be from cores taken from the open water zone. To fully undertake a dual core study, one would require the two cores to be dated and their stratigraphic records correlated to determine if sediments from similar periods were being analysed for different proxies in the two cores. This kind of analysis is particularly difficult to undertake as it is difficult to know whether the location chosen for the marginal core will contain a complete and accurate stratigraphic record before the cores are taken, dated and analysed.

Conclusions

From the results of this job it is clear that using single, open water cores for macrofossil analysis of sediments will be unlikely to produce sufficient material for the definition of reference conditions to be made using palaeolimnological techniques.

The positive results of Job 1.1.2 based on the biological surveys of the modern analogue sites for the UK AWMN lakes would indicate that it would not be warranted to try to use the full palaeolimnolgical record to define reference conditions using the method used in this study. Alternative palaeolimnological techniques exist that have been shown to work well in defining reference conditions (Bennion et al 2004a, 2004b) and these methods should be used in preference to the type of work undertaken here.

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Task 1.2: Chemical-biological database and interactive web page

Task 1.2: Chemical-biological database and interactive web page

Job 1.2.1: Chemical-biological database

Throughout the life of the CLAM2 project data holdings collected under previous DEFRA (DoE, DETR) Freshwater Umbrella contracts and other publicly funded projects have been compiled into an Microsoft SQL Server 2000 database. Currently 17 hydrochemical are distinguished within the database and these can be viewed on-line and downloaded through the CLAM2 project website (http://ecrc.geog.ucl.ac.uk/clam2/):

- Cairngorm Loch Survey
- CLAG Inflow-Outflow Study
- CLAG Mapping Dataset
- CLAG Sea Salt Study
- CLAG Within-square Variability Study
- CLAM Water Chemistry Data Set
- ED-Duddon/Glaslyn Study
- Emerge Scottish Lake District
- Exceedance Study Sites
- FAB Mapping (Screened Data Set)
- FAB Mapping Sites (1471)
- Galloway Cluster
- Galloway Loch Survey
- Lake District Lake Survey
- Nitrogen Network
- Pennines Lake Survey
- Welsh Random Survey 1995

Each data set has associated meta data included with it, including a description of each data set, periodicity of sampling, when samples were taken etc.

Data sets from this project have been included where they where available and harmonised with the CLAM2 database schema, such as the screened FAB mapping data set which was produced from the original FAB Mapping data set during this contract.

The Chemical-Biological data base used in previous contracts has also been uploaded to the server and can be downloaded from the project web site. Table 1.2.1 shows some summary meta data for the individual data sets that comprise the Chemical-Biological data base.

The Data and Methods section of the report on Job 1.2.2 describes these data holdings in more detail, and illustrates how these data holdings are being utilised to produce models of species response curves to hydrochemical data such as ANC. These models are subsequently used in national mapping exercises to illustrate the effect on different biological groups of emission reductions policies for example.

Wider access to these data via the web site is one outstanding issue that has not been addressed. These data are currently held in a secure area of the web site requiring a user-name and password for access. All members of the consortium involved in the current project have been supplied with a user-name and password and can access these data. Users without a user-name and password can access limited meta data for the data holdings, but cannot view or download the data sets.

Table 1.2.1: Metadata for current data holdings

CLAM2 biological – chemical database: Current holdings

Dataset	***Source***	***Sampling date***	***Site type***	***N***	***mean pH***	***min pH***	***max pH***
Scot Base	Scottish Baseline Survey (Doughty 1989)	1986	Streams	144	6.70	4.42	8.49
UKAWMN	UKAWMN Survey Data Stream sites (Patrick et al. 1991)	1990-92	Streams	33	5.52	4.53	6.68
IF / OF	Inflow / outflow validation study (CLAG)	1996	Streams	31	5.97	3.70	7.05
Sea Salt	Sea salt study (CLAG)	1996	Streams	17	5.77	4.89	6.98
WAWS	Welsh Acid Waters Resurvey	1995	Lakes & Streams	118	6.21	4.0	8.29
RSPB	RSPB survey (Allott & Rose 1993)	1992-94	Lakes	88	6.54	5.02	8.46
CCW	CCW Macrophyte survey	1998	Lakes	17	5.88	4.73	6.71
UKAWMN2	UKAWMN Survey Data Lake sites (macrophyte data)	1998	Lakes	11	5.44	4.61	6.48
Total				**459**	**6.35**	**3.7**	**8.49**

Job 1.2.2: Determine response curves / logistic regression equations from existing biology/chemistry data for national applications.

Introduction

The main goal of emission reduction is promote the recovery of impacted ecosystems. For acidified surface waters, recovery is taken to mean the re-establishment of a healthy flora and fauna, or a return to the taxonomic structure and function of the pre-impacted system. To achieve this implies knowledge of (a) the biological status of pre-impacted waters, and (b) the chemical conditions necessary to promote a return to the pre-acidification biological targets. Furthermore, to assess the biological damage resulting from a particular level of critical load exceedance we also need (c) information on the relationship between the occurrence of a wide range of biological taxa and their key chemical determinants.

For lake sites palaeolimnological analyses can yield information on the past occurrence of some biological groups, but this technique is labour intensive and cannot be applied to large numbers of sites. For stream sites the taxonomic composition of analogue sites located in non-acidified regions can provide some clues to the pre-acidification biology of impacted sites, but chemical and physical differences between targets and analogues makes the selection of the latter difficult. An alternative approach to addressing (a) and (b) above is to model the relationship between biology and chemistry in order to (i) predict the likely probability of occurrence of key components of the ecosystem under pre-impacted conditions, using hindcasts of pre-acidification chemistry, and (ii) measure the biological deviation from target conditions (ie. damage) under different reduction scenarios (ie. (c) above).

Relationships between biology and chemistry could be generated by field or laboratory experiment, but in either case the generation of sufficient data to relate the large number of potential biological targets to the full range of water chemistry parameters would be a vast undertaking. An alternative method is to derive empirical statistical relationships between biological status and chemical conditions using field survey data collected from a range of sites spanning the appropriate chemical gradients (Ormerod 1994).

To achieve this in CLAM2 we have continued to develop a database of high quality chemical – biological data focused on diatoms and invertebrates and have used this to derive statistical models for predicting the occurrence of key taxa. Diatoms and invertebrates have been used because these groups of organisms are key structural components of freshwater ecosystems and are extremely sensitive to changes in acidity (Battarbee 1984; Lien *et al*. 1996; Ormerod & Edwards 1987). They are thus excellent "indicator" groups for assessing and modelling acidification status of freshwaters and for assessing biological damage as a result of critical load exceedance.

Data and methods

The CLAM chemical – biological database has been assembled by merging existing datasets with data collected during the previous CLAM contract. After screening and taxonomic harmonisation, six datasets with matching chemical, diatom and invertebrate data are available (Table 1.2.2).

Table 1.2.2: Data sources for the CLAM biological – chemical database

Dataset	Source	Sampling date	Site type	N	mean pH	Min pH	Max pH
Scot Base	Scottish Baseline Survey (Doughty 1989)	1986	Streams	144	6.70	4.42	8.49
UKAWMN	UKAWMN Survey Data Stream sites (Patrick *et al.* 1991)	1990-92	Streams	33	5.52	4.53	6.68
IF / OF	Inflow / outflow validation study (CLAG)	1996	Streams	31	5.97	3.70	7.05
Sea Salt	Sea salt study (CLAG)	1996	Streams	17	5.77	4.89	6.98
WAWS	Welsh Acid Waters Resurvey	1995	Streams	118	6.21	4.0	8.29
RSPB	RSPB survey (Allott & Rose 1993)	1992-94	Streams	88	6.54	5.02	8.46
Total				431	6.35	3.7	8.49

Chemical data have been further screened and alkalinity determinations revised, and where possible, adjusted to a Gran titration equivalent value using the method of Henriksen (1982). Following CLAM2 discussions on ANC calculations, exploratory community ordination of the diatom and invertebrate datasets has been carried out using canonical correspondence analysis, based on the revised chemistry and including ANC calculated as "alkalinity + DOC" ("ANC1": McCartney *et al.* 2003) and as "alkalinity + DOC – Al" ("ANC2": Neal *et al.* 1999). Results indicated that measures of acidity, DOC and Al were all significant in explaining community-wide distribution patterns but that there was little difference in explanatory power between models developed using ANC1 or ANC2. Predictive logistic regression models for presence / absence of diatom and invertebrate taxa fitted using the revised chemical data also indicated that there is little difference in ability of these parameters to predict individual taxon distributions. Given that reliable aluminium determinations were not available at all sites to calculate ANC2 it was decided to develop the taxon predictive models using ANC1, using only sites where mean chemistry based on at least four samples was available. This final screening produced datasets of 315 matched biology / chemistry samples for diatoms and 187 samples for invertebrates. Figure 1.2.1 shows the distribution of ANC1 values in the final datasets.

A hierarchy of response models were fitted to the biological / ANC1 data to model the presence / absence of individual organisms using logistic regression (GLR) and generalised additive modelling (GAM). The hierarchy consisted of 4 models: (1) a null model, (2) a linear GLR to model a monotonic sigmoid response, (3) a quadratic GLR to model a symmetric unimodal response, and a GAM to model a non-symmetric unimodal or more complex monotonic response (Huisman *et al.* 1993; Yee & Mitchell 1991). This approach is an extension of generalised linear modelling previously used (e.g. Juggins *et al.* 1995) and has the advantage of being able to fit non-linear and non-symmetric response curves. The significance of each model was assessed using a chi-square test of the drop in deviance, and the most parsimonious model selected for each taxon. Response models were fitted to all taxa present in 30 or more samples.

In addition to fitting models to individual taxon distributions we have also developed predictive models for the sum of acid sensitive diatom and invertebrate taxa. These two models provide a convenient aggregate that summarises the occurrence of a range of acid sensitive indicator taxa based on literature reports (e.g. Stevenson *et al*. 1990, Lein *et al*. 1996) and distributions in the CLAM datasets. Table 1.2.3 lists the individual taxa summed in these aggregate categories.

Table 1.2.3 List of acid sensitive indicator taxa used in the aggregate "sum of acid sensitive taxa"

Acid sensitive diatom indicator taxa	Acid sensitive invertebrate indicator taxa
Achnanthes minutissima	*Gammarus pulex*
Achnanthes austriaca var. helvetica	*Baetis sp.*
Achnanthes saxonica	*Rhithrogena spp.*
Cymbella sinuata	*Heptagenia spp.*
Cymbella minuta	*Ecdyonurus sp.*
Cymbella lunata	*Isoperla grammatical*
Diatoma hyemale	*Oreodytes*
Eunotia pectinalis var. minor fo. impressa	*Hydraena gracilis*
Fragilaria vaucheriae	*Limnius volckmari*
Frustulia rhomboides var. viridula	*Oulimnius spp.*
Gomphonema angustatum	*Hydropsyche spp.*
Gomphonema parvulum	*Drusus annulatus*
Hannaea arcus	*Clinocera spp.*
Meridion circulare	*Scirtidae*

Results

A total of 38 diatom taxa and 29 invertebrate taxa meet the criteria of at least 30 occurrences. Tables 1.2.4 and 1.2.5 list the modelled diatom and invertebrate taxa respectively, together with the response type, and the regression coefficients for linear and quadratic logistic regression models. Tables 1.2.6 and 1.2.7 list, for those taxa with a statistically significant response to ANC, the probability of occurrence at different ANC values. These tables allow the probability of occurrence to be calculated for taxa that show complex non-linear responses fitted using non-parametric GAM models.

Figures 1.2.2 and 1.2.3 show the raw presence / absence data and fitted response models for the 38 diatom and 29 invertebrate taxa, and the aggregate sum of acid sensitive taxa.

A total of 36 diatom taxa exhibited a significant response to ANC: 16 had a linear or monotonic response, 5 a Gaussian symmetric unimodal response, and 15 had a complex linear or non-symmetric unimodal response. Only two taxa showed no significant response to ANC. Similarly, two invertebrate taxa showed a linear or monotonic response, 5 showed a Gaussian symmetric unimodal response, and 15 had a complex linear or non-symmetric unimodal response. Seven of the 29 invertebrate taxa modelled showed no significant response to ANC.

Discussion and conclusions

The main aim of the species - chemistry modelling is to develop models that allow us to predict the likely biological status of pristine, unimpacted waters, and to measure the amount of change or damage, in biological terms, that has occurred since the onset of acidification, and that will remain under different emission reduction scenarios. The inputs to such predictions are the chemical predictions from steady-state or dynamical hydro-chemical models that attempt to hindcast or forecast site chemistry under different boundary conditions. There is therefore a pragmatic requirement that the biological model be derived for the same chemical parameters that are output from the hydro-chemical models.

In many examples pH is often used as a simple measure of acidity because it can best account for the variation observed in biological datasets. However, both the steady state and dynamic models are formulated to predict ANC. ANC and pH are strongly correlated in the CLAM2 datasets, and although the exploratory ordination analysis demonstrated that both variables are uniquely significant in explaining variation in both diatom and invertebrate datasets, the two variables are confounded: it is thus difficult to separate their causal effects in these datasets. Given the strong correlation between ANC and pH, the evidence that ANC is significantly related to biological distributions after the effects of pH have been accounted for, and the need to link biological and hydrochemical models, the predictive models developed here have used ANC, rather than pH, as an explanatory variable.

The CLAM2 biology / chemistry database has been screened to derive a subset of sites with high-quality mean water chemistry data. This has been used to fit a hierarchical series of regression models to describe individual species response to ANC. These models, illustrated in Figures 1.2.2 and 1.2.3, can now be used to provide predictions of the probability of occurrence of key diatom and invertebrate taxa under different ANC chemistry. As such they provide a means of assessing likely biological response to past and future changes in ANC under different deposition reduction scenarios.

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Table 1.2.4 Summary of diatom taxa with significant response to ANC, showing response type and logistic regression coefficients for linear and unimodal responses.

Code	Name	Max percentage	Number of occurrences	Response type	b0	b1	b2
AC001A	Achnanthes lanceolata	36.5	34	Linear	-2.666294444	0.002184442	
AC013A	Achnanthes minutissima var. minutissima	95.7	227	GAM			
AC014B	Achnanthes austriaca var. minor	44.0	43	Linear	-1.641172268	-0.005809634	
AC014C	Achnanthes austriaca var. helvetica	52.3	110	Linear	-0.772365465	-0.002765456	
AC022A	Achnanthes marginulata	44.5	40	GAM			
AC028A	Achnanthes saxonica	84.7	91	Gaussian	-2.596890922	0.019553927	-4.23E-05
BR001A	Brachysira vitrea	59.6	139	GAM			
BR006A	Brachysira brebissonii fo. brebissonii	35.4	79	GAM			
CM031A	Cymbella minuta var. minuta	20.8	49	GAM			
CM048A	Cymbella lunata	8.6	59	Gaussian	-2.059923345	0.012966037	-3.44E-05
DT002A	Diatoma hyemale var. hyemale	67.1	55	GAM			
EU002A	Eunotia pectinalis var. pectinalis	9.1	55	Linear	-1.213807425	-0.003591749	
EU002B	Eunotia pectinalis var. minor	12.3	90	Linear	-0.627170406	-0.002726048	
EU002E	Eunotia pectinalis var. minor fo. impressa	11.2	62	GAM			
EU004A	Eunotia tenella	3.4	42	Gaussian	-2.07364093	0.006899404	-2.39E-05
EU009A	Eunotia exigua var. exigua	96.6	236	Linear	1.54056292	-0.007169641	
EU011A	Eunotia rhomboidea	50.0	148	Linear	0.389012571	-0.009277072	
EU040A	Eunotia paludosa	2.3	33	Linear	-1.648119951	-0.006277441	
EU047A	Eunotia incisa	35.3	149	Linear	0.514634509	-0.007425628	
EU048A	Eunotia naegelii	82.3	87	Linear	-0.705098211	-0.010116295	
EU049A	Eunotia curvata var. curvata	28.1	108	Linear	-0.264712688	-0.003804034	
EU051B	Eunotia vanheurckii var. intermedia	95.9	134	GAM			
EU056A	Eunotia minutissima	8.9	82	Linear	-0.676277288	-0.003785489	
FR005D	Fragilaria virescens var. exigua	26.1	41	Linear	-1.62429526	-0.002795712	
FR007A	Fragilaria vaucheriae var. vaucheriae	29.3	113	GAM			
FU002B	Frustulia rhomboides var. saxonica	50.0	125	Linear	-0.351244381	-0.006022239	
FU002F	Frustulia rhomboides var. viridula	14.1	68	GAM			
GO004A	Gomphonema gracile	9.0	42	Gaussian	-2.506518884	0.011269559	-2.25E-05
HN001A	Hannaea arcus var. arcus	19.2	37	GAM			
MR001A	Meridion circulare var. circulare	10.5	36	GAM			
NI005A	Nitzschia perminuta	5.2	53	NS			
PE002A	Peronia fibula	84.0	105	GAM			
PI022B	Pinnularia subcapitata var. hilseana	31.3	91	Linear	-0.500972071	-0.004356922	
PI023A	Pinnularia irrorata	84.9	73	Linear	-1.511048851	-0.003986283	
SU004A	Surirella biseriata var. biseriata	28.8	38	GAM			
SY003A	Synedra acus var. acus	12.3	35	NS			
SY010A	Synedra minuscula	48.3	138	GAM			
TA001A	Tabellaria flocculosa var. flocculosa	85.3	214	Gaussian	0.074536539	0.00766921	-3.33E-05
Sum Acid Sensitive		98.1	285	GAM			

Table 1.2.5 Summary of invertebrate taxa with significant response to ANC, showing response type and logistic regression coefficients for linear and unimodal responses.

Code	Name	Max percentage	Number of occurrences	Response type	b0	b1	b2
03120401	Phagocata vitta	6.8	40	GAM			
16000000	Oligochaeta	72.7	139	NS			
30020100	Baetis sp.	58.7	79	GAM			
30030100	Rhithrogena spp.	66.7	44	GAM			
30030200	Heptagenia	20.7	40	GAM			
31010302	Brachyptera risi	65.7	68	Gaussian	-1.337628832	0.005755697	-5.97E-06
31020103	Protonemura meyeri	37.9	90	Linear	0.114870079	-0.003508166	
31020202	Amphinemura sulcicollis	72.7	149	GAM			
31020400	Nemoura sp.	36.0	66	NS			
31030102	Leuctra inermis	69.5	135	Gaussian	0.273640107	0.006149928	-4.19E-06
31030103	Leuctra hippopus	72.5	112	Linear	0.301331264	-0.003266904	
31030104	Leuctra nigra	65.3	71	NS			
31050401	Isoperla grammatica	51.9	138	GAM			
31070102	Chloroperla tripunctata	19.0	67	Gaussian	-1.166993832	0.008584156	-9.66E-06
35050207	Hydraena gracilis	7.3	32	GAM			
35110101	Elmis aenea	35.5	78	Gaussian	-1.201077866	0.008720879	-6.90E-06
35110301	Limnius volckmari	53.2	77	GAM			
35110600	Oulimnus sp.	9.5	43	GAM			
38010100	Rhyacophila sp.	9.1	107	NS			
38030200	Plectrocnemia sp.	39.4	117	GAM			
38030301	Polycentropus flavomaculatus	34.9	33	NS			
38050100	Hydropsyche spp.	20.2	70	GAM			
38081100	Potamophylax sp.	20.2	61	NS			
40010000	Tipulidae	43.2	61	GAM			
40012100	Limonia sp	9.9	67	Gaussian	-1.310922699	0.007936443	-3.67E-06
40090000	Chironomidae	85.5	164	GAM			
40150000	Simuliidae	97.4	139	NS			
40171300	Clinocera spp	9.1	48	GAM			
SP016	Chloroperla torrentium	29.7	83	GAM			
Sum Acid Sensitive		100.0	157	Linear	-0.179050478	0.033618238	

Table 1.2.6 Modelled probability of occurrence of diatom taxa at different ANC values.

Taxon	ANC (ug/l)																											
Code	-200	-180	-160	-140	-120	-100	-80	-60	-40	-20	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340
AC001A	0.04	0.04	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.08	0.08	0.08	0.09	0.09	0.09	0.10	0.10	0.11	0.11	0.11	0.12	0.12	0.13
AC013A	0.00	0.01	0.01	0.02	0.02	0.04	0.06	0.08	0.12	0.18	0.26	0.36	0.47	0.58	0.68	0.76	0.81	0.85	0.88	0.90	0.91	0.92	0.92	0.93	0.93	0.94	0.94	0.94
AC014B	0.38	0.36	0.33	0.30	0.28	0.26	0.24	0.22	0.20	0.18	0.16	0.15	0.13	0.12	0.11	0.10	0.09	0.08	0.07	0.06	0.06	0.05	0.05	0.04	0.04	0.03	0.03	0.03
AC014C	0.45	0.43	0.42	0.40	0.39	0.38	0.37	0.35	0.34	0.33	0.32	0.30	0.29	0.28	0.27	0.26	0.25	0.24	0.23	0.22	0.21	0.20	0.19	0.18	0.18	0.17	0.16	0.15
AC022A	0.15	0.15	0.16	0.16	0.17	0.17	0.17	0.17	0.17	0.16	0.15	0.13	0.11	0.09	0.07	0.05	0.04	0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.06	0.06
AC028A	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.05	0.07	0.10	0.13	0.17	0.21	0.26	0.30	0.33	0.37	0.39	0.41	0.42	0.42	0.41	0.39	0.37	0.34	0.30
BR001A	0.09	0.10	0.12	0.14	0.16	0.19	0.21	0.24	0.28	0.31	0.34	0.38	0.41	0.43	0.44	0.43	0.42	0.40	0.38	0.35	0.33	0.30	0.28	0.27	0.25	0.24	0.23	0.22
BR006A	0.63	0.63	0.62	0.61	0.61	0.59	0.58	0.55	0.53	0.49	0.44	0.39	0.33	0.27	0.22	0.17	0.14	0.12	0.10	0.09	0.09	0.09	0.09	0.09	0.10	0.10	0.11	0.12
CM031A	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.10	0.14	0.18	0.22	0.27	0.31	0.36	0.40	0.44	0.47	0.50	0.53	0.55	0.57
CM048A	0.00	0.00	0.01	0.01	0.02	0.02	0.03	0.05	0.07	0.09	0.11	0.14	0.17	0.20	0.22	0.25	0.27	0.29	0.30	0.30	0.30	0.29	0.28	0.27	0.24	0.22	0.19	0.16
DT002A	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.10	0.12	0.15	0.18	0.20	0.22	0.24	0.25	0.25	0.25	0.25	0.25	0.24	0.23	0.23	0.23
EU002A	0.38	0.36	0.35	0.33	0.31	0.30	0.28	0.27	0.26	0.24	0.23	0.22	0.20	0.19	0.18	0.17	0.16	0.15	0.14	0.13	0.13	0.12	0.11	0.10	0.10	0.09	0.09	0.08
EU002B	0.48	0.47	0.45	0.44	0.43	0.41	0.40	0.39	0.37	0.36	0.35	0.34	0.32	0.31	0.30	0.29	0.28	0.27	0.26	0.25	0.24	0.23	0.22	0.21	0.20	0.19	0.18	0.17
EU002E	0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.05	0.06	0.08	0.10	0.13	0.16	0.20	0.24	0.27	0.30	0.31	0.32	0.32	0.31	0.30	0.28	0.27	0.25	0.24	0.22	0.21
EU004A	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.10	0.11	0.13	0.14	0.15	0.16	0.16	0.17	0.17	0.17	0.17	0.16	0.15	0.14	0.13	0.12	0.10	0.09	0.08
EU009A	0.95	0.94	0.94	0.93	0.92	0.91	0.89	0.88	0.86	0.84	0.82	0.80	0.78	0.75	0.72	0.69	0.66	0.63	0.60	0.56	0.53	0.49	0.46	0.42	0.39	0.35	0.32	0.29
EU011A	0.90	0.89	0.87	0.84	0.82	0.79	0.76	0.72	0.68	0.64	0.60	0.55	0.50	0.46	0.41	0.37	0.33	0.29	0.25	0.22	0.19	0.16	0.14	0.12	0.10	0.08	0.07	0.06
EU040A	0.40	0.37	0.34	0.32	0.29	0.26	0.24	0.22	0.20	0.18	0.16	0.15	0.13	0.12	0.10	0.09	0.08	0.07	0.07	0.06	0.05	0.05	0.04	0.04	0.03	0.03	0.03	0.02
EU047A	0.88	0.86	0.85	0.83	0.80	0.78	0.75	0.72	0.69	0.66	0.63	0.59	0.55	0.52	0.48	0.44	0.41	0.37	0.34	0.31	0.27	0.25	0.22	0.20	0.17	0.15	0.13	0.12
EU048A	0.79	0.75	0.71	0.67	0.62	0.58	0.53	0.48	0.43	0.38	0.33	0.29	0.25	0.21	0.18	0.15	0.13	0.11	0.09	0.07	0.06	0.05	0.04	0.03	0.03	0.02	0.02	0.02
EU049A	0.62	0.60	0.59	0.57	0.55	0.53	0.51	0.49	0.47	0.45	0.43	0.42	0.40	0.38	0.36	0.34	0.33	0.31	0.29	0.28	0.26	0.25	0.24	0.22	0.21	0.20	0.19	0.17
EU051B	0.30	0.32	0.34	0.36	0.37	0.39	0.41	0.42	0.43	0.43	0.43	0.42	0.40	0.37	0.34	0.30	0.26	0.22	0.19	0.17	0.16	0.15	0.14	0.14	0.13	0.13	0.12	0.12
EU056A	0.52	0.50	0.48	0.46	0.44	0.43	0.41	0.39	0.37	0.35	0.34	0.32	0.30	0.29	0.27	0.26	0.24	0.23	0.22	0.20	0.19	0.18	0.17	0.16	0.15	0.14	0.13	0.12
FR005D	0.26	0.25	0.24	0.23	0.22	0.21	0.20	0.19	0.18	0.17	0.16	0.16	0.15	0.14	0.14	0.13	0.12	0.12	0.11	0.11	0.10	0.10	0.09	0.09	0.08	0.08	0.07	0.07
FR007A	0.01	0.01	0.01	0.02	0.02	0.03	0.05	0.06	0.08	0.11	0.15	0.20	0.25	0.31	0.37	0.42	0.47	0.51	0.54	0.58	0.60	0.63	0.65	0.67	0.69	0.71	0.72	0.74
FU002B	0.70	0.68	0.65	0.62	0.59	0.56	0.53	0.50	0.47	0.44	0.41	0.38	0.36	0.33	0.30	0.28	0.25	0.23	0.21	0.19	0.17	0.16	0.14	0.13	0.12	0.10	0.09	0.08
FU002F	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.07	0.09	0.11	0.14	0.17	0.20	0.23	0.26	0.28	0.30	0.31	0.31	0.31	0.30	0.29	0.28	0.26	0.24	0.22	0.20	0.19
GO004A	0.00	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.08	0.09	0.11	0.13	0.15	0.17	0.19	0.20	0.22	0.23	0.24	0.25	0.25	0.25	0.25	0.24	0.23	0.22
HN001A	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.04	0.06	0.08	0.10	0.13	0.16	0.18	0.20	0.21	0.22	0.22	0.22	0.23	0.24	0.25	0.26	0.29
MR001A	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.08	0.10	0.12	0.15	0.17	0.20	0.23	0.25	0.26	0.28	0.29	0.29	0.30	0.30	0.30
PE002A	0.44	0.45	0.45	0.46	0.46	0.46	0.46	0.45	0.44	0.42	0.40	0.37	0.33	0.28	0.23	0.19	0.16	0.14	0.13	0.13	0.12	0.12	0.13	0.13	0.13	0.14	0.14	0.13
PI022B	0.59	0.57	0.55	0.53	0.51	0.48	0.46	0.44	0.42	0.40	0.38	0.36	0.34	0.32	0.30	0.28	0.26	0.25	0.23	0.22	0.20	0.19	0.18	0.16	0.15	0.14	0.13	0.12
PI023A	0.33	0.31	0.29	0.28	0.26	0.25	0.23	0.22	0.21	0.19	0.18	0.17	0.16	0.15	0.14	0.13	0.12	0.11	0.10	0.10	0.09	0.08	0.08	0.07	0.07	0.06	0.06	0.05
SU004A	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.05	0.07	0.10	0.13	0.16	0.19	0.20	0.21	0.20	0.19	0.17	0.15	0.14	0.12	0.11	0.10	0.10	0.09
SY010A	0.00	0.00	0.00	0.01	0.01	0.02	0.02	0.04	0.05	0.08	0.12	0.17	0.23	0.31	0.39	0.47	0.54	0.59	0.64	0.67	0.69	0.71	0.72	0.72	0.72	0.71	0.70	0.69
TA001A	0.06	0.08	0.12	0.16	0.21	0.26	0.32	0.38	0.43	0.48	0.52	0.55	0.58	0.60	0.62	0.62	0.63	0.62	0.61	0.59	0.57	0.54	0.50	0.45	0.40	0.35	0.29	0.24
Sum Acid Sensitive	0.00	0.01	0.01	0.02	0.04	0.06	0.11	0.17	0.27	0.39	0.54	0.69	0.81	0.89	0.93	0.96	0.97	0.98	0.98	0.98	0.99	0.99	0.99	0.98	0.98	0.98	0.98	0.98

Table 1.2.7 Modelled probability of occurrence of invertebrate taxa at different ANC values.

Taxon	ANC (ug/l)																												
Code	-200	-180	-160	-140	-120	-100	-80	-60	-40	-20	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380
3120401	0.02	0.03	0.03	0.04	0.05	0.06	0.07	0.09	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24	0.25	0.27	0.28	0.30	0.31	0.31	0.31	0.31	0.30	0.29	0.28	0.27	0.26	0.26
30020100	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.04	0.06	0.09	0.13	0.18	0.25	0.32	0.39	0.47	0.53	0.59	0.63	0.66	0.67	0.69	0.69	0.70	0.70	0.71	0.71	0.72	0.73	0.74
30030100	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.04	0.06	0.08	0.12	0.16	0.20	0.25	0.30	0.34	0.37	0.40	0.42	0.43	0.45	0.46	0.47	0.48	0.49	0.51	0.54	0.56
30030200	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.04	0.06	0.09	0.14	0.20	0.26	0.31	0.36	0.39	0.40	0.42	0.43	0.45	0.47	0.51	0.55	0.60	0.65	0.71	0.76
31010302	0.06	0.07	0.08	0.09	0.11	0.12	0.14	0.15	0.17	0.19	0.21	0.23	0.25	0.27	0.29	0.31	0.32	0.34	0.36	0.38	0.40	0.41	0.43	0.44	0.45	0.46	0.47	0.48	0.49	0.50
31020103	0.69	0.68	0.66	0.65	0.63	0.61	0.60	0.58	0.56	0.55	0.53	0.51	0.49	0.48	0.46	0.44	0.42	0.41	0.39	0.37	0.36	0.34	0.33	0.31	0.30	0.28	0.27	0.25	0.24	0.23
31020202	0.49	0.50	0.52	0.53	0.54	0.56	0.58	0.60	0.62	0.64	0.67	0.69	0.72	0.74	0.76	0.77	0.79	0.80	0.81	0.82	0.82	0.83	0.84	0.85	0.85	0.86	0.87	0.87	0.88	0.88
31030102	0.25	0.28	0.31	0.34	0.37	0.41	0.44	0.47	0.51	0.54	0.57	0.60	0.63	0.65	0.68	0.70	0.72	0.74	0.76	0.78	0.79	0.81	0.82	0.83	0.84	0.85	0.86	0.87	0.87	0.88
31030103	0.72	0.71	0.70	0.68	0.67	0.65	0.64	0.62	0.61	0.59	0.57	0.56	0.54	0.53	0.51	0.49	0.48	0.46	0.44	0.43	0.41	0.40	0.38	0.37	0.35	0.34	0.32	0.31	0.29	0.28
31050401	0.01	0.01	0.02	0.03	0.04	0.06	0.10	0.15	0.21	0.30	0.41	0.52	0.63	0.71	0.78	0.83	0.87	0.89	0.91	0.92	0.93	0.93	0.93	0.93	0.94	0.94	0.94	0.94	0.94	0.94
31070102	0.04	0.05	0.06	0.07	0.09	0.11	0.13	0.15	0.18	0.21	0.24	0.27	0.30	0.33	0.37	0.40	0.43	0.46	0.49	0.52	0.54	0.56	0.58	0.60	0.62	0.63	0.64	0.65	0.66	0.67
35050207	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.05	0.07	0.10	0.14	0.19	0.25	0.30	0.35	0.40	0.44	0.46	0.48	0.50	0.50	0.51	0.51	0.50	0.50	0.49
35110101	0.04	0.05	0.06	0.07	0.09	0.11	0.13	0.15	0.17	0.20	0.23	0.26	0.30	0.33	0.37	0.40	0.44	0.47	0.50	0.54	0.57	0.59	0.62	0.65	0.67	0.69	0.71	0.72	0.74	0.75
35110301	0.01	0.01	0.02	0.02	0.03	0.04	0.05	0.07	0.09	0.12	0.16	0.20	0.24	0.29	0.35	0.39	0.44	0.47	0.49	0.50	0.50	0.50	0.49	0.49	0.48	0.48	0.48	0.48	0.49	0.51
35110600	0.01	0.02	0.02	0.03	0.04	0.05	0.06	0.07	0.09	0.11	0.14	0.17	0.20	0.24	0.27	0.30	0.32	0.34	0.35	0.35	0.34	0.33	0.31	0.30	0.28	0.26	0.25	0.23	0.22	0.21
38030200	0.92	0.90	0.89	0.87	0.85	0.83	0.80	0.78	0.75	0.71	0.68	0.64	0.61	0.57	0.53	0.50	0.47	0.45	0.42	0.41	0.40	0.38	0.38	0.37	0.36	0.36	0.35	0.34	0.34	0.33
38050100	0.01	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.10	0.13	0.17	0.22	0.27	0.33	0.39	0.45	0.50	0.54	0.58	0.60	0.62	0.64	0.65	0.66	0.67	0.67	0.68	0.69	0.70	0.71
40010000	0.92	0.90	0.87	0.83	0.79	0.74	0.69	0.63	0.57	0.51	0.44	0.38	0.33	0.29	0.25	0.22	0.20	0.18	0.17	0.17	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.15
40012100	0.05	0.05	0.06	0.08	0.09	0.11	0.12	0.14	0.16	0.19	0.21	0.24	0.27	0.30	0.33	0.36	0.40	0.43	0.47	0.50	0.53	0.56	0.59	0.62	0.65	0.68	0.70	0.72	0.74	0.76
40090000	0.48	0.49	0.51	0.53	0.55	0.57	0.60	0.63	0.66	0.69	0.72	0.76	0.79	0.82	0.84	0.87	0.88	0.89	0.90	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.90	0.89	0.89
40171300	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.04	0.05	0.07	0.11	0.15	0.20	0.25	0.30	0.34	0.37	0.40	0.42	0.44	0.44	0.43	0.42	0.41	0.41	0.41	0.41	0.43	0.46	0.49
SP016	0.01	0.02	0.02	0.03	0.04	0.06	0.08	0.11	0.14	0.19	0.24	0.30	0.37	0.44	0.50	0.55	0.59	0.62	0.65	0.66	0.68	0.68	0.69	0.69	0.69	0.70	0.70	0.70	0.71	0.71
Sum Acid Sensitive	0.00	0.00	0.00	0.01	0.01	0.03	0.05	0.10	0.18	0.30	0.46	0.62	0.76	0.86	0.92	0.96	0.98	0.99	0.99	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Figure 1.2.1 Distribution of ANC in the diatom and invertebrate datasets.

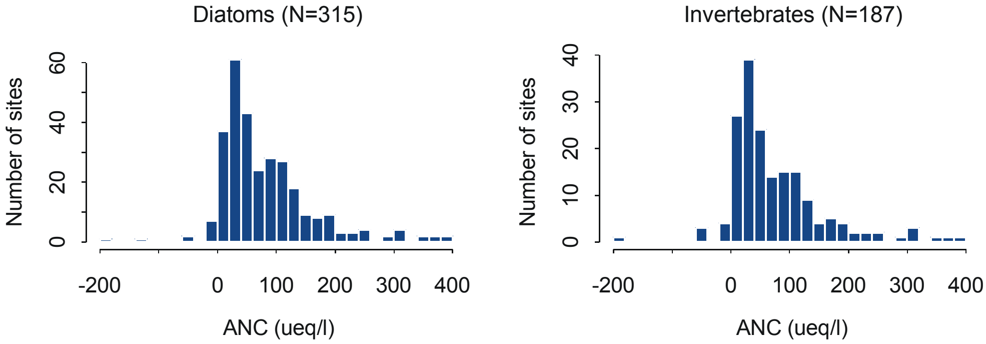


Figure 1.2.2 Diatom presence / absence data and fitted ANC response models (see Table 1.2.4 for taxon names)

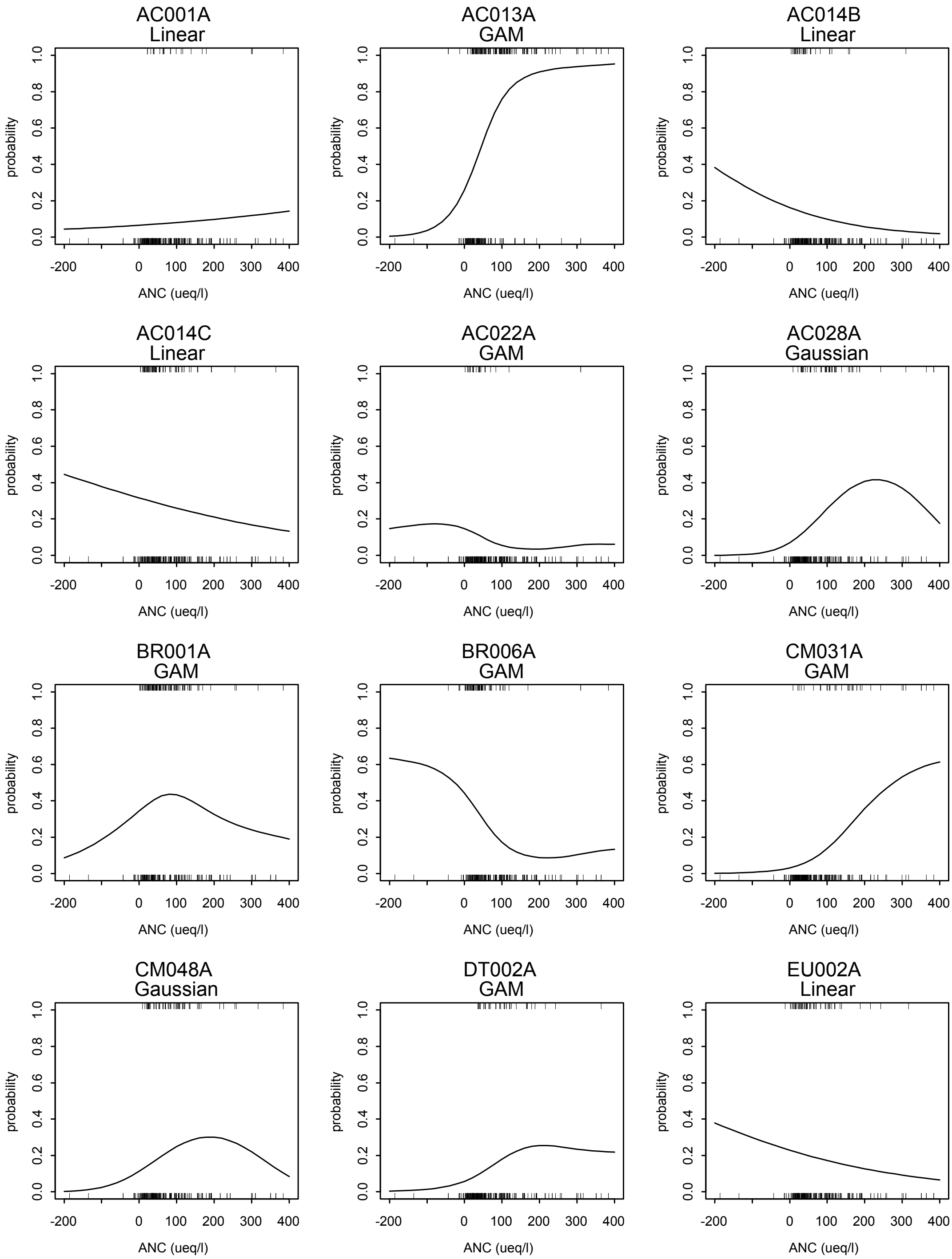


Figure 1.2.2 Continued

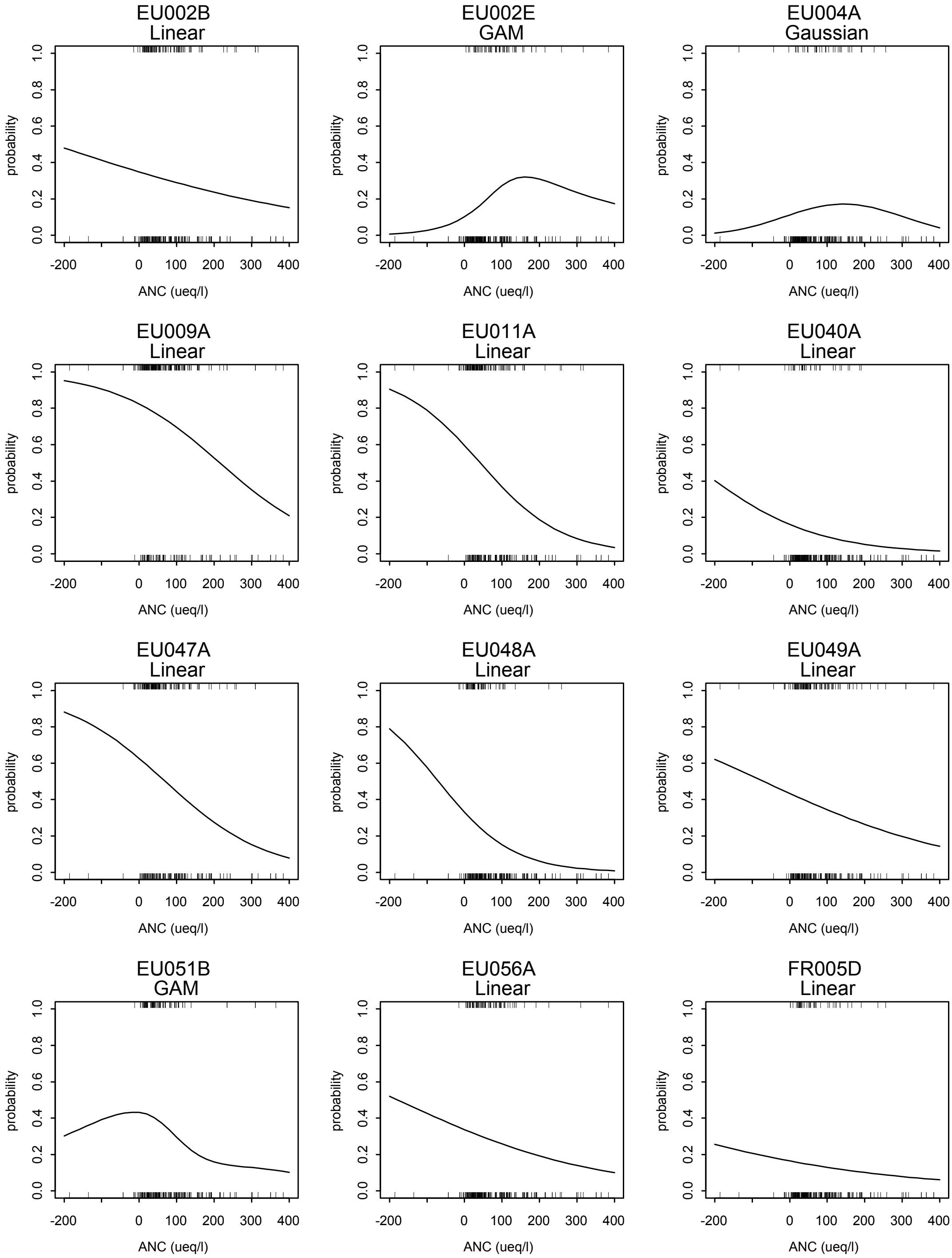


Figure 1.2.2 Continued

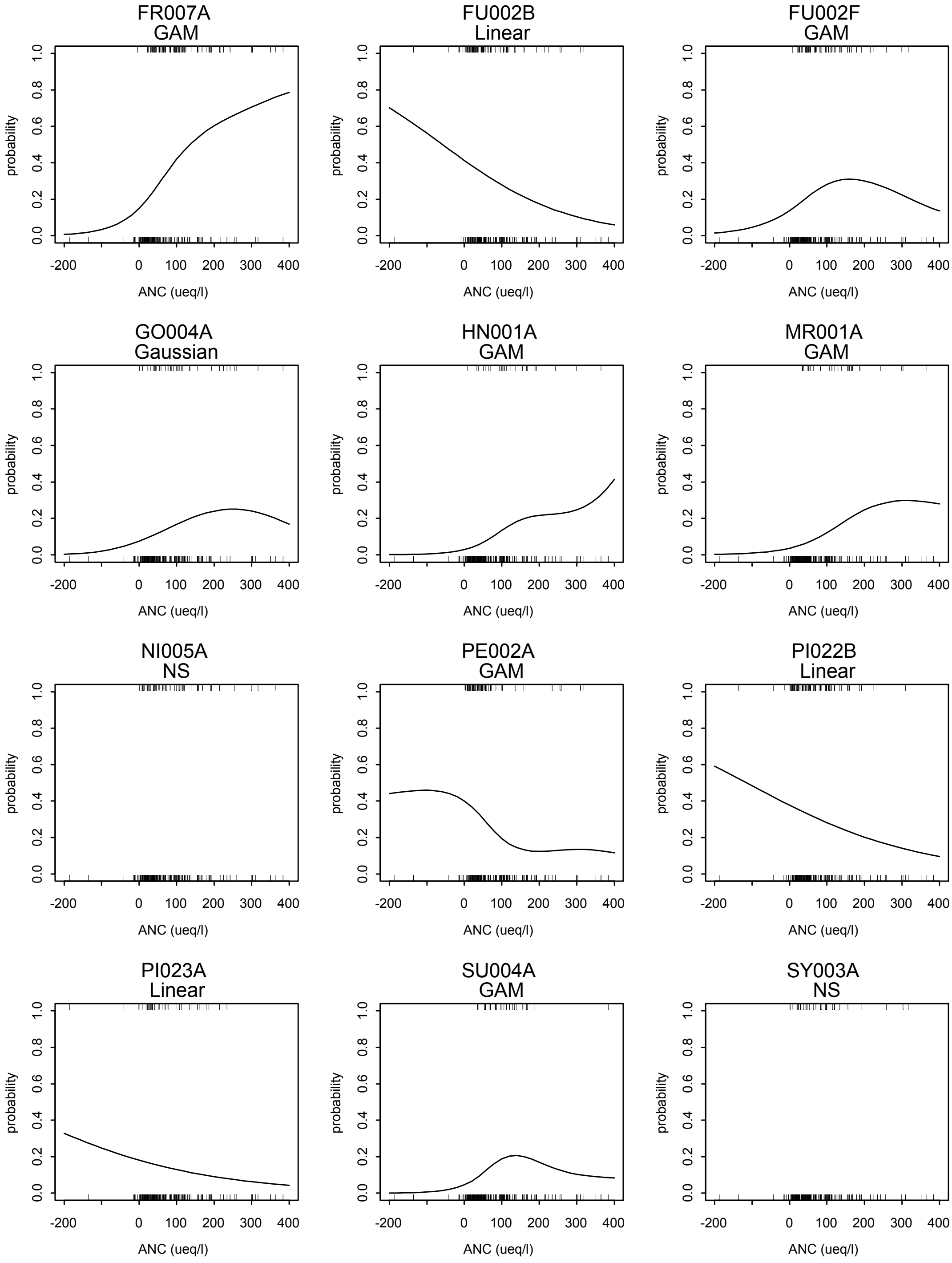


Figure 1.2.2 Continued

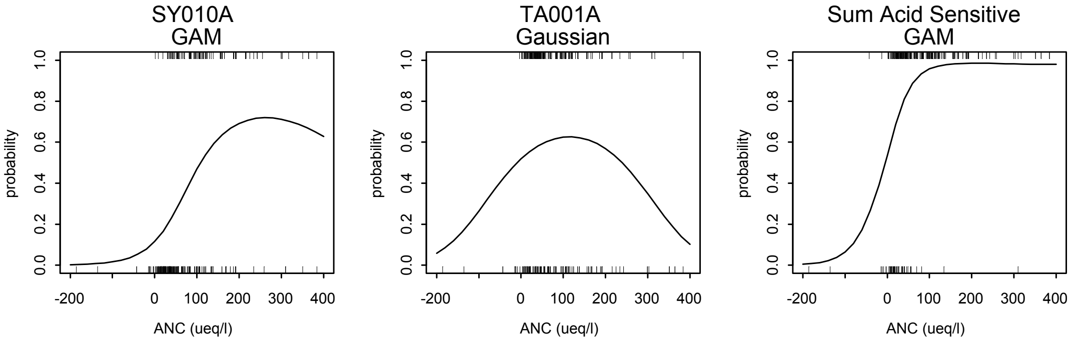


Figure 1.2.3 Invertebrate presence / absence data and fitted ANC response models (see Table 1.2.5 for taxon names)

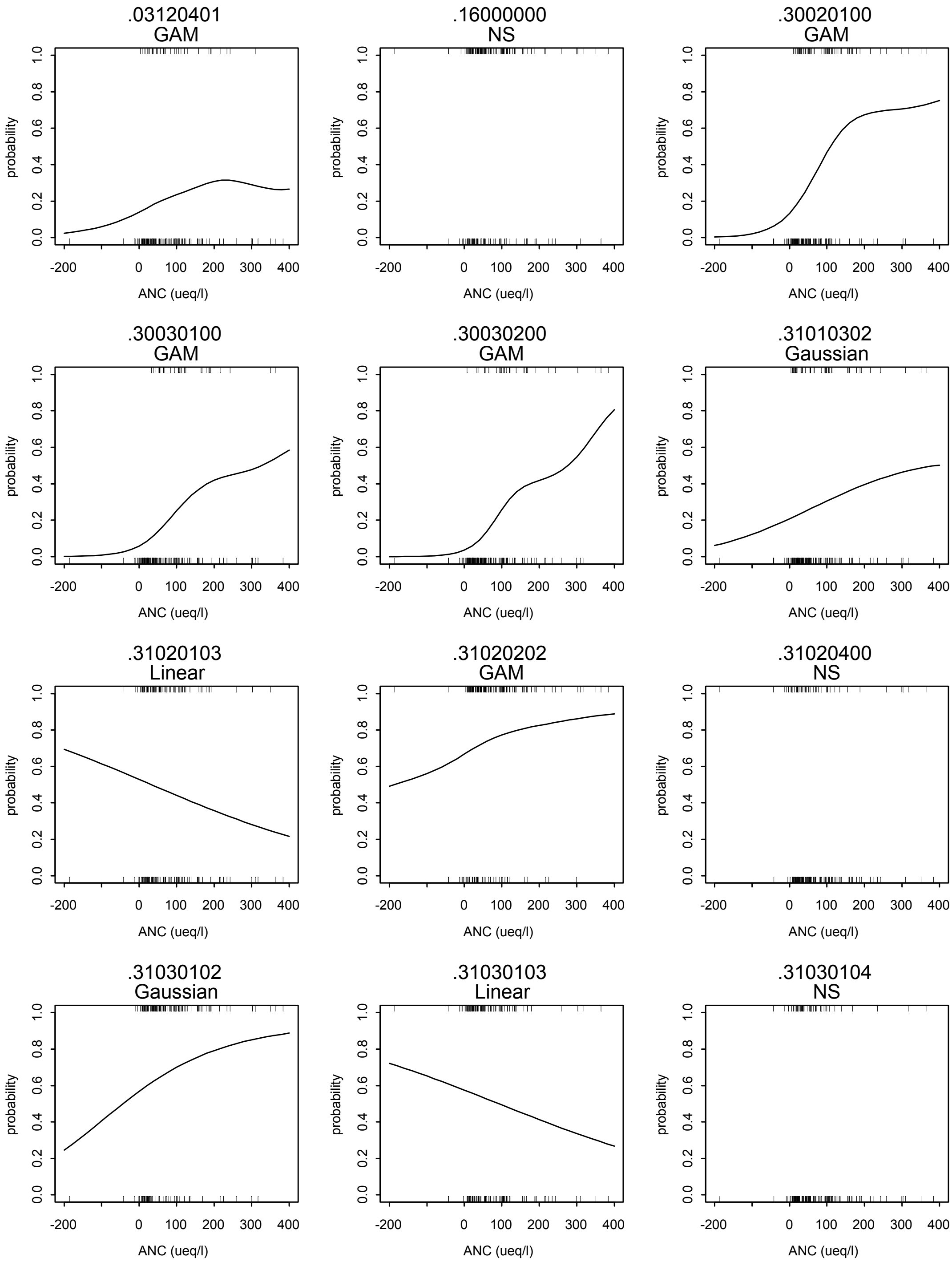


Figure 1.2.3 Continued

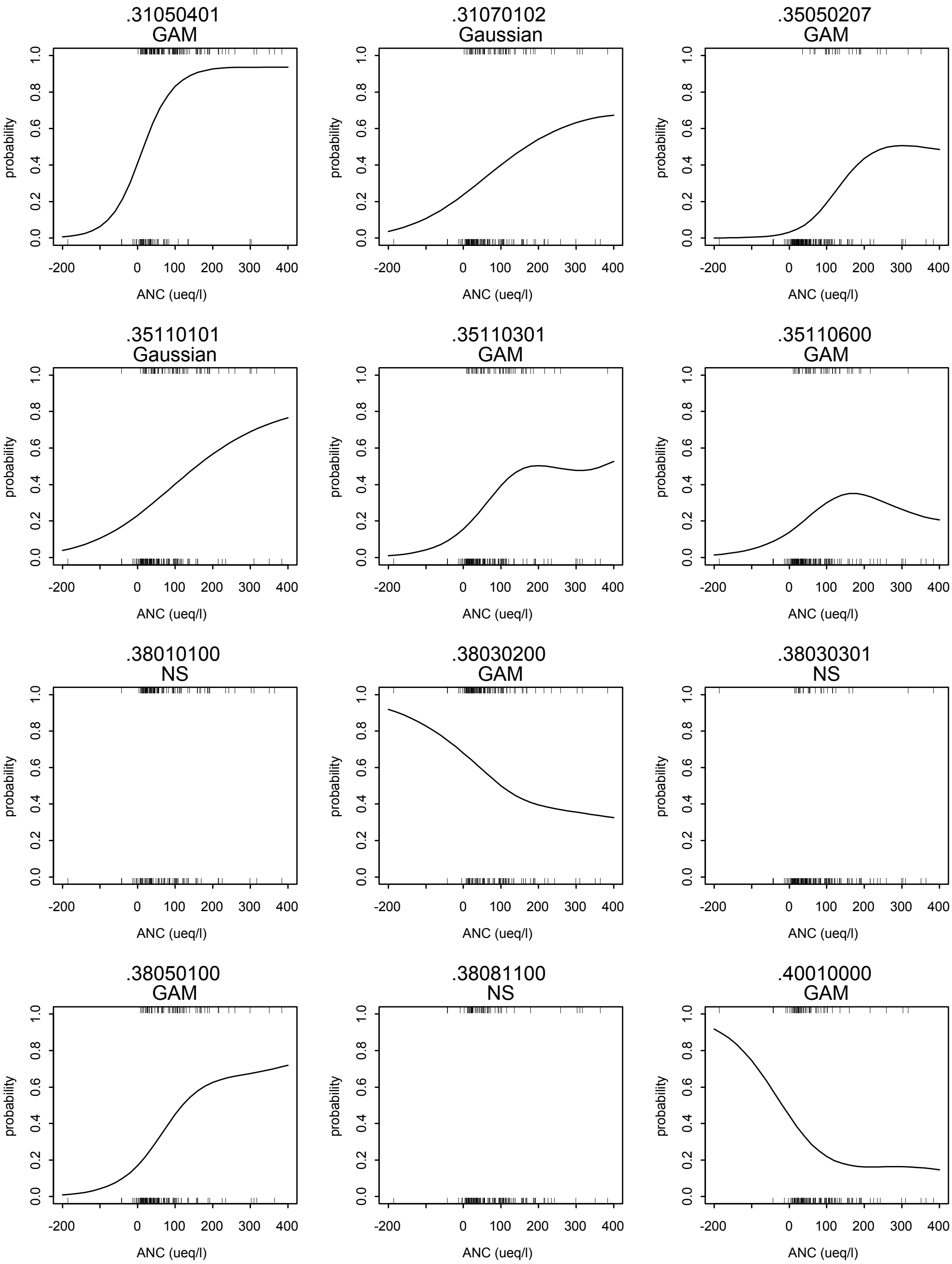
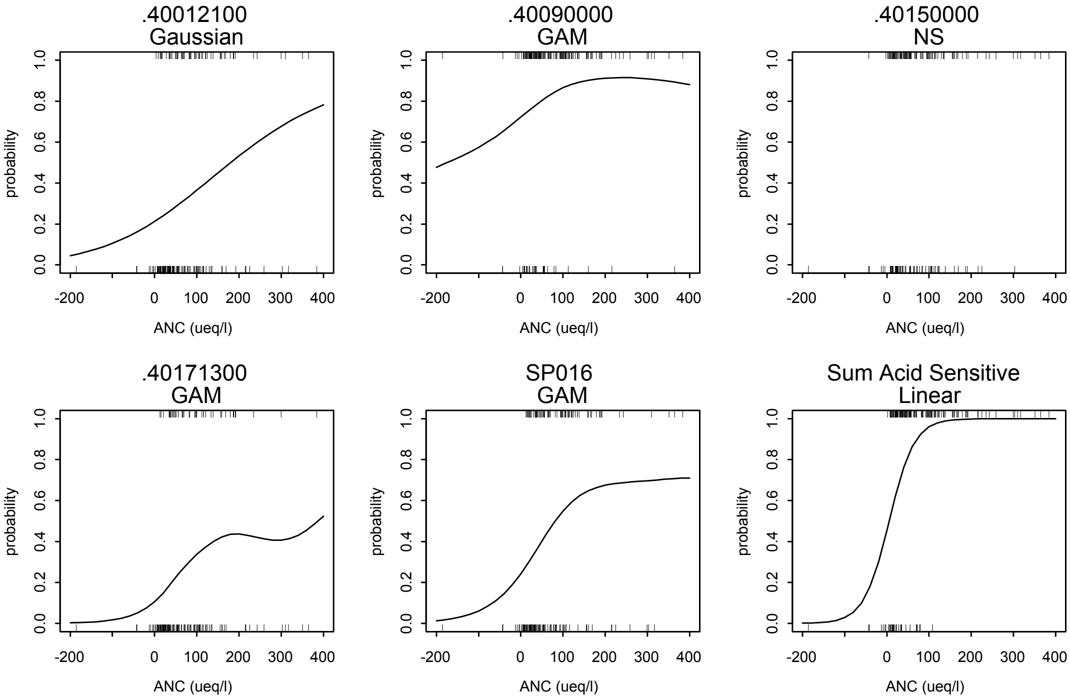


Figure 1.2.3 continued



Job 1.2.3: Re-evaluate critical loads/limits criteria for DEFRA workshop

This job was associated with the consideration of new data informing the choice of ANC_{crit} used for freshwater critical load modelling in the UK. Data collated within various parts of the Freshwaters Umbrella programme were presented at a workshop held at DEFRA on 27th February 2004, with the intention of gaining stakeholder consensus on the most appropriate value of ANC_{crit} to be used in critical loads. The summary stakeholder report from this workshop is presented below.

FRESHWATER CRITICAL LOADS: DEFRA WORKSHOP ON 2004 CCE DATA SUBMISSION

Aims of the workshop

In the 2003 freshwaters critical load data submission to CCE, the issue of the most appropriate value of ANC_{crit} for UK fresh waters was raised in the light of new work being done within the DEFRA sponsored Freshwaters Umbrella Programme. It was suggested that the current value used for all previous UK submissions of ANC_{crit}=0 μeql^{-1} provided a very modest level of protection to many freshwater organisms and that evidence was building for a review of the critical chemical threshold. In particular, the requirements of the EU Water Framework Directive for a return to "good ecological status" and of the Habitats Directive for protection of key organisms and habitats of conservation interest may not be well served by such a low level of protection.

This workshop provided the forum for the presentation of new research and discussions with stakeholders on the weight of evidence for an increase in ANC_{crit} to a higher value of 20 μeql^{-1}, as used widely elsewhere in Europe .

The aim of the workshop was to reach a consensus on the methodology and underlying principles to update the official UK dataset for critical loads for freshwaters, taking into account recent advances in understanding of biological response to surface water acidification and recovery within the UK.

Scientific presentations

The workshop presentations and discussions centred on three themes:

1. what were the pre-industrial conditions in acid sensitive freshwaters in the UK in terms of the critical chemical parameter, ANC?
2. what biological evidence is there for responses at ANC values of 0 and 20 μeql^{-1} including evidence for recovery in waters with declining sulphate and increasing ANC?
3. what is the current state of UK freshwaters in terms of ANC and critical load exceedance?

<u>1. Baseline conditions</u>

Knowledge of pre-industrial, baseline (or reference) conditions is of great importance for setting recovery targets, for defining "good ecological status" under the WFD and crucially, for setting an appropriate value of ANC_{crit}. Two approaches have been employed here; palaeolimnological reconstruction of water chemistry (pH and ANC) from lake sediments and dynamic modelling using MAGIC.

Palaeolimnological data for 114 lakes across the UK were collated and provide reconstructed lakewater pH from diatom-pH transfer functions for the pre-industrial baseline of 1850. While a direct transfer function for ANC is still under development, it is possible to derive ANC from reconstructed pH indirectly using relationships found in modern water chemistry. It was concluded that the great majority of sites would have had a pre-industrial ANC of > 20 μeql^{-1}, in many cases much higher. In a small number of sites, pre-industrial ANC could have been lower than 20 μeql^{-1}, but always greater than 0 μeql^{-1}.

Regional applications of the MAGIC model provided hindcast ANC distributions for lake populations in several key regions impacted by acidification; Wales, the South Pennines, the Lake District, Galloway, the Cairngorms and the Mourne Mountains of Northern Ireland. In Wales and Galloway, no lakes had a modelled ANC below 20 μeql^{-1} in 1850. In the other regions a very small number of sites had modelled pre-industrial ANC values in the range 0-20 μeql^{-1} while the great majority had values >20 μeql^{-1}.

2. Biological evidence

A chemical-biological database collated specifically for the purpose provided evidence of more acid-sensitive elements of the biota than the widely used indicator species, brown trout. Several invertebrate species including the mayfly *Baetis rhodani*, as well as the diatom *Achnanthes minutissima*, rarely occur in waters with a mean ANC of <20 μeql^{-1}. Even brown trout in the Welsh Acid Waters Survey were found to be largely absent in streams with mean ANC <20 μeql^{-1}. Experimental work in Wales and elsewhere has demonstrated that invertebrate populations may be impacted more by minimum pH and ANC values during acid episodes in streams so that mean water chemistry is a poor predictor of biological status. A lower level of protection is therefore afforded to invertebrates in streams than in lakes for a given mean value of ANC, requiring a higher value of ANC_{crit} for streams to provide an equivalent level of protection as for lakes.

Data from the UK Acid Waters Monitoring Network (AWMN) show chemical recovery in surface waters in response to declining sulphur deposition since 1995, with sulphate concentrations decreasing and a corresponding increase in ANC in many sites. Early signs of biological recovery are also apparent, especially in diatom communities and subtle changes in invertebrate communities. In a number of sites, elodeid macrophytes have re-appeared where ANC has increased above the range 15-20 μeql^{-1}, suggesting a possible recovery threshold.

3. Current status of UK freshwaters and effects of ANC_{crit} on critical load exceedance

Most acid sensitive regions of the UK have sites where recent water chemistry data show negative ANC values and hence critical load exceedance for recent deposition levels even with the low (modest) ANC_{crit} value of 0 μeql^{-1}.

Of 1797 UK sites modelled using ANC_{crit} = 0 μeql^{-1}, 29% show exceedance with 1998-2000 deposition data and 16% with 2010 deposition data under the National Emissions Ceiling Directive (NECD). England has the highest proportion of exceeded sites under both deposition levels.

If ANC_{crit} = 20 μeql^{-1} is used, the exceedance figures are 38% (1998-2000) and 24% (2010). The largest proportional increases in exceedance with ANC_{crit} raised from 0 to 20 μeql^{-1}occur in Scotland (19 to 30%) and Wales (38 to 51%). Regional differences in sensitivity to choice of ANC_{crit} occur. Heavily acidified regions like the Pennines, where large negative ANC values are recorded at present, are insensitive to the choice of ANC_{crit}, as most sites exceed their critical loads regardless. Other regions like Snowdonia and the Cairngorms show large differences in the proportion of exceeded sites depending on the selected value of ANC_{crit}.

The static critical load models provide a rough estimate of pre-industrial ANC in that they derive the pre-industrial base cation leaching rate, which is assumed to be equivalent to the rate of production of bicarbonate from weathering. If an ANC_{crit} value greater than this figure is selected, a negative critical load results, suggesting that the critical ANC value could not be attained even without anthropogenic deposition. Several regions include a small number of sites where negative critical loads result from the use of the higher value of ANC_{crit} = 20 μeql^{-1} suggesting that in these cases the threshold is too high. The Mourne Mountains of Northern Ireland, a dataset of only 8 sites, is the only region where a large proportion of negative critical loads result from the use of ANC_{crit} = 20 μeql^{-1}.

Summary of new data

All the evidence from palaeolimnological, static and dynamic models suggests that the great majority of surface waters in the UK had a pre-industrial ANC of >20 μeql^{-1}. Biological data suggest that a number of organisms may be adversely affected when mean ANC declines to 0 μeql^{-1} but an increase from 0 to 20 μeql^{-1} represents a major improvement in biological status. Hence while ANC = 0 μeql^{-1} may represent a high probability of change from good ecological status, ANC_{crit} = 20 μeql^{-1} may reasonably be considered to provide a defensible threshold for acidity.

It is recognised that in a small number of sites, pre-industrial ANC may have been less than 20 μeql^{-1} (but greater than 0 μeql^{-1}) and in such cases ANC_{crit} = 20 μeql^{-1} provides an unachievable critical load.

Discussion and agreement of new ANC_{crit}

In the context of the research findings presented above, several options for updating the value of ANC_{crit} employed in the 2004 critical loads submission to CCE were considered.

1. Blanket value of ANC_{crit} = 0 μeql^{-1} (status quo)

The workshop considered that the weight of evidence no longer supported the blanket use of ANC_{crit} = 0 μeql^{-1} for the UK, given the relatively high probability of damage allowed and the large distance from "good ecological status" implied.

2. Blanket value of ANC_{crit} = 20 μeql^{-1}

A blanket value of ANC_{crit} = 20 μeql^{-1} is inappropriate because of the resultant zero critical loads that are impossible to meet for a small number of sites that may not have had a pre-industrial ANC as high as 20 μeql^{-1}.

3. ANC_{crit} = 20 μeql^{-1} for streams and 0 μeql^{-1} for lakes

While the data suggest that ANC_{crit} = 20 μeql^{-1} should be a minimum value for streams the continued use of 0 μeql^{-1} for lakes was deemed inappropriate as providing too low a level of protection (see 1 above).

4. ANC_{crit} = 20 μeql^{-1} with exceptions at 0 μeql^{-1}

The workshop agreed that this option provides a pragmatic and widely acceptable solution, with a more appropriate level of protection for all sites. Where site-specific modelling work suggests than an ANC of 20 μeql^{-1} is unattainable through emissions reductions because of a lower pre-industrial (reference) value, then the lower threshold of 0 μeql^{-1} should be used.

5. Site-specific ANC_{crit}, using reference conditions and/or specific indicator species

While this option provides the optimal level of protection appropriate for each site, the necessary data are lacking for a large proportion of sites in the mapping dataset, so there are great practical limitations to its application. However, for site-specific assessments at individual sites of high conservation or amenity value, this option is the most appropriate.

6. Assign ANC_{crit} according to typology

The requirement to assign typologies to surface waters under EU directives would suggest that ANC_{crit} based on typologies may bring critical loads modelling into line with EU thinking. However, it was agreed that typology definitions were currently too broad and poorly defined to make this option feasible at present.

Conclusion

The workshop supported the adoption of Option 4 – a general ANC_{crit} value of 20 μeql^{-1} except where site-specific data suggest that the pre-industrial value was lower, in which case ANC_{crit} = 0 μeql^{-1} should be used.

Job 1.2.4: Project web site

The project web site has been created and improved throughout the life of this contract, and it is hoped that further additions to the site can be made as part of future Freshwater Umbrella work, particularly to maintain on-line access to the Biological-Chemical database and the large collection of hydrochemical data collected over the course of previous Freshwater Umbrella and other public funded projects.

The project web site is hosted on a Windows 2000 server running the Apache web server software. The PHP web scripting language has been used to allow the creation of dynamic page content, searching of the project database and management of secure access to data via user-names and passwords for example. The URI (Uniform Resource Identifier or web address) of the site is currently http://ecrc.geog.ucl.ac.uk/clam2/. The home page of the site is shown in Figure 1.2.4.

The following few pages illustrate some of the main features of the project website. Figures 1.2.5 and 1.2.6 show two pages describing some of the background material for the project, specifically the processes of acid deposition (Figure 1.2.5) and how the diatom critical loads model is calculated and applied to sites (Figure 1.2.6).

Figure 1.2.7 illustrates one page of project output, specifically the sites selected as part of Job 1.1 for the modern analogue survey. Most of these sections remain incomplete as this report is only in draft status. When the report is approved, summaries of the output and a key figure or two will be included on the project website as part of the wider dissemination process, alongside an electronic copy of the report.

Figure 1.2.8 illustrates a user accessing the secure section of the website to look at the various datasets available for download. Another area of the secure site allows users to search for sites in the dataset that match user-supplied parameters (e.g. type of sites, pH > 5.5 etc.). Figure 1.2.9 illustrates the advanced search page allowing for more complex queries to be asked of the database. Figure 1.2.10 illustrates the results of a search for all lake sites in Scotland. The web site creates the map of the results each time a query is run and this is displayed as an image in the web page so that users can copy the map to another application. The main part of the results page displays a scrollable list of sites that matched the query results (in this case, all lake sites in Scotland are displayed). Each site name displayed is an active hyperlink, which when clicked will display the information contained in the database such as physical site characteristics and a list of all the water chemistry samples available for the site in question.

Figure 1.2.11 illustrates and example of such a page, showing the information stored in the project database for the Round Loch of Glenhead, an upland site in the Galloway region of Scotland. Each of the entries in the hydrochemistry table displayed on this page is an active hyperlink, which when clicked will take the user to a page which displays the data for the selected record.

It is hoped that the current website can be maintained and expanded under future DEFRA Freshwater Umbrella contracts to provide a vehicle for dissemination of the work undertaken as part of the Umbrella science programmes. One area that the web site could improve upon is in linkages with the GB Lakes Inventory database (Hughes et al. 2004, http://ecrc.geog.ucl.ac.uk/gblakes/), which contains a wide range of data for all lakes in Great Britain larger than 1 hectare in size. Some progress has been made internally between these two initiatives so that sites within the Freshwater Umbrella database can be linked to the relevant data in the GB Lakes Inventory database (and the Inventory was used in Task 2.1 to define the "Stock at Risk" and sites of conservation importance) so that both databases can benefit from the exchange of data – water chemistry and biological data from the Freshwater Umbrella data holdings, and catchment and other lake information from the GB Lakes Inventory. As yet there is no public interface to these two data sets via either of the project websites, however.

References

- Hughes, D. D. Hornby, H. Bennion, M.Kernan, J. Hilton, G. Phillips and R. Thomas (2004) The Development of a GIS-based Inventory of Standing Waters in Great Britain together with a Risk-based Prioritisation Protocol. *Water, Air and Soil Pollution: Focus* 4 (2-3): 73-84

Figure 1.2.4: Screen grab of the project web site showing the home page

Figure 1.2.5: Screen grab of the project web site showing a page and pop-up describing the process of acid deposition.

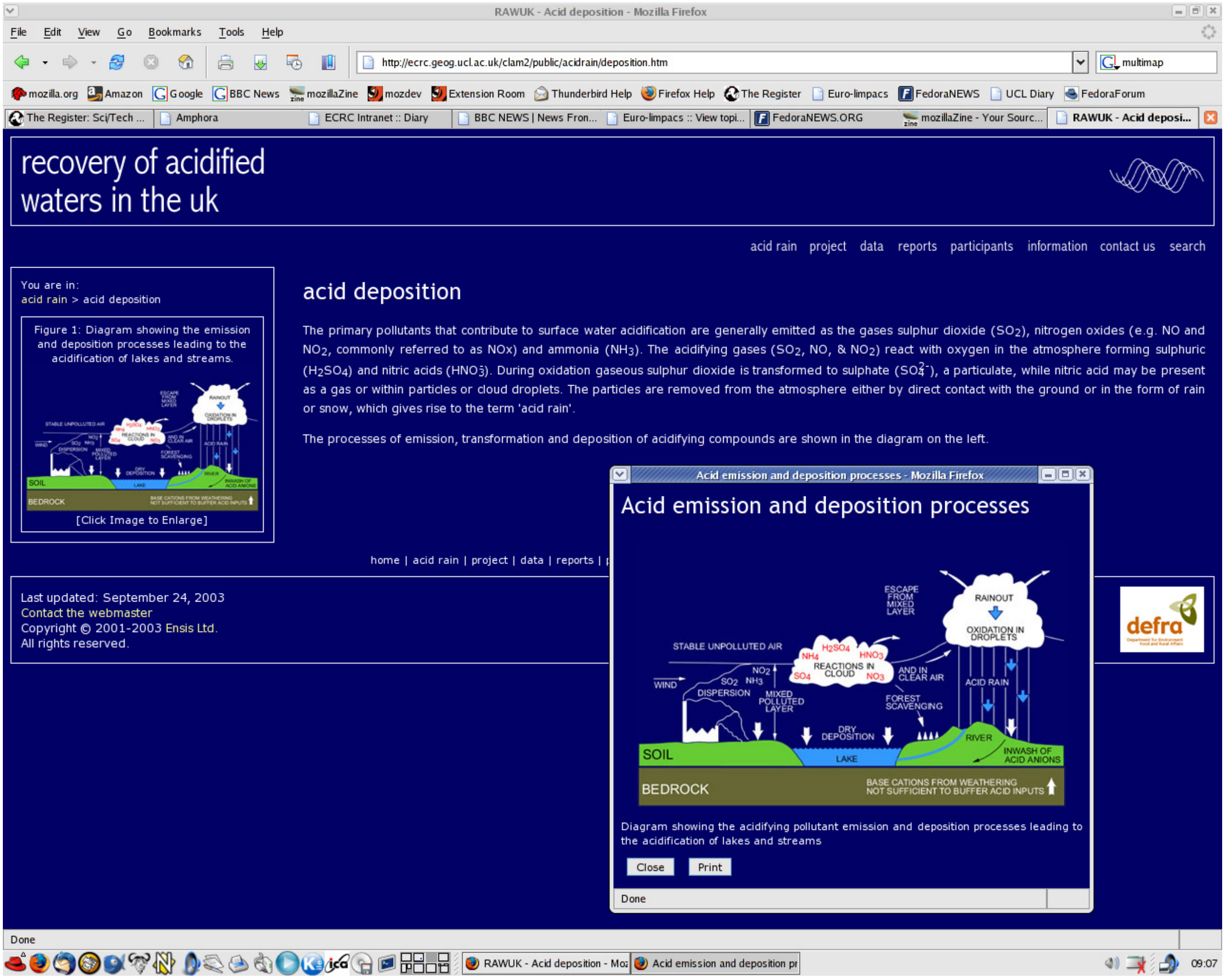


Figure 1.2.6: Screen grab of the project web site showing a page and pop-up describing the diatom critical load model.

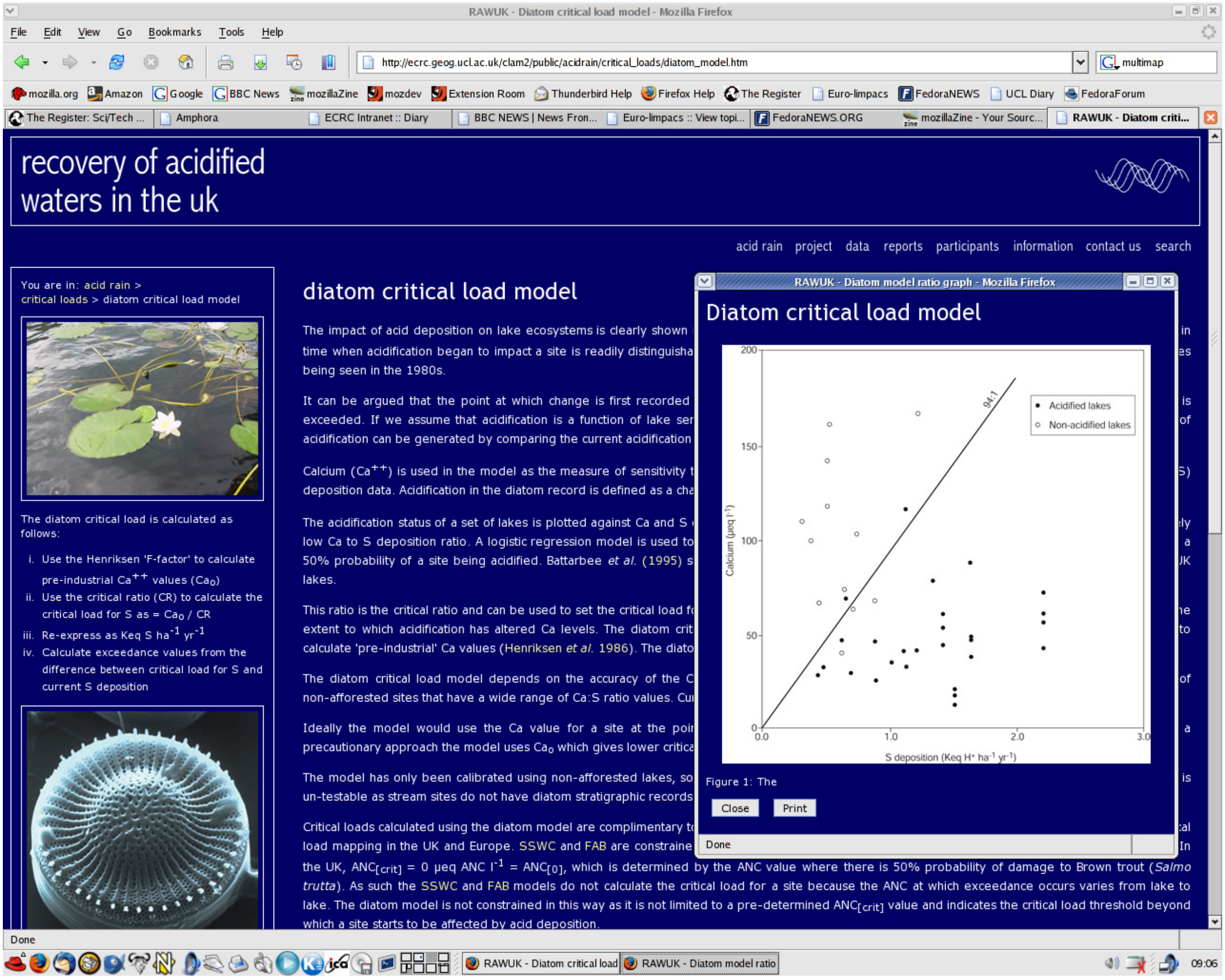
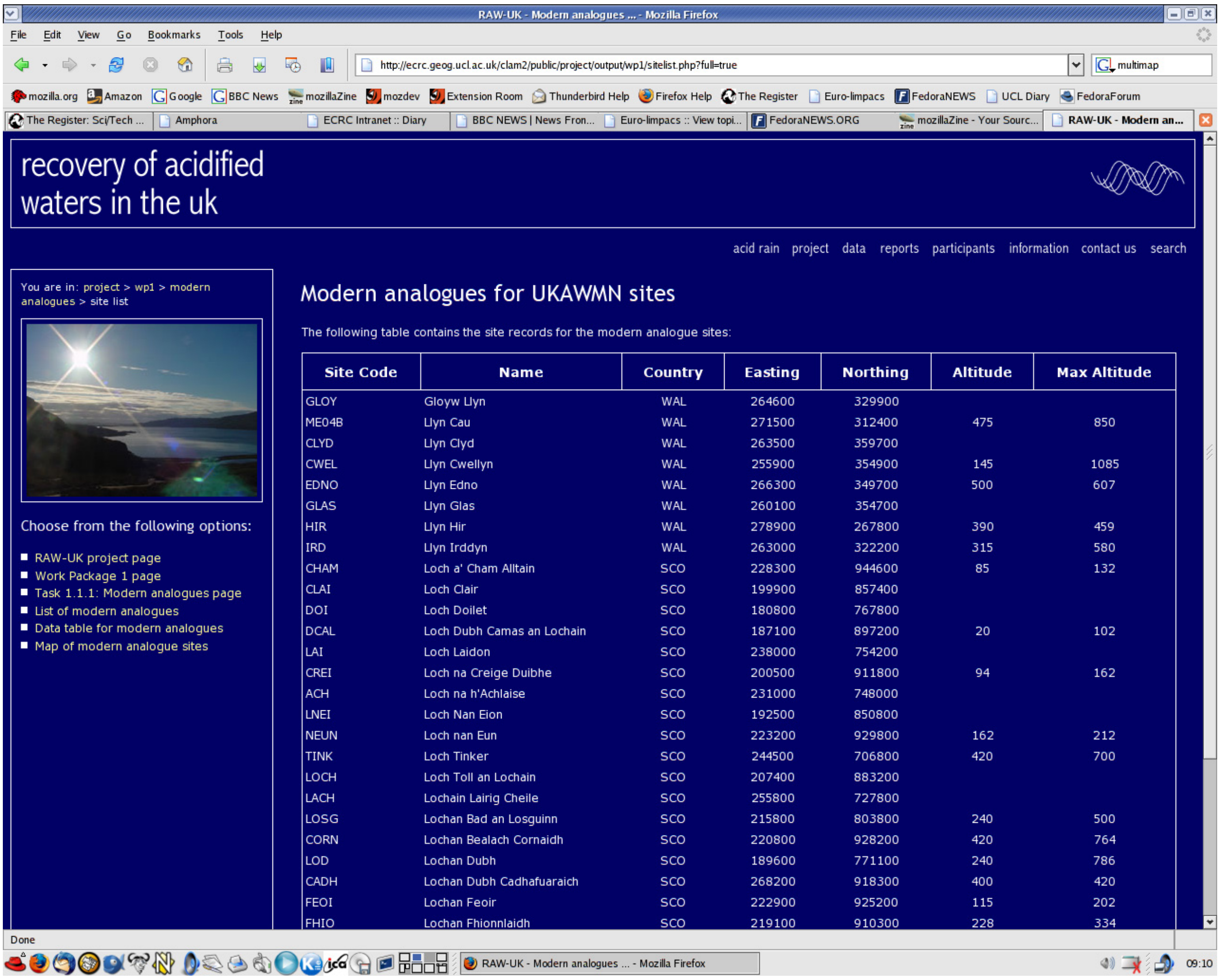


Figure 1.2.7: Screen grab of the project web site showing a page describing the modern analogue sites sampled as part of Task 1.1.



Site Code	Name	Country	Easting	Northing	Altitude	Max Altitude
GLOY	Gloyw Llyn	WAL	264600	329900		
ME04B	Llyn Cau	WAL	271500	312400	475	850
CLYD	Llyn Clyd	WAL	263500	359700		
CWEL	Llyn Cwellyn	WAL	255900	354900	145	1085
EDNO	Llyn Edno	WAL	266300	349700	500	607
GLAS	Llyn Glas	WAL	260100	354700		
HIR	Llyn Hir	WAL	278900	267800	390	459
IRD	Llyn Irddyn	WAL	263000	322200	315	580
CHAM	Loch a' Cham Alltain	SCO	228300	944600	85	132
CLAI	Loch Clair	SCO	199900	857400		
DOI	Loch Doilet	SCO	180800	767800		
DCAL	Loch Dubh Camas an Lochain	SCO	187100	897200	20	102
LAI	Loch Laidon	SCO	238000	754200		
CREI	Loch na Creige Duibhe	SCO	200500	911800	94	162
ACH	Loch na h'Achlaise	SCO	231000	748000		
LNEI	Loch Nan Eion	SCO	192500	850800		
NEUN	Loch nan Eun	SCO	223200	929800	162	212
TINK	Loch Tinker	SCO	244500	706800	420	700
LOCH	Loch Toll an Lochain	SCO	207400	883200		
LACH	Lochain Lairig Cheile	SCO	255800	727800		
LOSG	Lochan Bad an Losguinn	SCO	215800	803800	240	500
CORN	Lochan Bealach Cornaidh	SCO	220800	928200	420	764
LOD	Lochan Dubh	SCO	189600	771100	240	786
CADH	Lochan Dubh Cadhafuaraich	SCO	268200	918300	400	420
FEOI	Lochan Feoir	SCO	222900	925200	115	202
FHIO	Lochan Fhionnlaidh	SCO	219100	910300	228	334

Figure 1.2.8: Screen grab of the project web site showing part of the interface to the hydrochemistry database. The screen shows which users is logged in to the site on the left of the page.

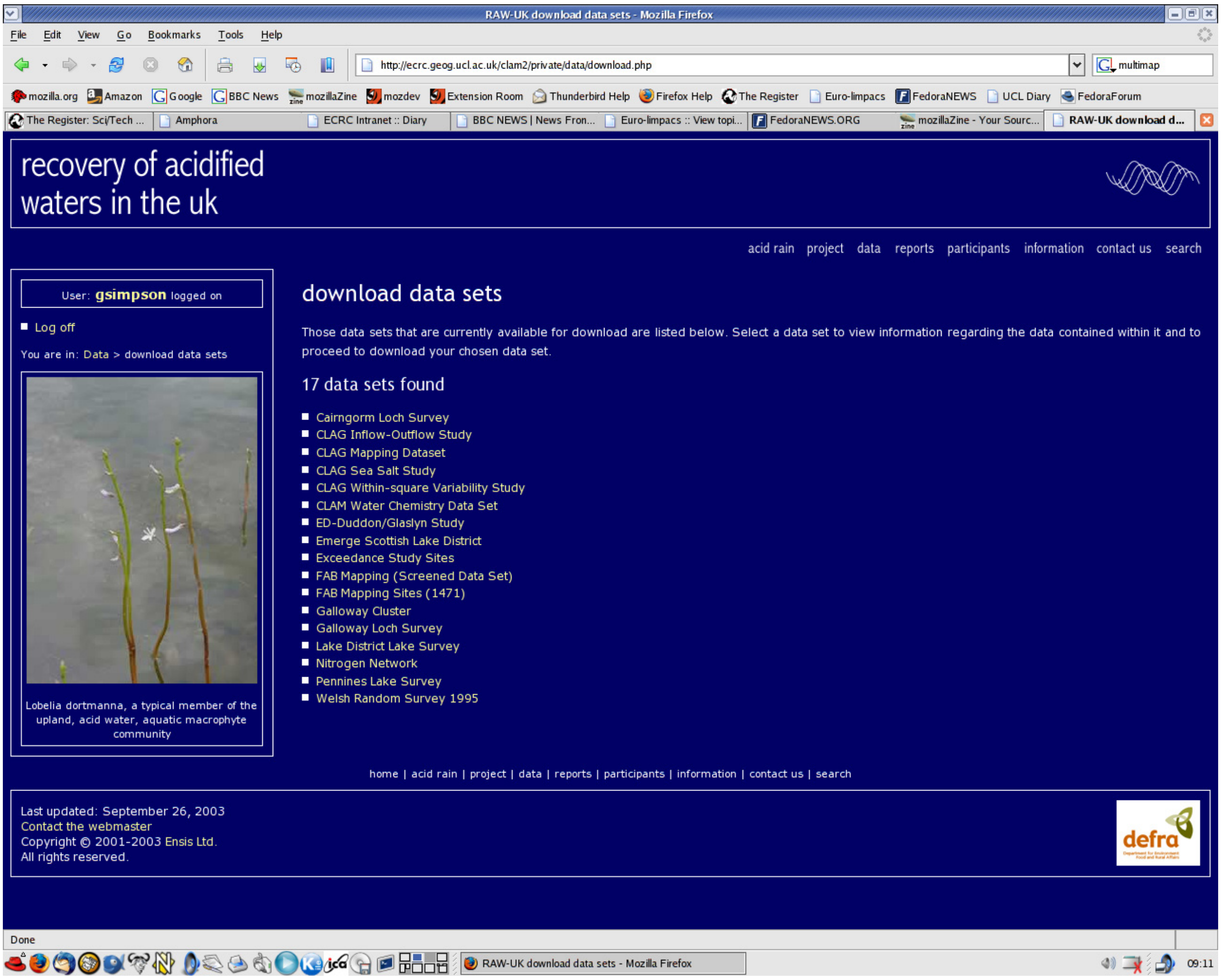


Figure 1.2.9: Screen grab of the project web site showing the advanced search facility allowing users to search the hydrochemistry database.

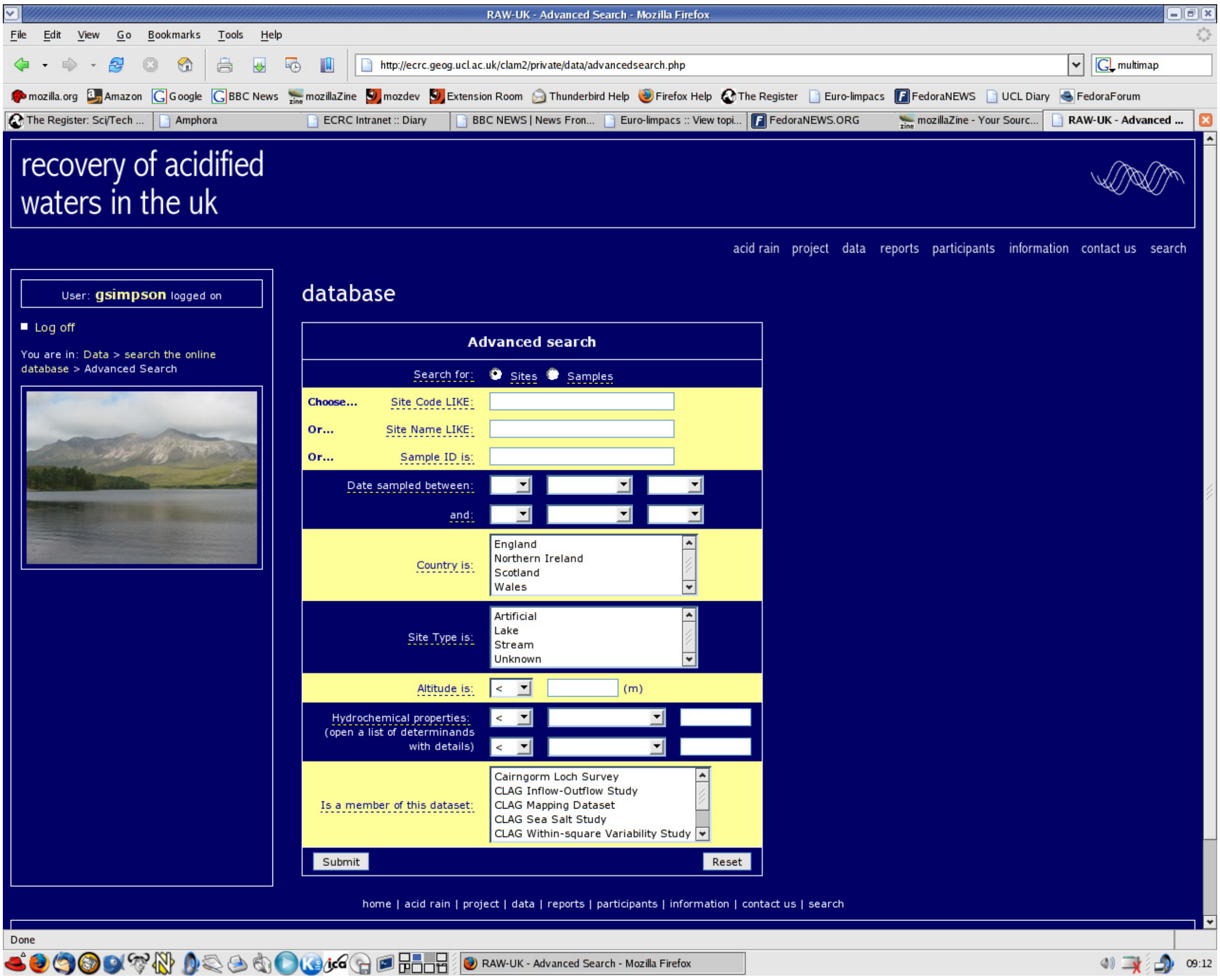


Figure 1.2.10: Screen grab of the project web site showing the results of a search for all lake sites in Scotland. A map showing the locations of all the sites returned in the query is displayed on the left and a scrollable list of sites is presented in the main page section.

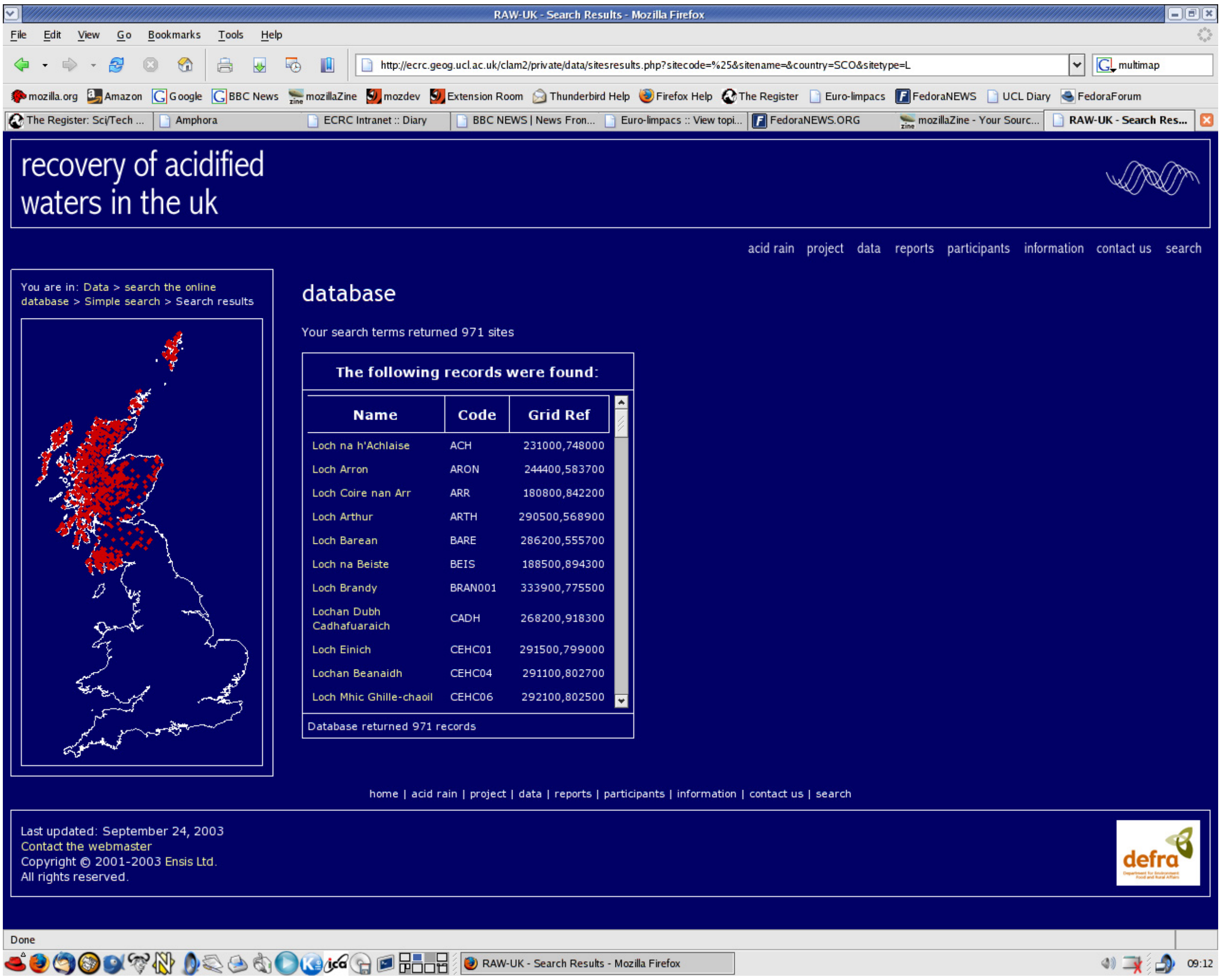
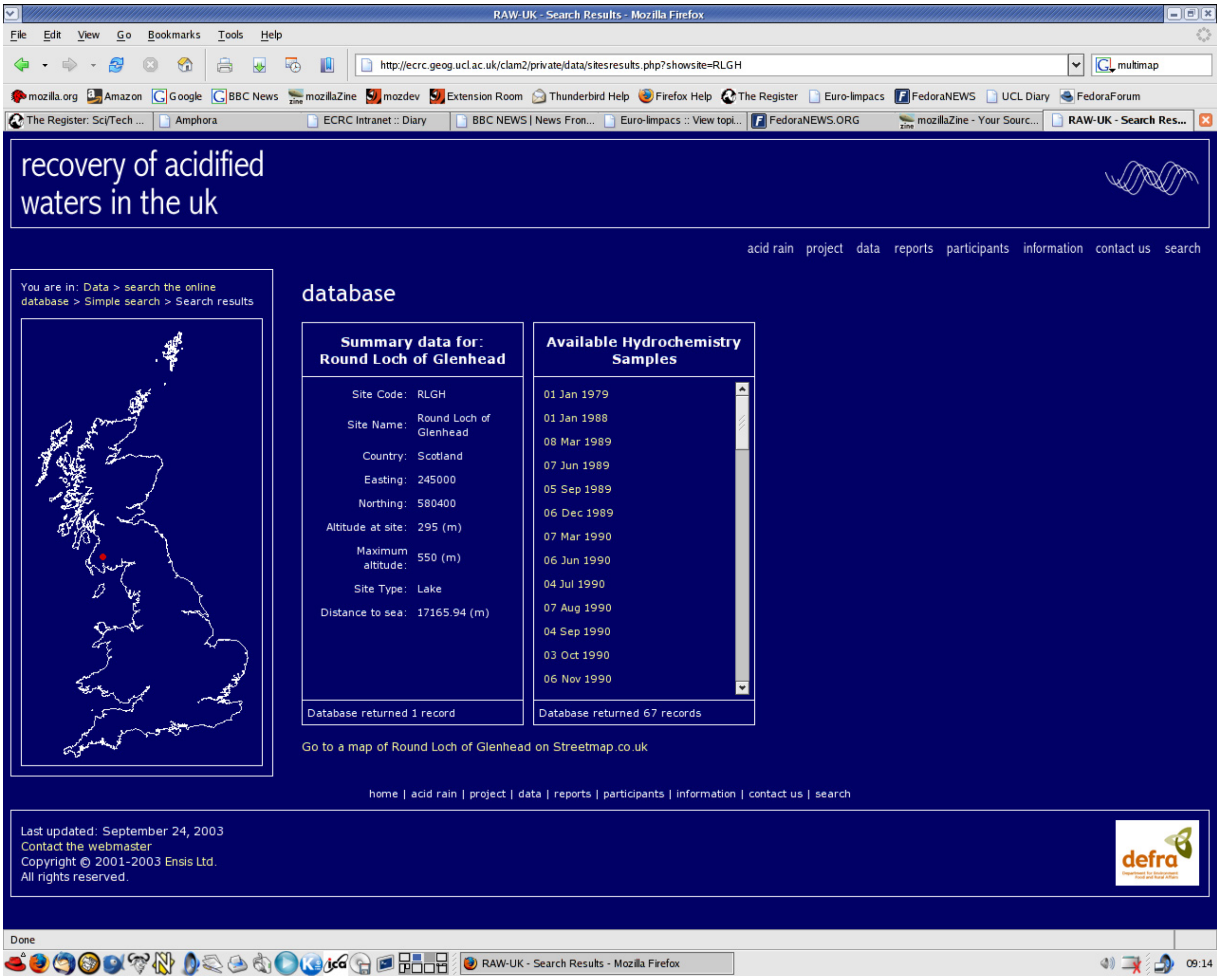


Figure 1.2.11: Screen grab of the project web site showing the site summary page displaying the data holdings for the Round Loch of Glenhead, Galloway, Scotland.



Task 2.1: Regional assessment of lake status

Task 2.1: Regional assessment of lake status

Job 2.1.1: Define stock at risk on a regional basis

Job 2.1.2: Identification of sites to be sampled in regions where data are sparse

Job 2.1.3: Calculate critical loads with various deposition datasets and ANC_{crit} values

Job 2.1.5: Sample standing waters of conservation importance in acidified regions

While these Jobs were completed early within the project, new developments later in the project led to their combination and expansion as reported below:

1) new deposition data became available for calculation of critical load exceedances (1998-2000, 1999-2001 and revised figures for 1995-97 and 2010);
2) the DEFRA Workshop reported under Job 1.2.3 recommended a revised ANC_{crit} of 20 μeql^{-1} except for sites with site-specific evidence of a lower pre-industrial ANC, in which case 0 μeql^{-1} should be used;
3) a revised version of the FAB model accounting for direct deposition to lake surfaces was used; and
4) the new CCE call for data in 2004 required an expansion of the mapping dataset to ensure that all sites used for application of the VSD model were also FAB critical loads sites – hence regional MAGIC datasets were added to the mapping dataset, allowing a more thorough assessment of stock at risk.

The final assessment under Jobs 2.1.1 (stock at risk) and 2.1.3 (range of FAB critical loads) included both the new regional datasets (Job 2.1.2) and the conservation sites (Job 2.1.5), and is therefore reported last.

Job 2.1.2: Identification of sites to be sampled in regions where data are sparse.

The purpose of this Job was to identify potentially important regions where acidification may be an issue but that were previously under-represented in the critical loads mapping dataset. The new regional datasets would provide samples to expand the national "stock at risk" assessment.

This exercise used the existing CLAM Chemistry database (1893 sites) and the GB lakes Inventory (43738 sites) to examine the geographical spread of sites on the CLAM database in relation to the full population of lakes in sensitive areas (Fig.2.1.1). The latter was overlaid onto national digital maps of freshwater sensitivity to acidification, deposition and land cover. Sites in areas of low sensitivity and low deposition were screened out together with those where there is potentially an agricultural input. 'Sensitive' and potentially impacted areas with relatively few CLAM sites were identified. In autumn 2002 water samples were collected from standing waters in three regions;

1. Surrey and Sussex Heaths (21 sites)
2. New Forest / Dorset (19 sites)

3. Trossachs (30 sites)

Southern England has relatively poor coverage and a significant number of sites emerge as potentially sensitive during the mapping exercise. Additionally the mapping dataset shows there are number of sites with low critical loads in these areas. The Trossachs region exhibits elevated deposition levels and is located between Galloway and the Cairngorms both of which have regional datasets on the CLAM database. The recently designated Trossachs and Loch Lomond National Park is also testament to the conservation value attached to this area. Table 2.1.1 provides summary chemistry for each of the three regions.

These three new regional datasets were added to the new UK Mapping Dataset to expand the stock at risk assessment and critical loads exercises in Jobs 2.1.1 and 2.1.3.

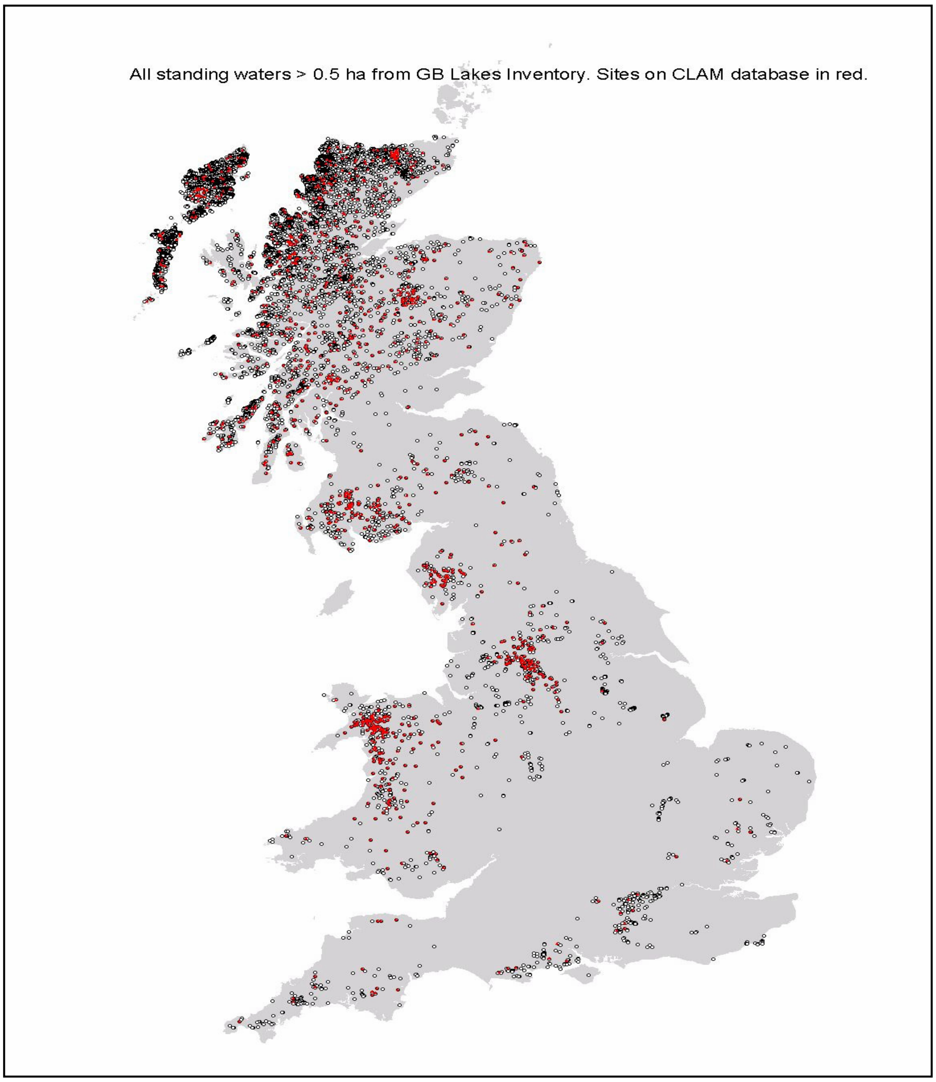


Figure 2.1.1: Map showing all standing waters in Great Britain in areas sensitive to acidification (Freshwater Sensitivity Classes 1, 2 and 3). Sites with chemistry on the CLAM database are shown in red.

Table 2.1.1: Summary statistics - chemistry for regional stock at risk sites

	pH	Alk2	Cond	Na	NH4	K	Mg	Ca	Cl	NO3	SO4	SiO2	PO4-P	TP	TORGP	TN	TORGN	Al-TM	Al-NL	Al-L	Abs-250	TOC
Surrey/Sussex Heaths																						
Mean	5.30	444	147	512	27	76	191	651	584	31.7	251	4262	70.6	111.5	40.9	1493.1	1403.3	83.3	50.2	33.1	0.67	15.3
Median	6.26	141	121	532	7	67	189	413	585	0.3	188	2560	4.0	34.0	26.0	805.0	698.0	34.0	18.0	5.0	0.43	14.7
St Dev	0.97	760	90	175	68	41	85	989	199	127.0	230	4411	245.6	249.4	58.6	2584.4	2615.1	102.2	82.0	69.5	0.66	10.3
Min	4.52	-32	48	135	0	18	66	71	160	0.0	14	40	0.0	2.5	0.5	155.0	120.0	4.0	0.0	0.0	0.01	1.2
Max	7.99	3160	453	879	313	184	324	4442	971	584.0	702	13150	1130.0	1150.0	255.0	12220.0	12220.0	342.0	312.0	257.0	2.10	36.0
Dorset Heath/New Forest																						
Mean	5.27	150	117	617	16	46	167	262	697	1.0	145	1445	12.3	46.0	33.7	829.2	810.3	46.1	30.1	16.1	0.43	12.8
Median	5.81	53	93	436	6	44	140	165	466	0.0	124	660	2.0	25.0	20.0	494.0	494.0	25.0	16.0	7.0	0.34	10.8
St Dev	0.88	237	62	434	41	27	105	275	515	1.8	87	1426	25.4	85.4	61.2	1200.5	1170.4	48.4	33.9	19.5	0.34	7.2
Min	4.63	-24	53	159	0	7	14	29	165	0.0	40	80	0.0	6.0	2.0	91.0	91.0	3.0	1.0	0.0	0.02	2.5
Max	7.29	799	237	1609	161	113	337	985	1847	5.5	390	4320	100.0	351.0	251.0	4920.0	4780.0	168.0	112.0	56.0	1.13	24.0
Trossachs																						
Mean	5.53	68	28	113	1	7	51	121	103	3.8	47	905	2.2	9.2	7.0	304.4	257.4	32.3	22.9	9.8	0.37	8.4
Median	6.09	45	26	100	0	7	48	98	86	2.0	43	710	1.0	4.3	2.5	287.5	261.0	23.5	18.0	5.5	0.32	7.8
St Dev	0.72	101	10	45	2	3	24	98	45	3.9	22	664	4.9	10.5	9.7	86.0	76.3	33.6	21.3	17.5	0.22	3.9
Min	4.85	-14	16	66	0	3	25	39	56	0.0	21	70	0.0	2.5	1.5	157.0	136.0	0.0	0.0	0.0	0.06	2.9
Max	7.42	480	61	261	8	15	140	529	233	16.0	124	3080	21.0	50.0	50.0	481.0	426.0	166.0	87.0	98.0	0.93	18.0

Job 2.1.5: Identify all standing waters of conservation importance in acidified regions & sample 50 of these

The intention in Job 2.1.5 was to identify all sites of conservation interest and sample up to 50 of these in sensitive or 'acidified' areas for water chemistry. The objective was to assess whether these may have been impacted by acid deposition prior to a palaeolimnological analysis of biological assemblages (Job 2.1.7). However, the focus of the study moved away from SSSIs towards an examination of standing waters in SACs. The sampling strategy involved:

- Identification of all standing waters in SACs designated for freshwater aquatic habitats within the three most acid-sensitive classes of the UK freshwater sensitivity map.
- Identification all sites where agricultural inputs are less than 10%
- Identification all sites where deposition is high relative to sensitivity
- Selection of a random subset (out of a total of 1045 stranding waters) of sites for sampling (excluding Orkney and Shetland for logistical purposes)

One standing water body, selected at random from each SAC designated for freshwaters was included in the sampling list of 29 sites (see Table 2.1.2).

There are also a number of sites in SACs with freshwater designations in the regional datasets. The locations of the SACs and sampled sites are mapped in Figure 2.1.2. Sampling was completed in 2002 for these sites. Table 2.1.3 shows summary statistics for the conservation sites.

Critical load exceedance figures are provided in the Results section of Jobs 2.1./1/3 below.

Table 2.1.2: Standing waters of conservation interest sampled under CLAM2

Country	Sitecode	WBID	Easting	Northing	Site Name	OS Map	SAC Name
WAL	HIR	38394	278900	267600	Llyn Hir	147	Afon Teifi / River Teifi
SCO	CONV4	13857	225377	882168	Un-named	20	Beinn Dearg
SCO	CZNN64	23612	264493	742634	Lochan nan Cat	51	Ben Lawers
SCO	CZNN17	22173	214393	772781	Lochan Meall an t-Suidhe	41	Ben Nevis
WAL	CZSH71	36182	270787	313542	Llyn y Gadair	124	Cadair Idris
SCO	CONV21	20920	318700	803500	Loch Builg	36	Cairngorms
SCO	CONV20	2635	273200	958400	Lochan Airigh na Creige	10	Caithness and Sutherland Peatlands
SCO	CONV8	21623	243711	788163	Lochan a Choire	34	Creag Meagaidh
WAL	CONV3	38309	283991	269301	Llyn Cerrigllwydion Uchaf	147	Elenydd
WAL	WSH7601	33537	270034	366561	Dulyn Reservoir	115	Eryri / Snowdonia
SCO	CONV13	26023	125569	669639	Un-named	60	Feur Lochain
SCO	CONV9	2919	229668	955712	Loch Tarbhaidh	9	Foinaven
SCO	CONV11	22893	214244	756725	Loch Achtriochtan	41	Glencoe
SCO	SCR084	20860	283063	804450	Loch Insh	35	Insh Marshes
SCO	CONV12	11759	217500	906800	Loch Dhonnachaidh	15	Inverpolly
ENG	CEHL46	29157	322158	509853	Styhead Tarn	90	Lake District High Fells
SCO	CZNG96	16140	194300	860800	Loch Coire Mhic Fhearchair	19	Loch Maree Complex
SCO	NARR	27912	245234	581552	Loch Narroch	77	Merrick Kells
WAL	CONV19	34845	275912	338742	Llyn Conglog-mawr	124	Migneint a Dduallt
SCO	CONV15	20104	167904	820741	Un-named	32	Mointeach nan Lochan Dubha
SCO	CONV6	21189	344135	799404	Loch Kinord	37	Muir of Dinnet
SCO	CONV2	23225	231300	751200	Lochan Beinn Chaorach	41	Rannoch Moor
WAL	CONV16	35225	265772	330306	Llyn Morwynion	124	Rhinog
SCO	CONV18	19804	149766	824001	Un-named	32	Sligachan Peatlands
SCO	CONV10	20012	213300	821600	Loch Coulavie	25	Strathglass Complex
SCO	CONV17	25168	180123	691031	Loch Fidhle	55	Taynish and Knapdale
ENG	CONV5	45332	425207	111065	Un-named	195	The New Forest
ENG	CONV7	29183	316262	505902	Wast Water	89	Wast Water
ENG	CRAN	44464	479326	132385	Cranmer Pond	186	Woolmer Forest

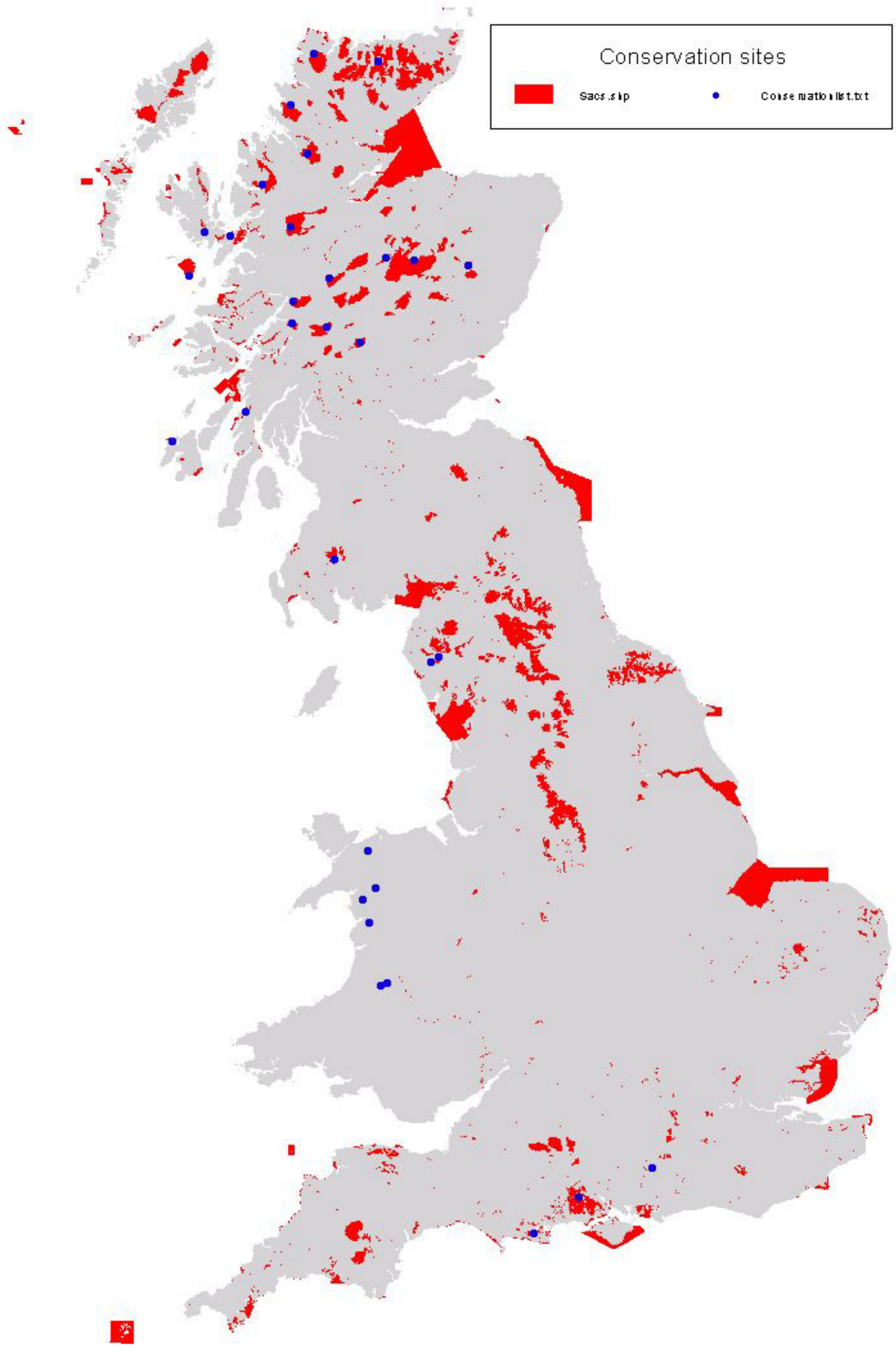


Figure 2.1.2: Location of conservation sites

Table 2.1.3: Summary statistics - chemistry for conservation sites

	pH	Alk2	Cond	Na	NH4	K	Mg	Ca	Cl	NO3	SO4	SiO2	PO4-P	TP	TORGP	TN	TORGN	Al-TM	Al-NL	Al-L	Abs-250	TOC
Conservation																						
Mean	5.54	79	51	270	2	12	82	124	287	4.9	52	790	1.6	7.4	5.7	367.5	302.8	22.7	13.5	9.2	0.23	6.4
Median	6.20	57	42	176	0	8	66	95	192	2.7	47	570	0.5	6.0	5.0	319.5	255.5	8.0	6.0	1.5	0.18	4.6
St Dev	0.74	97	27	164	3	9	45	94	198	6.5	26	851	3.0	5.3	4.2	202.1	210.9	33.8	15.3	20.5	0.25	4.8
Min	4.74	-19	19	98	0	3	33	27	80	0.0	19	150	0.0	2.5	0.5	90.0	60.0	3.0	1.0	0.0	0.01	1.1
Max	7.28	312	105	632	8	43	226	366	808	26.0	121	4300	13.0	23.0	19.0	1063.0	1058.0	132.0	51.0	81.0	0.99	19.0

Job 2.1.1: Define stock at risk on a regional basis

Job 2.1.3: Calculate critical loads with various deposition datasets and ANC_{crit} values

As part of the UK response to the 2004 CCE call for data, the freshwaters mapping dataset for critical loads was updated and revised in early 2004. This process involved the incorporation of additional lakes datasets which facilitated a much more thorough assessment of stock at risk than had previously been possible. Furthermore, the new datasets included many more sites used in MAGIC model and palaeololimnological reconstructions, providing information on baseline ANC values to inform the Stakeholder Workshop and review of ANC_{crit} described under Task 1.2 (Job 3). Changes to the national dataset and results from the new stock at risk assessment are presented below.

Updates to mapping dataset

The additional datasets contributing to the 2004 freshwaters critical loads submission for the UK are listed in Table 2.1.4. These include both the new regional and conservation sites sampled under this programme, plus the additional dynamic modelling datasets provided from other projects.

Since many of the datasets overlap in terms of sites sampled, consistent criteria had to be employed in the selection of the chemistry data used for the calculation of critical loads. The most recent, best estimate of annual mean chemistry data were selected where multiple datasets for a site were available. The quality of the chemistry data took precedence over the sampling date, e.g. annual mean chemistry based on monthly samples for 1995 would be used in preference to one-off water samples from 1998.

Seasalts screening

The presence of exceeded sites in north-west Scotland in 2010 using an ANC_{crit} value of 20 μeql^{-1} drew attention to the problem of seasalt induced acidity in certain sites that was not distinguishable in the critical load models from anthropogenic acidity. Hence to maintain the rigour of data screening and quality assurance, a screening criterion bases on seasalt impacts was applied. All sites where the sum of non-marine (seasalt-corrected) base cations was < -20 μeql^{-1} were removed from the mapping dataset because of the lack of confidence in calculated critical loads. It should be noted that these sites are often genuinely acid and are removed only because of the model's inability to distinguish between sources of acidification (anthropogenic deposition versus natural seasalt inputs). It cannot be said with confidence that these sites are *not* impacted by anthropogenic acid deposition.

The screening criterion led to the removal of 75 sites from the Great British mapping dataset, mainly in northern and north-west Scotland. No sites were screened out from the Northern Irish dataset on this basis. The resultant mapping dataset includes 1595 sites in Great Britain and 127 sites in Northern Ireland, with a UK total of 1722 sites.

Table 2.1.4: datasets contributing to 2004 CCE freshwater critical loads data submission

Dataset	No. of sites	Streams	Lakes/ reservoirs	Chemistry used	Sampling date(s)	Selection criteria	Funding
FAB Mapping GB	1044	200	844	CLAG one-off	1990-94	10km/20km grid, FWS	DEFRA
NI 2000	119	50	69	DoE NI one-off	March 2000	10km grid: FWS	EHS, DoE NI
AWMN GB	19	8	11	Annual mean	2002	Spatial / sensitivity gradient	DEFRA
AWMN NI	4	3	1	Annual mean	2002	Spatial / sensitivity gradient	EHS, DoE NI
Seasalts	18	0	18	CLAG Annual mean	Quarterly 1992-93	Distance to sea / altitude	DEFRA
CLAG Nitrogen Network	13	0	13	CLAG 2 year mean	Monthly 1996-97	N deposition / Ca sensitivity	DEFRA
MK Snowdonia	76	0	76	Spring sample	February 1996	All in key grid squares	DEFRA
Analogue	27	0	27	CLAM one-off	Spring 2002	AWMN analogues	DEFRA
Trossachs	32	0	32	CLAM one-off	October 2002	All lochs in region	DEFRA
Southern England	35	0	35	CLAM one-off	September 2002	All sensitive sites in 2 regions	DEFRA
Conservation	29	0	29	CLAM one-off	Sept/Oct 2002	Random lakes in SACs	DEFRA
Pennines	64	0	64	One-off / quarterly mean	April 1998 / 2002	Most reservoirs in region	DEFRA / CEH / GANE
GANE Snowdonia	25	0	25	Quarterly mean	2002	Remote, high altitude	NERC GANE
GANE Mournes (NI)	8	0	8	Quarterly mean	2002	All in region	NERC GANE
Galloway 1998 / GANE	61	0	61	3 years 1-off / Quart. mean	1996/7/8 or 2002	Most in region	SEERAD / NERC GANE
Cairngorms	38	0	38	One-off	April-June 1999	Most in region	SEERAD
Lake District	53	0	53	One-off	May 2000	Most in region	DEFRA / CEH
WAWS lakes	16	0	16	Annual mean	Monthly 1995	Most sensitive areas: FWS	CCW/EA/Welsh Office
WAWS streams	102	102	0	Annual mean	Monthly 1995	Most sensitive areas: FWS	CCW/EA/Welsh Office
Scottish Random Survey	135	0	135	One-off	Winter 1995/96	Random subsample	NIVA/FRS-FL/ECRC
Welsh Random Survey	52	0	52	CLAM one-off	Nov/Dec 1995	Random subsample	NIVA/FRS-FL/ECRC

AWMN: UK Acid Waters Monitoring Network
CLAG: DoE/DETR Critical Loads Advisory Group
CLAM: DEFRA Freshwaters Umbrella (Critical Loads of Acidity and Metals)
FWS: Freshwater Sensitivity Map based on soils and geology (Hornung *et al.*, 1995)

Nested catchments

The amalgamation of various datasets in certain regions led to the occurrence of a number of nested catchments in the mapping dataset. 118 "father" catchments were found to have one or more subcatchments ("sons") in the mapping dataset for which ecosystem area would be double-accounted if reported separately. It was decided that only the exclusive area for the larger "father" catchments should be reported for calculation of ecosystem area exceeded (average accumulated exceedance, AAE). Hence the exclusive area was calculated as the difference between the total area of the father catchment and the area of the separately submitted ("son") subcatchment. Where more than one subcatchment occurred, the sum of subcatchment areas was subtracted from that of the father catchment.

Stakeholder review of ANC_{crit}

As suggested in the 2003 submission report, a stakeholder workshop was held prior to submission of the 2004 freshwaters critical loads dataset. The workshop was hosted by DEFRA at Ashdown House, London on 27th February 2004. The summary report from this workshop is presented above under Task 1.2 (Job 3), but the key outcome was the decision to adopt a new critical chemical threshold of ANC_{crit} = 20 μeql^{-1} to replace the previously used value of 0 μeql^{-1}, except where site specific evidence for a pre-industrial ANC of less than 20 μeql^{-1} could be found. Details of ecosystem areas and site numbers with each of these ANC_{crit} values are provided in Table 2.1.5 below.

Table 2.1.5: Summary of numbers and areas of freshwater sites in the UK mapping data sets for the February 2003 and February 2004 updates, and the ANC_{crit} values applied to sites in 2004.

Site information	Site statistics by country and for the UK				
	England	Wales	Scotland	NI	UK
Number sites 2003	268	116	660	119	1163
Total area (km^2) 2003	660	179	1430	149	2417
Number sites 2004	395	344	856	127	1722
No. sites ANC 0 μeql^{-1}	21	2	15	5	43
No. sites ANC 20 μeql^{-1}	374	342	841	122	1679
Total area (km^2) 2004	1042	1225	5338	186	7791

Updates to parameters in FAB model

1. *Adoption of new version of FAB*

For the 2004 critical loads submission, the reformulated FAB model of Henriksen & Posch (2001) was applied. This version of FAB takes account of direct deposition to the lake surface, whereas the previous version (Posch *et al.*, 1997) assumed that all deposited N had first to pass through the terrestrial catchment before reaching surface waters.

The key difference between the two formulations is in the interpretation of $CL_{min}N$. In the previous version of FAB, $CL_{min}N$ represented the level of deposition at the first point of nitrate leaching into waters, so that below this deposition load, N did not contribute to critical load exceedance. In the new formulation, for lake catchments there is always some flux of N into surface waters via direct deposition. Since in-lake retention is a first-order term and a fixed proportion of inputs to the lake, there must always be a flux of nitrate from the lake outflow that contributes to a decline in ANC. In this case, $CL_{min}N$ simply represents the first point of terrestrial nitrate leaching that increases the N load to the lake and increases exceedance when the critical threshold is crossed. Hence there is no longer a category in the Critical Load Function corresponding to "reduce S deposition only" for exceeded sites; exceedance must always be due to a combination of S and N deposition where both are non-zero.

Note that in the published reformulation of Henriksen and Posch (2001), three possible scenarios of N deposition and leaching are envisaged and these are utilized in the published equations for the parameters of the Critical Load Function:

i) no terrestrial N leaching: $N_{dep} < (N_{imm}+N_{den})$

ii) terrestrial N leaching except from forested areas:

$(N_{imm}+N_{den}) < N_{dep} < (N_{imm}+N_{den}+N_{upt})$

iii) terrestrial N leaching from all areas:

$N_{dep} > (N_{imm}+N_{den}+N_{upt})$

The second case may underutilize the potential sink for N in forests by assuming that the only N input to forested areas is via direct deposition. However, if N leaching occurs from moorland areas within a catchment that are upslope of forested areas, there may be further scope for uptake of N beyond that which is directly deposited (i.e. in case ii). Hence the existing formulation provides a "worst-case" nitrate leaching scenario for forested catchments. For the UK application of FAB we have therefore modified the published equations to assume that the terrestrial N sink including forest uptake is averaged over the whole terrestrial catchment. Although this is a "best-case" nitrate leaching scenario for forested catchments, it is more consistent with the approach taken in FAB for modelling soil-based sinks for N, where the whole-catchment value for N_{imm} and N_{den} is the catchment-weighted mean for all soils.

Under this adaptation of FAB there are only two possible scenarios for N deposition and leaching. The corresponding critical load equations are given below. Note that for stream catchments where direct deposition to the water surface is negligible, the equations remain the same as in the previous formulation of FAB.

The equation for $CL_{min}N$ remains the same – only the interpretation of it changes:

$$\mathbf{CL_{min}N = (1\text{-}r)\ (N_{imm} + N_{den}) + fN_{upt}}$$

Case 1: $N_{dep} <= CL_{min}N$ (no terrestrial nitrate leaching)

$$CL(A) = (1\text{-}\rho_S)S_{dep} + r(1\text{-}\rho_N)N_{dep}$$

$$CL_{max}S = L_{crit} / \ (1\text{-}\rho_S)$$

$$CL_{max}N = L_{crit} / \ r(1\text{-}\rho_N)$$

Case 2: $N_{dep} > CL_{min}N$ (terrestrial nitrate leaching occurs)

With terrestrial N leaching the critical loads for S and N become:

$$CL(A) = (1-\rho_S)S_{dep} + (1-\rho_N)N_{dep} - (1-\rho_N)\ \{(1-r)\ (N_{imm} + N_{den}) + fN_{upt}\}$$

$$CL_{max}S = L_{crit} / (1-\rho_S)$$

$$CL_{max}N = (L_{crit}/(1-\rho N)) + CL_{min}N$$

The equations used for $CL_{max}S$ and $CL_{max}N$ are therefore dependent on deposition load relative to $CL_{min}N$.

2. *Updated forestry data*

Updated forest cover data for 2004 were used in this application of FAB. A reclassification of managed broadleaf woodland on deep peats to a more probable class of managed coniferous woodland resulted in minor changes to forest cover distributions in some catchments.

For managed coniferous woodland a net N uptake rate of 0.21 keq ha^{-1} yr^{-1} (2.94 kgN ha^{-1} yr^{-1}) was used, while for managed broadleaf woodland the rate was 0.42 keq ha^{-1} yr^{-1} (5.88 kgN ha^{-1} yr^{-1}).

Results I: Calculation of critical loads and exceedances with baseline (1970), 1998-2000 and 2010 deposition data for ANC 0, 20 and 40 μeql^{-1}

Under the requirements of Job 2.1.3, critical load exceedances were calculated for the new mapping dataset using baseline (1970), most recent (1998-2000, replacing 1995-97) and 2010 deposition datasets, using fixed ANC_{crit} values of 0, 20 and 40 μeql^{-1}. Note that all Figures and maps within this results section refer to the pre-screening mapping dataset of February 2004 (n=1797), but 75 sites in England (4) and Scotland (71) were subsequently removed on the basis of a seasalts screening threshold for the April 2004 CCE submission (n=1722). Also, the 1998-2000 and 2010 deposition datasets were subsequently modified and the new exceedances are presented in the next results section. The general patterns observed here do, however, remain true.

The 1970 deposition was calculated using a current dispersion model with re-scaled emissions. The pattern of emissions has, however, changed over the intervening period, with a substantial decline in urban emissions since 1970 due, for example, to reductions in the use of coal to heat houses. It is therefore likely that the estimated deposition for 1970 will be too large for remoter areas of the UK (e.g. Wales) and too small close to urban areas (e.g. the midlands of England). The 1970 data do, however, provide a general picture of the broad regional patterns in critical load exceedance during the assumed period of maximum deposition.

Summary exceedance statistics by subproject / region are provided in Table 2.1.6 below. Note that the figures for each subproject may include duplicated sites that occur under more than one subproject heading, so the sum for all subprojects does not provide the total for the mapping dataset where such sites are only represented once (n=1797).

Table 2.1.6: % of 2004 mapping sites exceeding critical loads by subproject

		$ANC_{crit} = 0\ \mu eql^{-1}$			$ANC_{crit} = 20\ \mu eql^{-1}$			$ANC_{crit} = 40\ \mu eql^{-1}$		
Subproject	**n**	**1970**	**1998-2000**	**2010**	**1970**	**1998-2000**	**2010**	**1970**	**1998-2000**	**2010**
PREVIOUS MAPPING										
FAB Mapping GB	**1043**	43	25	13	49	35	21	54	41	31
NI 2000	**119**	16	10	7	16	12	8	18	13	11
OTHER DEFRA DATA										
AWMN	**23**	78	74	43	87	78	65	96	91	74
Seasalts	**18**	17	11	0	44	33	11	61	39	39
CLAG Nitrogen network	**13**	54	23	15	54	23	15	54	38	38
MK Snowdonia	**75**	79	48	27	89	61	41	93	79	59
NEW CLAM2 DATA										
Analog	**27**	44	15	4	70	48	11	81	63	44
Trossachs	**32**	50	22	0	63	31	0	66	41	25
Southern	**35**	83	60	31	83	63	31	83	63	31
Conservation	**29**	34	21	10	34	21	17	48	28	21
ADDITIONAL DATA										
Pennines	**64**	100	97	86	100	98	88	100	98	92
GANE Snowdonia	**25**	96	76	52	100	96	72	100	96	96
GANE Mournes (NI)	**8**	100	100	100	100	100	100	100	100	100
Galloway 1998/GANE	**61**	92	61	31	95	72	51	98	84	59
Cairngorms	**38**	68	53	18	79	71	39	79	76	63
Lake District	**53**	83	53	45	85	64	55	87	74	64
WAWS Lakes	**16**	100	31	25	100	63	31	100	81	69
WAWS Streams	**102**	79	42	13	80	59	33	84	67	47
Scottish Random Survey	**129**	10	2	1	13	5	2	17	10	2
Welsh Random Survey	**49**	59	27	12	65	35	24	69	51	37

There is a large variation in the proportion exceeded between subprojects, between years and for each value of ANC_{crit}. The least impacted groups of sites include the CLAG Seasalts dataset in remote north-west Scotland, the Northern Ireland 10km grid survey (NI 2000) and the Scottish Random Survey. While low deposition explains the low proportion of exceedances for the Seasalt sites, the inclusion of a large proportion of sites in non-sensitive areas accounts for the low exceedance figures in the other two datasets.

The most impacted groups of sites include the Pennines, the Mournes, the WAWS Lakes, the GANE Snowdonia lakes, the Galloway sites and the Southern England sites. The eight sites in the Mournes are all exceeded under every scenario, even for $ANC_{crit} = 0\ \mu eql^{-1}$ (the least demanding critical load) in 2010 (the lowest deposition scenario).

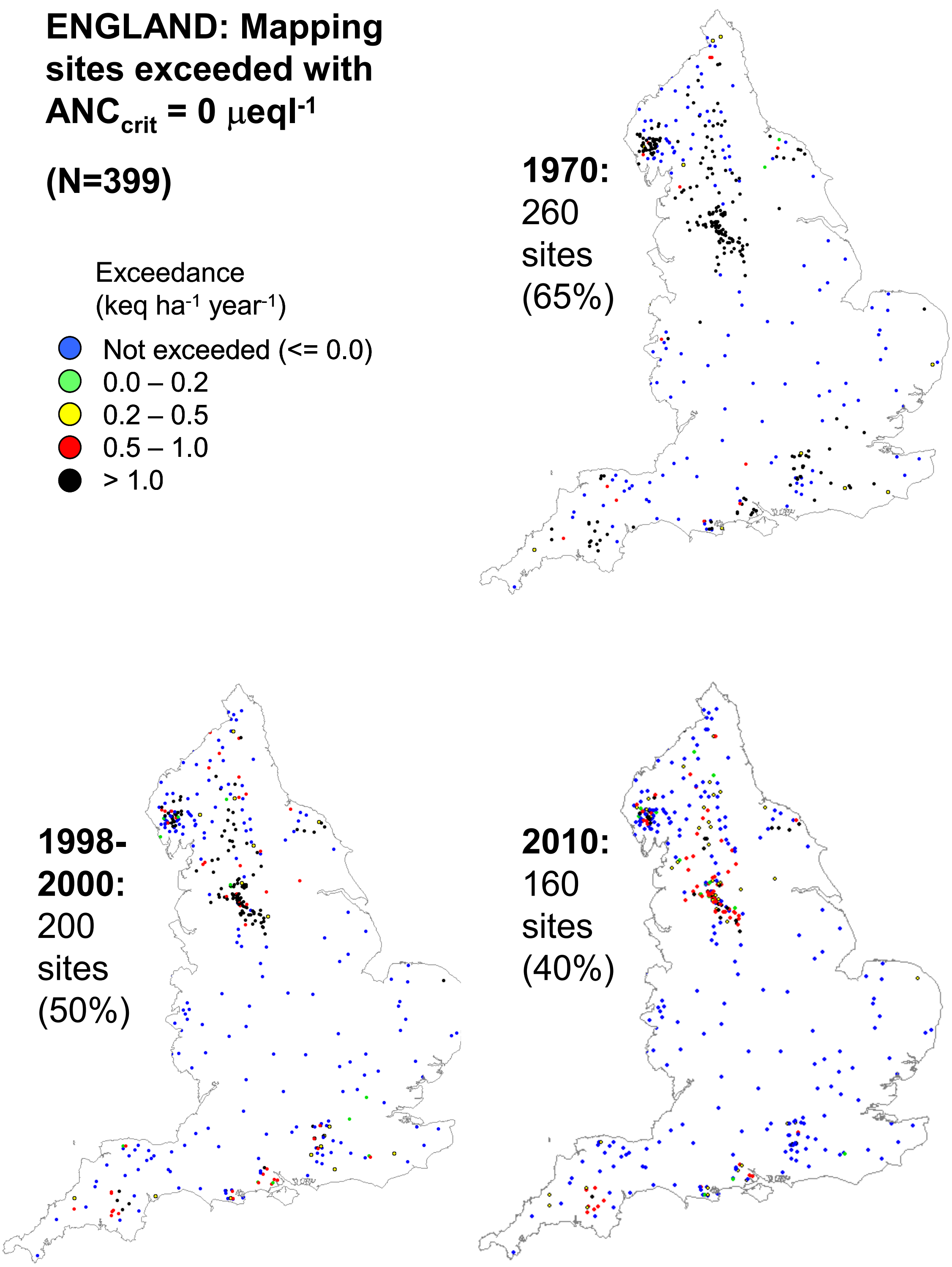
In the highest deposition year modelled, 1970, many of the 20 subprojects / regions showed critical load exceedance in more than half of their sites; 14 with $ANC_{crit} = 0\ \mu eql^{-1}$, 15 with $ANC_{crit} = 20\ \mu eql^{-1}$ and 17 with $ANC_{crit} = 0\ \mu eql^{-1}$. By 2010 following emission reductions under the NECD these figures are much reduced, to 3 with $ANC_{crit} = 0\ \mu eql^{-1}$, 6 with $ANC_{crit} = 20\ \mu eql^{-1}$ and 9 with $ANC_{crit} = 40\ \mu eql^{-1}$. Hence the major benefits in terms of reduced critical loads exceedance following emissions reductions from the assumed worst-case year of 1970 are apparent. The subprojects / regions showing the greatest proportion of exceeded sites remaining in 2010 are the Pennines, GANE Snowdonia and the Mournes.

Aggregated exceedance statistics and maps for England, Scotland, Wales and Northern Ireland are shown below (Table 2.1.7; Figs. 2.1.3-2.1.10); since $ANC_{crit} = 40\ \mu eql^{-1}$ was not considered as a feasible option for the UK mapping submission to CCE, only maps for 0 and 20 μeql^{-1} are given. The choice of ANC_{crit} greatly affects the reductions in exceedance achieved by 2010 relative to 1970 or current deposition levels, mainly in Scotland and Wales. England and Northern Ireland are relatively insensitive to the choice of ANC_{crit}.

With $ANC_{crit} = 0\ \mu eql^{-1}$, just under a half of UK mapping sites are exceeded in 1970, decreasing to 16% by 2010. With $ANC_{crit} = 20\ \mu eql^{-1}$ the UK figures are 54% in 1970 and 24% by 2010, while for $ANC_{crit} = 40\ \mu eql^{-1}$ they increase to 58% of sites exceeded in 1970 and 34% still exceeded in 2010. In 1970, Wales was the most impacted region regardless of ANC_{crit}, with 73-81% of sites exceeded. Under recent deposition levels (1998-2000), England has a greater proportion of exceeded sites than Wales with $ANC_{crit} = 0\ \mu eql^{-1}$, but not with higher values of ANC_{crit}. By 2010, England has the greatest proportion of exceedances for all values of ANC_{crit}.

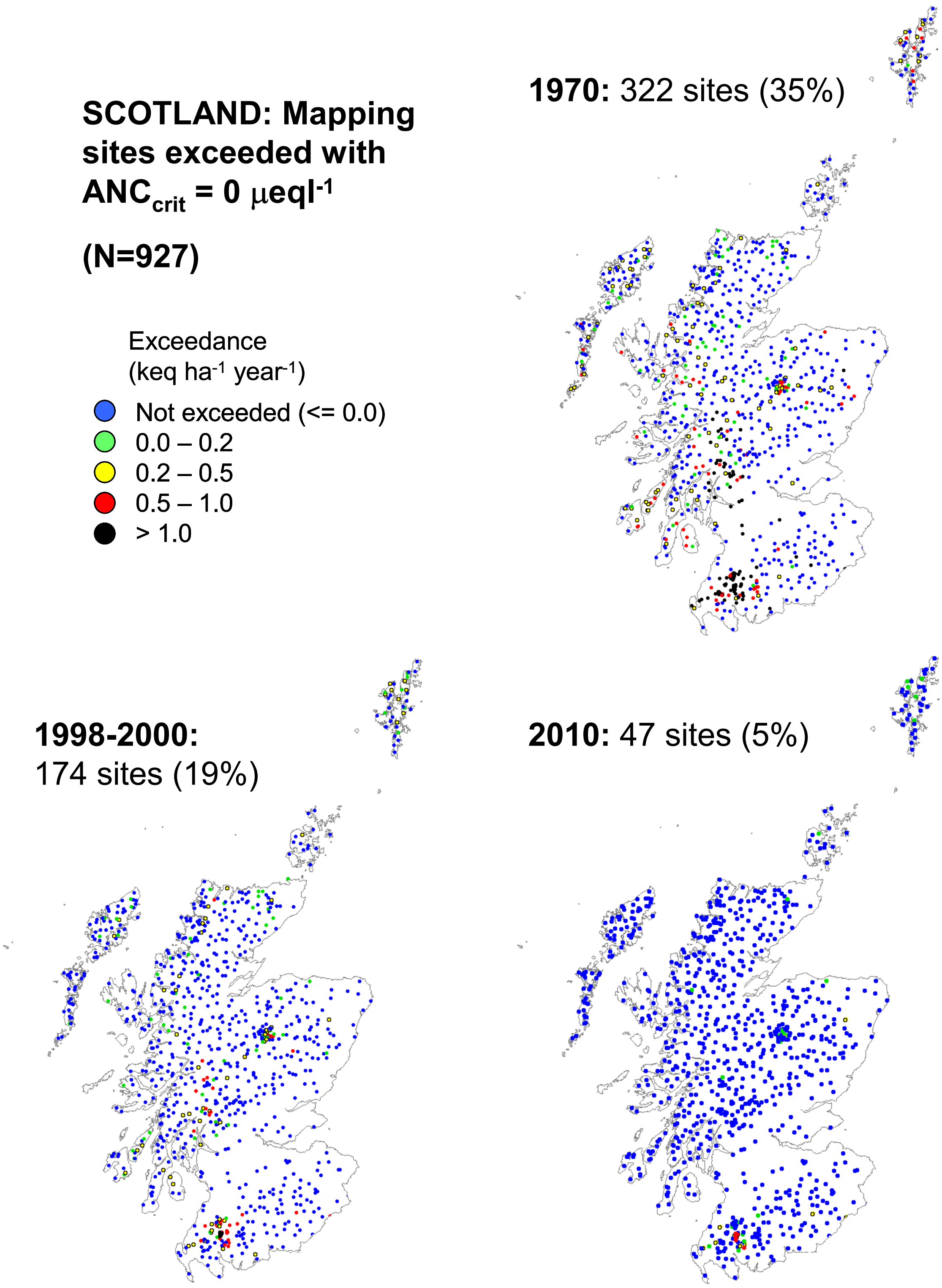
These differences, along with the maps in Figs. 2.1.3-2.1.10, show that Wales has a wider distribution of sensitive sites across a gradient of sensitivity, with a broad range of low critical loads. The population of exceeded sites is highly sensitive to changes in ANC_{crit} or deposition. England has regional clusters of extremely low critical loads and highly impacted sites that are insensitive to the choice of ANC_{crit} or national changes in deposition, because local deposition levels are still high enough to cause exceedance in 2010, even with the least demanding value of ANC_{crit}.

Figure 2.1.3: Critical load exceedances for English sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 0 μeql^{-1}



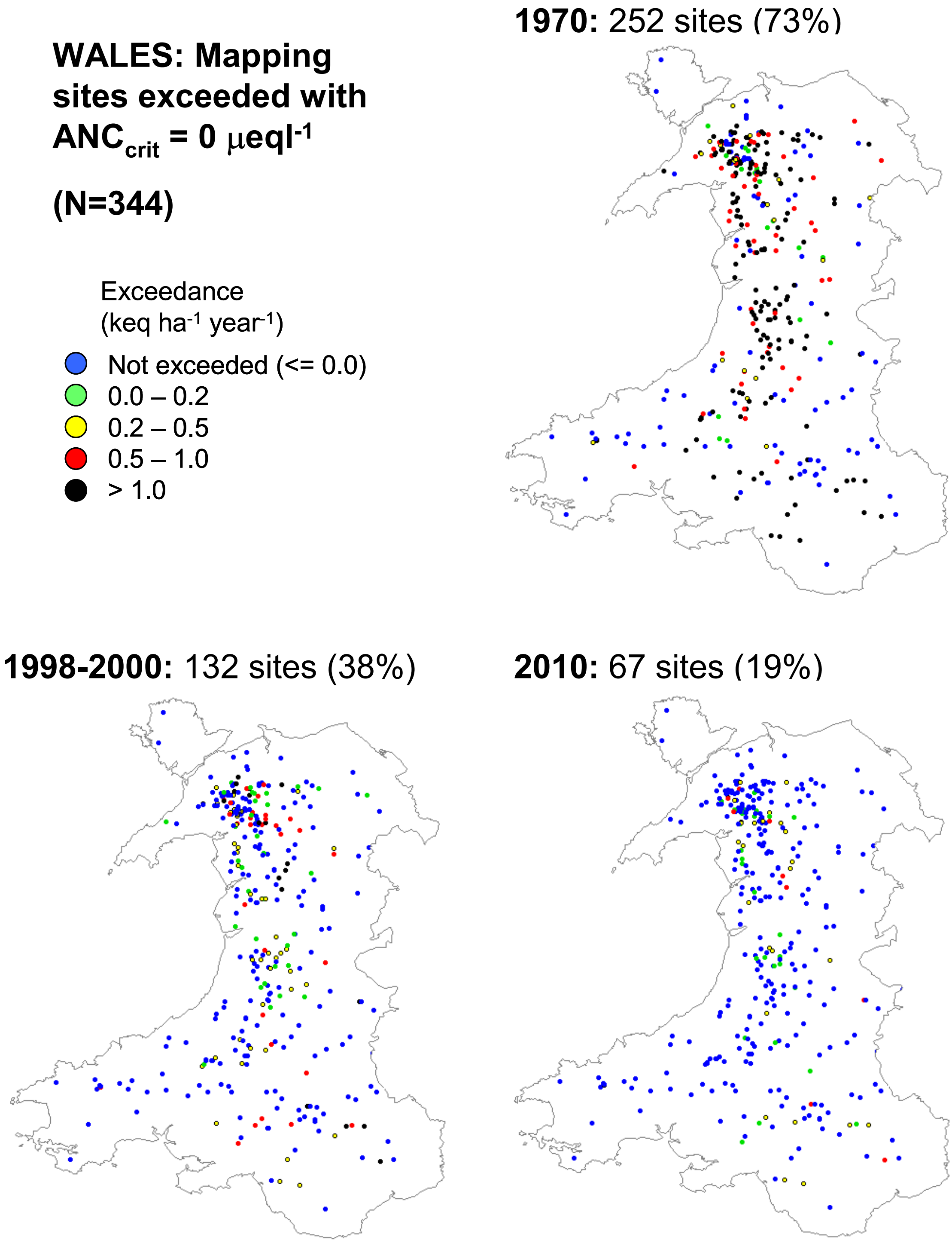
Source: CEH Monks Wood

Figure 2.1.4: Critical load exceedances for Scottish sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 0 μeql^{-1}



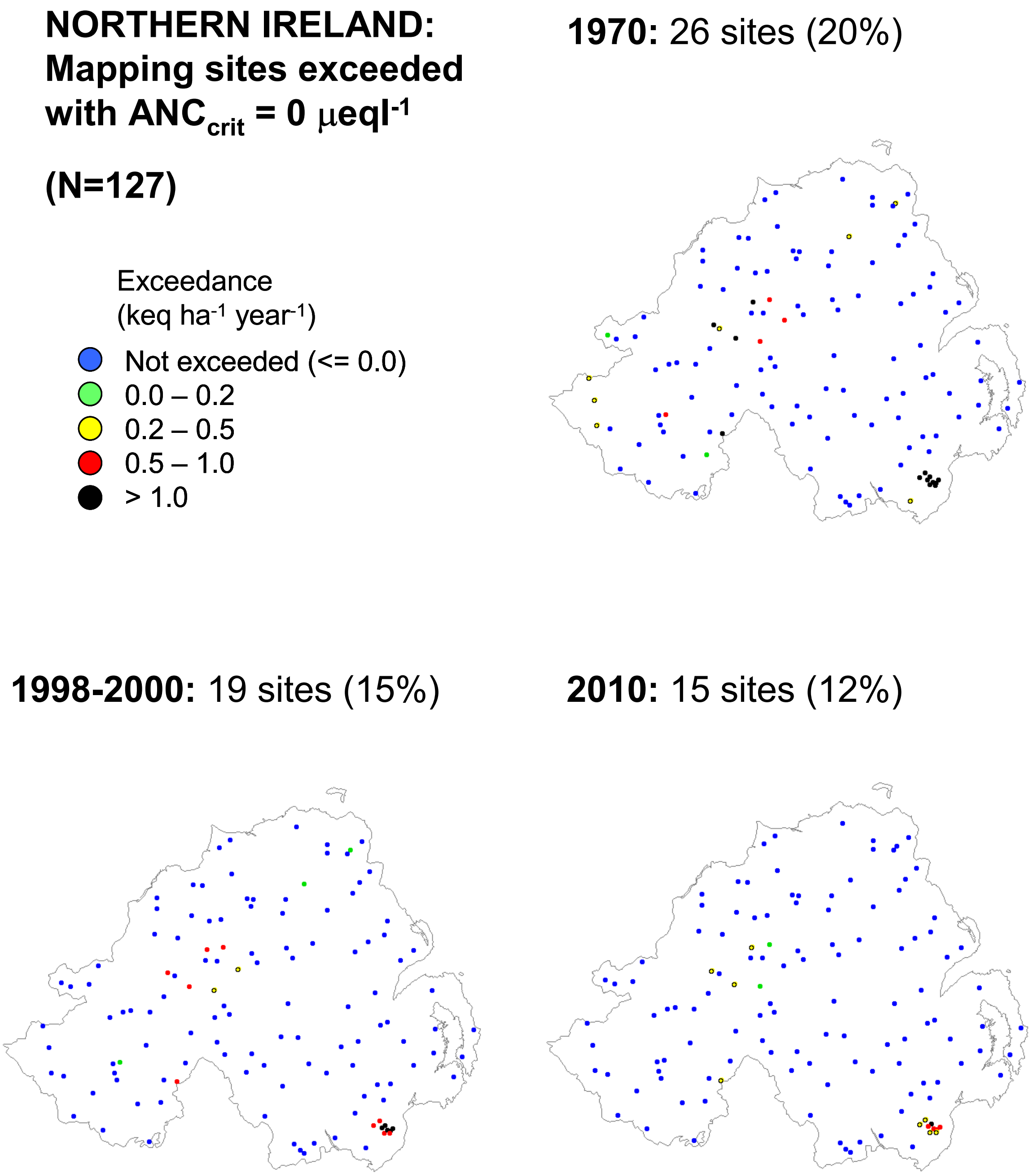
Source: CEH Monks Wood

Figure 2.1.5: Critical load exceedances for Welsh sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 0 μeql^{-1}



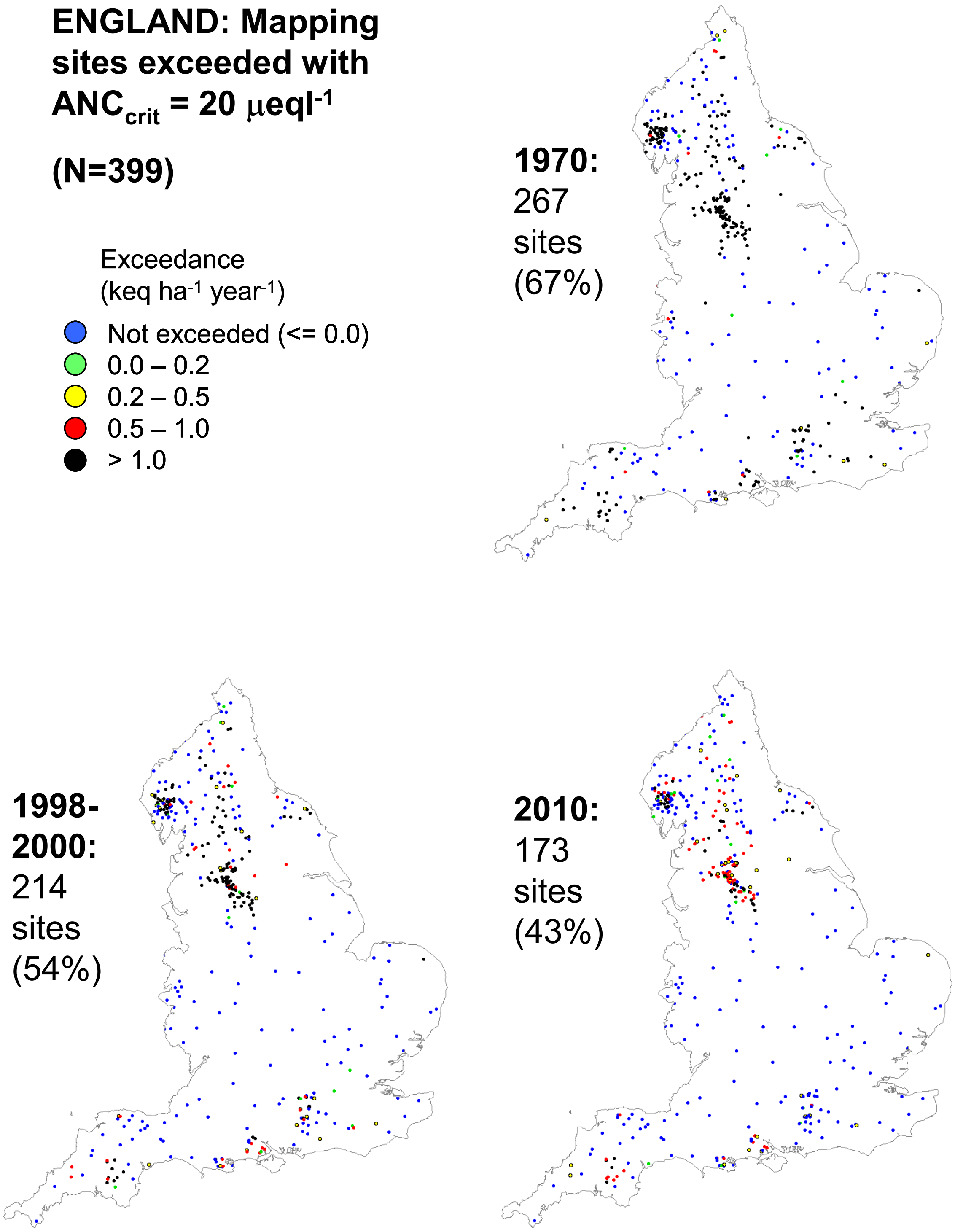
Source: CEH Monks Wood

Figure 2.1.6: Critical load exceedances for Northern Irish sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 0 μeql^{-1}



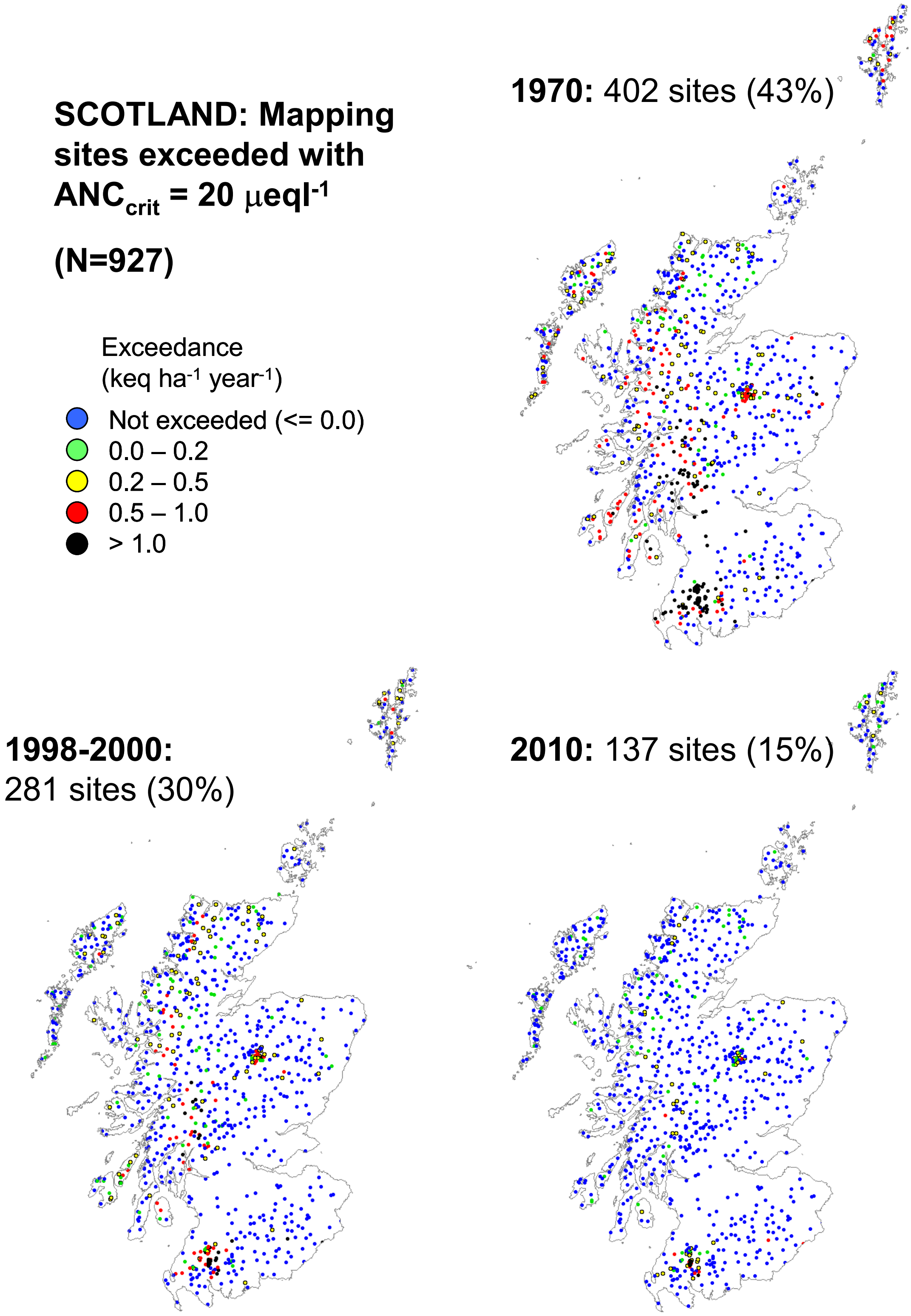
Source: CEH Monks Wood

Figure 2.1.7: Critical load exceedances for English sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 20 μeql^{-1}



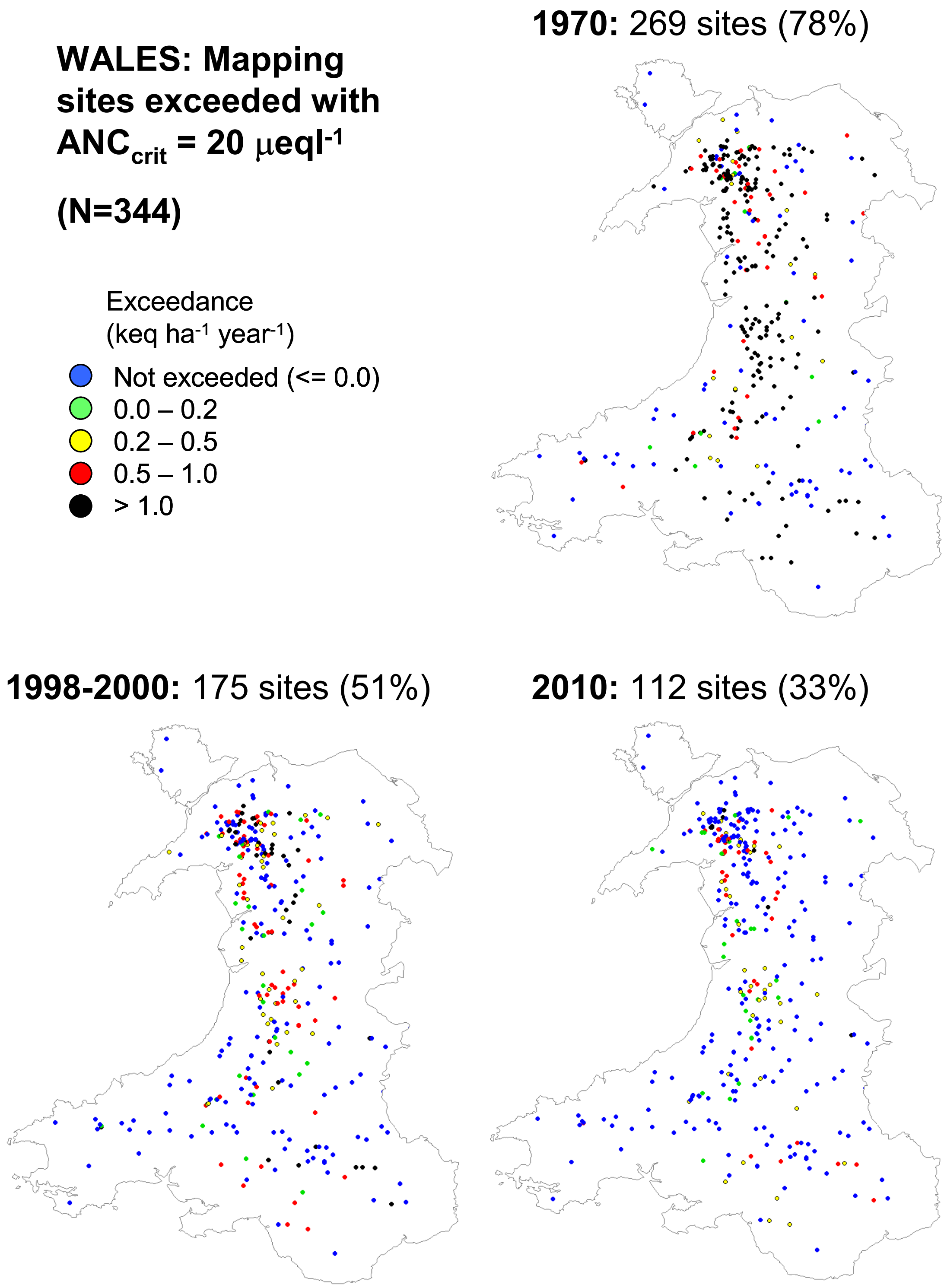
Source: CEH Monks Wood

Figure 2.1.8: Critical load exceedances for Scottish sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 20 μeql^{-1}



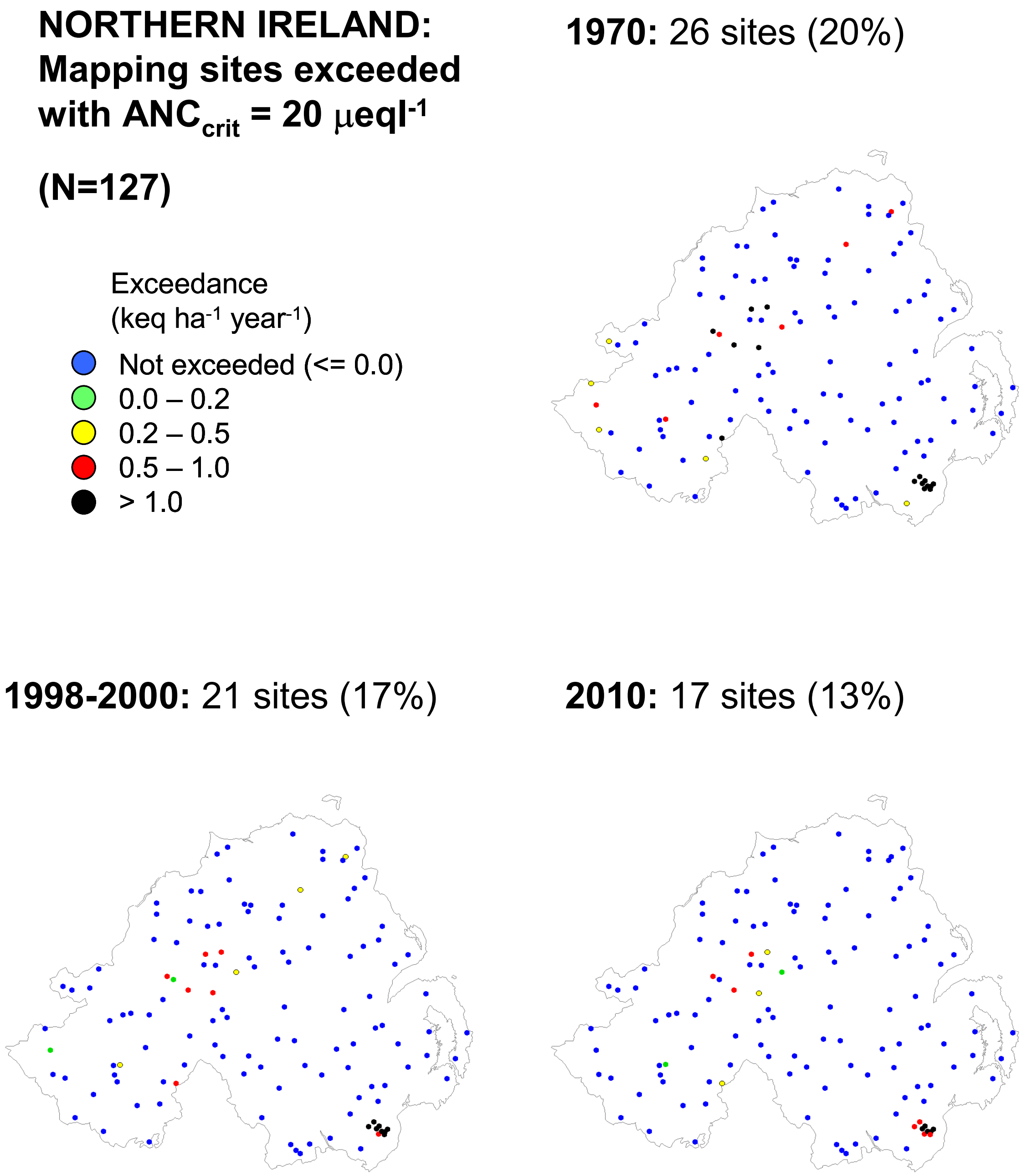
Source: CEH Monks Wood

Figure 2.1.9: Critical load exceedances for Welsh sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 20 μeql^{-1}



Source: CEH Monks Wood

Figure 2.1.10: Critical load exceedances for Northern Irish sites in 1970, 1998-2000 and 2010 (NECD) with fixed ANC_{crit} of 20 μeql^{-1}



Source: CEH Monks Wood

Table 2.1.7a: Critical load exceedance for ANC_{crit} = 0 μeql^{-1}

	Sites	1970	%	1998-00	%	2010	%
England	399	260	65	200	50	160	40
Scotland	927	322	35	174	19	47	5
Wales	344	252	73	132	38	67	19
N.Ireland	127	26	20	19	15	15	12
UK	**1797**	**860**	**48**	**525**	**29**	**289**	**16**

Table 2.1.7b: Critical load exceedance for ANC_{crit} = 20 μeql^{-1}

	Sites	1970	%	1998-00	%	2010	%
England	399	267	67	214	54	173	43
Scotland	927	402	43	281	30	137	15
Wales	344	269	78	175	51	112	33
N.Ireland	127	26	20	21	17	17	13
UK	**1797**	**964**	**54**	**691**	**38**	**439**	**24**

Table 2.1.7c: Critical load exceedance for ANC_{crit} = 40 μeql^{-1}

	Sites	1970	%	1998-00	%	2010	%
England	399	270	68	222	56	186	47
Scotland	927	461	50	356	38	251	27
Wales	344	279	81	212	62	156	45
N.Ireland	127	28	22	23	18	20	16
UK	**1797**	**1038**	**58**	**813**	**45**	**613**	**34**

Scotland, like Wales, has a broad spatial distribution of sensitive sites but deposition levels are generally much lower so that only a small proportion of sites at the regional scale are affected. Northern Ireland has an even more localised distribution of sensitive sites than England, which are again extremely sensitive and located in high deposition areas so that they are exceeded whatever value of ANC_{crit} is used.

Results II: FAB model application to new mapping dataset with variable ANC_{crit}, using most recent deposition data

In the first results section, exceedance statistics and maps were provided for three fixed ANC_{crit} values (0, 20 and 40 μeql^{-1}). However, the DEFRA Workshop (Job 1.2.3) recommended a variable ANC_{crit} with a value of 20 μeql^{-1} except where palaeolimnological or dynamic modelling data suggested a lower pre-industrial value on a site-specific basis, in which case 0 μeql^{-1} was used. By the time of the April 2004 submission to CCE, 75 further sites had been removed from the mapping datasets on the basis of a new seasalt screening criterion (see above) and revised deposition figures for 1995-97, 1998-2000 and 2010 had been generated by CEH Edinburgh. The effects of these revisions on national scale exceedance figures are shown in Table 2.1.8 and Figure 2.1.11. Details of ANC_{crit} values used were provided in Table 2.1.5.

Table 2.1.8: Critical loads exceedance figures by country for the UK using original and revised deposition datasets

Scenario	Site exceedance statistics by country and for the UK (and percentage of total sites by country and UK)				
	England	Wales	Scotland	NI	UK
1995-1997 (original)	231 (58.5%)	227 (66.0%)	291 (34.0%)	28 (22.0%)	777 (45.1%)
1995-1997 (vMar04)	232 (58.7%)	225 (65.4%)	308 (36.0%)	26 (20.5%)	791 (45.9%)
1998-2000 (vMar04)	208 (52.7%)	184 (53.5%)	247 (28.9%)	21 (16.5%)	660 (38.3%)
1999-2001 (vMar04)	208 (52.7%)	176 (51.2%)	244 (28.5%)	20 (15.7%)	648 (37.6%)
2010 (vApr04)	186 (47.1%)	135 (39.2%)	182 (21.3%)	18 (14.2%)	521 (30.3%)

All sites with ANC_{crit} = 0 μeql^{-1} are exceeded for all deposition scenarios except for Scotland, where in 2010 only 13/15 are exceeded. It can be seen that the revision of the 1995-97 deposition dataset had very minor effects on the overall proportion of exceeded sites, although numbers increased slightly for the UK as a whole. For 1998-2000 deposition, similarly small changes in exceedance occurred with the revised deposition figures (cf. Table 2.1.7b). Changes were, however, more significant for 2010 exceedance figures, with the number of exceeded sites increasing by 82 (from 24 to 30%) from the previous dataset using the old deposition figures and ANC_{crit} = 20 μeql^{-1}.

In the dataset submitted to CCE the proportion of exceeded sites decreases with national deposition patterns from 1995-97 to 1998-2000 and 1999-2001. By 2010, almost a half of mapping sites in England still exceed their critical loads, while for Wales the figure is nearly 40%. Only a fifth of Scottish mapping sites are exceeded and the proportion is even lower for Northern Ireland at 14%. The overall figure of 30% for the UK indicates that while substantial reductions in exceedance will be achieved relative to a 1970 baseline (see above), less than a quarter of sites currently exceeded will be protected following implementation of the NECD. Acidification will still be a major problem in several highly sensitive regions by 2010.

Finally, critical load exceedance statistics with new deposition data in separate mapping subprojects is provided in Table 2.1.9.

References

Henriksen, A. and Posch, M. (2001) Steady-state models for calculating critical loads of acidity for surface waters. *Water, Air and Soil Pollution: Focus* **1**, 375-398.

Posch, M., Kämäri, J., Forsius, M., Henriksen, A. and Wilander, A. (1997) Exceedance of critical loads for lakes in Finland, Norway, and Sweden: reduction requirements for acidifying nitrogen and sulphur deposition. *Environmental Management* **21(2)**, 291-304.

Figure 2.1.11: Critical load exceedances in new 2004 mapping dataset submitted to CCE for new deposition data (www.critloads.ceh.ac.uk)

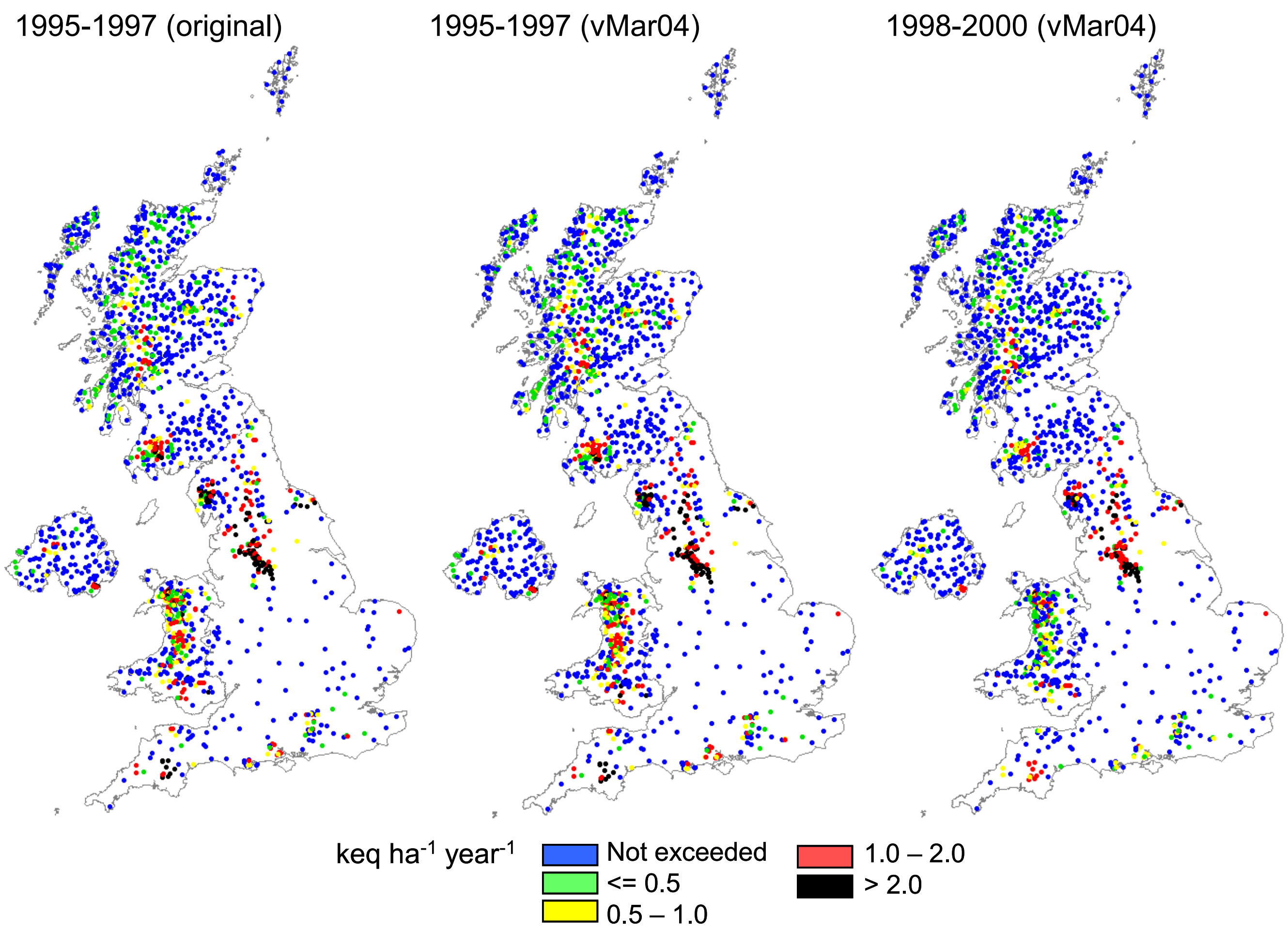


Figure 2.1.11 (continued): Critical load exceedances in new 2004 mapping dataset submitted to CCE for new deposition data (www.critloads.ceh.ac.uk)

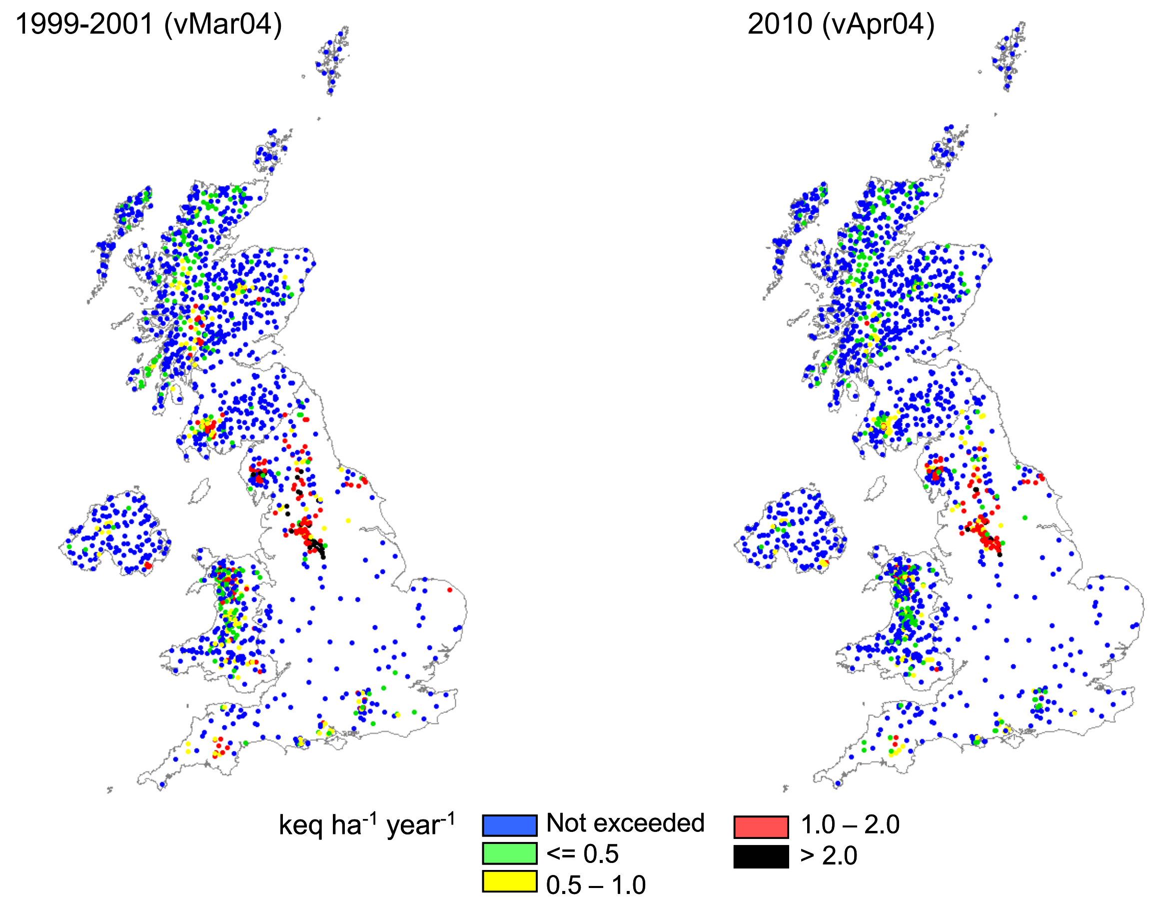


Table 2.1.9: Critical load exceedance by region / subproject for various deposition datasets

Region / Subproject	Total no. sites	Number exceeded				% exceeded			
		1995-97	1998-00	1999-01	2010	1995-97	1998-00	1999-01	2010
Analog	27	18	13	12	7	66.7	48.1	44.4	25.9
AWMN	23	21	18	18	18	91.3	78.3	78.3	78.3
Cairngorms	38	30	27	28	24	78.9	71.1	73.7	63.2
Galloway 1998/GANE	61	52	45	45	36	85.2	73.8	73.8	59.0
Lake District	52	43	33	32	29	82.7	63.5	61.5	55.8
GANE Snowdonia	25	24	24	24	21	96.0	96.0	96.0	84.0
Seasalts	15	6	5	5	4	40.0	33.3	33.3	26.7
Conservation	29	8	6	6	5	27.6	20.7	20.7	17.2
FAB Mapping GB	971	387	325	322	256	39.9	33.5	33.2	26.4
MK Snowdonia	75	55	48	47	37	73.3	64.0	62.7	49.3
Mournes	8	8	8	8	8	100.0	100.0	100.0	100.0
NI 2000	119	19	14	13	11	16.0	11.8	10.9	9.2
CLAG Nitrogen network	13	7	5	3	3	53.8	38.5	23.1	23.1
Pennines	64	64	63	63	60	100.0	98.4	98.4	93.8
Scottish Random Survey	129	14	8	6	3	10.9	6.2	4.7	2.3
Southern	35	24	21	21	19	68.6	60.0	60.0	54.3
Trossachs	32	14	10	10	7	43.8	31.3	31.3	21.9
WAWS Lakes	16	15	12	8	7	93.8	75.0	50.0	43.8
WAWS Streams	102	78	64	61	42	76.5	62.7	59.8	41.2
Welsh Random Survey	49	26	17	18	14	53.1	34.7	36.7	28.6
TOTAL	**1883**	**913**	**766**	**750**	**611**	**48.5**	**40.7**	**39.8**	**32.4**

Conservation sites

Of the 29 conservation sites sampled under this programme, a maximum of 10 exceeded their critical loads in 1970 (Table 2.1.6). This figure declined to 8 by 1995-97 and 6 at present (1999-2001 deposition: Table 2.1.9). No further sites are protected by emissions reductions up to 2010; the same 6 sites still show critical load exceedance (Table 2.1.10).

Table 2.1.10: Conservation sites exceeding critical loads in 2010

Sitecode	Name	Country	SAC Name	Exceedance (keq ha^{-1} yr^{-1})
CONV5	(un-named)	ENG	The New Forest	0.94
CRAN	Cranmer Pond	ENG	Woolmer Forest	0.66
NARR	Loch Narroch	SCO	Merrick Kells	1.63
CONV16	Llyn Morwynion	WAL	Rhinog	0.76
CONV3	Llyn Cerrigllwydion Uchaf	WAL	Elenydd	0.38
CZSH71	Llyn y Gadair	WAL	Cadair Idris	0.61

If it is assumed that the 29 lakes sampled in SACs for this project are representative of the lakes within each SAC, then over 20% (6/29) of freshwater designated SACs are still exceeding critical loads by 2010. Hence the emissions reductions required under the NECD are insufficient to protect freshwater SACs in the UK.

Job 6: Regional case study – high resolution analysis of sediment cores

Introduction

Palaeolimnological studies (e.g. Charles and Whitehead 1986; Battarbee and Renberg 1990) have proved conclusively that acid deposition has resulted in the widespread acidification of surface waters. The timing of acidification in lakes has always occurred after the onset of the Industrial Revolution and the record of carbonaceous particle deposition in lake sediments clearly demonstrates atmospheric contamination from industrial sources in parallel to acidification (Rose et al. 1995; Rose 1996).

Evidence of recovery in sites remote from point source pollution was described at the Round Loch of Glenhead (Battarbee *et al.* 1988; Allott et al 1992). In sediment cores with high sediment accumulation rates recent changes in the diatom flora of the loch were identified, including an increase in the abundances of several acid sensitive taxa. These studies have indicated that recovery from acidification should happen in lake systems following emissions reductions, though detecting this may be more difficult in sites remote from point-source emissions.

Monitoring data from the UK AWMN demonstrate that whilst some sites on the network are showing signs of chemical recovery, other sites show little or no signs of recovery and some sites are still acidifying (Monteith and Evans 2000). It is not clear what the underlying causes of these inconsistencies are, but clearly catchment characteristics of individual sites play a role as do so called “confounding factors” such as climatic fluctuations and changes observed in other hydrochemical properties such as DOC changes.

The sites in the UK AWMN cover a wide geographical region from southern England to north west Scotland. This job aims to investigate whether a number of sites from the same geographical region exhibit similar patterns in pH change in the recent sediment record, and whether there is any evidence for recovery in the sedimentary record.

Much palaeolimnological work has been undertaken in the Galloway region of Southern Scotland (e.g. Flower et al 1987). Long time-series of monitored hydrochemical data also exist for many lakes within the region (Job 2.1.8, this report). As a result of this legacy and availability of data, the Galloway region has been chosen for this study. As part of Task 1.1 a number of sites from the Galloway region were cored for use in determining palaeolimnological reference conditions. Five of these sites were selected for use in this job and sites were analysed for diatom and zooplankton remains to assess signs of biological recovery or recent change within lakes in the Galloway region.

Methods

Study sites

Of the sites cored as part of Task 1.1, five were selected for high resolution analysis of the uppermost sediment slices to investigate recovery from acidification within the Galloway region. The sites and associated summary information are displayed in Table 2.1.11.

Laboratory analyses

Sediment cores from the five study sites were taken from the deepest part of the lake basin and were subsequently sliced at fine intervals (2mm). The uppermost 1 or 2 centimetres of sediment in these cores represents the most recent period of lake history. Samples within the uppermost 2 centimetres were selected for analysis in this job. The samples were then prepared for diatom and zooplankton analysis and mounted on microscope slides using standard methods (Batterbee et al 2001, Korhola and Rautio 2001). At least 300 diatom valves were counted in each sample using a Leitz research microscope with a x100 oil immersion objective and phase contrast. Diatom taxonomy and nomencalture principally follows Krammer and Lange-Bertalot (1986-1991).

The Cladocera samples were prepared using the standard deflocculation of 1 cubic centimetre of sediment in 100 ml hot potassium hydroxide (KOH) with gentle manual agitation for approximately 30 minutes. Following deflocculation, the solution containing the cladoceran remains was passed over a 33 µm sieve. The residue on the sieve was wash under a gentle flow of water to remove as much of the fine inorganic matter as possible.

The residue collected on the sieve was transferred to a 10 ml container. This was allowed to settle out overnight and the supernatant was pipetted off to remove as much water as possible. The samples were then stored in methanol with a few drops of safranin stain. Known amounts of a sample were plated onto six cover slips and mounted on slides using a small amount of glycerol jelly.

All cladoceran remains on a slide were enumerated. Slides were counted until at least 200 remains had been found. Exuviae were identified using the standard texts, including Frey (1959; 1960; 1962a; 1962b; 1965), Goulden and Frey (1963) and Alonso (1996). Taxonomy follows that of Flößner (1972).

The diatom and zooplankton data were expressed as percentage relative abundances in the subsequent numerical analysis.

Numerical Analysis

The Surface Waters Acidification Project (SWAP) Palaeolimnology Programme diatom pH transfer function (Stevenson et al 1991) model was used to estimate lake water pH from the diatoms species abundance data enumerated from the sediment samples (Birks et al 1990). A one component weighted-average partial least squares (WA-PLS; Ter Braak and Juggins 1993) model derived from the SWAP modern training set was used to reconstruct pH for each sample in each sediment core. The WA-PLS model was then applied to the sediment samples in each core. Estimates of the prediction error were derived using boostrap resampling techniques with 999 permutations. The diatom-pH transfer functions were applied using the C^2 software of Juggins (2003).

Results

Figures 2.1.12 – 2.1.16 show stratigraphic plots for each of the five sites studied. The y-axis illustrates depth from the top of the core, with the top of the core containing the most recent sediments. The x-axis for species variables is in percentage abundance units. A separate graph unit is displayed for each separate species. Only those taxa that occur at abundances greater than 5% of the total diatom community are displayed in these diagrams. On the right of each plot, the diatom inferred pH derived from the diatom community composition and the application of the SWAP transfer function model is shown.

Of the five study sites, only Loch Narroch exhibits a continuing decrease in pH over the period of time spanned by the uppermost 2 cm of the sediment core (Figure 2.1.12), with diatom inferred pH declining from 4.85 to 4.65 over the period. This change is well within the prediction error of the SWAP model (RMSEP +/- 0.35 pH units), but the consistent trend in the results is indicative of a reduction in pH. The decreasing pH is driven by the increase in the acidobiontic diatom taxon *Tabellaria binalis* from 10% abundance in the lowermost sample to 30% at the top of the core. *T. binalis* has a pH optima of 4.7 in the SWAP training set and is particularly common in very acid lakes.

The remaining 4 lakes (Loch Enoch, Long Loch of Glenhead, the Round Loch of the Dungeon and the Round Loch of Glenhead) all show similar patterns of fluctuating pH to one another in the uppermost sedimentary samples. Again, the magnitude of the fluctuations (of the order of 0.1 pH units) are well within the prediction error of the transfer function model and so must be interpreted with care, but little overall change in pH appears to have taken place in any of the lakes, with the possible exception of the Round Loch of the Dungeon (Figure 2.1.14), where pH is predicted to have increased from pH 4.95 to 5.1 in the present day.

Tabellaria quadriseptata and *Eunotia incisa* are the dominant taxa in these lakes and both are indicative of acid conditions. It is the fluctuations in the percentage abundances of these two taxa and other acid tolerant taxa, such as *Frustulia rhomboides* var. *saxonica* and *Navicula hoefleri* that appear to be important in determining the fluctuations in the diatom inferred pH.

The results of the analysis of the sedimentary zooplankton remains showed that no discernible changes in community structure were found in any of the five sites studied as part of this work. This is not totally unexpected given the results of the diatom data, which showed only minor changes in pH, and that chydorid zooplankton common in acid upland lakes are not particularly sensitive to minor changes in lake water acidity (c.f. Simpson 2004). As such the zookplankton data are not considered further in this report.

Discussion

Of the five studied sites, four sites (Loch Enoch, Long Loch of Glenhead, the Round Loch of the Dungeon and the Round Loch of Glenhead) showed similar responses in terms of their diatom communities. None of the sites showed a clear recovery, with only the Round Loch of the Dungeon showing an increase in pH in the samples analysed as part of this study. Loch Narroch appears to have acidified further in recent years.

These results are in stark contrast to the consistent hydrochemical recovery of lakes in the Galloway region reported under Job 2.1.8, a study which incorporates four of the five sites included in this study (the Round Loch of the Dungeon is not routinely sampled in the Galloway cluster). pH has been increasing in these lakes since the 1980's (Figure 2.1.17) yet this regional improvement in hydrochemical conditions is not reflected in the sedimentary diatom assemblages presented in this report.

It is difficult to account for this inconsistency in the response of the diatoms and the increase in the measured pH at sites in the Galloway region. Diatoms have been shown to respond rapidly to changes in lake water pH and long term trends in pH are faithfully reflected in sediment records of lakes (e.g. Cameron 19958, Dixit et al 1992). Allott et al (1992) demonstrated that in rapidly accumulating cores within the Round Loch of Glenhead that slight recovery could be seen in the diatom assemblages of recent sediment samples. This recovery is not apparent in the core analysed in this study.

It is possible that mixing of the uppermost sediments through bioturbation or potential re-suspension of older material from marginal sources may be smoothing the diatom response illustrated in the sediment cores shown in Figures 2.1.12 – 2.1.16.

Conclusions

The work presented demonstrates that four of the five study sites appear to show consistent fluctuations in diatom inferred pH suggesting that the diatoms are responding to some regional forcing factor. None of the studied sites has seen a significant increase in pH over the period studied and that this is inconsistent with the measured hydrochemistry, which shows a consistent and significant increase in pH since the early 1980s.

Further work is required to understand the reasons for the discrepancy between the measured pH recovery and the lack of response shown in the diatom sediment samples. The effect of climatic fluctuations associated with, for example, the North Atlantic Oscillation, and the observed increases in dissolved organic carbon (See Job 2.1.8 and Figure 2.1.18) may all act to mask diatom recovery and untangling these effects will require a greater understanding of diatom ecology and responses to these other forcing factors.

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Table 2.1.11 – List of sites sampled as part of Job 2.1.6 and summary information. WBID = the lake Water Body ID identifier as recorded in the GB Lakes Inventory.

Code	WBID	Name	Grid Reference	Altitude
NARR	27192	Loch Narroch	NX452815	328
RLDN	27824	Round Loch of the Dungeon	NX466847	277
RLGH	27927	Round Loch of Glenhead	NX449803	298
ENO	27808	Loch Enoch	NX445851	498
LLGH	27922	Long Loch of Glenhead	NX445808	298

Figure 2.1.12: Summary diatom stratigraphy diagram for Loch Narroch. Only species whose minimum abundance was 5% or more in any single sample are displayed. Diatom inferred pH is also illustrated. Units for the species graphs are percentage abundance in the sample.

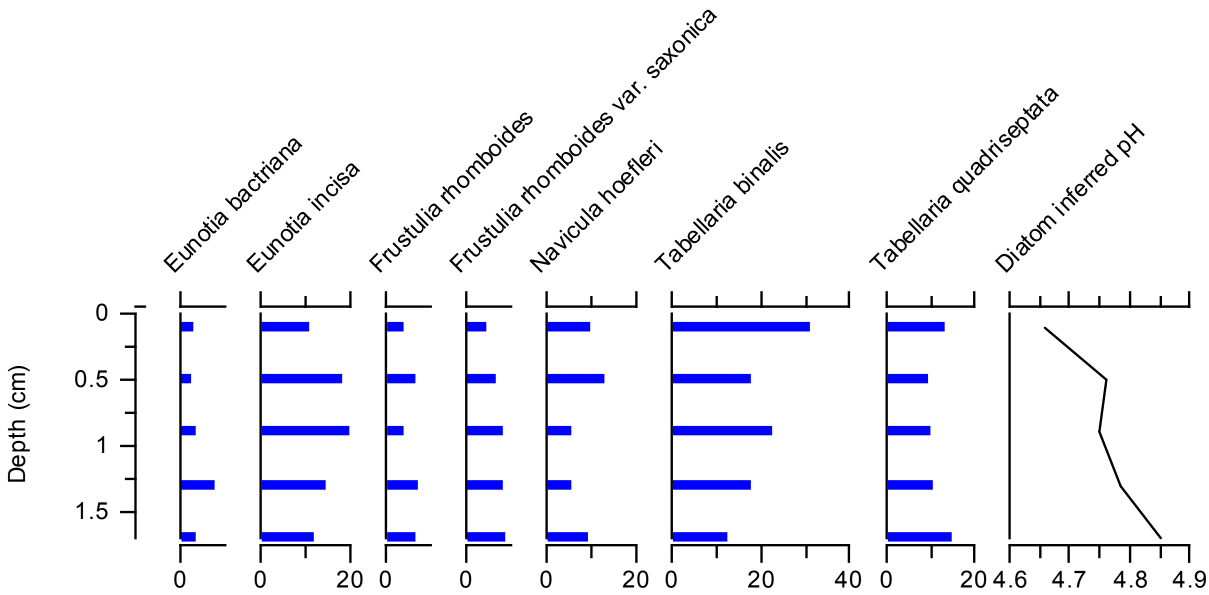


Figure 2.1.13: Summary diatom stratigraphy diagram for Loch Enoch. Only species whose minimum abundance was 5% or more in any single sample are displayed. Diatom inferred pH is also illustrated. Units for the species graphs are percentage abundance in the sample.

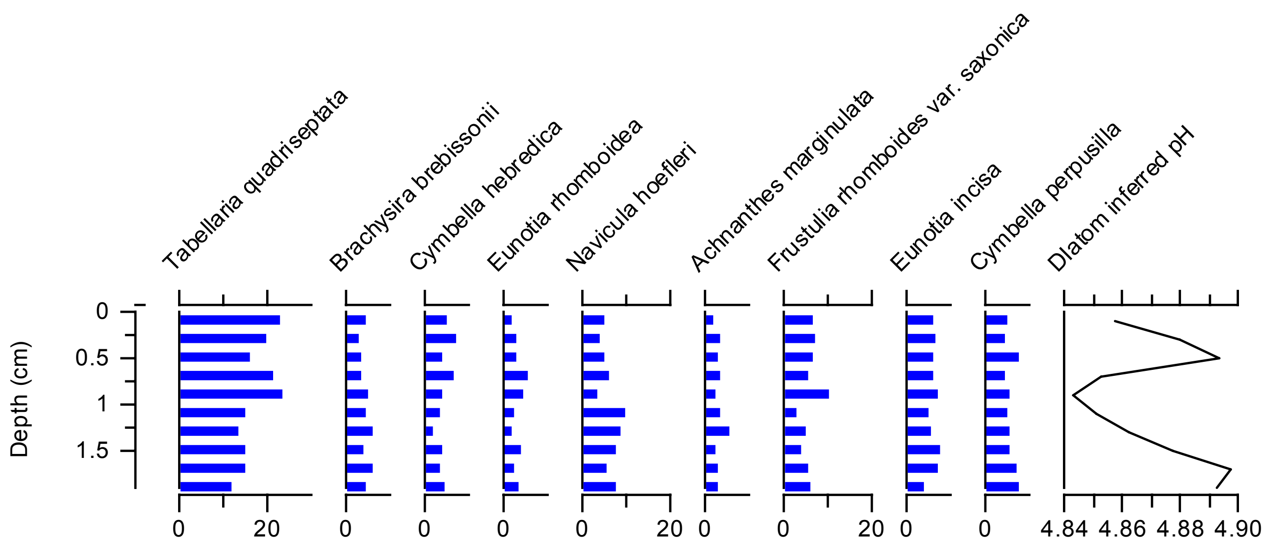


Figure 2.1.14: Summary diatom stratigraphy diagram for the Long Loch of Glenhead. Only species whose minimum abundance was 5% or more in any single sample are displayed. Diatom inferred pH is also illustrated. Units for the species graphs are percentage abundance in the sample.

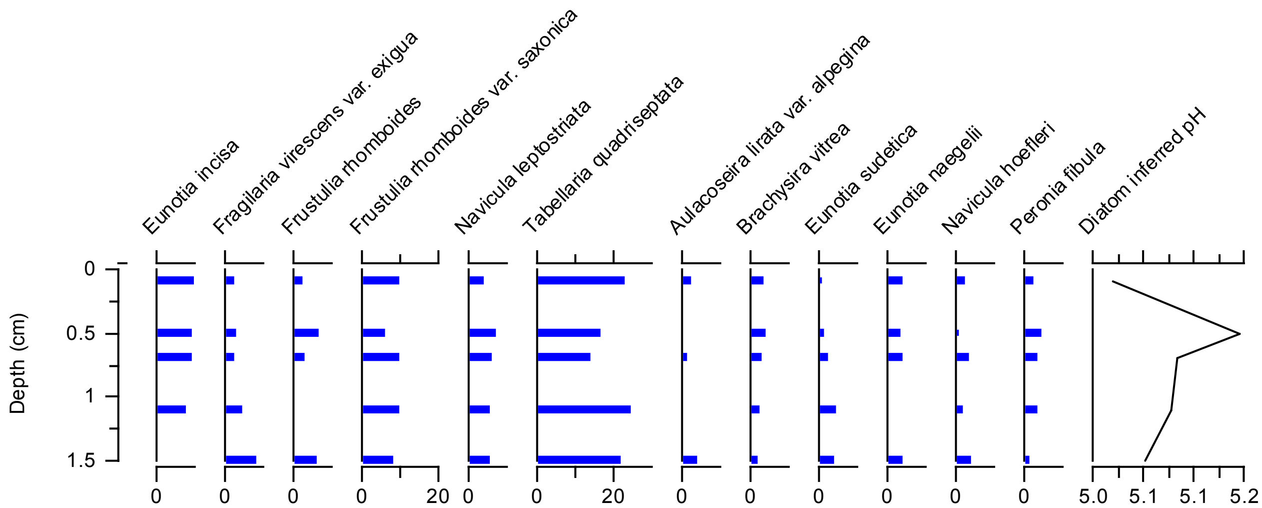


Figure 2.1.15: Summary diatom stratigraphy diagram for the Round Loch of the Dungeon. Only species whose minimum abundance was 5% or more in any single sample are displayed. Diatom inferred pH is also illustrated. Units for the species graphs are percentage abundance in the sample.

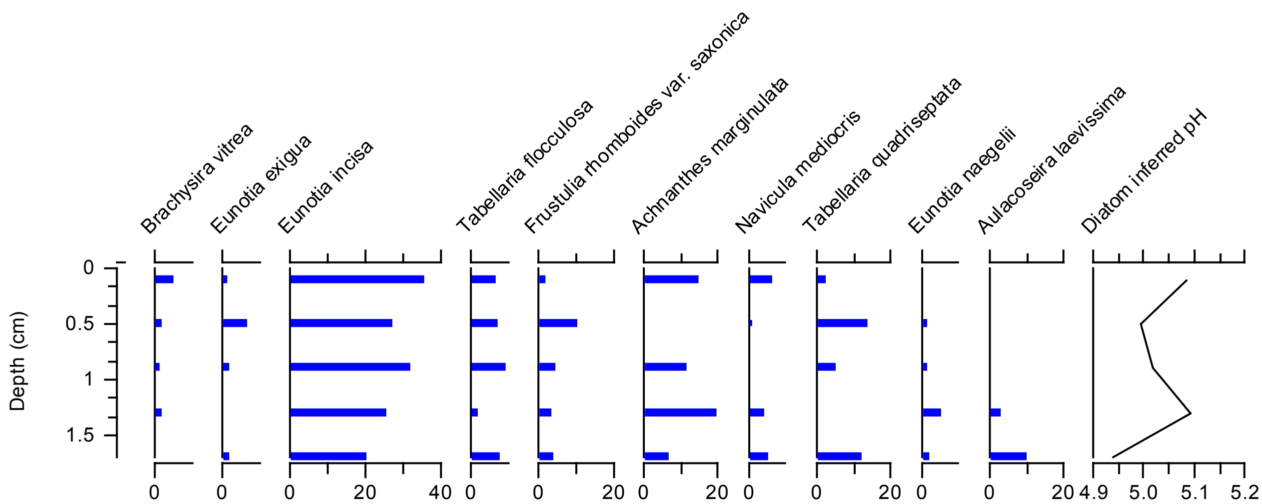
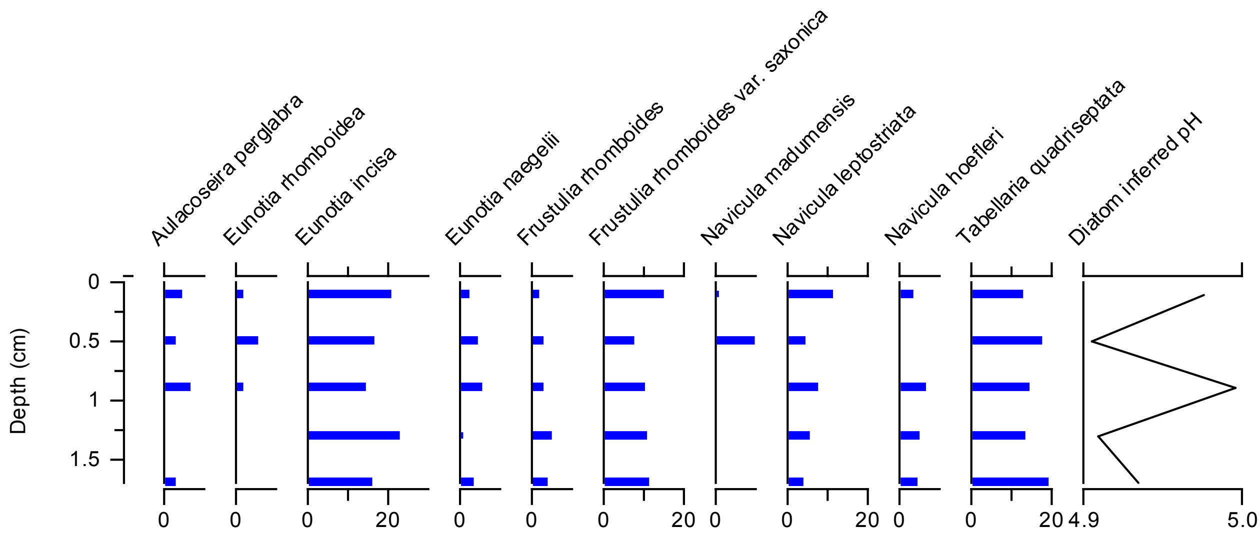


Figure 2.1.16: Summary diatom stratigraphy diagram for the Round Loch of Glenhead. Only species whose minimum abundance was 5% or more in any single sample are displayed. Diatom inferred pH is also illustrated. Units for the species graphs are percentage abundance in the sample.



Job 7: Assess acidification in a subset of conservation sites (from Job 5 above)

Introduction

The work present in this section follows on naturally from the results of Job 2.1.5. Of the 29 sites in SACs sampled for hydrochemistry in Job 2.1.5, ten of sites were also cored for palaeolimnological analysis. The aim of this small study was to ascertain whether biological change had taken place at each of these ten SAC sites by using the so-called top-bottom approach. In the top-bottom approach, the surface sample from a sediment core and a sample chosen to represent pre-disturbance conditions are prepared for palaeolimnological analysis using standard methods. The amount of biological change indicated from the fossil records of the two samples is then calculated using a suitable dissimilarity coefficient, such as the chord distance (Overpeck et al 1985, Gavin et al 2003, Wahl, 2004). This re-expresses the multivariate species data into a measure of species change over time between the reference sample (core bottom) and the surface sample (core top).

The advantage of the top-bottom approach is that it is relatively quick and cheap to implement compared to standard palaeolimnological methods where greater numbers of samples are analysed to provide a more complete history of species change. As such the approach can be applied in regional studies such as this one where the aim is to generate a snapshot of change over a wide geographical range or at a large number of sites.

Methods

Study Sites

Ten of the original 29 conservation sites that were sampled for hydrochemistry in Job 2.1.5 were selected for sediment coring. The ten sites were selected to cover as wide a geographical and hydrochemical range as possible from the original list of 29 sites. The following sites were selected for analysis: CZNN27, CZNG96, CONV8, CONV3, CONV21, CONV19, CONV16, CONV15, and CEHL46 (See Table 2.1.2 for more details). CONV5 was originally selected for coring but was found to unsuitable during the fieldwork campaign. Little Sea Mere (LITT, WBID = 46102, Grid ref SZ 029846) was subsequently selected as a replacement site, located in the Dorset Heaths (Purbeck & Wareham) & Studland Dunes SAC.

As an additional exercise, Amphora, the Environmental Change Research Centre's (ECRC) diatom database was queried to produce a list of all lake sites in the UK for which diatom core top and bottom data were available. This list of sites was then used to query against the GB Lakes Inventory (Hughes et al 2003) database to select only those lakes that were designated as part of a SAC and which were also classified as belonging to freshwater sensitivity classes 1-3. This resulted in an additional list of 32 sites for which the chord distances could be calculated, bringing the total number of sites analysed as part of this job to 42. Summary site details for the 32 additional sites are presented in Table 2.1.12.

Diatom analysis

Sediment cores from the main ten study sites were sliced at fine intervals (2mm) in the field. The surface sample (the uppermost 2mm slice in the core) and a sample from 20cm core depth were used as the top and bottom samples respectively (the bottom sample from LITT was located at a depth of 10cm because of prior knowledge of the palaeolimnology of this site). The samples were then prepared for diatom analysis and mounted on microscope slides using standard methods (Batterbee et al 2001). At least 300 valves were counted in each sample using a Leitz research microscope with a x100 oil immersion objective and phase contrast. Diatom taxonomy and nomencalture principally follows Krammer and Lange-Bertalot (1986-1991). The diatom data were expressed as percentage relative abundances in the subsequent numerical analysis.

Numerical Methods

The degree of similarity (or dissimilarity) in the diatom communities between the top and bottom sample from each of the 42 study sites was then calculated using the chord distance (CD) (Overpeck et al 1985, Gavin et al 2003, Wahl, 2004):

$$d_{ij}=\sqrt{\sum_{k=1}^{m}\left(y_{ik}^{0.5}-y_{jk}^{0.5}\right)^2}$$

where the CD between the i^{th} and j^{th} samples (d_{ij}) is the square root of the sum of the differences between the square root of the proportion of taxon *k* in samples *i* and *j*.

Results

Figure 2.1.17 shows the results of the core top bottom analysis for the ten newly cored sites, and Figure 2.1.18 shows similar results for the 32 sites we have existing data for. These figures illustrate the differences in the diatom species compositions of the top and bottom samples for each lake. The units on the axes are the CD between the top and bottom samples. Values for the CD range from 0, where the two samples are perfectly identical and 2 where sites are perfectly dissimilar (i.e. they have no species in common). The dashed lines on the plots illustrate certain critical levels of the CD derived from simulated random data. The process used to determine these critical values is identical to that used in the analysis of the modern analogue lakes and the reader is directed to the section on Analogue matching in the Methods for Task 1.1 Jobs 1 and 2 for further information regarding how these critical values are calculated.

The two lines at 0.29 and 0.47 are derived from the 1st and the 5th percentiles of the distribution of simulated CD values. The value of 0.47 has been used to determine whether samples from two different lakes are sufficiently similar to one another. Where we are interested in producing a guide as to whether two samples from the same lake are sufficiently similar to one another we should choose a lower critical value for the CD because we no longer need to account for the fact that any two lakes will never be perfectly similar due to natural variation between sites.

Within a site, and especially over such short time scales reflected by the difference in age between core top and bottom samples in this study, we would expect, under circumstances of no or little change, that the CD between the two samples could indeed be zero or be lower than 0.47. The line plotted at 0.29 is indicated as a possible critical value (1st percentile of the simulated CD values), but this allows a fair degree of difference between two samples before we would suggest that change has taken place, and Bennion et al (2004) demonstrate that in a number of low alkalinity sites that have not acidified that the CD between reference or pre-disturbance conditions and the core top sample is around 0.2 and often around 0.1. As such we use a value of less than 0.2 to indicate very minor change of reference conditions, 0.2-0.29 to indicate minor change over reference conditions and 0.29-0.47 to indicate moderate change. Values greater than 0.47 indicate considerable change over reference conditions.

From Figure 2.1.17 we can see that none of the ten newly analysed lakes has a CD between reference conditions and the present day of less than 0.2, indicating that all sites have experienced at least minor changes in diatom community composition. One site (CONV21) has a CD of less than 0.29, which would indicate that only minor change had taken place in the lake. The CDs for LITT, CZNG96 and CONV19 are all lower than 0.47, which would suggest that in these sites moderate changes in diatom community composition have taken place. The CDs for the remaining six sites all exceed the 0.47 critical value, which indicates that substantial change in the diatom communities of these samples has taken place. CONV8 is perhaps a borderline site where the change in the diatom assemblage between reference and present day conditions could be taken to be moderate, in the same class as LITT, CZNG96 and CONV19.

In the six sites where substantial change is observed, the change is associated with increases in the percentage abundance of acid tolerant diatom species such as *Tabellaria quadriseptata*, *Tabellaria binals*, *Eunotia incisa* and *Frustulia rhomboides*, at the expense of taxa assocated with more circumneutral conditions, such as *Achnanthes minutissima* and planktonic *Cyclotella* species. These results suggest that these sites have acidified during the period between reference conditions and the present day, although it is not possible to state with certainty that these sites have been impacted by acid deposition without further, more detailed palaeolimnological analysis of sediment samples throughout the core profile.

Of the six sites that are suggested to still be exceeding their critical load in 2020, CONV3 and CONV16 are included in this study and these two sites have seen the greatest change in the diatom community over reference conditions of the ten sites for which the core top-bottom approach has been applied.

Figure 2.1.18 illustrates the results of the chord distance analysis on the additional 32 sites for which data already existed. The dashed lines reflect the same critical values as described above. Two of these 32 sites have experienced very minor change over reference conditions (SAID and MARE), with FHIO being borderline between very minor and minor change. The remaining 29 sites have all experienced at least moderate change over reference conditions (9 sites) with many sites experiencing substantial changes in diatom community composition over time (20 sites).

Conclusions

The results of the core top-bottom analysis has shown that many acid sensitive lakes in designated SCAs have experienced substantial change in their diatom communities over reference conditions. These results indicate that 62 % (26 out of 42 sites) of sites in SACS have undergone substantial change, with a further 28% (12 out of 42 sites) having undergone moderate change. Only 10% of the study sites illustrate only minor or very minor change in their diatom communities over reference conditions. It is not possible to make direct inferences on the total population of sites in SACS regarding the extent and magnitude of biological change based on these results because the initial site selection was not randomised. The additional 32 sites taken from the existing data holdings of the ECRC are likely to be biased towards sites that have been affected by acidification as much of the ECRC's work in low alkalinity sites has focused onlooking for the effects of acid deposition. As such these results are perhaps at the pessimistic end of the spectrum of possible results, but they do indicate that a considerable proportion of sites of conservation importance may have been adversely affected by acid deposition and that substantial biological change has taken place.

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Table 2.1.12: Summary site details for the 32 additional sites analysed as part of Job 2.1.7. The WBID field is the Water Body ID for each site from the GB Lakes Inventory

Site Code	WBID	Name	Grid reference
SAID	6759	Loch Coire na Saidhe Duibhe	NC 450360
FHIO	11424	Lochan Fhionnlaidh	NC 191103
MARE	14057	Loch Maree	NG 985675
BHAR	16452	Loch Bharranch	NG 977575
DAVA	21123	Loch Davan	NJ 442007
COR	21160	Loch Coire an Lochan	NH 943004
KINO	21189	Loch Kinord	NO 442995
EINI	21191	Loch Einich	NN 913990
UAI	21265	Lochan Uaine	NO 001981
LAI	22839	Loch Laidon	NN 380542
BUTT	23531	Loch of Butterstone	NO 058449
MARL	23553	Marlee Loch	NO 145443
CRAI	23557	Loch of Craiglush	NO 042444
LOWE	23559	Loch of Lowes	NO 049439
CLUN	23561	Loch of Clunie	NO 115442
ENO	27808	Loch Enoch	NX 446853
RLDN	27824	Round Loch of the Dungeon	NX 466846
NELD	27872	Loch Neldricken	NX 445829
VAL	27900	Loch Valley	NX 445817
NARR	27912	Loch Narroch	NX 453816
RLGH	27927	Round Loch of Glenhead	NX 450804
BASS	28847	Bassenthwaite Lake	NY 214296
WAST	29183	Wast Water	NY 165060
IDWA	33836	Llyn Idwal	SH 645596
CWEL	34002	Llyn Cwellyn	SH 560549
CLAP	35046	Clarepool Moss	SJ 435343
YBI	35439	Llyn y Bi	SH 670265
HIR	36710	Llyn Hir	SN 789675
GYN	38525	Llyn Gynon	SN 800647
CRAN	44464	Cranmer Pond	SU 794324
WOOL	44482	Woolmer Pond	SU 788321
HATC	45652	Hatchet Pond	SU 367016

Figure 2.1.17: Barplot showing the calculated chord distances between top and bottom sediment samples for the main ten sites studied. The dashed lines illustrate various critical values indicative of change. See text for more details.

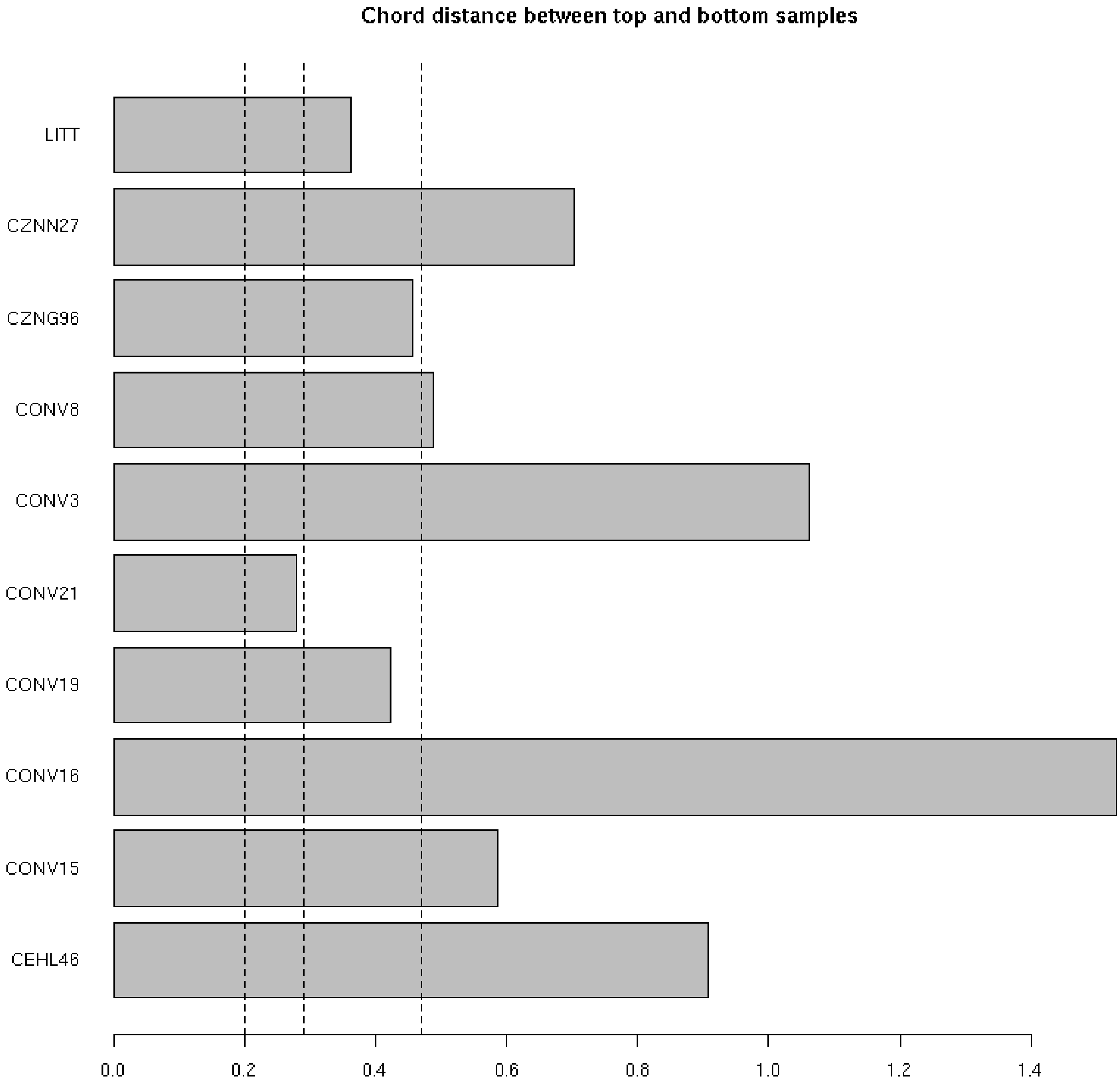
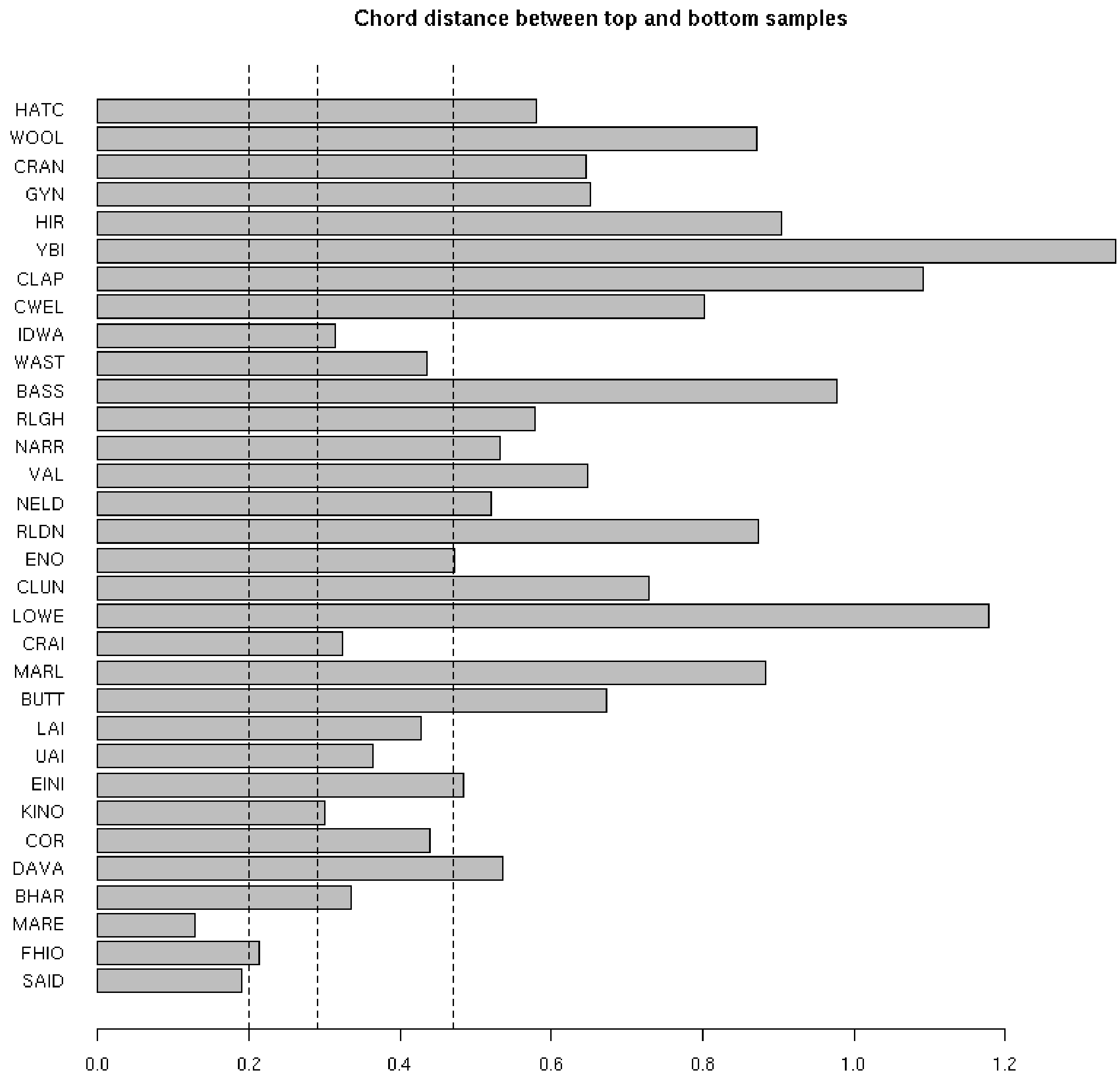


Figure 2.1.18: Barplot showing the calculated chord distances between top and bottom sediment samples for the 32 additional sites studied. . The dashed lines illustrate various critical values indicative of change. See text for more details.



Job 2.1.8 Continue chemical sampling and analysis of sites in the Galloway cluster

Iain A Malcolm, Alistair McCartney & Jill Watson

Introduction

Fisheries Research Services Freshwater Laboratory (FRS FL) has been monitoring water quality and the status of fish populations in the Galloway region since 1978. Particular focus has been placed on 7 high elevation lochs (the Galloway Cluster) where changes in land use and land management activities are unlikely to substantially impact on water quality (Harriman *et al.,* 1995, 2001). Consequently these locations provide a valuable insight into the effects of climate change and changing patterns of atmospheric deposition on surface water quality. Sampling frequency varied substantially in the years preceding 1990. However, post-1990 sampling has been more frequent and regular with a monthly sampling programme supported by successive DOE / DEFRA contracts (CLAG, CLAM, CLAM2) and continued support from SOAFD / SEERAD.

Changes in water quality for lochs in the Galloway region are well documented. Most studies have focussed on improvements in water quality associated with a reduction in atmospheric deposition of non-marine sulphate (Harriman *et al.,* 1987, 1995, 2001). However, other climate change effects such as changing inputs of sea salts and nitrate deposition have also been investigated (Ferrier *et al.,* 2001). There is little value in replicating this information. Consequently, this report will simply focus on updating existing information to include the period of time covered under the CLAM2 contract in order to investigate whether previously reported trends in water quality persist.

Methodology

Sampling and chemical analysis
Water samples were taken infrequently and at irregular intervals between 1978 and 1979. Between 1980 and 1983 there was no sampling carried out at the Galloway high lochs. Irregular sampling resumed in 1984 and carried on until 1989. Between spring 1990 and 2003 sampling took place on the first week of each month. Sampling was interrupted by the occasional month where heavy snow prevented access to sites and a three-month period in 2001 where foot and mouth also prevented access.

Water samples were collected in clean polyethylene bottles and analysed according to standard laboratory procedures as described by Harriman *et al.,* (1987, 1990). ANC was calculated according to the methodology described by Cantrell *et al* (1990).

ANC = Alk2 + (5xDOC)

DOC analysis was conducted by SEPA until May 2003 and by the Macaulay Institute thereafter. Due to technical problems between June and Oct 2003, DOC data during this period were derived from Absorbance 250 data using site specific regression relationships.

Trend analysis
Chemical data were initially inspected visually to determine consistency of response over time. Data were plotted as mean annual values to remove seasonal complexity (Fig. 2.1.19). Data were included for the pre-1990 period although careful interpretation is required due to the infrequent and irregular sampling that places seasonal bias on the data. Particular care is

required for interpretation of the small (Arron and Narroch) and medium (Round Loch of Glenhead, Long Loch of Glenhead) sized lochs. Seasonal variability is less marked for the larger lochs (Enoch, Valley and Neldricken) due to longer turnover times, mixing and moderating effects on seasonal chemistry.

Trends were analysed statistically using the Seasonal Kendall test as described by Harriman *et al* (1990) and McCartney *et al* (2003). The test is non-parametric, can be used despite missing data, removes seasonal cycles and determines rate, direction and significance of trends. Data were firstly analysed for the period 1978-2003 to maximise the length of the dataset and secondly for the period 1990-2003, which corresponds to the period of frequent regular sampling assisted by successive DOE/DEFRA contracts (including CLAM2). For DOC, ANC (which required DOC values) and labile aluminium trend analysis was carried out firstly for the period 1984-2003, which corresponds to the longest available dataset for these determinands and secondly for the period 1990-2003.

Trends 1978-2003

Non-marine sulphate exhibited clear and significant ($P<0.01$) declines since 1978 although concentrations appear to have stabilised since 1999 (Fig. 2.1.19a, Table 2.1.13). Associated with this decline were statistically significant ($P<0.01$) increases in pH, Alkalinity, ANC and DOC, and significant decreases in toxic labile aluminium (Fig. 2.1.19 Table 2.1.13). ANC and DOC appeared to show a stepwise response mirroring that of non-marine sulphate, with increasing gradients post-1994, while pH appears to exhibit a more linear trend over time (Fig. 2.1.19).

Nitrate concentrations exhibited significant increases at Loch Enoch, Long loch of Glenhead ($P<0.05$) and Round Loch of Glenhead ($P<0.01$) although not at other sites (Fig. 2.1.19, Table 2.1.13). Marine derived salt concentrations, (Na, Cl, not shown) exhibited significant ($P<0.05$) downward trends at Round Loch of Glenhead, Loch Narroch, Long Loch of Glenhead and Loch Enoch. Changes to base cations concentrations were generally insignificant and exhibited no consistency among sites.

Trends 1990-2003

Trends for the period 1990 to 2003 (Fig. 2.1.19, Table 2.1.14) generally replicated those found for the period 1978-2003, but with increasing rates of change. Non-marine sulphate and labile aluminium continued to exhibit clear and significant ($P<0.01$) declines, while pH, Alkalinity, ANC and DOC continued to increase (Fig. 2.1.19 Table 2.1.14). Marine derived salt concentrations exhibited significant declines at all sites ($P<0.05$). There were no significant trends in nitrate concentrations except at Round Loch of Glenhead where small increases were observed.

Summary

The "Galloway Cluster" of high lochs continues to exhibit recovery from acidification in response to stable nitrate concentrations and reduced sulphur deposition. The rate of recovery has increased in recent years (post-1994) and in terms of water quality, the lochs are at their healthiest since monitoring began in 1978. For the first time, Loch Enoch (2003) obtained a mean annual ANC of >0. These continued improvements are re-assuring for the recovery process. However, reductions in non-marine sulphate appear to have reached a plateau since 1999 with unknown consequences for further recovery. Step-changes in sulphur deposition, combined with unknown effects of climatic variation will continue to have a substantial affect on the recovery signal in the Galloway lochs. Continued monitoring is required to further understand the interactions between climate change, reduced sulphur deposition and recovery.

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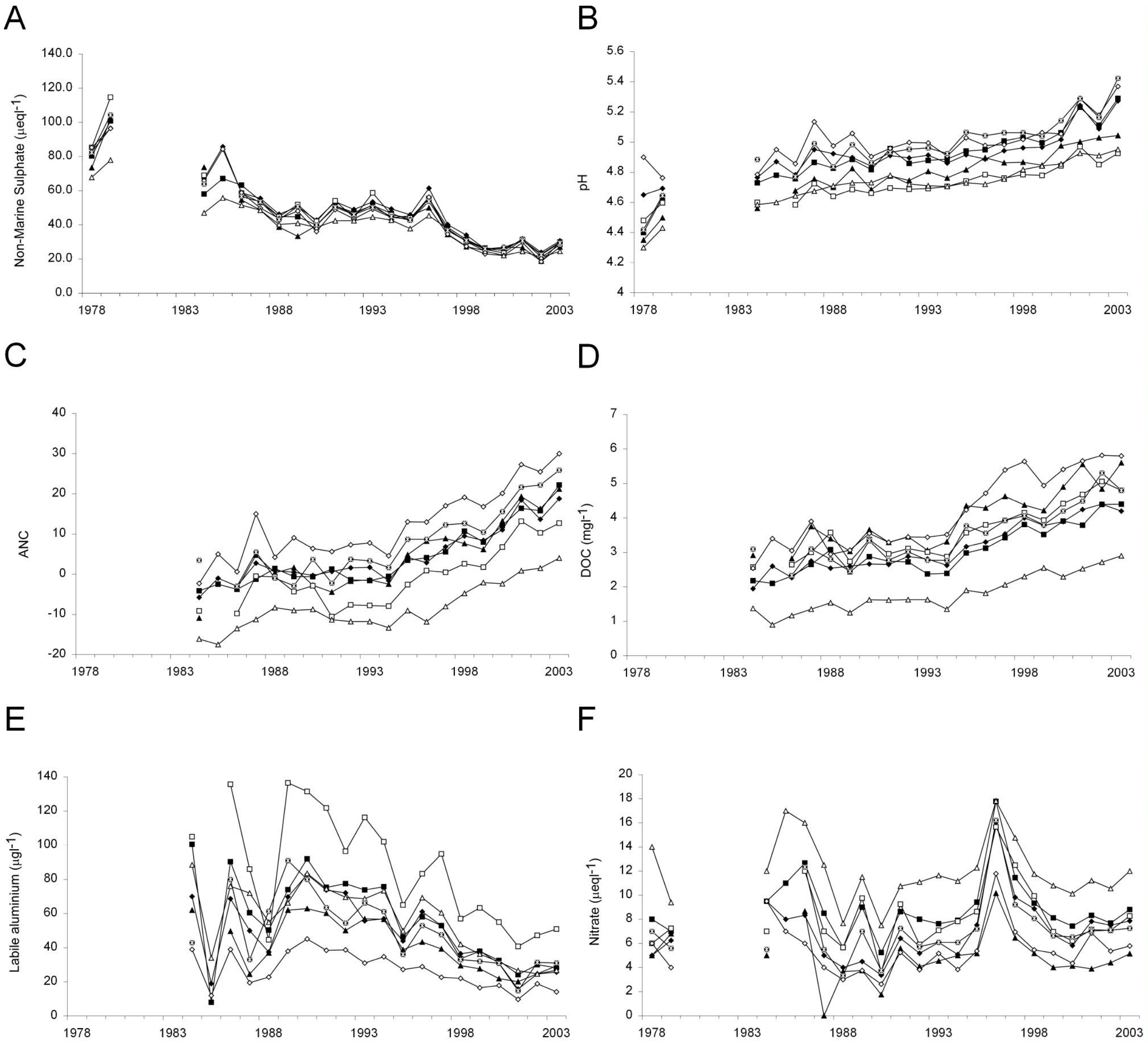

Figure 2.1.19: Mean annual chemistry data for Lochs Valley (■), Narroch (□), Neldricken (○), Arron (▲), Enoch (∆), Round Loch of Glenhead (♦) and Long Loch of Glenhead (◊), showing non-marine sulphate (A), pH (B), ANC (C), DOC (D), Labile Aluminium (E) and Nitrate (F).

Table 2.1.13: Significance, direction and rate of change for selected chemical determinands measured at sites in the Galloway high loch cluster (1978-2003 unless otherwise stated).

		Loch Valley	Round Loch of Glenhead	Loch Arron	Loch Narroch	Long Loch of Glenhead	Loch Enoch	Loch Neldricken
Non-marine sulphate	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	-1.87	-1.98	-1.979	-2.26	-1.79	-1.6	-1.84
pH	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	0.022	0.015	0.019	0.016	0.013	0.014	0.02
Alk 2	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	0.833	0.5	0.361	0.619	0.429	0.333	0.79
ANC (1984-2003)	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	1.83	1.25	1.78	1.75	1.75	0.82	1.75
NO3	*P<0.05*	x	✓	x	x	✓	✓	x
	P<0.01	x	✓	x	x	x	x	x
	Median Slope	NA	0.225	NA	NA	0.117	0.111	NA
DOC (1984-2003)	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	0.14	0.13	0.16	0.15	0.21	0.1	0.16
Labile Aluminium (1984-2003)	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	-4.17	-3	-2.17	-5.45	-1.85	-3.875	-3.33

Table 2.1.14: Significance, direction and rate of change for selected chemical determinands measured at sites in the Galloway high loch cluster (1990-2003).

		Loch Valley	Round Loch of Gleanhead	Loch Arron	Loch Narroch	Long Loch of Glenhead	Loch Enoch	Loch Neldricken
Non-marine sulphate	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	-2.09	-2.75	-2.47	-2.59	-2.156	-1.74	-2.25
pH	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	0.028	0.018	0.020	0.018	0.020	0.016	0.025
Alk 2	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	1.00	0.60	0.90	0.82	0.67	0.42	0.92
ANC	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	1.90	1.50	1.84	1.75	2.00	0.83	1.67
NO3	*P<0.05*	x	✓	x	x	x	x	x
	P<0.01	x	x	x	x	x	x	x
	Median Slope	NA	0.195	NA	NA	NA	NA	NA
DOC	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	0.15	0.14	0.17	0.16	0.23	0.10	0.16
Labile Aluminium	*P<0.05*	✓	✓	✓	✓	✓	✓	✓
	P<0.01	✓	✓	✓	✓	✓	✓	✓
	Median Slope	-5.43	-3.90	-2.79	-7.00	-2.50	-1.00	-4.20

Job 2.1.4: Calculate probability of occurrence for indicator taxa, species richness for indicator groups, and explore for rare taxa.

Job 2.1.9: Assess gap closure in relation to targets.

Introduction

Regression analysis in Task 1.2 Job 2 above demonstrated that a large number of diatom and invertebrate taxa have statistically significant responses, or distributional relationships, to ANC. Models for predicting the occurrence of these taxa were derived using logistic regression and generalised additive modelling. The aim of this job is to identify models that can be applied to a large number of sites for a synoptic study, the results of which should be easy to map and visualise. To this end we have selected predictive models for four biological entities (Fig. 2.1.20):

1. Occurrence of the diatom *Achnanthes minutissima*.
2. Occurrence of the macroinvertebrate *Baetis* spp.
3. Occurrence of the sum of acid sensitive diatom taxa (Listed in Task 1.2, Job 2, Table 1.2.3).
4. Occurrence of the sum of acid sensitive invertebrate taxa (Listed in Task 1.2, Job 2, Table 1.2.3).

Achnanthes minutissima and *Baetis* spp. are both common in streams above pH 6.0, and are among the first taxa to decline in response to lowered pH (e.g. Battarbee *et al*., 1988; Raddum *et al*., 1994). The sum of acid sensitive diatom and invertebrate taxa represent aggregates of acid sensitive taxa identified from the literature and from their distribution in the CLAM datasets. They fulfil the requirements of indicator taxa in that they are sensitive to the impact under study and they are widespread in nature. In addition, by using an aggregate the effect of secondary chemical variables and site-specific "noise" that influences the distribution of individual taxa is reduced. These aggregate categories also provide an alternative and more robust measure to the richness of indicator groups whose occurrence may be overly influenced by site-specific factors and the taxonomic expertise of the original analyst.

Rare diatom and invertebrate taxa could not be identified in the CLAM2 database and there is insufficient data on the distribution of other organisms (e.g. fish or macrophytes) to explore the potential for predicting the occurrence of rare taxa.

Biological predictions for the national chemical database

Taken together the four indicators listed above provide a general indication of ecosystem health, and are thus important and appropriate for use in assessing the overall biological status of soft waters. Response models for these taxa have been applied to the CLAM national chemical database to predict probability of occurrence under baseline (pre-acidification), 1970, and future (2010: Gothenburg Protocol) conditions using ANC predictions from the steady state water chemistry model (SSWC).

Results of biological predictions are shown graphically in Figures 2.1.21-2.1.25 and are summarised in Table 2.1.15. Figures 2.1.21-2.1.24 show maps of the predicted probability of occurrence of each biological target organism under baseline (pre-industrial), current and future (Gothenburg) conditions. These figures encapsulate the spatial distribution of the shifts in probability of occurrence for the different time periods, and clearly show the loss of the acid sensitive taxa between baseline and 1970, and the predicted recovery, or partial recovery under the Gothenburg protocol.

Gap closure in relation to targets

Figure 2.1.25 shows the cumulative frequency distributions of the modelled biological predictions for the four target organisms under baseline, 1970 and Gothenburg ANC conditions. These plots summarise the distributional information plotted in Figures 2.1.21-2.1.25 and allow comparison of biological status under different ANC scenarios. Table 2.1.15 presents the same summaries in tabular form.

We take two target scenarios. The first assesses the gap between baseline and Gothenburg for a probability of occurrence of the target organism of 0.3. The second scenario takes a target probability of 0.5. Table 2.1.16 shows the number of sites achieving the target probabilities for each organism.

Results indicate that during the mid 19th century the acid sensitive diatom *Achnanthes minutissima* had a probability of occurrence of at least 0.3 in the majority of sites (1056 sites or 93%) in the national dataset. By 1970 this figure had fallen to 681: it's distribution was severely reduced in over one third of the dataset. Predictions under Gothenburg suggest partial recovery and that it will achieve a probability of at least 0.3 in 856 sites (75%). Similarly *Baetis* spp. had a baseline distribution of predicted probability of occurrences of greater that 0.3 in 772 sites (68%). This fell to 620 sites in 1970 (54%) and is predicted to recover to 709 sites (62%) under the Gothenburg reductions.

The sum of acid sensitive diatom taxa had a predicted probability of greater than 0.3 in virtually all sites under baseline conditions. This fell to 885 (75%) in 1970 and is predicted to recover to 982 sites (86%) under Gothenburg. Similarly, the sum of acid sensitive invertebrate taxa also had a predicted probability of greater than 0.3 in virtually all sites under baseline conditions. This fell to 764 (67%) in 1970 and is predicted to recover to 953 sites (84%) under Gothenburg conditions.

Predictions of the number of sites supporting *Achnanthes minutissima* and *Baetis* spp. at a probability of occurrence of at least 0.5 are similar for baseline and Gothenburg conditions, indicating substantial recovery for these organisms under a more stringent biological target. However, even under 0.5 probability of occurrence the aggregate indicator groups suggest that substantial biological damage will remain under Gothenburg conditions: for example, an additional 209 sites have a probability of occurrence of acid sensitive diatom taxa of less that 0.5 and an additional 213 sites for the sum of acid sensitive invertebrates.

Conclusions

Gap analysis using ANC predictions derived from the national mapping dataset using the SSWC model are used to assess the magnitude and spatial distribution of biological damage resulting form surface water acidification, and the likely recovery under the Gothenburg protocol. Results suggest that between 10 and 20 percent of the sites in the mapping dataset will fail to reach the various baseline biological targets and that water quality will not improve sufficiently to support acid sensitive diatom and invertebrate taxa in geological sensitive parts of the country.

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Table 2.1.15: Summary cumulative probabilities of occurrence for *Achnanthes minutissima*, *Baetis* spp. and the sum of acid sensitive diatom and invertebrate taxa, showing numbers of sites in the CLAM national dataset with a given predicted probability of occurrence for each taxon under baseline (pre-acidification, 1970 and Gothenburg ANC conditions.

Cumulative	*Achnanthes minutissima*			*Baetis* spp.		
Probability	Baseline	1970	Gothenburg	Baseline	1970	Gothenburg
0.0-0.1	2	214	125	17	385	192
0.1-0.2	17	396	196	195	470	338
0.2-0.3	81	456	281	365	517	428
0.3-0.4	218	472	347	471	547	480
0.4-0.5	325	497	401	538	581	532
0.5-0.6	398	529	438	587	608	578
0.6-0.7	472	550	486	726	693	679
0.7-0.8	544	585	535	1137	1137	1137
0.8-0.9	636	630	606	1137	1137	1137
0.9-1.0	1137	1137	1137	1137	1137	1137

Cumulative	Sum acid sensitive diatom taxa			Sum acid sensitive invertebrate taxa		
Probability	Baseline	1970	Gothenburg	Baseline	1970	Gothenburg
0.0-0.1	0	163	91	1	201	116
0.1-0.2	2	209	123	6	276	154
0.2-0.3	8	282	155	15	373	184
0.3-0.4	17	376	185	22	428	226
0.4-0.5	26	437	235	56	453	269
0.5-0.6	74	456	278	139	462	305
0.6-0.7	164	464	326	239	473	355
0.7-0.8	289	487	377	331	500	403
0.8-0.9	401	530	441	420	533	456
0.9-1.0	1137	1137	1137	1137	1137	1137

Table 2.1.16: Gap closure under Gothenburg ANC for targets of 0.3 and 0.5 probability of occurrence. Gap closure is measured in number of sites (and % of total) failing to reach target.

		Number of sites			
	Target organism	Baseline	1970	Gothenburg	Gap (Baseline-Gothenburg)
Target 1:Probability of occurrence = 0.3	*Achnanthes minutissima*	1056	681	856	200 (18%)
	Baetis spp.	772	620	709	63 (6%)
	Sum of acid sensitive diatoms	1129	855	982	147 (13%)
	Sum of acid sensitive invertebrates	1122	764	953	169 (15%)
Target 2:Probability of occurrence = 0.5	*Achnanthes minutissima*	812	640	736	76 (7%)
	Baetis spp.	599	529	605	0 (0%)
	Sum of acid sensitive diatoms	1111	700	902	209 (18%)
	Sum of acid sensitive invertebrates	1081	684	868	213 (19%)

Figure 2.1.20: Presence / absence data and fitted response model for *Achnanthes minutissima*, *Baetis* spp., and the sum of acid sensitive diatom and invertebrate taxa.

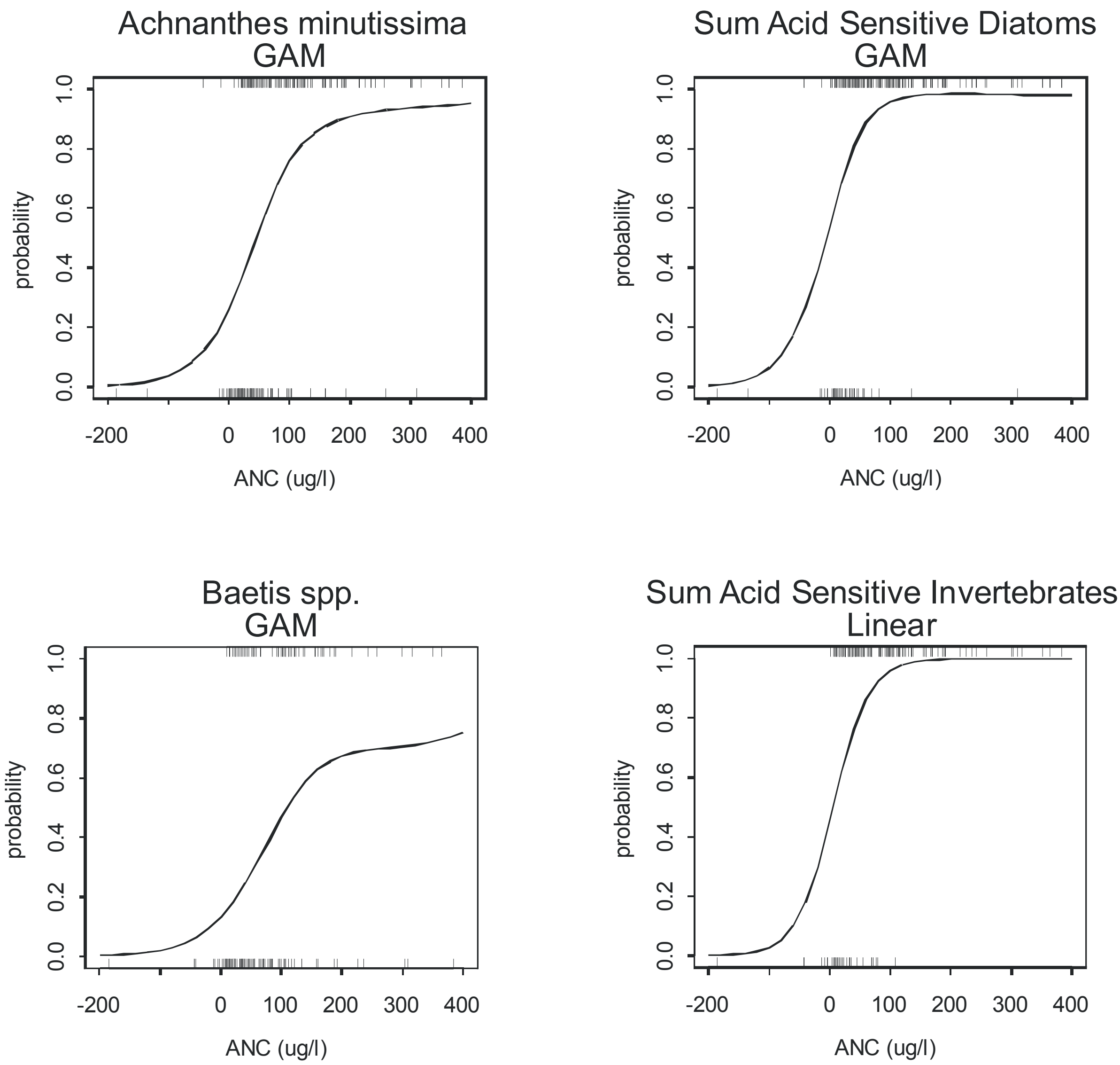
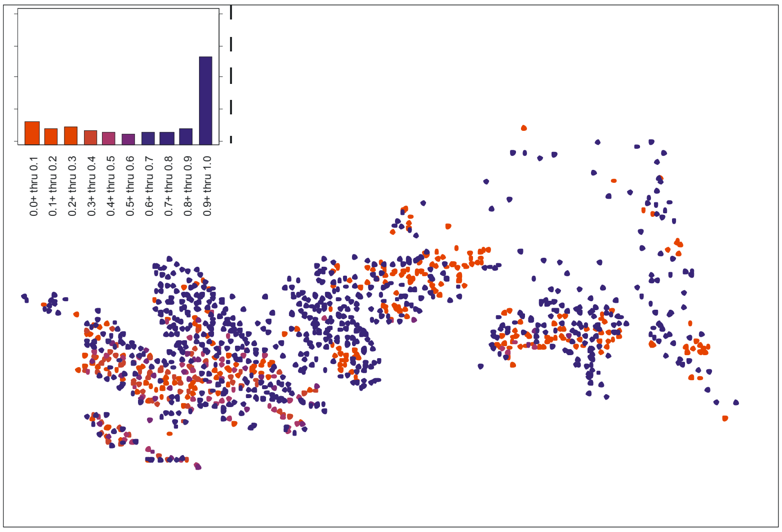
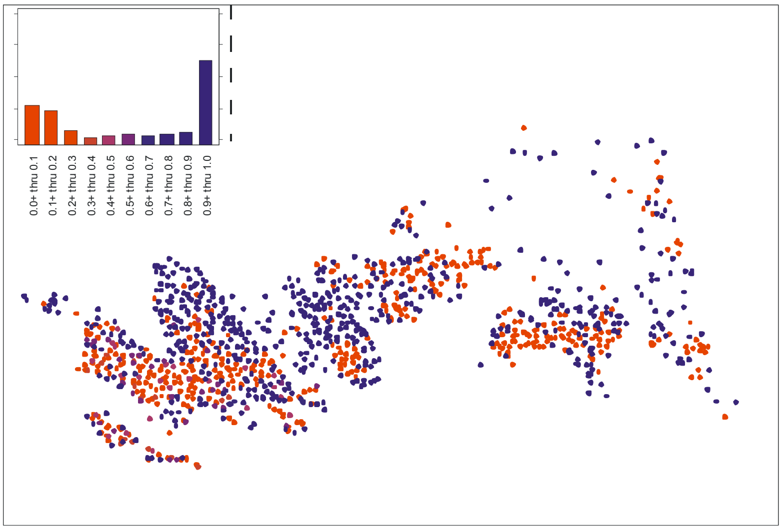


Figure 2.1.21: Probabilities of occurrence of *Achnanthes minutissima* under baseline (pre-acidification, left), 1970 (middle) and future (Gothenburg, right) modelled ANC conditions.





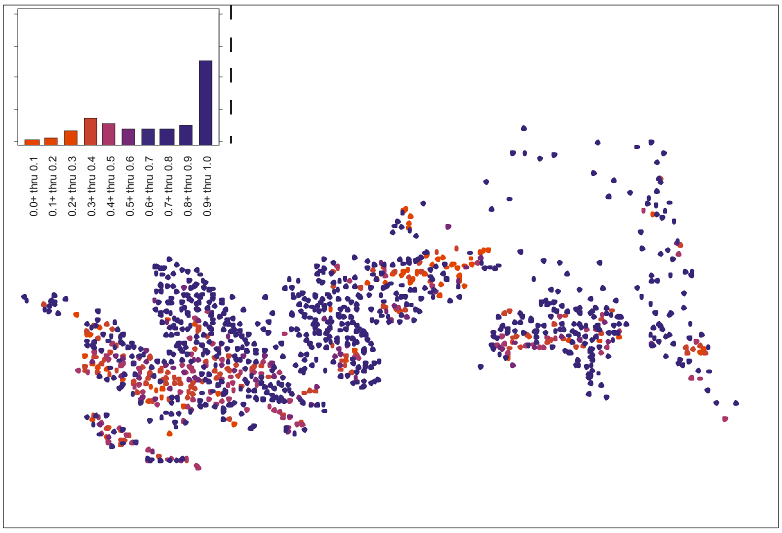


Figure 2.1.22: Probabilities of occurrence of *Baetis* spp. under baseline (pre-acidification, left), 1970 (middle) and future (Gothenburg, right) modelled ANC conditions.

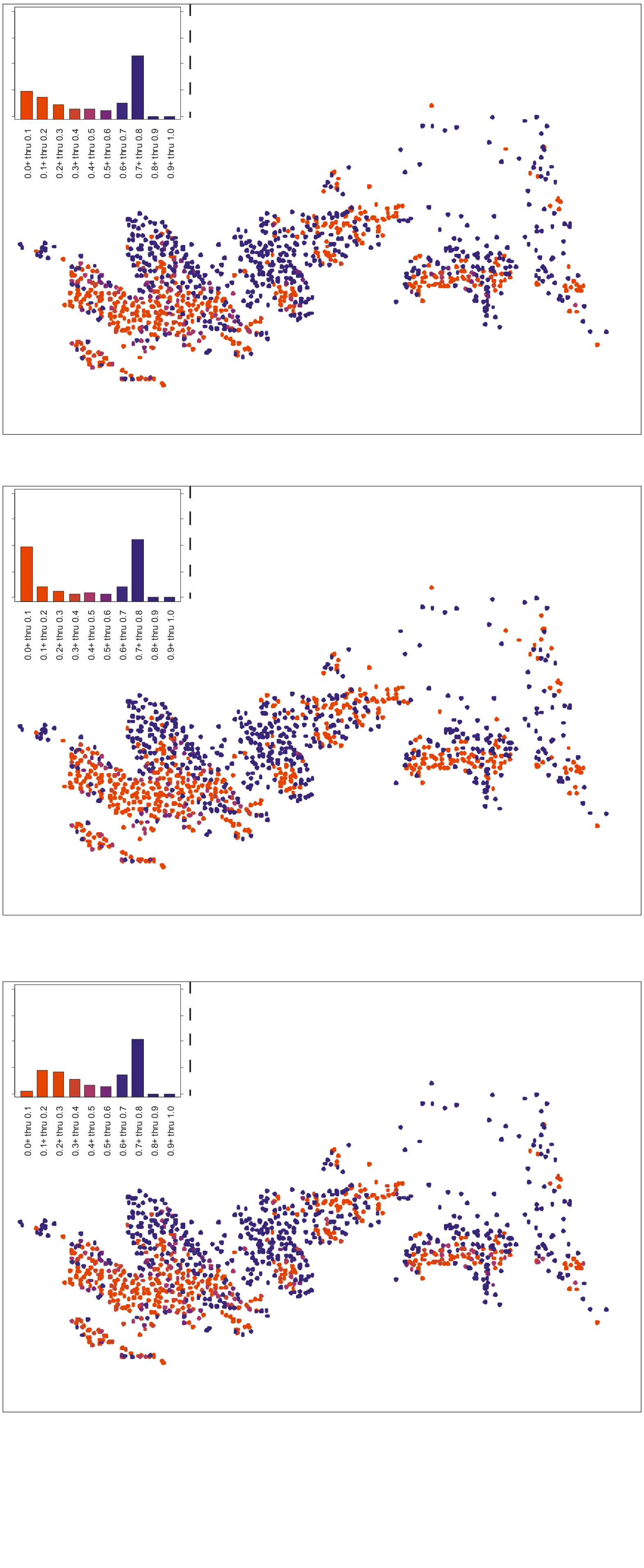


Figure 2.1.23: Probabilities of occurrence of the sum of acid sensitive diatom taxa under baseline (pre-acidification, left), 1970 (middle) and future (Gothenburg, right) modelled ANC conditions.

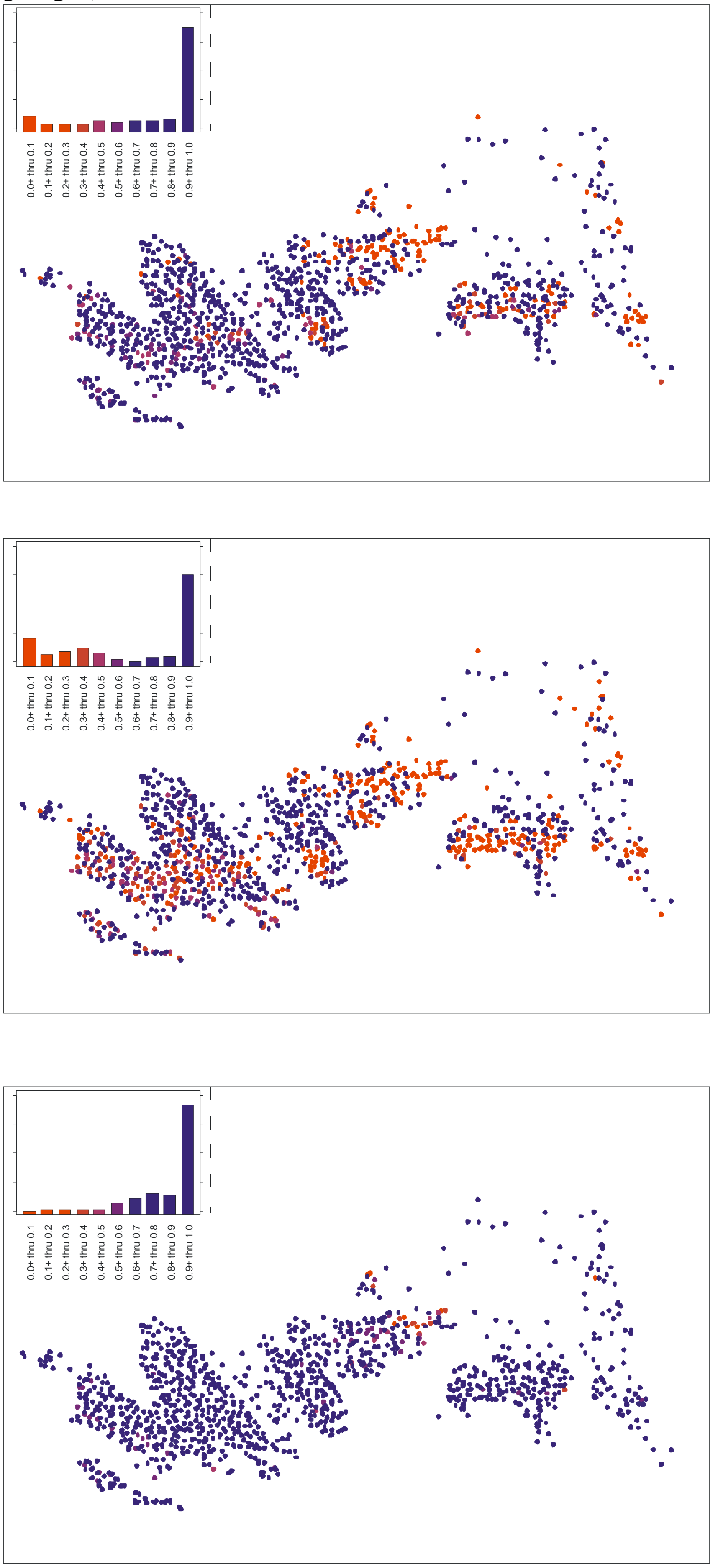
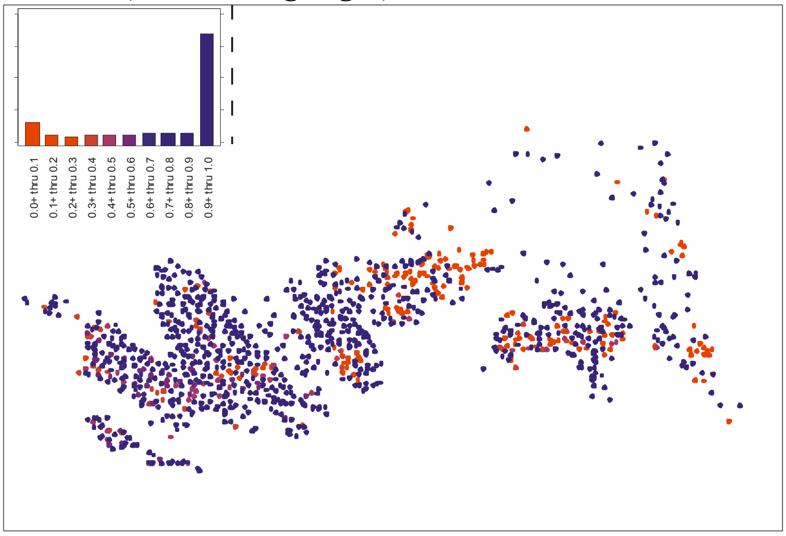
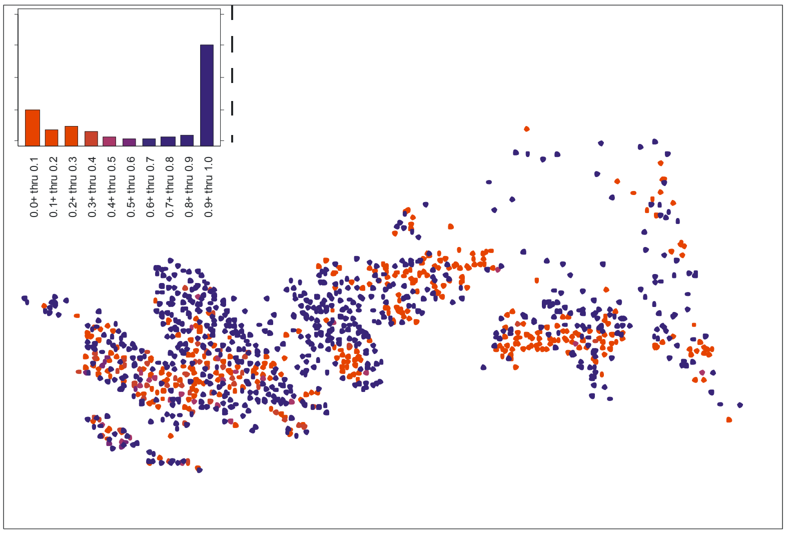


Figure 2.1.24: Probabilities of occurrence of the sum of acid sensitive invertebrate taxa under baseline (pre-acidification, left), 1970 (middle) and future (Gothenburg, right) modelled ANC conditions.





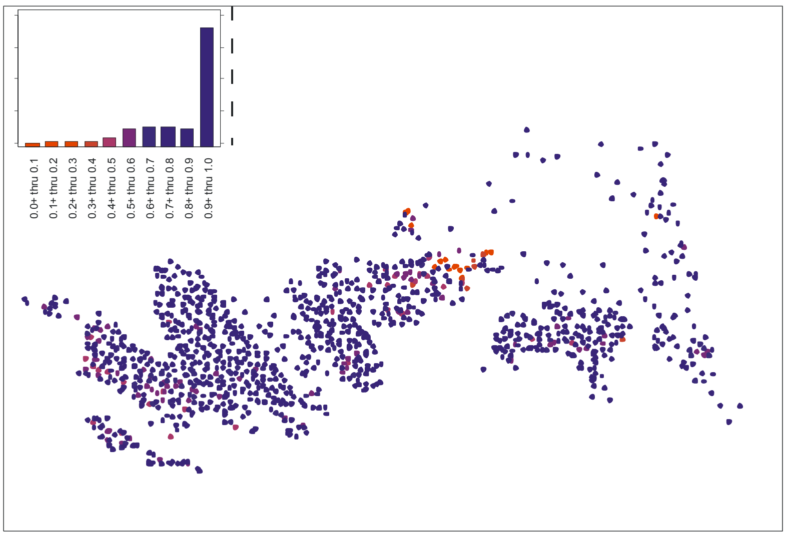
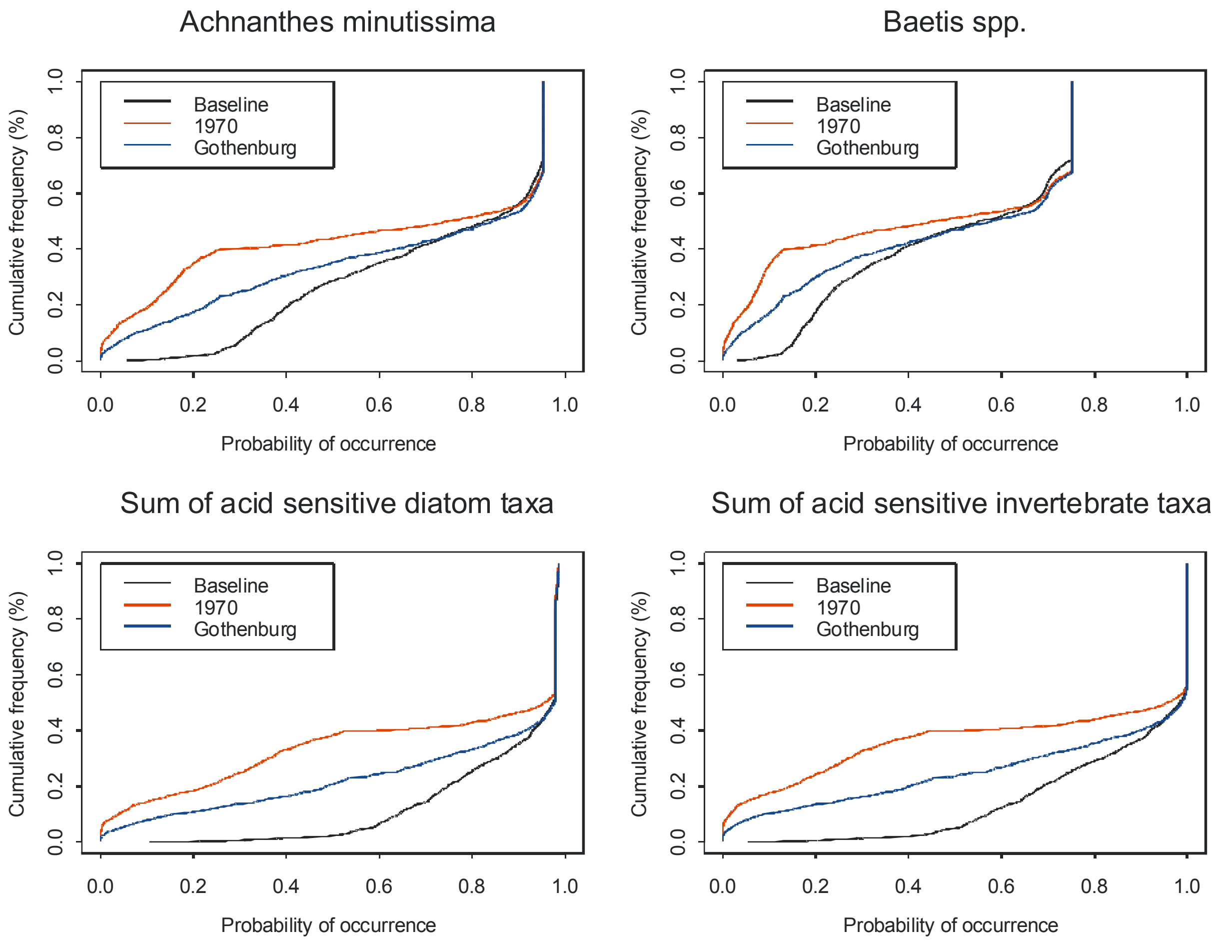


Figure 2.1.25: Summary cumulative frequency distributions for indicator organisms under baseline, 1970 and Gothenburg ANC conditions.



Task 2.1.10: Develop a framework that integrates biological model predictions with sediment core biological time series and analogue matching approaches to produce a unified "methodology" that can be used to present concepts and results to end users.

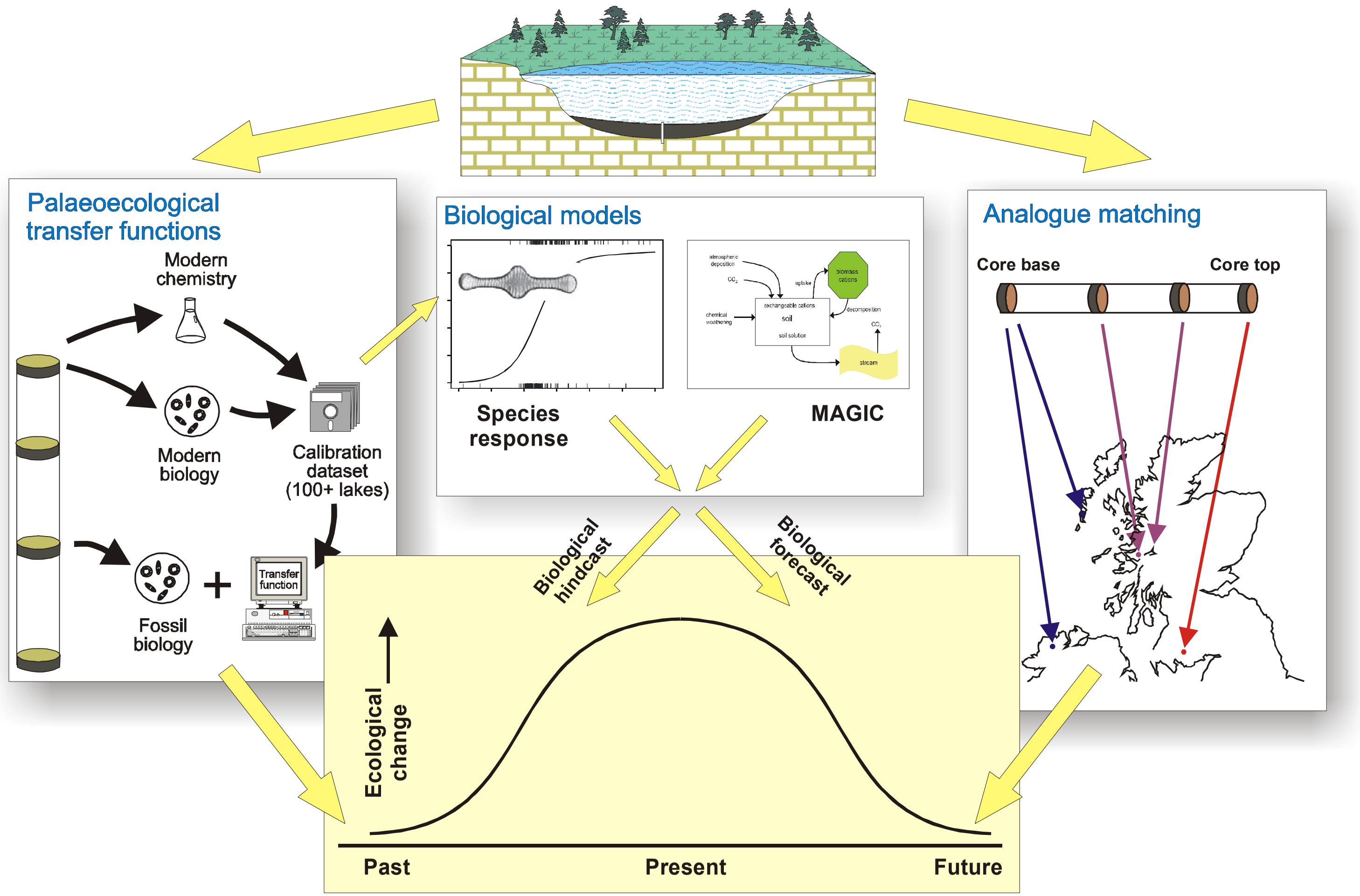
The conceptual framework that integrates environmental reconstructions based on sediment core times series, analogue matching approaches, and biological model predictions is shown in Figure 2.1.26. The framework illustrates the relationship between the three approaches used in CLAM2 to assess magnitude of biological impacts, biological forecasts and estimates of gap closure, and identification of appropriate targets for recovery.

The first of these approaches is the use of palaeoecological transfer functions. These are ecological response functions that model the relationship between organisms preserved in the surface sediments of a range of lakes with the chemistry of the overlying waters. Once derived, the transfer functions can be applied to fossil organisms extracted from dated levels in a sediment core to "reconstruct" or hindcast pH or ANC. Such reconstructions provide a time-series of acidification at individual sites and also values for background, or pre-acidification, chemistry that can be used as a restoration target or to test dynamic models.

The second approach is based on palaeoecological analogue matching. In this approach, fossil biological assemblages from pre-acidification levels of cores from impacted lakes are "matched" to assemblages derived from the surface sediments of lakes in "clean" or unimpacted areas. Thus lakes which today have a similar surface-sediment assemblage to that of the pre-acidification levels can be used as analogues for the pre-acidification biological status of impacted lakes. Appropriate analogues can then be used as restoration targets.

The final approach illustrated in the centre of the diagram is based on ecological response models. These models are also derived from the contemporary distribution of organisms across a range of lakes and streams of varying chemistry in impacted and unimpacted areas. These distributions are used to derive statistical response functions that model the relationship between the probability of occurrence of individual organisms and water chemistry. Linked to the hydrochemical prediction from MAGIC simulations the models can then be used to predict the likely occurrence of organisms under varying chemistry predicted by MAGIC. When linked to MAGIC hindcasts the models can provide an assessment of biological status under baseline conditions. When linked to MAGIC predictions the models provide an assessment of recovery and time to gap closure.

Figure 2.1.26: Conceptual framework showing relationship between approaches to biological and chemical hindcasts, forecasts and recovery targets using palaeoecological transfer functions, analogue matching approaches, and species response models.



Task 2.2: Regional assessment of stream status and risk of episodes

2.2 Regional assessment of stream status and risk of episodes

2.2.1 Determine study catchments, calculate HRUs, determine soil, land use, geology and deposition characteristics

Regional analysis – approach to water quality estimation

A full inventory of stream acidification status is not achievable within the normal constraints on field activity. Regional status must be inferred from limited stream sampling, and spatial coverage of catchment characteristics, possibly augmented by deposition estimates. The PEARLS approach (Cooper *et al*., 2000, 2004) adopted here determines empirical relationships between stream water concentrations and catchment characteristics in the form of landscape classes. The relationships are then used to simulate acidification in unsurveyed river reaches using simple mixing of drainage water from a small number of landscape classes within a catchment. To accommodate uncertainty within the modelling framework, drainage from each landscape class is assigned a probability distribution with values distributed in space. This distribution is usually not available from past studies and is estimated by sampling replicate subcatchments of a single landscape class. Application of PEARLS provides estimates of the probability distribution of concentrations within each reach at the time of sampling. Derived statistics include, for example, the expected total length of river having a concentration less than some threshold value. The PEARLS approach does not account for temporal variation and includes no transformation processes within rivers beyond simple mixing.

Before PEARLS can be applied in a selected region, suitable landscape classes must be identified, and if a field sampling programme is required, suitable locations selected. Following sampling and inspection of measured concentration values, landscape classes may be merged or split to better account for the variability in the data. Interpolation throughout a river network, once drainage chemistry from each landscape class has been estimated, is achieved through knowledge of the spatial distribution of landscapes, and the geometry of the drainage network. This can be achieved using GIS techniques. At present, catchment geometry is discretised into a spatial cover of hydrological response units (HRUs) (Cooper and Naden, 1998) draining to a river network. The coverage and network are defined from DTM elevations, each HRU draining to an identified reach in the schematic river network. The landscape coverage and HRU coverage are overlain to provide estimates of the proportion of each landscape in each HRU.

Water quality in drainage from a landscape class varies not only in space, but also over time, and this variation may be greater than between-landscape spatial variability. Field sampling campaigns, unless they become a very major undertaking, cannot characterise this variability. They can only provide a small number of "snapshots". It may be possible to select sampling times to capture the expected range of events, usually high and low flows. This is sufficient to generate scenarios, but cannot with confidence provide estimates of such ecologically important characteristics as the duration of individual water quality extreme events.

Landscape class selection based on soil, land use and other classifications does not explicitly account for a number of important variables which are expected to be associated with water quality differences. These include rainfall, slope and distance from the sea. These can be classified by range to generate new classes, or used as covariates.

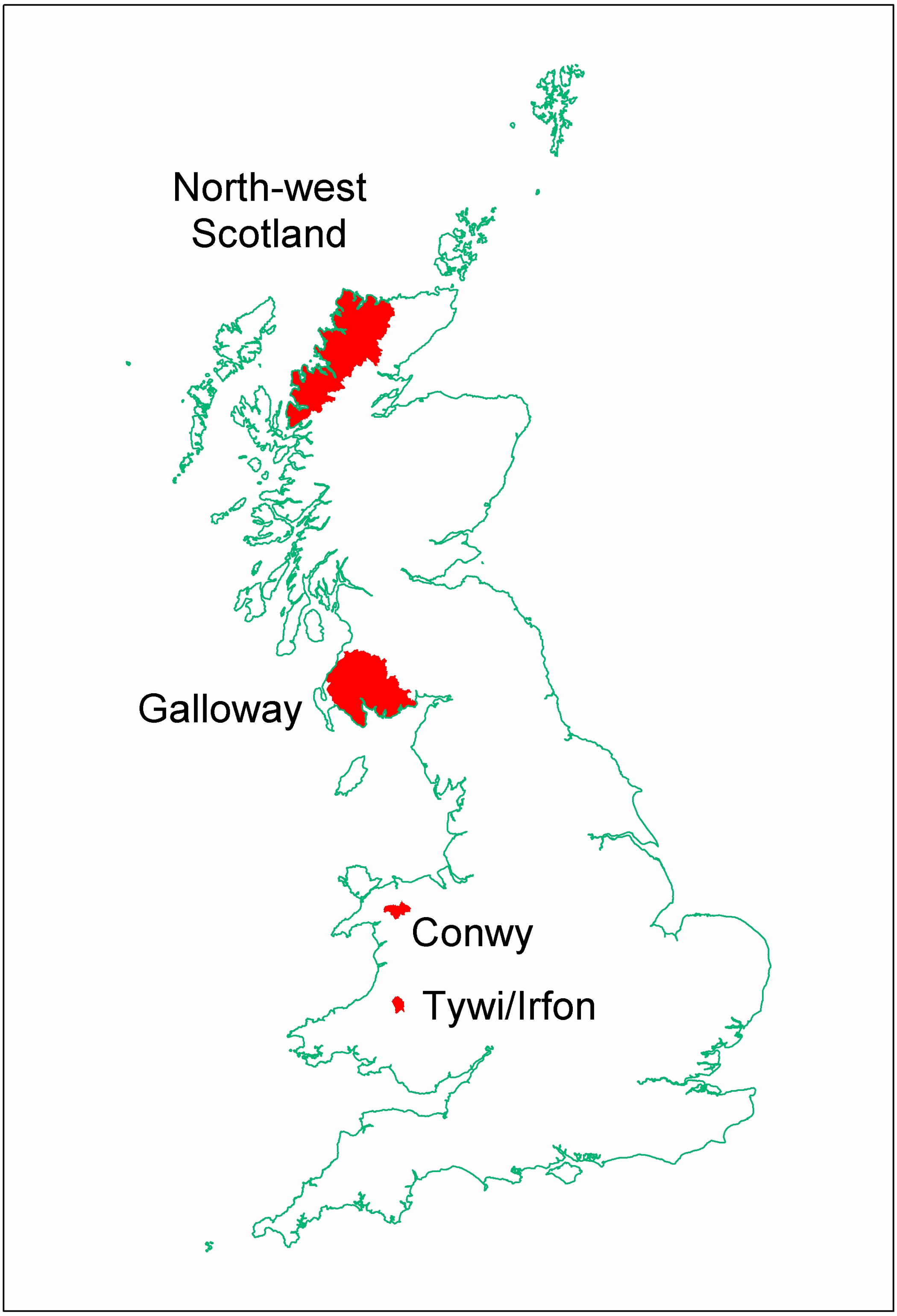
Regions selected for CLAM2

Four regions were initially selected for study and potential application of PEARLS: north-west Scotland, Galloway, the Conwy valley and the upper Tywi/Irfon. Figure 2.2.1
shows the locations of these regions. Galloway and the Tywi/Irfon are areas with a known history of acidification. The Conwy, while less well studied, included substantial forestry and acidic headwaters. North-west Scotland was thought to have been little affected by acid deposition, but to have large areas of naturally acid soils.

NW Scotland
North-west Scotland was chosen as a region where acid deposition has been low and streams were expected to show little change in acidification following emissions reductions. Sampling in this region was expected to reveal the extent of natural variability in water quality, particularly the incidence of acid episodes. The selected region covers some 6000 km^2, extending along the western seaboard from Loch Carron to Strathnaver on the north coast. Most catchments included drain west and north to the Atlantic coast, but the region also includes the rivers Oykell, Cassley and Shin, draining eastward to the Dornoch Firth and the North Sea. These three catchments include significant coniferous plantation forestry. Much of the remainder of the region is semi-natural moorland, with some crofting along the coast and inland where soils allow. Geology is particularly diverse along the Moine thrust, running roughly N-S through the region. East of this, Moine schists predominate, though there are some substantial inliers. To the west is largely Torridonian sandstone on a bed of Lewisian gneiss, which includes numerous volcanic intrusions of varied geochemistry. Soil cover includes peats, peaty podzols, poorly developed soils and rocky outcrops.

Galloway
The portion of Galloway chosen for study includes approximately 4000 km^2 in the south west of Scotland, covering much of the western half of Dumfries and Galloway, the southern part of South Ayrshire and the south west corner of East Ayrshire. This includes some of the most heavily forested landscape in the United Kingdom, much of it planted on peaty soils. Geology comprises granite and base-poor Palaeozoic fine-grained sediments, with some more weatherable formations in the north-west of the region. Soils at higher altitudes include substantial areas of peats and peaty podzols. There is a history of high acidic deposition (Helliwell *et al.*, 2001).

Figure 2.2.1: Location of study regions



Conwy

The Conwy catchment (256 km^2) contains a number of relatively distinct landscape types ranging from an extensive area of blanket peat (the Migneint) in the southwest through rough grazed hill and mountain land to extensive coniferous forestry and improved pasture at lower altitudes. Geology is a mixture of lower Palaeozoic igneous and sedimentary formations. These catchment characteristics, together with an established sensitivity to surface water acidification in headwater areas, make it highly suitable for this assessment approach. Additionally, due to its proximity to CEH Bangor, it was possible to target sampling times in order to capture both low flow and peak high flow conditions, to an extent that was not possible in more remote regions. Sampling, and subsequent modelling, were focused on the catchment upstream of Betws-y-Coed incorporating the Conwy, and the major Afon Lledr and Machno tributaries.

Tywi/Irfon

The upland region drained by the adjacent headwaters of the Tywi (94 km^2) and Irfon (50 km^2) in mid-Wales is a well-established acidification research area, with a mixture of moorland and plantation forestry as land cover. Soils are largely peats, peaty podzols and podzols, with a small area of stagnogley. Previous studies (Edwards *et al.*, 1990) have shown the hydrochemical differences in drainage from moorland and forestry in this region, and these have been linked to ecological differences.

Landscape definition

North-west Scotland and Galloway

Spatial information used to define landscapes was provided by Land Cover of Scotland (1988) data held at the Macaulay Institute and a 1:250 000 scale soil map coverage of Scotland. In defining landscape classes for inclusion in PEARLS modelling, the existing Skokloster classification scheme for Scotland (Nilsson *et al.*, 1988; Langan *et al.*, 2001) was first considered. This classification gives an indicator on a scale of 1 to 5 of acidification susceptibility, and is based on soil classification but excludes land use. However, in both north-west Scotland and Galloway it was found that a single Skokloster class dominated. To allow for possible discernable variation within these classes, and also to account for significant within-class vegetation differences, the two regions were reclassified into 12 and 13 classes respectively. While some classes might prove indistinguishable, this initial classification allows the possibility of more refined estimation if this is justifiable. Although some land uses, particularly forestry, are associated with acidification, a division of existing Skokloster classes on the basis of land use alone for north-west Scotland gave a very limited presence for many of the landscapes generated. The larger soil groupings were therefore split, and an altitude factor included. This gave classifications based on land use, soils/geology and elevation. Galloway includes more varied land use, and this was a more important factor in the reclassification of landscapes in this region. Tables 2.2.1 and 2.2.2 show the selected landscape classes for north-west Scotland and Galloway. Initial landscape classes for the two regions are shown in Figures 2.2.2 and 2.2.3.

Table 2.2.1: Initial landscape classes for north-west Scotland

Class	%	Altitude	Soil class	Geology	Land use
1	3	Low	BFS/HIP	Schist/gneiss/granulite/quartzite	forest
2	14	Low	BFS/HIP	Schist/gneiss/granulite/quartzite	all vegetation types except forest
3	1	Medium	PP/PG	Schist/gneiss/granulite/quartzite	forest
4	16	Medium	PP/PG	Schist/gneiss/granulite/quartzite	moorland/peat
5	3	High	SUB/ALP/RANK	Schist/gneiss/granulite/quartzite	moorland/montane
6	19	Low-high	BFS/PG/PT/SUB	Granite and Lewisian gneiss	moorland/montane
7	7	Low	BCS/BFS	Old red sandstone/limestone/shelly sands	moorland/grassland/improved pasture
8	17	Low-medium	BFS/HIP/PP/PG	Torridonian sandstone/grit	moorland
9	4	High	SUB/ALP	Torridonian sandstone/grit	moorland/montane
10	1	Low-high	PT	Mixed	forest
11	10	Low-high	PT	Mixed	all vegetation types except forest
12	5	Low-high	BFS/PG/PP/PT/SUB	Quartzite and quartzose grit	moorland/montane

Key to soil classes

PT-Peat; PG-Peaty Gley; PP-Peaty Podzol; HIP-Humus Iron Podzol; BFS-Brown Forest Soil; BFSG-Brown Forest Soil with Gleying; NCG-Non Calcareous Gley; RANK-Ranker; REG-Regosol; ALL-Alluvial Soil; SUB-Sub-alpine Soil; ALP-Alpine Soil; BCS-Brown Calcareous Soil

Table 2.2.2: Initial landscape classes for Galloway

Class	% Area	Altitude	Soils	Geology	Land Cover
1	6	low-high	PT	Mixed	forest
2	5	low-high	PT	Mixed	grassland/peat
3	2	low	BFS/BFSG/NCG	Greywacke/shale	forest
4	20	low	BFS/BFSG/NCG	Greywacke/shale	improved pasture
5	4	low	BFS/BFSG/NCG	Greywacke/shale	grassland/montane/moorland/peat
6	15	med-high	PT/PG/PP/BFS/NCG/RANK/SUB	Greywacke/shale	forest
7	8	med-high	PT/PG/PP/BFS/NCG/RANK/SUB	Greywacke/shale	improved pasture
8	17	med-high	PT/PG/PP/BFS/NCG/RANK/SUB	Greywacke/shale	grassland/montane/moorland/peat
9	4	low-high	HIP/PG/PP/BFS/NCG/RANK/SUB	Granite	forest
10	6	low-high	HIP/PG/PP/BFS/NCG/RANK/SUB	Granite	grassland/improved pasture
11	2	low-med	BFS/BFSG/NCG/HIP/PG/PP/ALL/REG	Basalt, mixed drift	forest
12	6	low-med	BFS/BFSG/NCG/HIP/PG/PP/ALL/REG	Basalt, mixed drift	improved pasture
13	4	low-med	BFS/BFSG/NCG/HIP/PG/PP/ALL/REG	Basalt, mixed drift	grassland/montane/moorland/peat

Key to soil classes

PT-Peat; PG-Peaty Gley; PP-Peaty Podzol; HIP-Humus Iron Podzol; BFS-Brown Forest Soil; BFSG-Brown Forest Soil with Gleying; NCG-Non Calcareous Gley; RANK-Ranker; REG-Regosol; ALL-Alluvial Soil; SUB-Sub-alpine Soil; ALP-Alpine Soil; BCS-Brown Calcareous Soil

Figure 2.2.2: Landscape classes and sampling sites in north-west Scotland

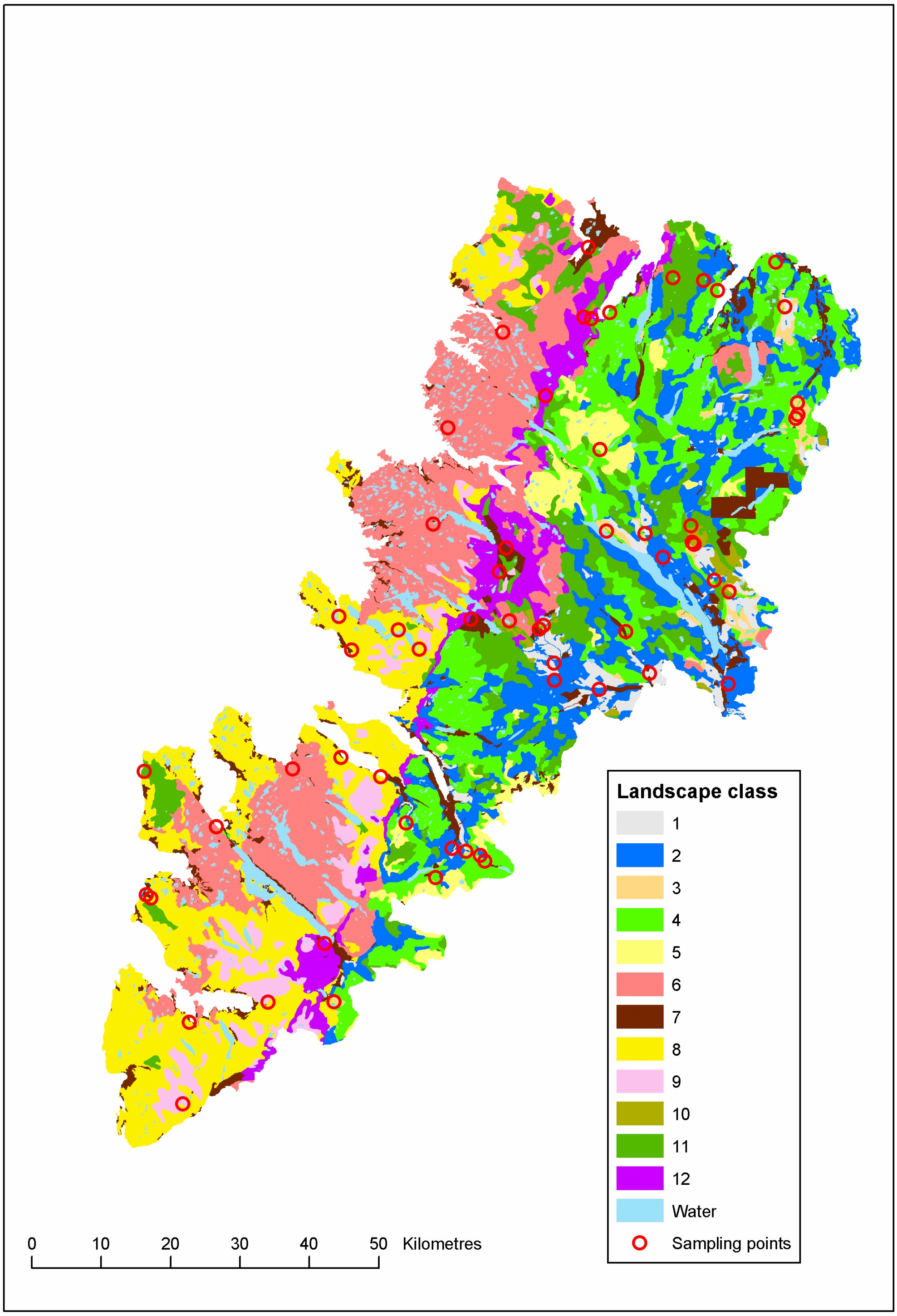
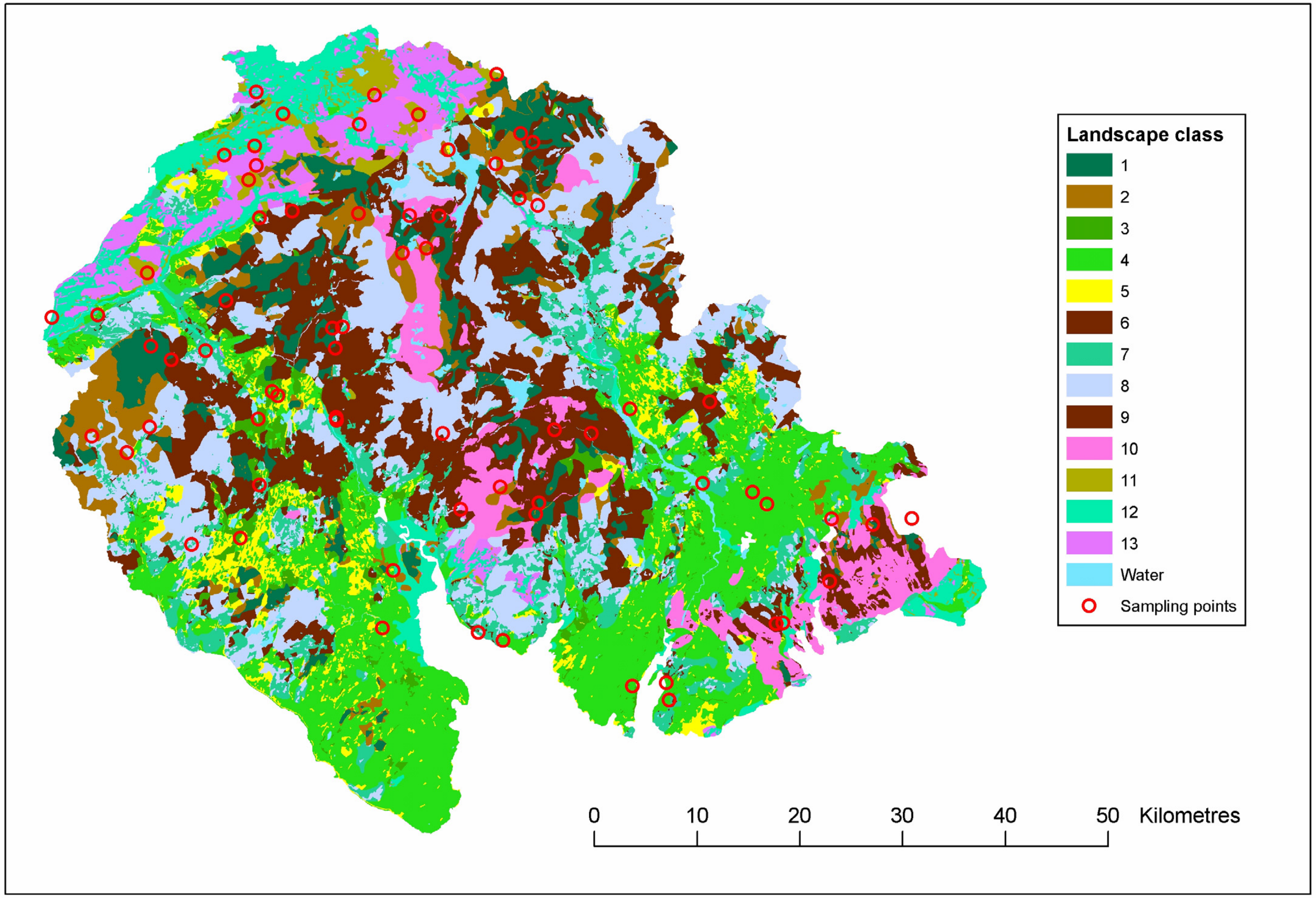


Figure 2.2.3: Landscape classes and sampling sites in Galloway



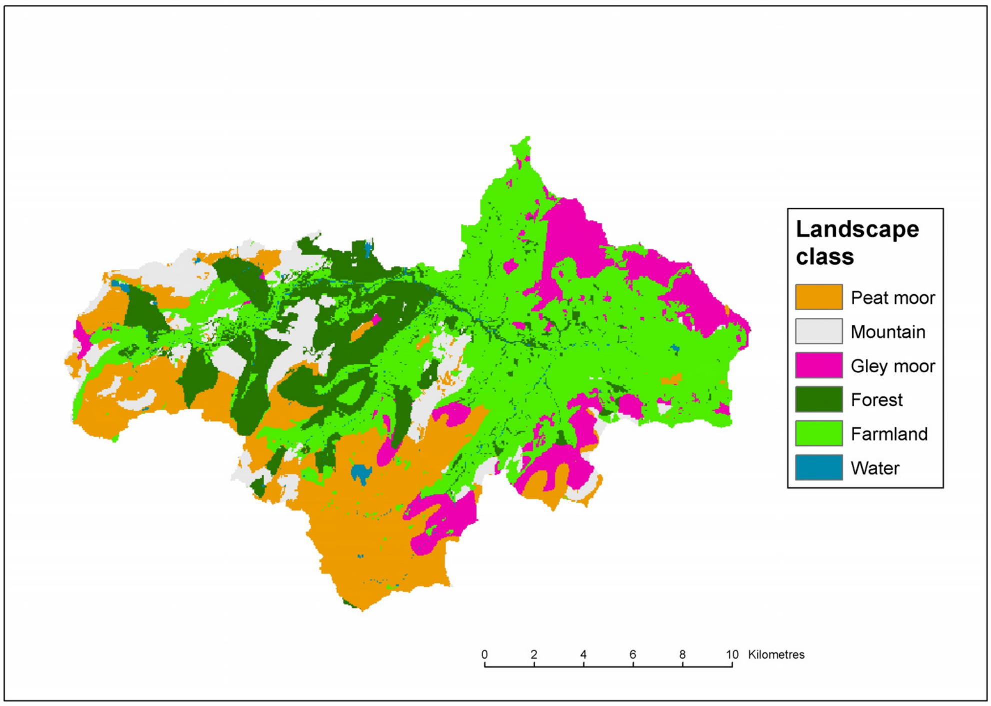
Conwy

Soils for this area were derived from the NSRI 1:250,000 digitial soils map (NATMAP), whilst land-use was derived from a detailed survey undertaken in the mid 1980s (Phase 1 Habitat Survey, JNCC, 1993). This land-cover dataset has the advantages that it was mapped at a high resolution, and primarily based on ground-level surveys rather than on satellite imagery as in the CEH Landcover datasets, but is only available for Wales. Based on an assessment of variations in soil and land-use within the Conwy catchment, six provisional landscape types were identified. These included two coniferous forest landscape types (on organic and mineral/organo-mineral soils respectively), however these could not be clearly differentiated in terms of runoff chemistry, so were merged to give five final landscape types (Table 2.2.3 and Figure 2.2.4).

Table 2.2.3: Landscape classes for the Conwy catchment

Class	Soils	Land cover	Notes
1. Peat moorland	Peat	All non-forest	S and W of catchment, mainly Migneint
2. Montane	Rankers, peaty podzols	Moorland/montane	Relatively small areas in W of catchment
3. Peaty gley moorland	Peaty gleys, some peaty podzols	Moorland	Characteristic low-relief moorland landscape, mainly in NE of catchment
4. Forest	All soils under forest	Forest	Extensive in Lledr valley
5. Farmland	All soils under farmland	Improved pasture	Extensive at lower elevation in E of catchment

Figure 2.2.4: Landscape classes in the Conwy catchment



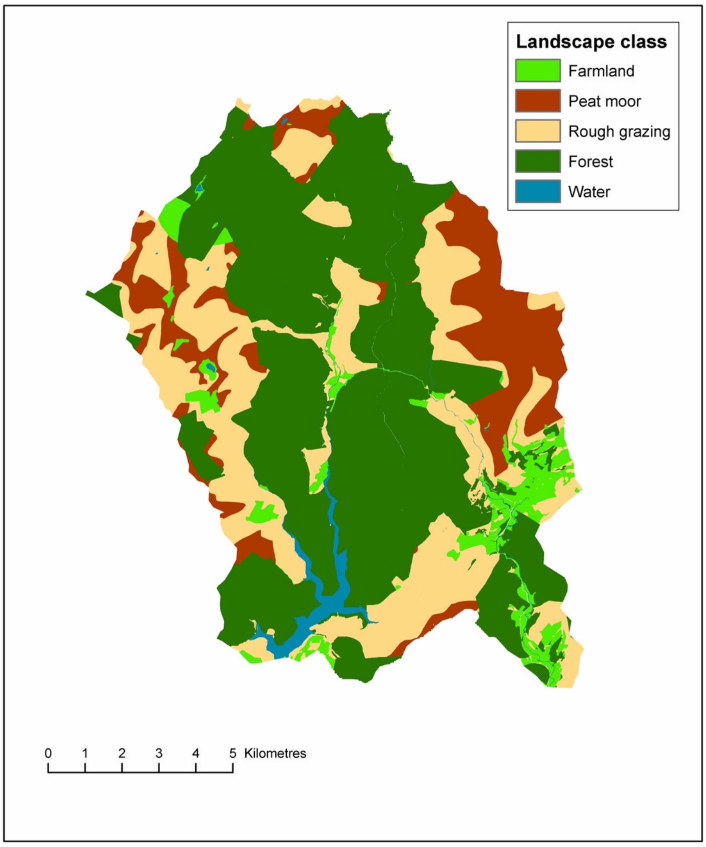
Tywi/Irfon

Landscape classes were selected using the same data sets as for the Conwy. The Tywi/Irfon catchments form a small region with rather uniform geology of lower Palaeozoic fine-grained sediments, and dominated by two land uses, semi-natural moorland, and plantation coniferous forestry. There is a small amount of improved pasture at lower altitudes. Drainage of the moorland is varied, with some steeper and better-drained valley sides, and poorly-drained plateau-like moorland between valleys. On the basis of this, moorland has been divided into two landscapes, poorly drained peats and better drained hillslopes. The remaining two landscape classes are farmed land and forestry. The Tywi catchment also includes the substantial Brianne reservoir. Table 2.2.4 and Figure 2.2.5 show the landscape classes selected for the Tywi/Irfon.

Table 2.2.4: Landscape classes for the Tywi/Irfon catchments

Class	Soils	Land cover	Notes
1. Farmland	All soils under farmland	Improved pasture	Small area in valley bottoms
2. Peat moorland	Peat	Moorland/peat	Upland plateau and some valley bottoms
3. Rough grazing	Podzols and stagnopodzols	Moorland/grassland	Better-drained valley slopes
4. Forest	All soils under forest	Forest	Extensive

Figure 2.2.5: Landscape classes in the Tywi/Irfon catchments



Choice of sampling sites

In order to apply the PEARLS model, estimates of the distribution of water quality from each landscape class are required. These may be available from past studies, or a field sampling programme may be required to provide the necessary estimates.

The Tywi/Irfon region has a number of subcatchments which have been used in previous studies. Many of these were originally selected as draining exclusively either moorland or forestry, so as to compare drainage water quality from these two landscapes. No new subcatchments were selected in this region for CLAM2.

In each remaining region, an attempt was made to identify a number of replicate subcatchments draining a single landscape. This was intended to give a measure of the within-landscape variability in drainage water quality, and identify those landscapes which were not statistically distinguishable on the basis of concentrations of selected determinands. The population of streams within each landscape class is not well-defined, and those selected are not a random sample, but are chosen as easily accessible and "representative". This is not ideal, and has the potential to introduce bias. Where possible the streams sampled exclude those draining lakes whose chemistry is likely to be strongly influenced in the short term by storage. Subcatchments were selected by comparing landscape class maps with OS 1:50000 Landranger or 1:25000 Explorer series maps, both of which show main surface features and contours.

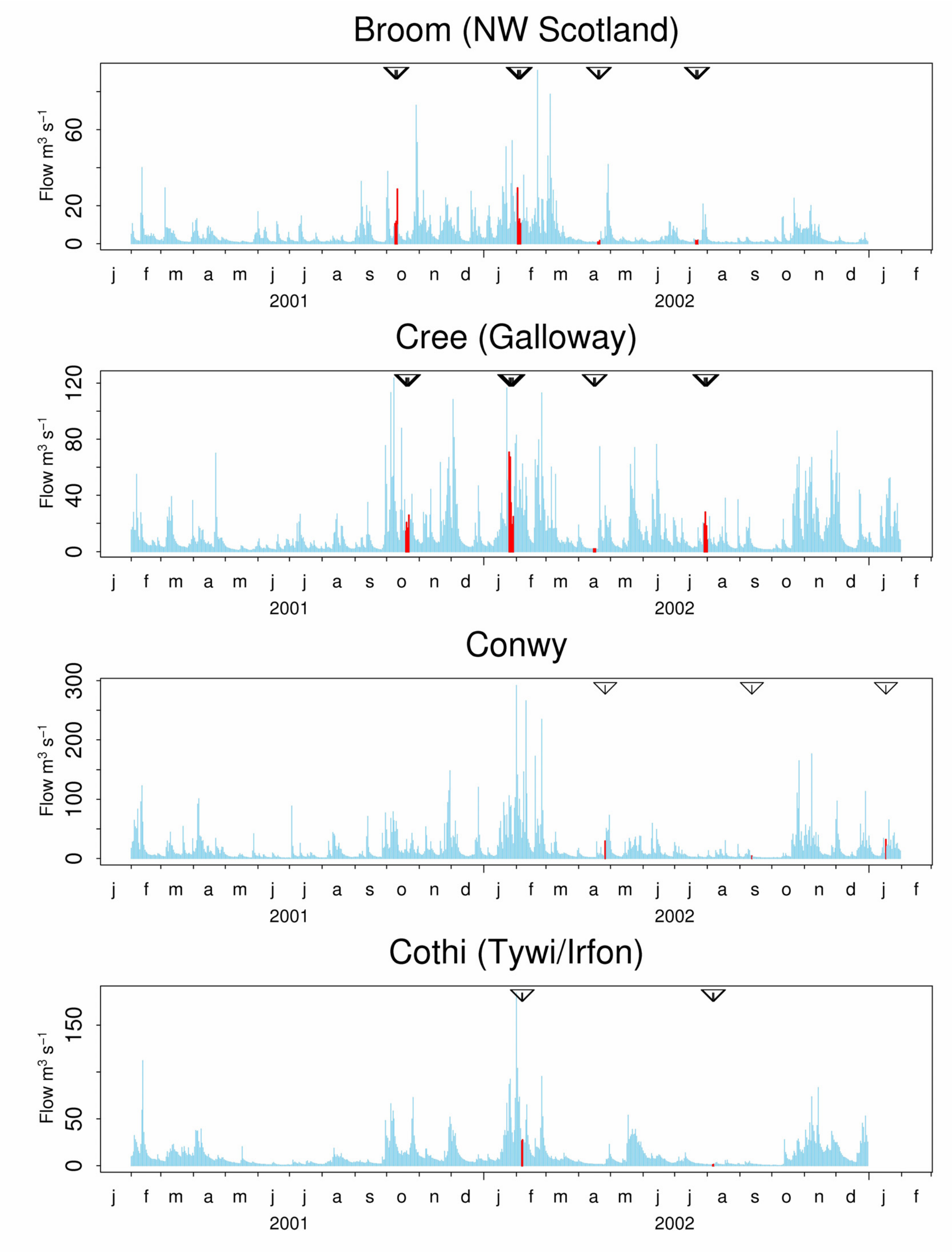
Many water quality variables are strongly influenced by quite localised and minor geological features. Where this occurs, the water quality of some streams may be poorly characterised by reference to the dominant landscape, or be predictable only within wide error margins. Such sites do not form part of a well-identified statistical population, so their characteristics cannot be inferred from a modest sampling programme. The way forward for full characterisation of water quality characteristics of streams is a gradually increasing sampling program, accounting for the multiplicity of geological conditions. For some determinands not having geological origin, losses may be independent of geology and more readily predictable. In general, this may be true of nutrients and sulphate, but not, for example, alkalinity or ANC.

Experience and data from the first field visit suggested that some sites were unsuitable, and a revised network of sampling sites was selected for the second and subsequent samplings. Reasons for exclusion of sites might be because they are for a landscape which is of little interest, or one which is well represented. In some cases the subcatchment did not have the characteristics expected from the initial desk study. Additional sites were included where the first set of data collected suggested a particularly interesting feature. For example, some extremely high DOC values and low pHs were measured at sites in NW Scotland draining forested peat. While this landscape class does not cover a large part of the region, it has something to tell us about processes occurring.

<u>North-west Scotland</u>
Thirty-nine subcatchments were initially selected in north-west Scotland. Following the first sampling, a further 18 sites were added and 5 sites removed, mainly because of accessibility problems. There were four sampling campaigns: 9-11 Oct 2001

(autumn); 2-5 Feb 2002 (winter); 19-21 Apr 2002 (spring); 21-23 Jul 2002 (summer). Autumn and winter flows were moderate to high. Spring flow was low, following a long dry period, and summer low to moderate during a showery spell of weather. Figure 2.2.6 shows daily discharge on the Broom, Ullapool during 2001-2002, with the periods of sampling highlighted. Figure 2.2.2 includes the location of the final selection of sampling sites.

Figure 2.2.6: Discharge in representative rivers, showing times of sampling



Galloway

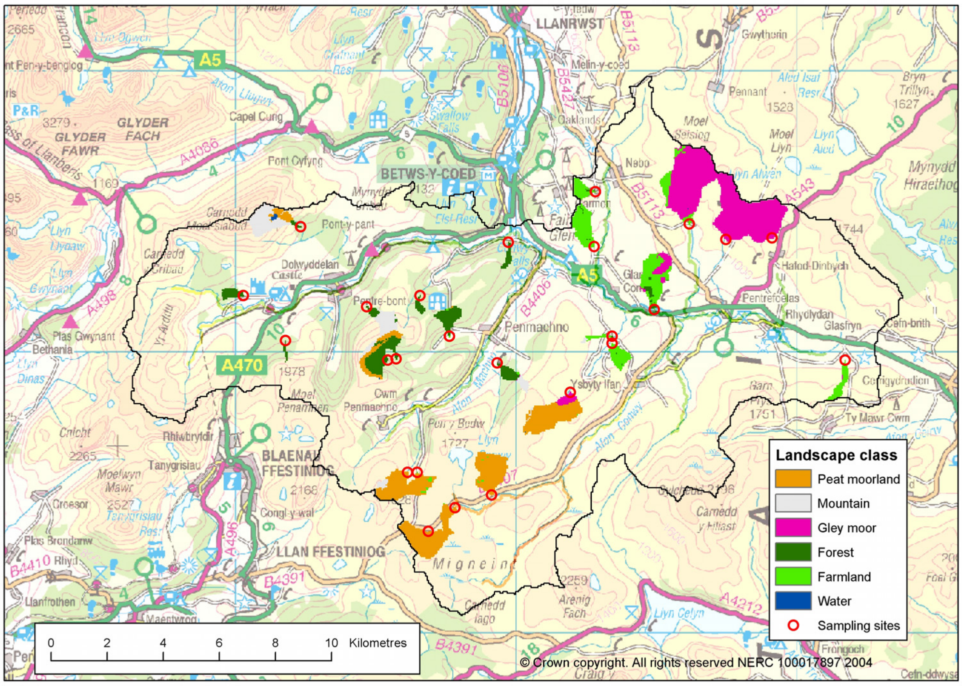
In Galloway 46 sites were chosen, with 8 dropped and 21 added after the first sampling trip. There were later minor changes in sites sampled on subsequent visits to the region. Samples were taken on four occasions: 19-22 Oct 2001; 25-29 Jan 2002; 15-17 Apr 2002; 29 Jul-1 Aug 2002. Flow conditions were similar to north-west Scotland, with the exception of the summer sampling, when flow was moderate to high following rain. Figure 2.2.3 shows the sampling sites and Figure 2.2.6 discharge in the Cree covering the sampling periods.

Conwy

Based on the observed range of soils and land-use within the catchment, 24 subcatchments were identified which, insofar as possible, represented one particular soils-land use combination (e.g. moorland on peat, coniferous forest on mineral soils). The subcatchments and their landscape class are shown in Figure 2.2.7.

Streams were sampled on three occasions, targeted to periods of typical high and low flows: a spring high flow (April 26 2002), late summer low flow (September 12 2002), and a winter high flow (January 17 2003). During both high flow surveys, overbank flooding was observed in floodplain areas. Measurements for the Conwy at the Cwm Llanerch Environment Agency gauge (Figure 2.2.6) within the catchment indicate that discharge during the low flow sampling was exceeded 72% of the time. Discharge in both high flow events was an order of magnitude higher, with the April 26th discharge exceeded 15% of the time, and the January 17th discharge 12%. Observed streamwater chemistry for these surveys should therefore, to a reasonable extent, represent the extremes of baseflow and episode chemistry.

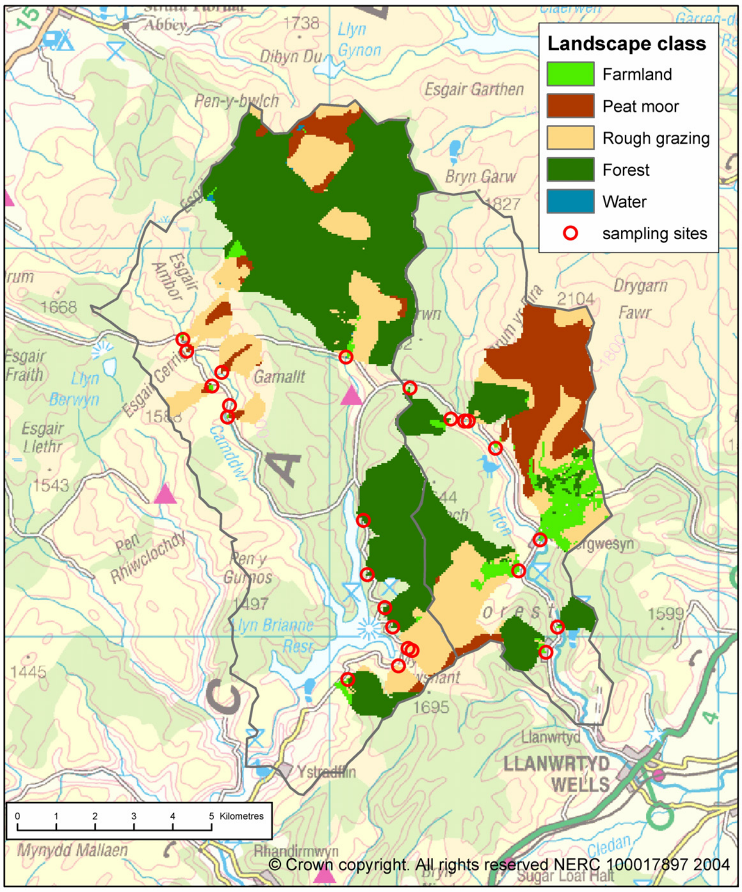
Figure 2.2.7: Subcatchments for sampling and their landscape class – Conwy



Tywi/Irfon

The subcatchments used for the Tywi/Irfon are a well-established group of 24 used in previous acidification studies. Two were discarded since they included several of the remaining subcatchments. A further two, classified as moorland, were also omitted since their stream chemistry suggested a residual effect of past liming. The remaining 20 subcatchments included none which were entirely or substantially improved farmland, and none which were exclusively peat. However, moorland and forestry were well represented. Two samples were collected at each site, on 6-7 February 2002, when discharge was high, and 6-7 August 2002 at low flow. Figure 2.2.6 shows discharge in the Cothi, a nearby tributary of the Tywi, and the subcatchments and their landscapes in Figure 2.2.8.

Figure 2.2.8: Subcatchments for sampling and their landscape class – Tywi/Irfon



2.2.2 Sampling and analysis of chemistry and biology from streams in 3 regions at high and low flows

Samples collected in north-west Scotland and Galloway were analysed at MLURI laboratories in Aberdeen. During transit of up to 5 days, they were kept in cool boxes. Water samples were filtered through a 0.45 µm Whatman cellulose nitrate filter on site. They were analysed by ICP-OES to provide concentrations of Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Si and Zn. Analysis by ion chromatography gave concentrations of the anions chloride, sulphate and nitrate. Ammonium and phosphate were determined by flow colorimetry. DOC was measured using non-dispersive infra-red spectroscopy, and alkalinity determined by Gran titration.

Samples collected in Wales were analysed at the CEH Bangor laboratories. On site filtering and transit storage were as for the Scottish samples. Na, K, Ca and Mg were measured by flame atomic emission spectrophotometry. Aluminium (total monomeric) was determined colorimetrically by catechol violet using UV-visible spectrometry. Chloride, NO_3-N, PO_4-P, SO_4 and ammonium were measured by ion chromatography, and silicon by Autoanalyser using a standard molybdate-blue method and colorimetric detection. DOC was determined by Autoanalyser following a UV-digestion technique, and colorimetric detection. Alkalinity was determined by Gran-titration.

2.2.3 Analysis of chemistry data and application of flow routing model

Data description

<u>NW Scotland</u>
Measured concentrations from samples in north-west Scotland suggested that some landscape classes were not distinguishable from their water chemistry. The between-landscape variability was no greater than within-landscape. There was therefore little justification in retaining the full original classification, and a reclassification was carried out. Revised classes are shown in Table 2.2.5, comprising montane, forest and limestone and two moorland landscapes. Moorland is essentially divided in that to the west and to the east of the Moine thrust, Moorland I and Moorland II.

<u>Table 2.2.5: Revised landscape classes for north-west Scotland and Galloway</u>

North-west Scotland			**Galloway**		
Revised class	*Original classes*	*Name*	*Revised class*	*Original classes*	*Name*
1	1,3,10	Forest	1	1,3,6,9	Forest I
2	2,4	Moorland I	2	4,5,7,12	Farmland
3	5,9,12	High altitude	3	2,8,10	Moorland I
4	6,8,11	Moorland II	4	11	Forest II
5	7	Limestone	5	13	Moorland II

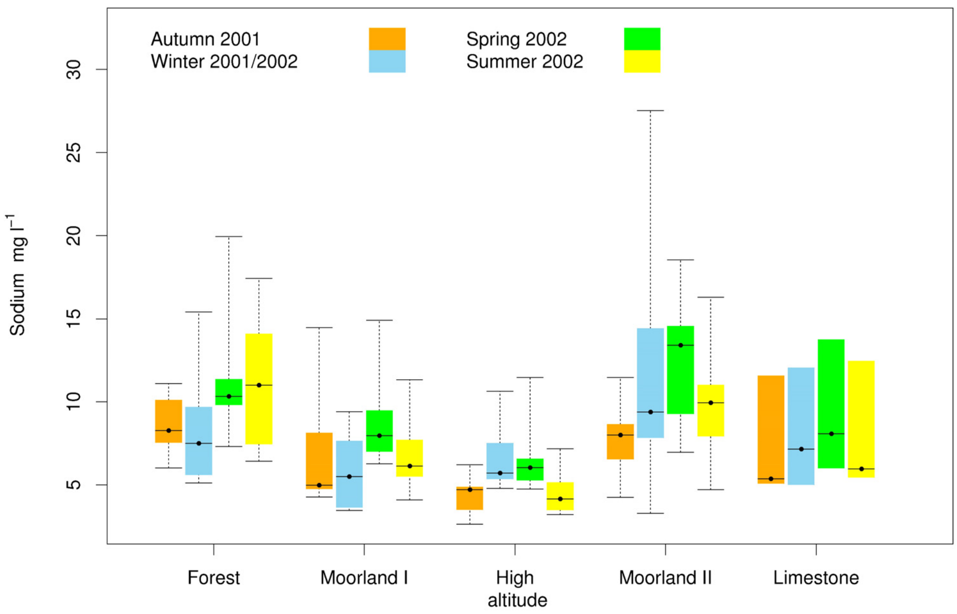
There is a strong marine influence in many of the sampled catchments in north-west Scotland, and this is partly confounded with landscape class. Forested subcatchments, which elsewhere would show elevated sea salt concentrations, are largely some distance from the sea and in sheltered glens. For this reason there is less evidence of, for example, higher chloride concentrations at forested sites than might be expected. In addition, some of the marine influence cuts across the landscape classification, contributing to within-class variability.

Figures 2.2.9a to 2.2.9k shows box and whisker plots of concentrations by landscape class for samples from north-west Scotland. In these plots, sample subcatchments are grouped by their dominant landscape class, which in most cases is overwhelmingly dominant. Even after reducing the number of classes from 12 to 5, for many determinands there is little perceptible (and no statistically significant) difference between landscapes. Particular characteristics by landscape are:

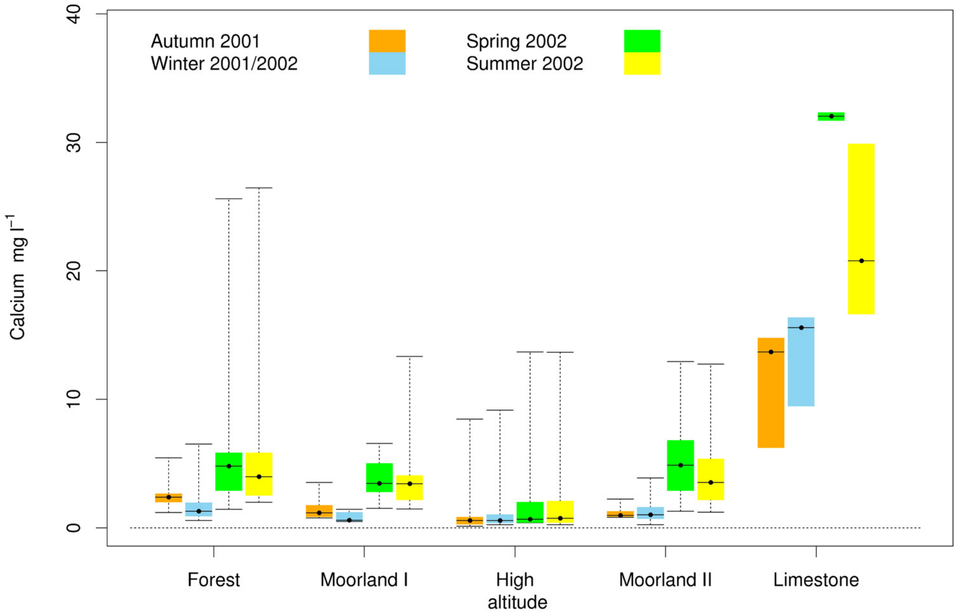
- <u>Forest</u>: Moderate sea salt component, considering the land cover. Concentrations maintained in summer, when falls are seen in other classes. Some loss of base cations, particularly at low flow. Aluminium losses higher than other classes, and also some nitrate loss. Significant non-marine sulphate except during summer. ANC never below zero. High DOC in comparison with other classes, with some exceptionally high summer values. Several sites show pH below 5 during autumn and winter, although these are not associated with negative ANC.
- <u>Moorland I</u>: This class has a westerly distribution, with a greater marine influence than Moorland II. Base cation losses are similar to Forest and Moorland II classes, and nitrate losses are low. There is effectively no non-marine sulphate. A summer decline to negative values is shared by Forest and Moorland II classes. ANC values are similar to Forest and Moorland II, but in common with Moorland II show some negative values in the winter sampling. pH is neutral at low flows
- <u>High altitude</u>: These show the least marine influence, although not notably distant from the sea. Higher rainfall may account for this. They also show the lowest base cation loss, with little increase in spring and summer. Nitrate losses are significant in all seasons. This is assumed to be atmospheric nitrogen which in these hostile catchments is not limiting to plant growth. There is also significant non-marine sulphate, which may be present for the same reason. ANC is low in all seasons, but rarely falls below zero, and pH is relatively stable though higher at low flows. DOC is present, but in lower concentrations than other classes.
- <u>Moorland II</u>: There is little to distinguish this from Moorland I, other than a less significant marine influence, and lower aluminium concentrations.
- <u>Limestone</u>: This class has a major geological contribution in the form of base cation weathering, particularly apparent at low flows. Excess sulphur may also be from this source. While not improved, these catchments have greater biological activity, and have some nitrate loss. Aluminium concentrations are low, and DOC high in summer, though not at other times of year.

Figure 2.2.9: Sample chemistry by landscape class & sampling period – North-west Scotland

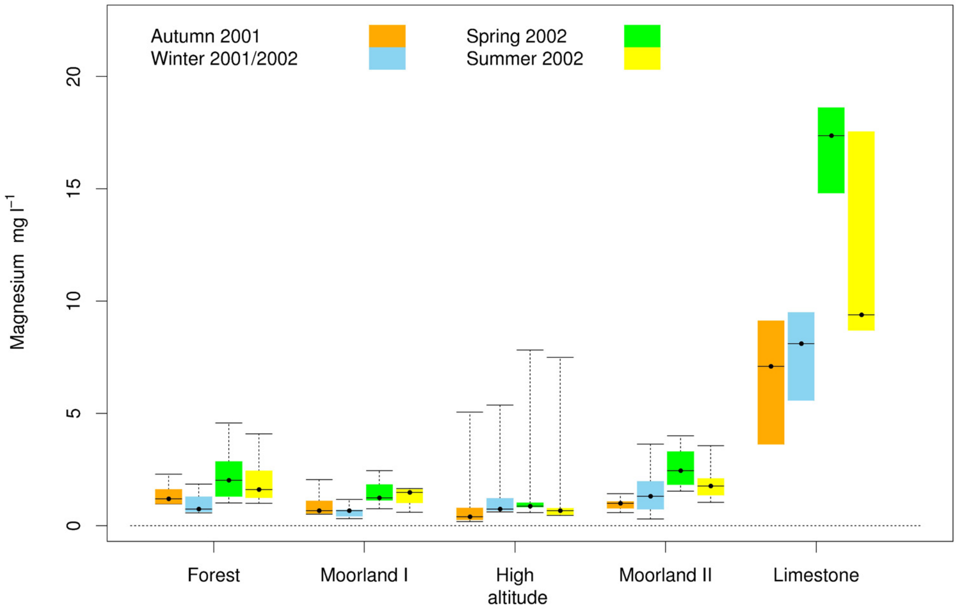
a: Sodium



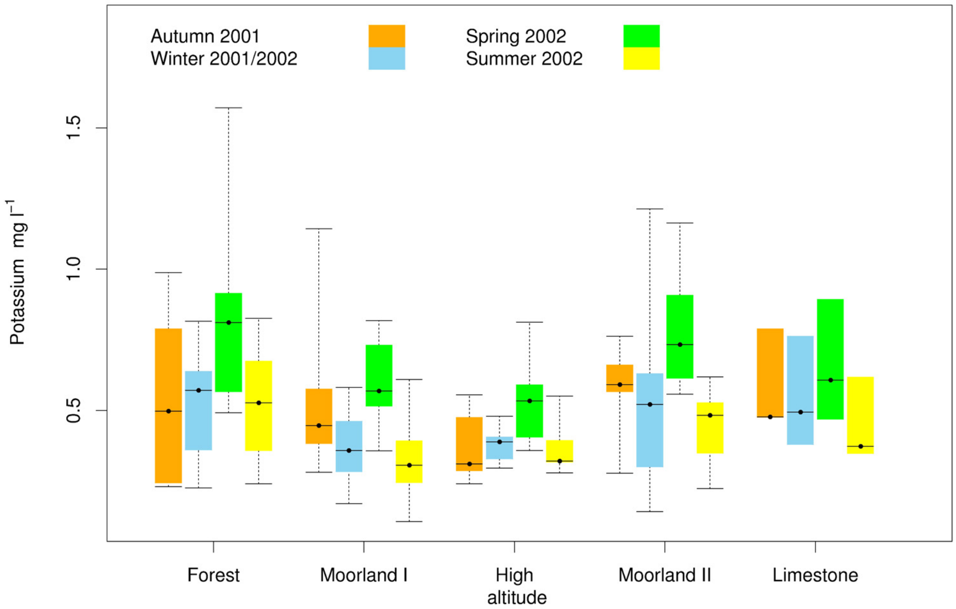
b: Calcium



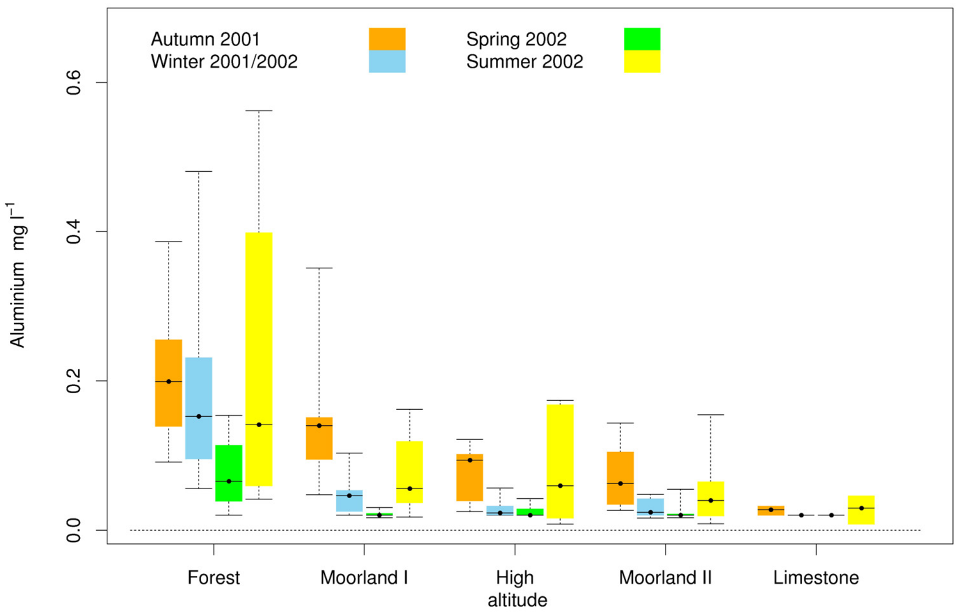
c: Magnesium



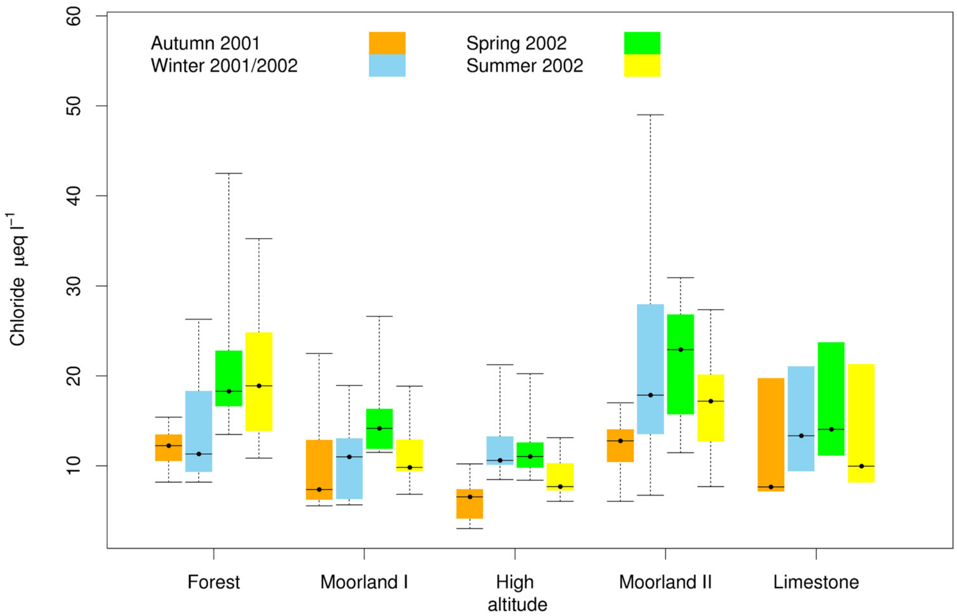
d. Potassium



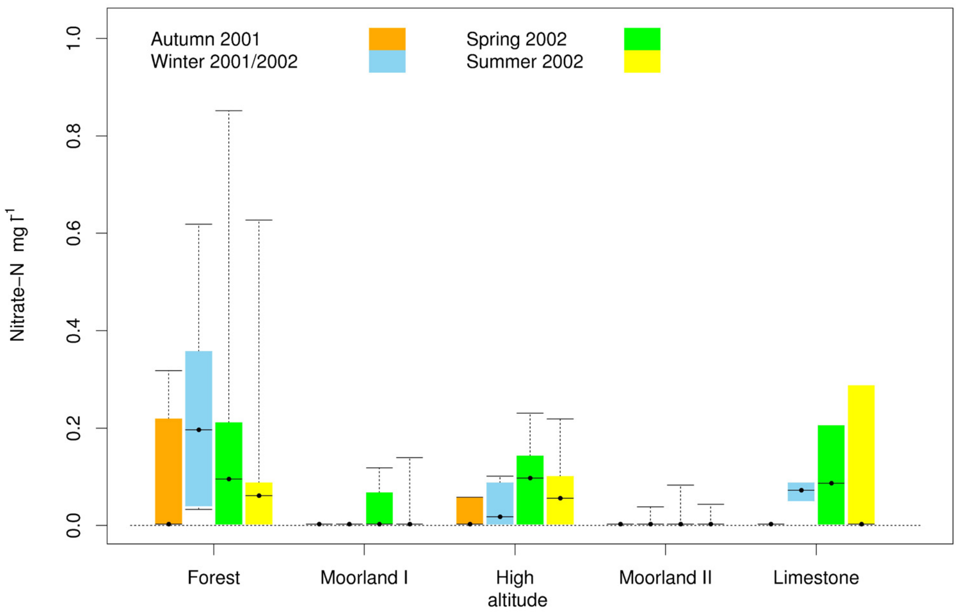
e. Aluminium



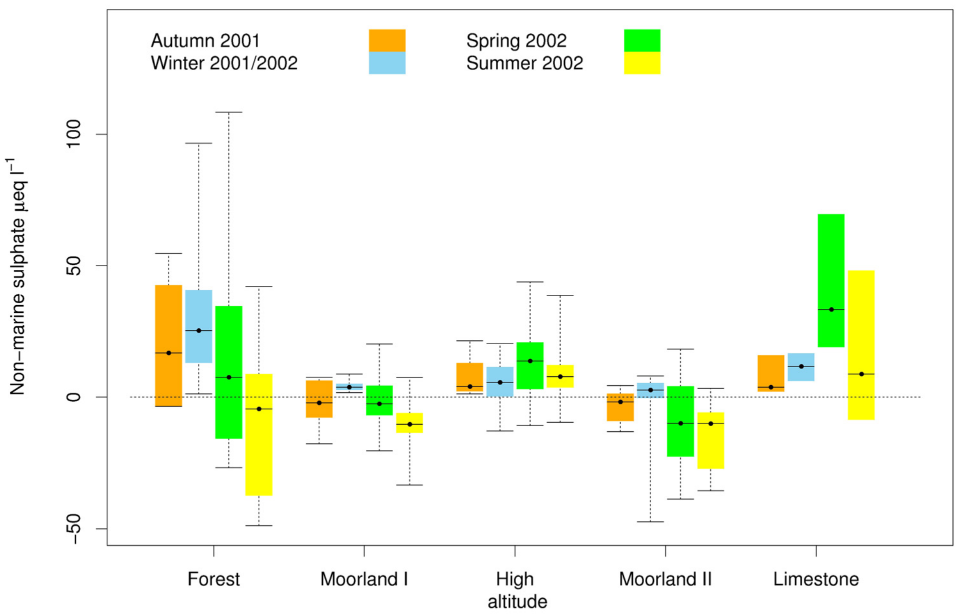
f. Chloride



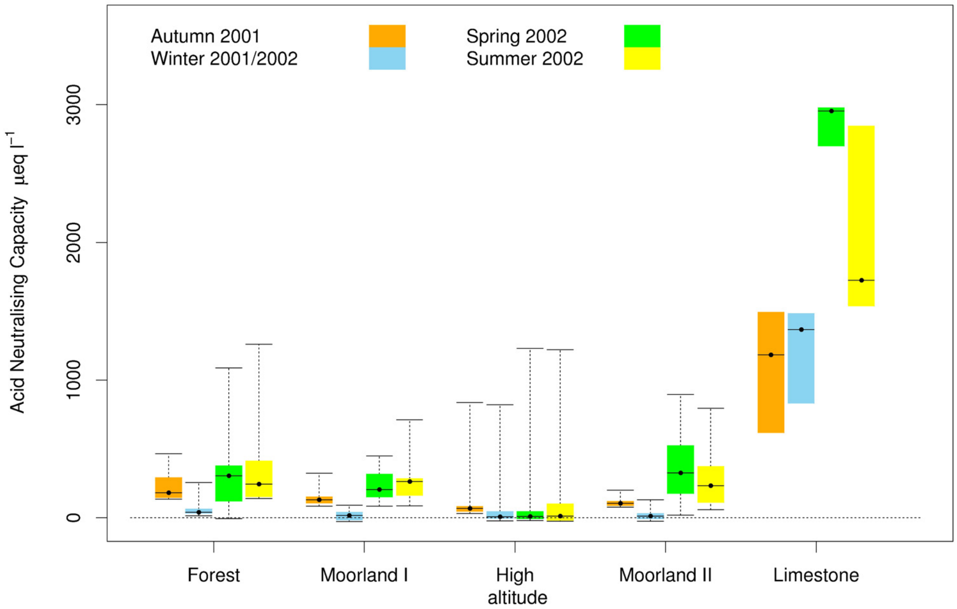
g. Nitrate



h. Non-marine sulphate

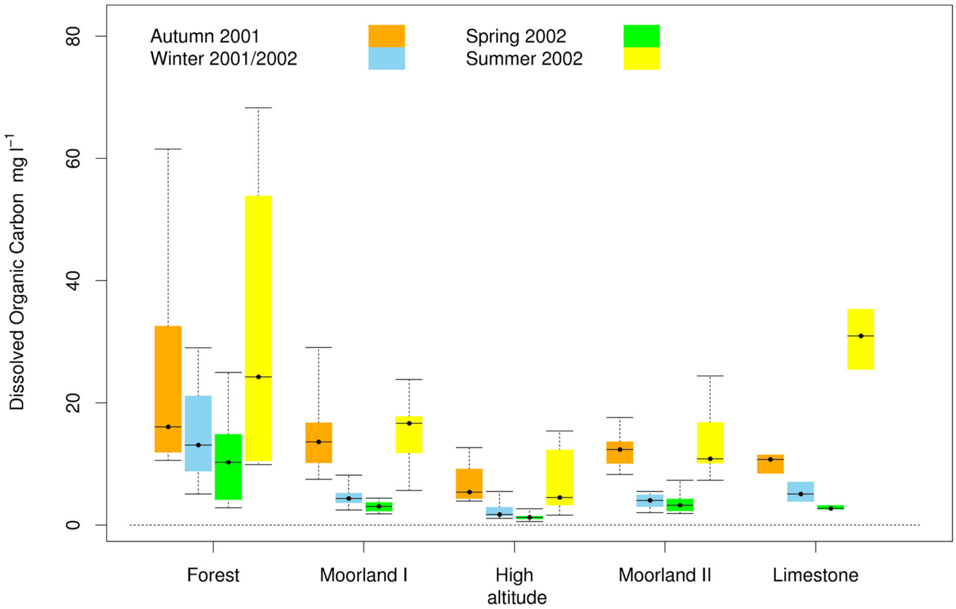


i. ANC



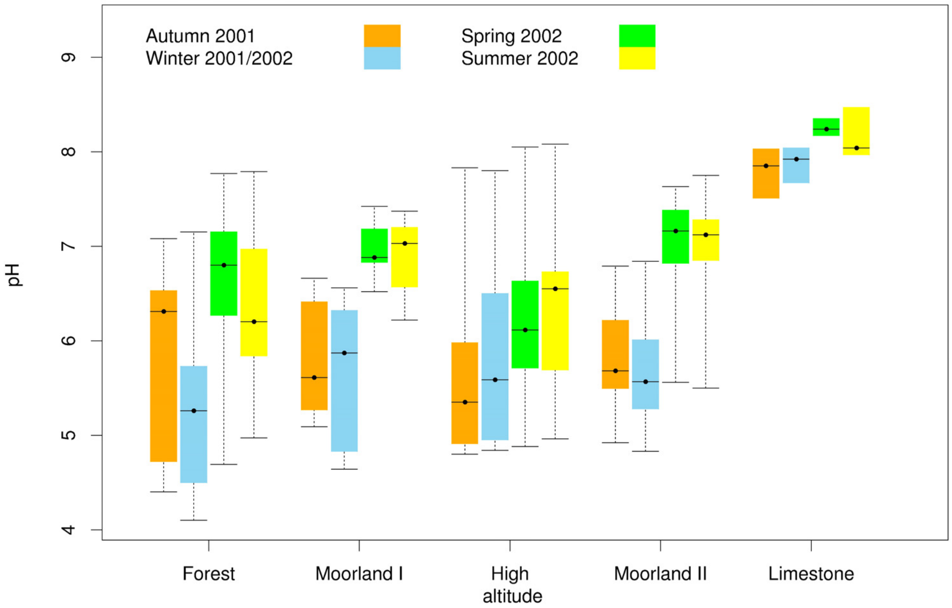
Autumn 2001
Winter 2001/2002
Spring 2002
Summer 2002
Acid Neutralising Capacity µeq l^{-1}
0
1000
2000
3000
Forest
Moorland I
High altitude
Moorland II
Limestone

j. DOC



Autumn 2001
Winter 2001/2002
Spring 2002
Summer 2002
Dissolved Organic Carbon mg l^{-1}
0
20
40
60
80
Forest
Moorland I
High altitude
Moorland II
Limestone

k. pH



Autumn 2001
Winter 2001/2002
Spring 2002
Summer 2002
pH
4
5
6
7
8
9
Forest
Moorland I
High altitude
Moorland II
Limestone

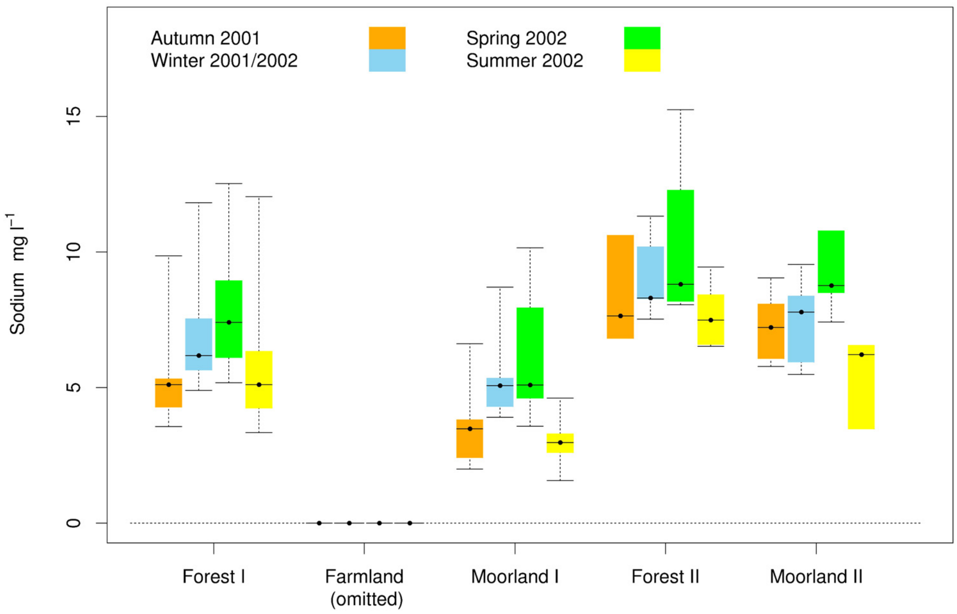
Galloway

In common with north-west Scotland, many of the original landscape classes proved indistinguishable from concentration measurements, and a group of 5 merged classes was generated, as shown in Table 2.2.5. The classes include two each of forestry and moorland, the distinction being based largely on soils and geology, but also location, with a higher marine component in the more north-westerly Moorland II and Forest II. A farmland class accounts for the remainder of the region. Figure 2.2.10 shows concentrations of a range of determinands by sampling visits for each of the 5 revised landscapes. Data for Farmland are excluded since they are not vulnerable to acidification. However, they are retained for modelling in order to generate the mixing required to estimate water quality in rivers. General observations from Figure 2.2.10 are:

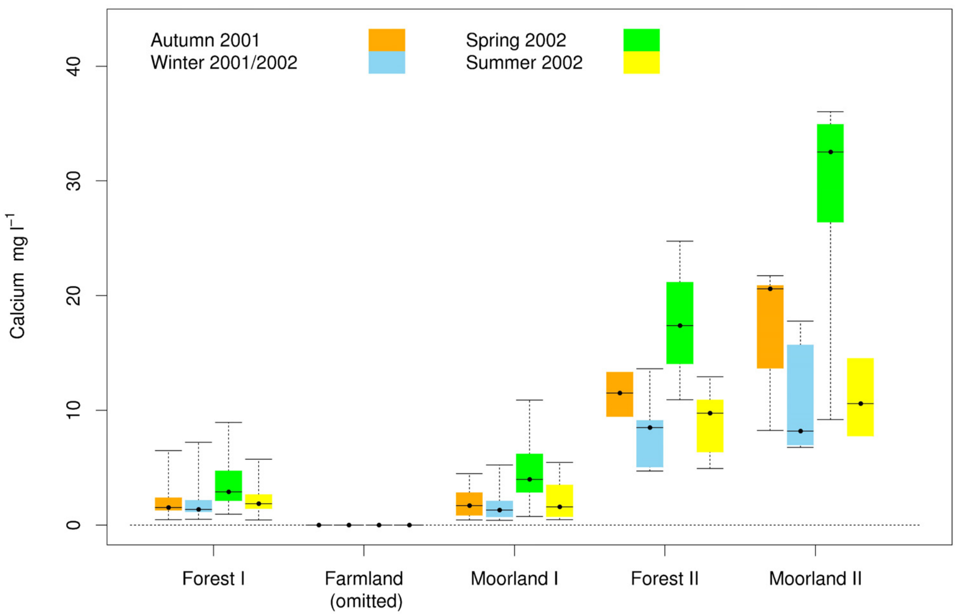
- Forest I: Marine component slightly higher than Moorland I, with slightly lower base cation losses. Both marine and base cation losses are lower than for Forest II. Aluminium losses higher than remaining forest and moorland classes, and related to flow conditions. Note that summer was a high-flow sampling. Some nitrate leaching, and significant concentrations of non-marine sulphate, higher than Moorland I, but comparable to or lower than Forest II. Some negative ANC in winter. ANC generally lower and DOC higher than remaining landscapes, with some negative ANC values in all seasons. pH very variable between subcatchments at high flows, suggesting variable influence of deeper weathering.
- Farmed: Omitted. High concentrations of major ions, high pH and ANC
- Moorland I: Characterised by low base cation weathering and a low marine component. It also shows the lowest nitrate and non-marine sulphate concentrations. ANC is higher than Forest I. DOC is lower than other classes, and pH is very variable, with some sites below 5 under high flow conditions.
- Forest II: This is influenced by more weatherable geology and a marine influence in the north-west of the region. This results in a higher marine component, higher base cation loss and higher ANC and pH. Although excess sulphate concentrations are quite high, this class is not susceptible to acidification.
- Moorland II: Comparable to Forest II for most determinands, but with a lower aluminium and marine component, and higher base cation concentrations. Particularly high non-marine sulphate concentrations at low flows may be due to internal sources.

Figure 2.2.10: Sample chemistry by landscape class and sampling period – Galloway

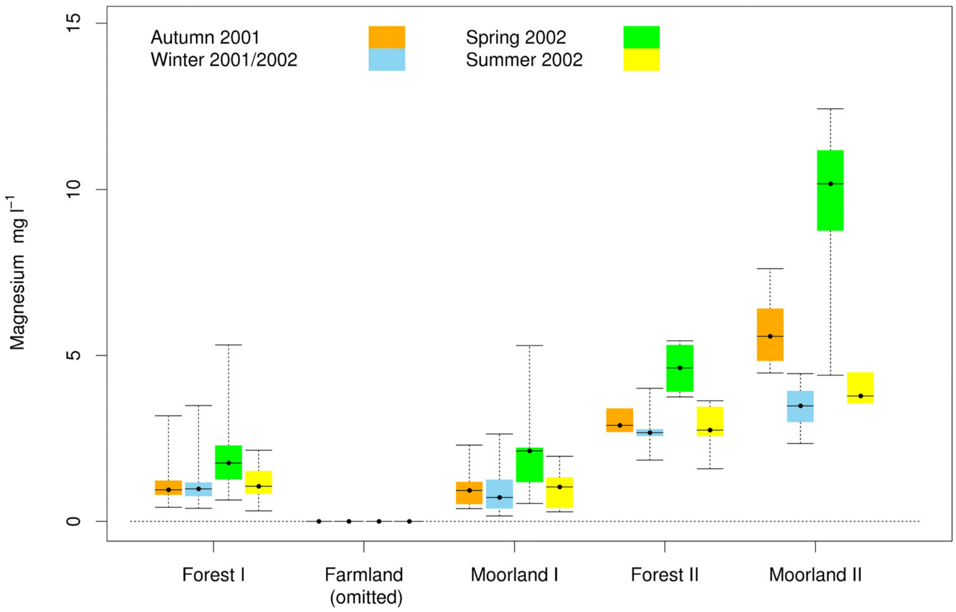
a. Sodium



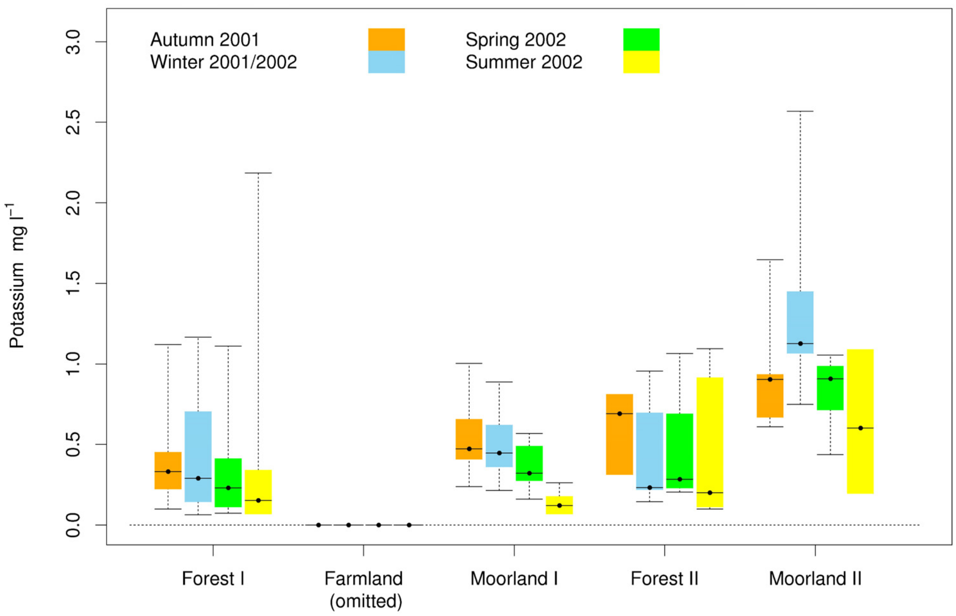
b. Calcium



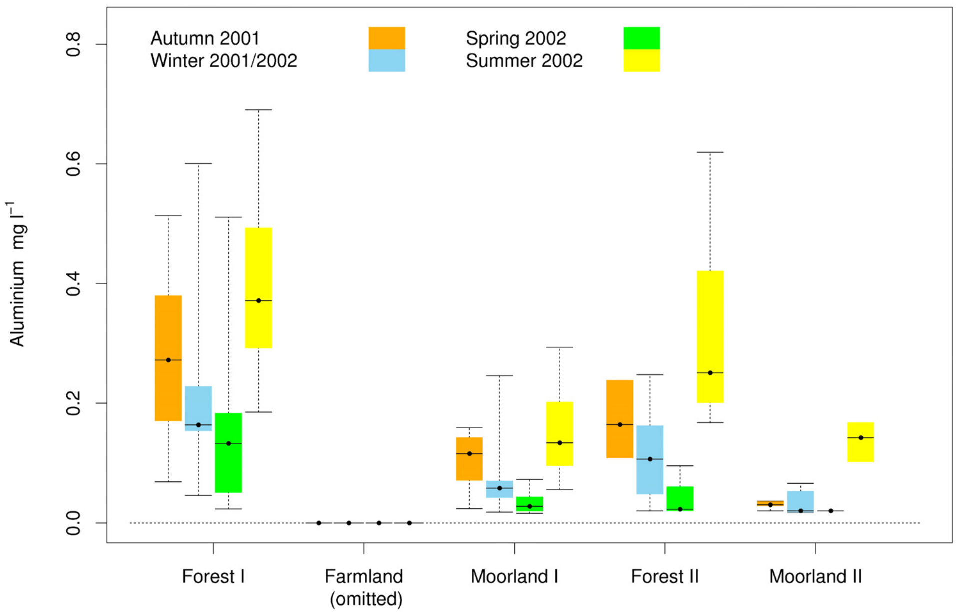
c. Magnesium



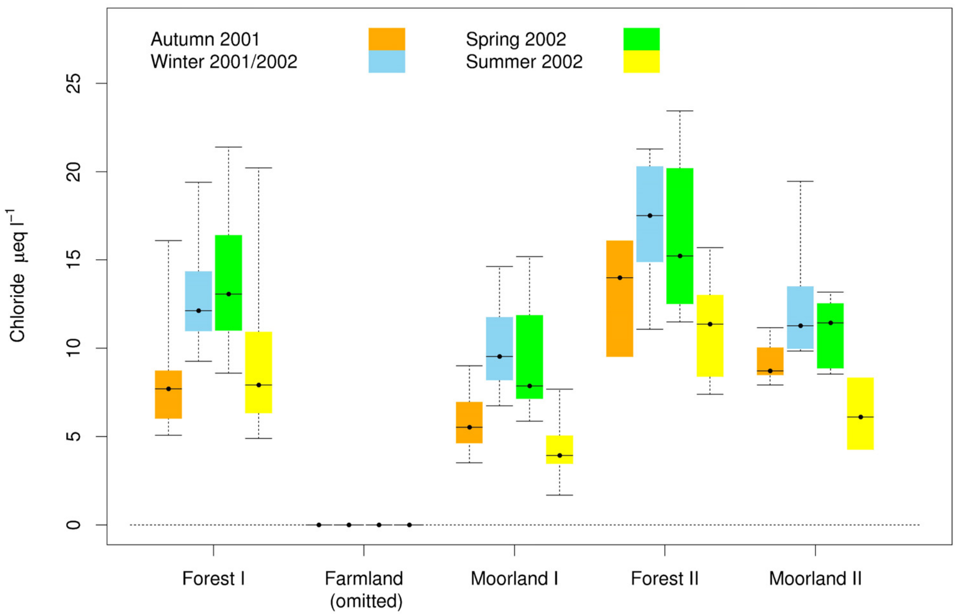
d. Potassium



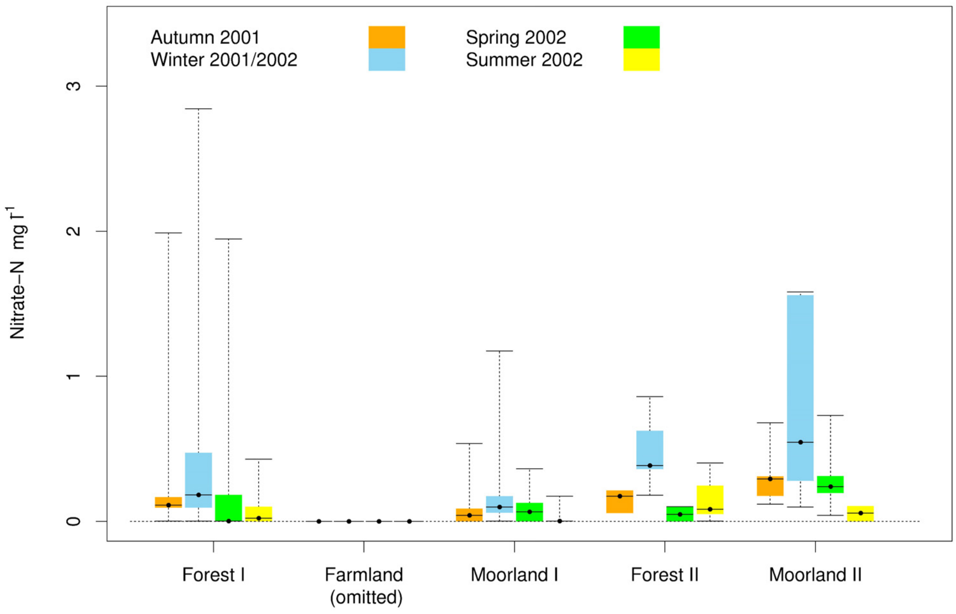
e. Aluminium



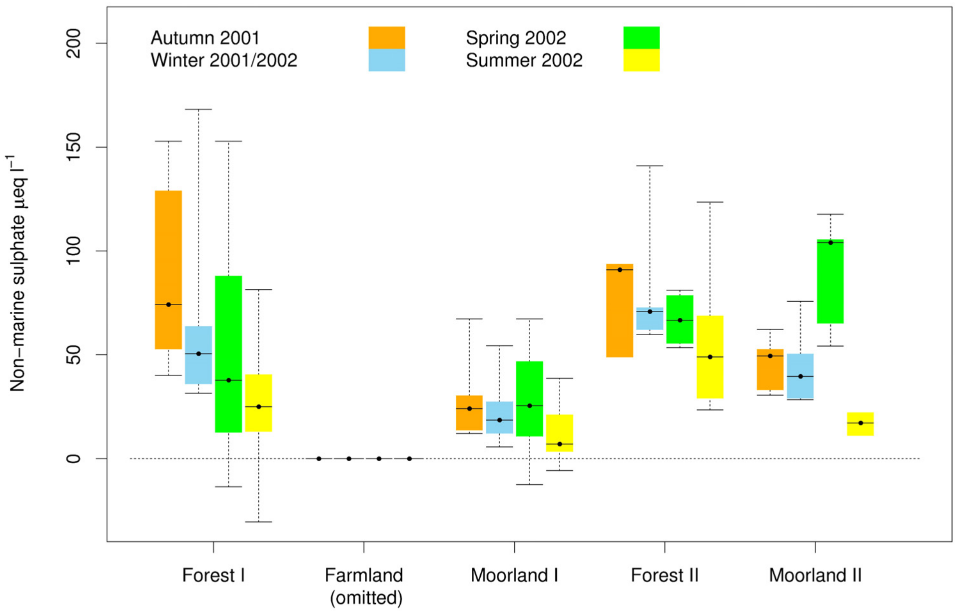
f. Chloride



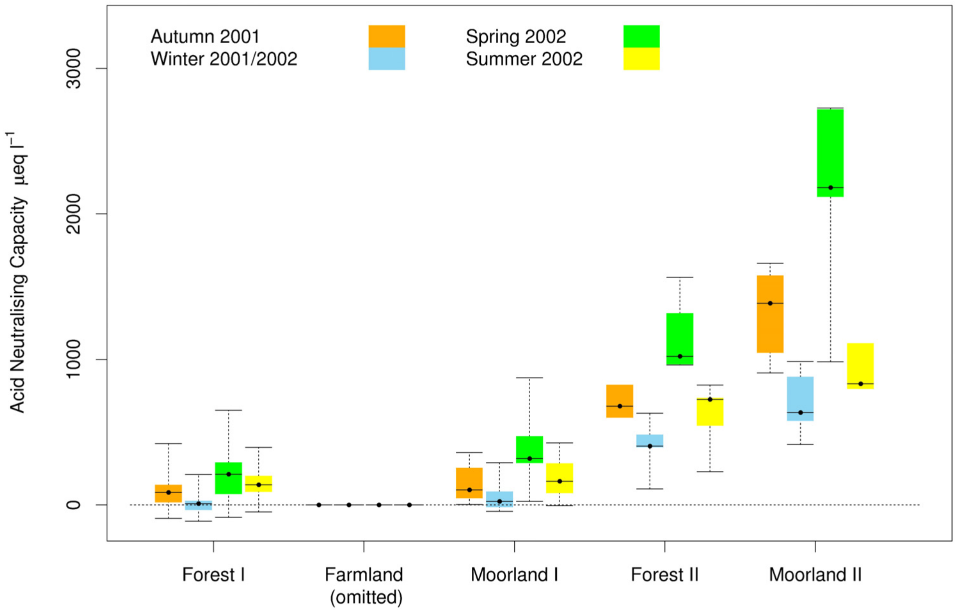
g. Nitrate



h. Non-marine sulphate

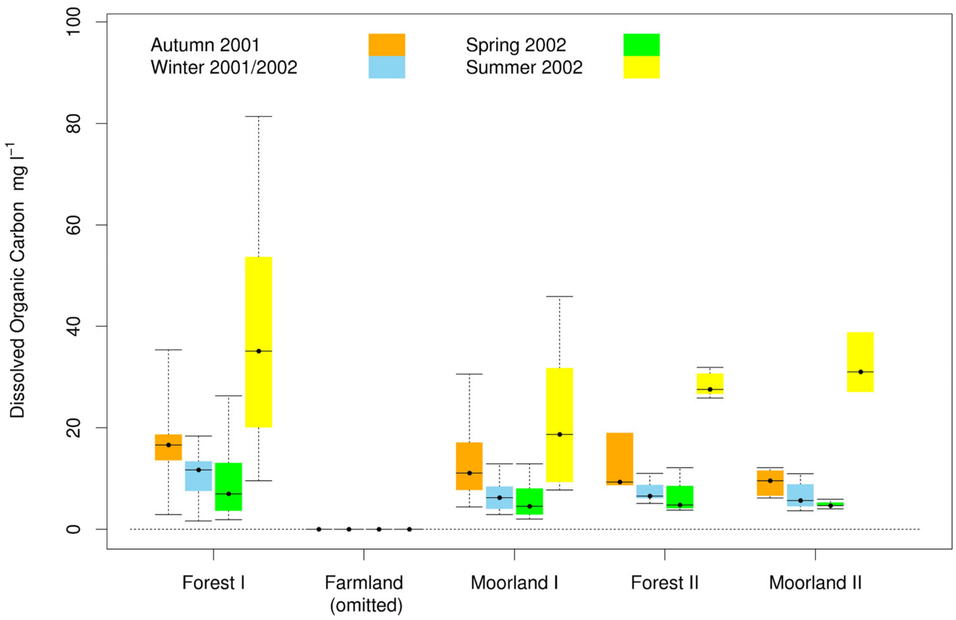


i. ANC



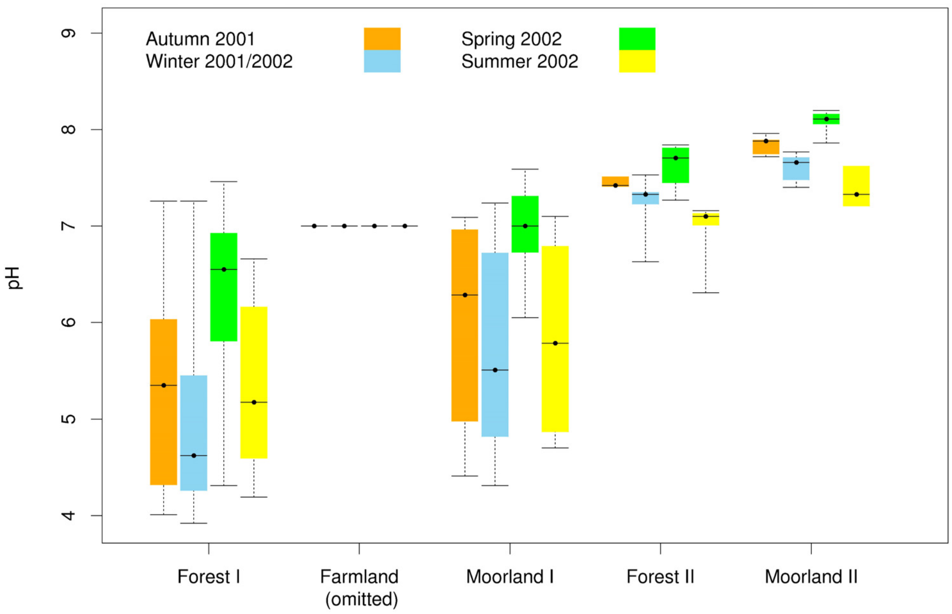
Autumn 2001
Winter 2001/2002
Spring 2002
Summer 2002
Acid Neutralising Capacity µeq l⁻¹
0
1000
2000
3000
Forest I
Farmland
(omitted)
Moorland I
Forest II
Moorland II

j. DOC



Autumn 2001
Winter 2001/2002
Spring 2002
Summer 2002
Dissolved Organic Carbon mg l⁻¹
0
20
40
60
80
100
Forest I
Farmland
(omitted)
Moorland I
Forest II
Moorland II

k. pH


Autumn 2001
Winter 2001/2002
Spring 2002
Summer 2002
pH
9
8
7
6
5
4
Forest I
Farmland
(omitted)
Moorland I
Forest II
Moorland II

Conwy

Box and whisker plots for stream chemistry within each of the landscape classes (Figure 2.2.11) indicate reasonably consistent and distinct runoff chemistry for each of the landscape types. Additionally, a simple assessment of the role of different chemical drivers of acid episodes was made by comparing solute concentrations in the most acid samples (January high flow) to site means. Since charge balance ANC is defined from the constituent base cations and acid anions, the proportion of a change in ANC caused by the change in a particular ion can be determined. As a simple example, if ANC falls by 20 μeql^{-1}, NO_3 rises by 10 μeql^{-1}, Ca falls by 10 μeql^{-1} and other ions remain constant, 50% of the ANC decrease can be accounted for by increasing NO_3, the other 50% by base cation dilution. Ideally this analysis would be undertaken based on pre- and peak-episode samples, but the analysis undertaken here on episodic versus mean chemistry (Figure 2.2.12) provides some indication of the drivers of low ANC conditions. Results for each landscape type can be summarised as follows:

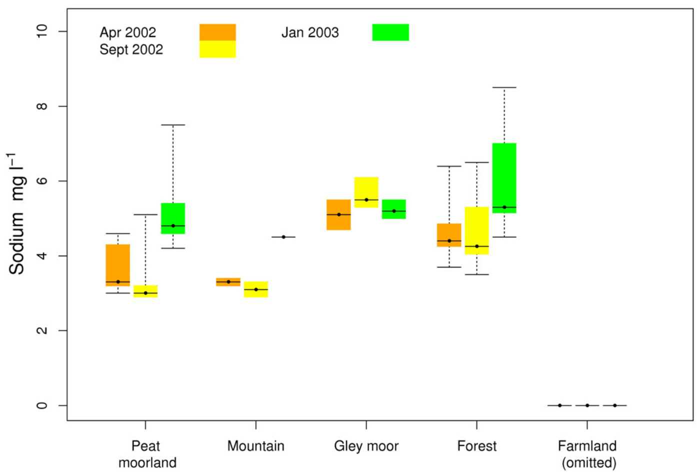
- Peat moorland: Characterised by generally low solute concentrations, low alkalinity and (charge balance) ANC, high H^+, high DOC and intermediate total Al. indicative of an ombrotrophic system with minimal terrestrial inputs (e.g. of base cations, Al), dominated by deposition inputs and organic acidity. Alkalinity and ANC became negative in both high flow events, with 'sea salt effect' exchange of marine base cations and hydrogen an important driver of acid episodes.
- Montane moorland: Low mean ANC and alkalinity, and moderately low base cations. DOC is lower, and NO_3 higher, than the peat streams, both of which are thought to reflect smaller amounts of organic matter in the catchments (Evans *et al.*, submitted). ANC and alkalinity fell to around zero at high flows, with episodic ANC decreases apparently driven by a combination of base cation dilution and the seasalt effect. However, since only two montane catchments were sampled, inferences for this landscape type are considered uncertain.
- Gley moorland: Much less acidic than the other moorland landscape types, with markedly higher base cations (especially Mg). Most of this landscape area, and all of the sampled subcatchments, are located on the Denbigh Moors in the northeast of the catchment. It is possible that this area, located on Silurian sediments, may be less geologically sensitive than the rest of the catchment, which is on Ordovician sedimentary or igneous bedrock. Large areas of this landscape type are also characterised by *Juncus*-dominated grassland, which could also indicate past improvement. High DOC and low NO_3 levels draining the relatively peaty soils, however, correspond to those in the peat streams. Episodic ANC decreases in this landscape type are driven primarily by base cation dilution, and ANC was not found to fall below zero in any sampled catchment.
- Forest: High SO_4 and NO_3 concentrations in the forest streams lead to low alkalinity and ANC despite relatively high base cation concentrations. These enhanced acid anion losses, and consequent acidification, reflect the established impacts of afforestation on deposition inputs and nutrient cycling. All eight forested streams experienced negative ANCs during high flows, with biologically-important Al concentrations markedly higher in the forest streams than in moorland streams at the same ANC and pH. The ANC depression observed at

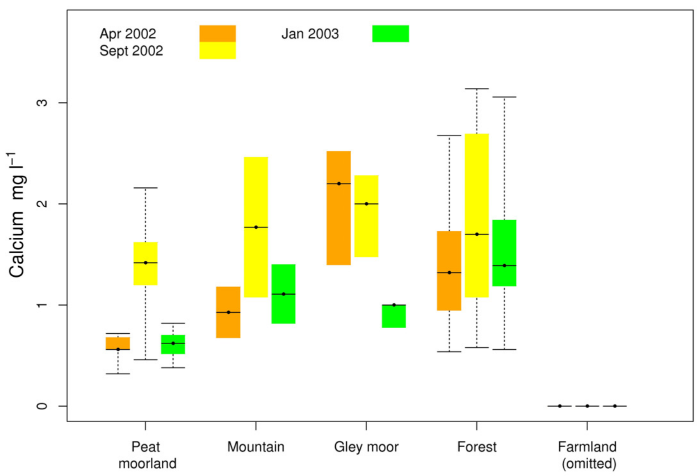
high flows can be attributed to a combination of the sea-salt effect, and increases in acid anion concentrations.

- Farmland: Farmed catchments were invariably alkaline, with high concentrations of base cations and also NO_3, SO_4 and Cl. Spatial variability was high, probably due to variations in agricultural (e.g fertiliser, lime) inputs. Base cation concentrations decreased at high flows but ANC remained above 150 μeql^{-1} at all times in all six sampled streams.

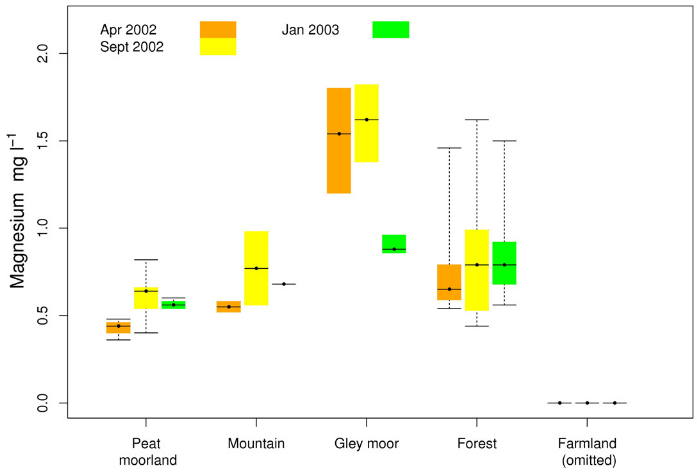
Figure 2.2.11. Sample chemistry by landscape class and sampling period – Conwy

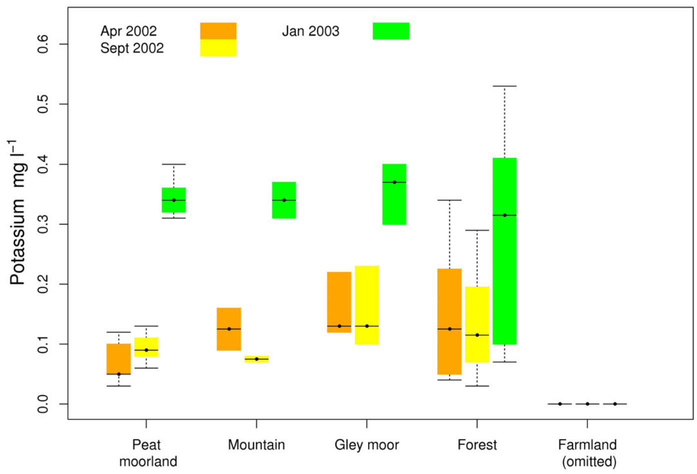
a. Sodium and calcium



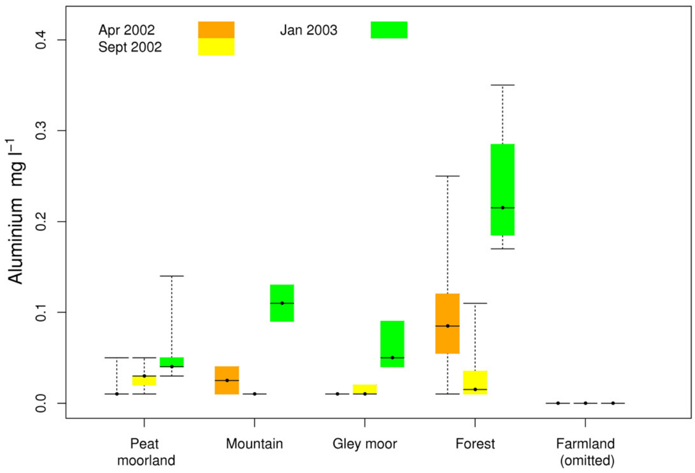


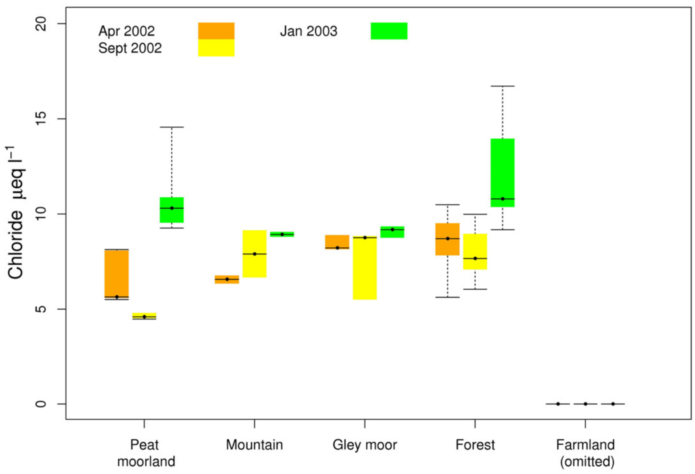
b. Magnesium & potassium



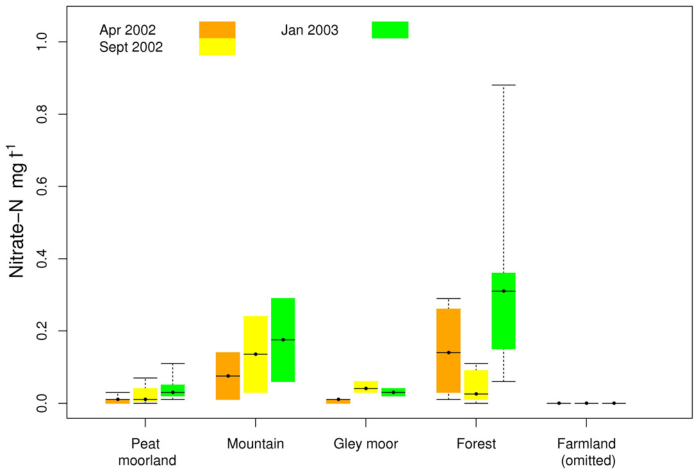


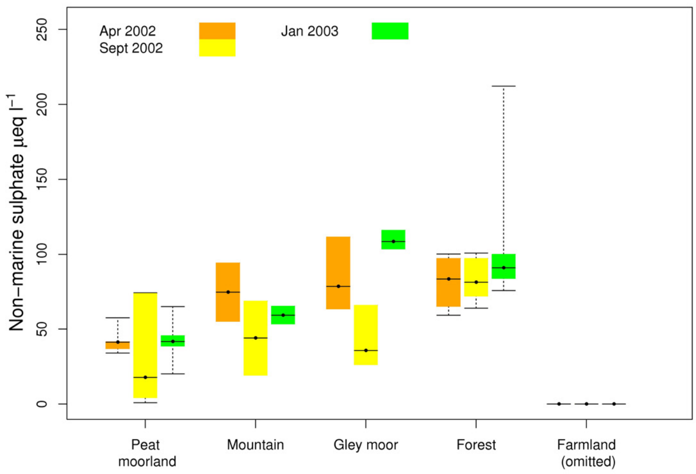
c. Aluminium & chloride



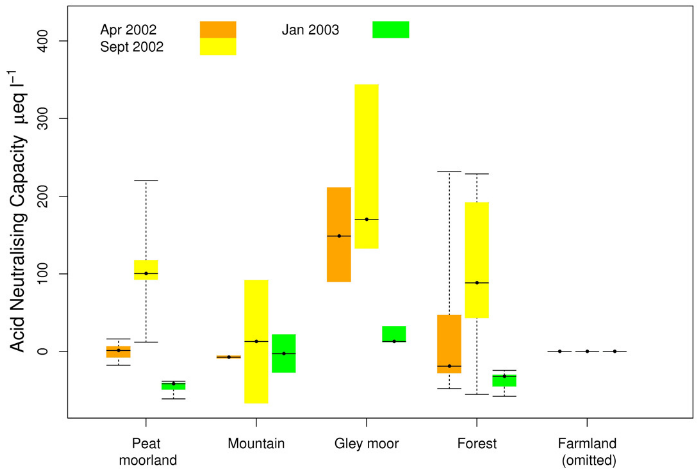


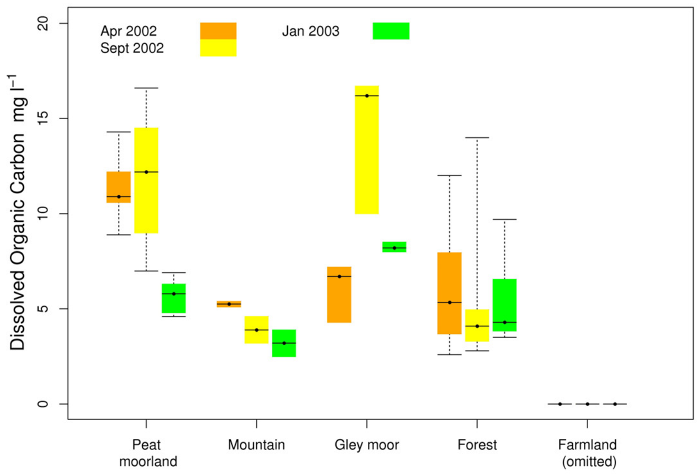
d. Nitrate & non-marine sulphate





e. ANC & DOC


Apr 2002
Sept 2002
Jan 2003
Acid Neutralising Capacity µeq l⁻¹
400
300
200
100
0
Peat moorland
Mountain
Gley moor
Forest
Farmland (omitted)


Apr 2002
Sept 2002
Jan 2003
Dissolved Organic Carbon mg l⁻¹
20
15
10
5
0
Peat moorland
Mountain
Gley moor
Forest
Farmland (omitted)

f. pH

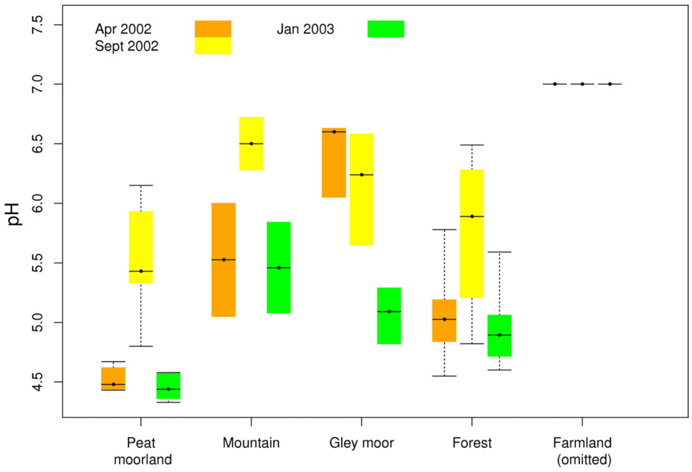
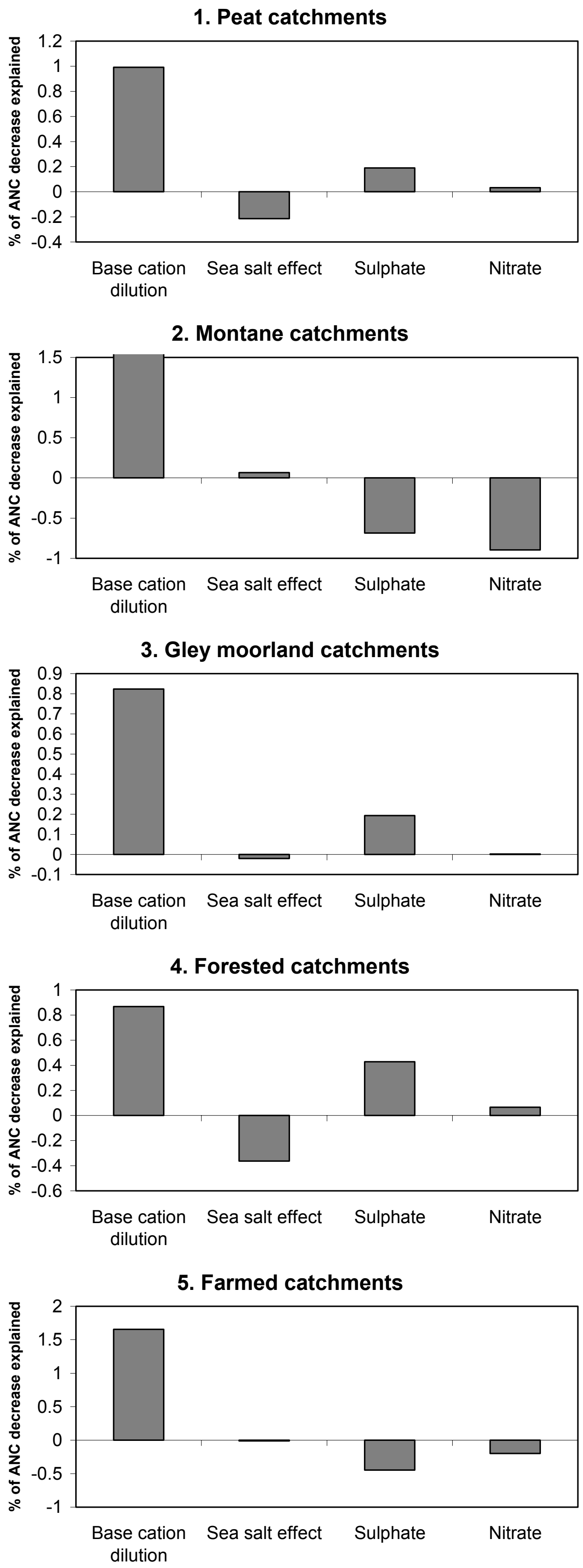

Apr 2002
Sept 2002
Jan 2003
pH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
Peat moorland
Mountain
Gley moor
Forest
Farmland (omitted)

Figure 2.2.12: Sources of change in ANC between high and average flow – Conwy



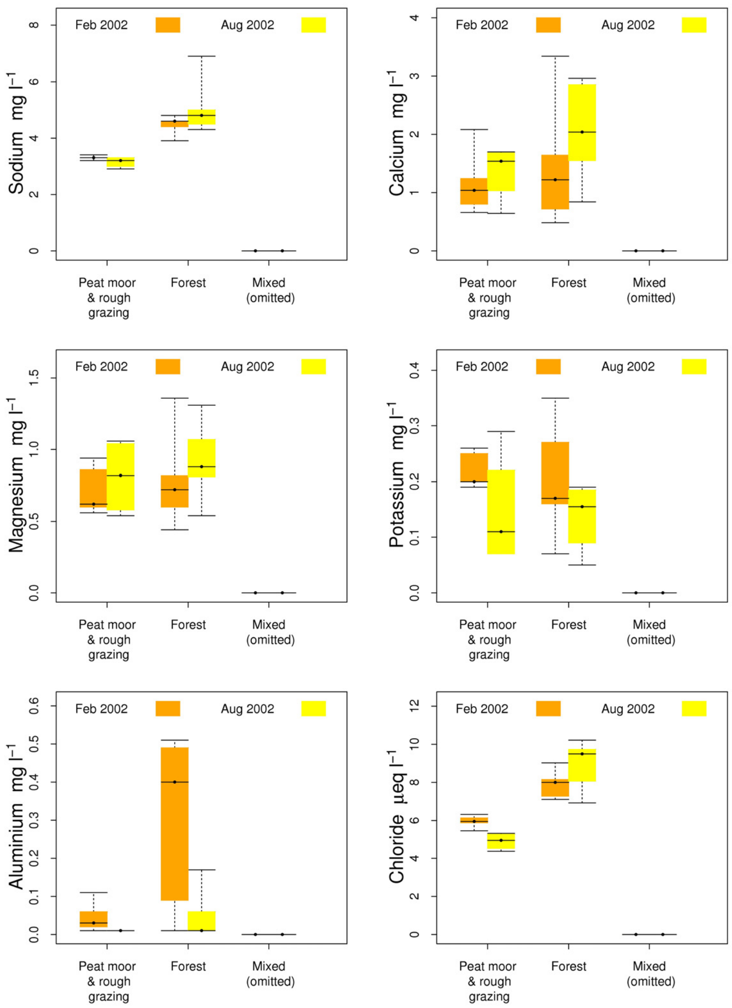
Tywi/Irfon

The subcatchments were not selected for the CLAM2 project, and some landscape classes are not well covered. In addition, some subcatchments have a mixture of landscapes, and no subcatchment is dominated by either Peat moor or Farmland. For comparison of drainage chemistries, those catchments which are overwhelmingly Peat moor and Rough grazing have been identified, together with those which are essentially forest. The chemistry of these two groups of subcatchments is shown in Figure 2.2.13. General observations are:

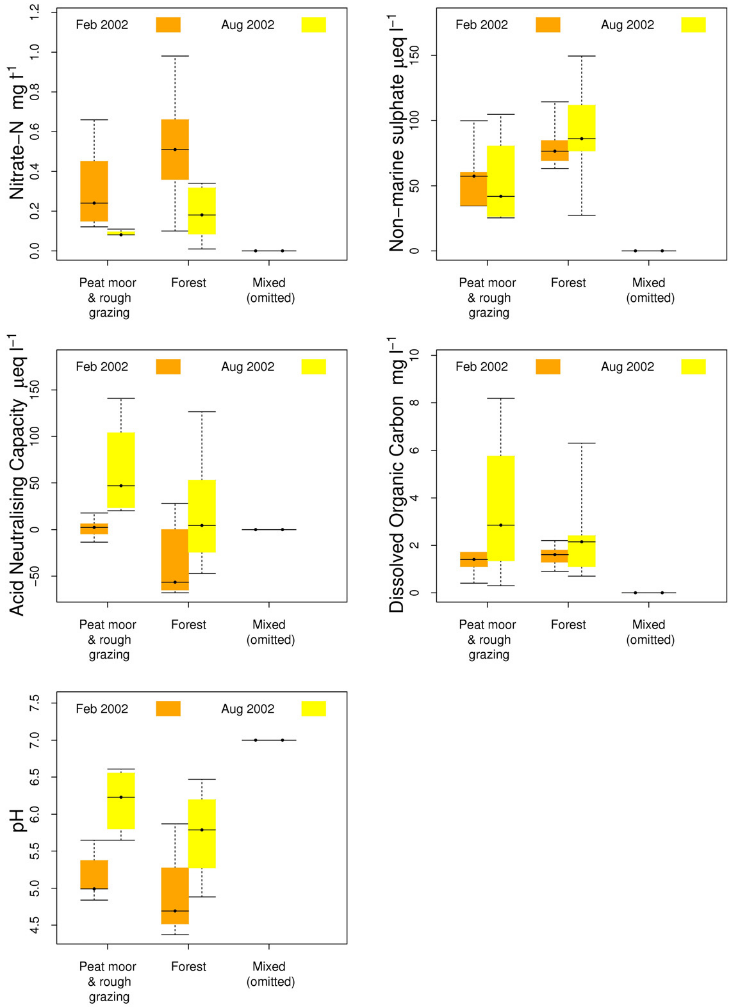
- Peat moor and rough grazing: This shows lower marine influence than forestry, and this is not related to location. It also shows higher concentrations of non-marine sulphate. These characteristics have been observed elsewhere in mid-Wales. Aluminium concentrations are lower than for Forest. ANC fell below zero only at the high flow sampling, and was higher than Forest ANC.
- Forest: Defined against peat moor and rough grazing above. ANC falls below -50 μeql^{-1} at some sites during the high flow sampling.

Figure 2.2.13. Sample chemistry by landscape class and sampling period – Tywi/Irfon

a. Sodium, calcium, magnesium, potassium, aluminium & chloride



b. Nitrate, non-marine sulphate, ANC, DOC & pH



Application of PEARLS

Cooper *et al.* (2000) describe the mixing model procedure for estimating regional acidification status which developed into the PEARLS approach. This was extended to include uncertainty estimation under the CLAM2 project, as described by Cooper *et al.* (2004). Once the characteristic chemistry of each landscape class has been determined, mixing in the river network is simulated using a topographically-based network of HRUs and river reaches derived from a DEM. The proportion of each landscape class in each HRU is known, and the HRUs present upstream of each reach are also known. The discretisation into reaches and HRUs was originally chosen to reduce computational requirements, but recent developments in GIS software suggest this intermediate stage may be eliminated.

In order to demonstrate its application, the PEARLS approach was used in all regions except NW Scotland. While PEARLS generates concentrations of a range of determinands, the focus here is on ANC, which is of critical ecological interest.

Galloway

The PEARLS approach to stream status estimation was applied for ANC to the Cree catchment in Galloway, as described by Cooper *et al.* (2004). The catchment includes little enclosed agricultural land, but substantial forestry and moorland, on lower Palaeozoic sedimentary formations, and intrusive granite. Application of PEARLS includes Monte Carlo simulation, giving a probability distribution of ANC in each reach of the river network, from which the probability of ANC falling below a selected threshold may be computed. Figure 2.2.14 shows such probabilities for the Cree for a threshold of 0 $\mu eq\ l^{-1}$. The simulation uses data collected in January 2002, a period of high flow and low ANC. It should be emphasised that this is a spatial interpolation at the time of sampling, though it is also likely to be indicative of ANC under similar flow conditions. Lowest ANCs are simulated in those streams in the east draining granite, and forested areas over peat in the north-west of the catchment, where probabilities exceed 0.6. Probability of exceedence for large areas of moorland and forest are in the range 0.45 to 0.6.

The total length of river is defined under the PEARLS procedure as a coarser network to which HRUs deliver, and a finer within-HRU network. The length of river within an HRU associated with each landscape class is assigned by proportion. So 40% of the river network in an HRU with 40% forestry is assigned the ANC value associated with the value for drainage from forestry. For the main river network, the ANC within a reach is assigned the value achieved by mixing, by proportion, the water from all upstream HRUs, their landscape class and rainfall being known. Monte Carlo simulation assigns a different value for each landscape class for each HRU, depending on the probability distribution derived from analysis of the subcatchment data. This is a simple procedure, assuming HRUs and subcatchments are statistically equivalent. The development of a more rigorous treatment would be desirable.

One derived output from PEARLS is a distribution of total river length having ANC below a selected threshold. Figure 2.2.15 shows a histogram of the overall probability distribution of river length with ANC below 0 $\mu eq\ l^{-1}$ in the Cree, based on Monte

Carlo simulation. This provides a useful and valuable indicator of interpolation uncertainty.

Figure 2.2.14. ANC status of the Cree using PEARLS, January 2002

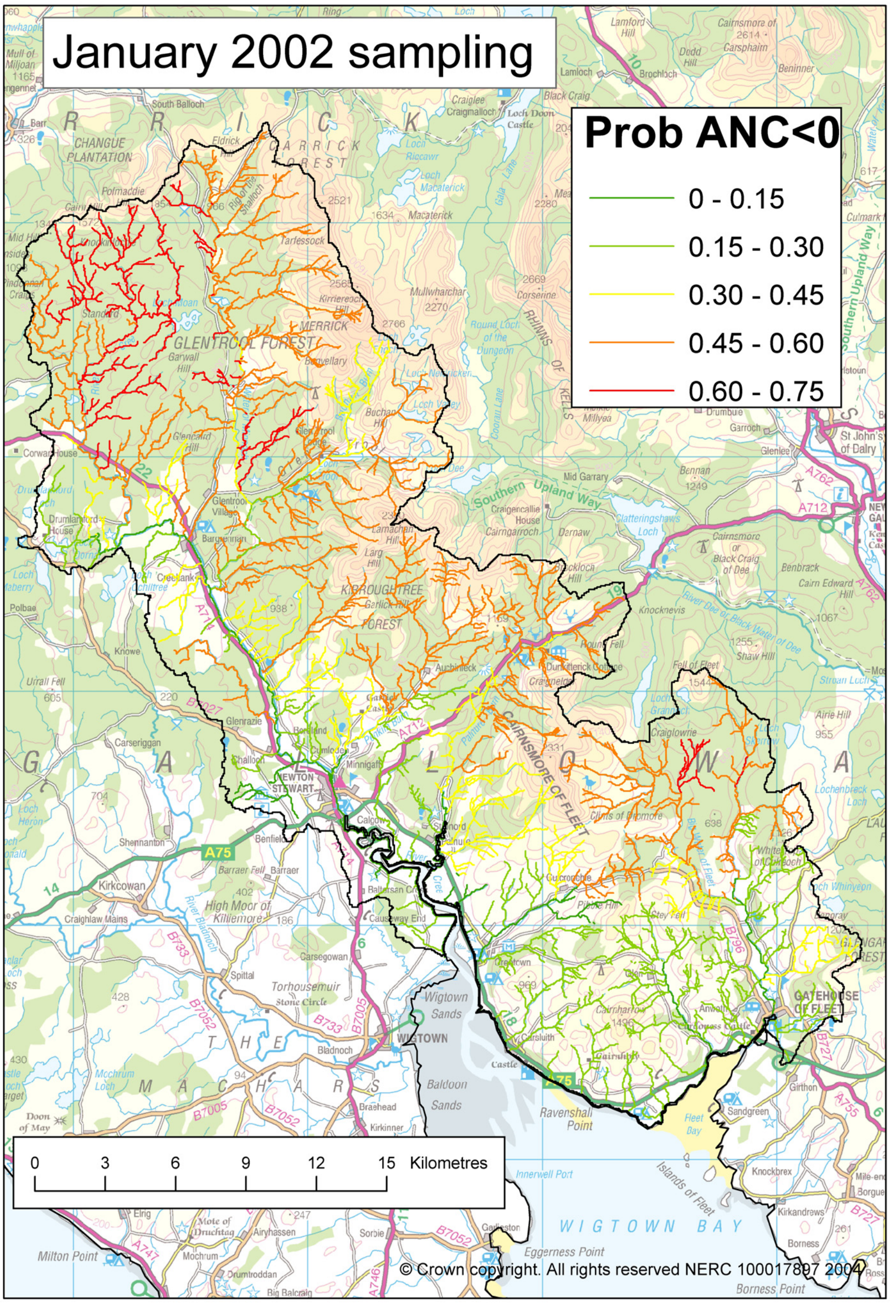
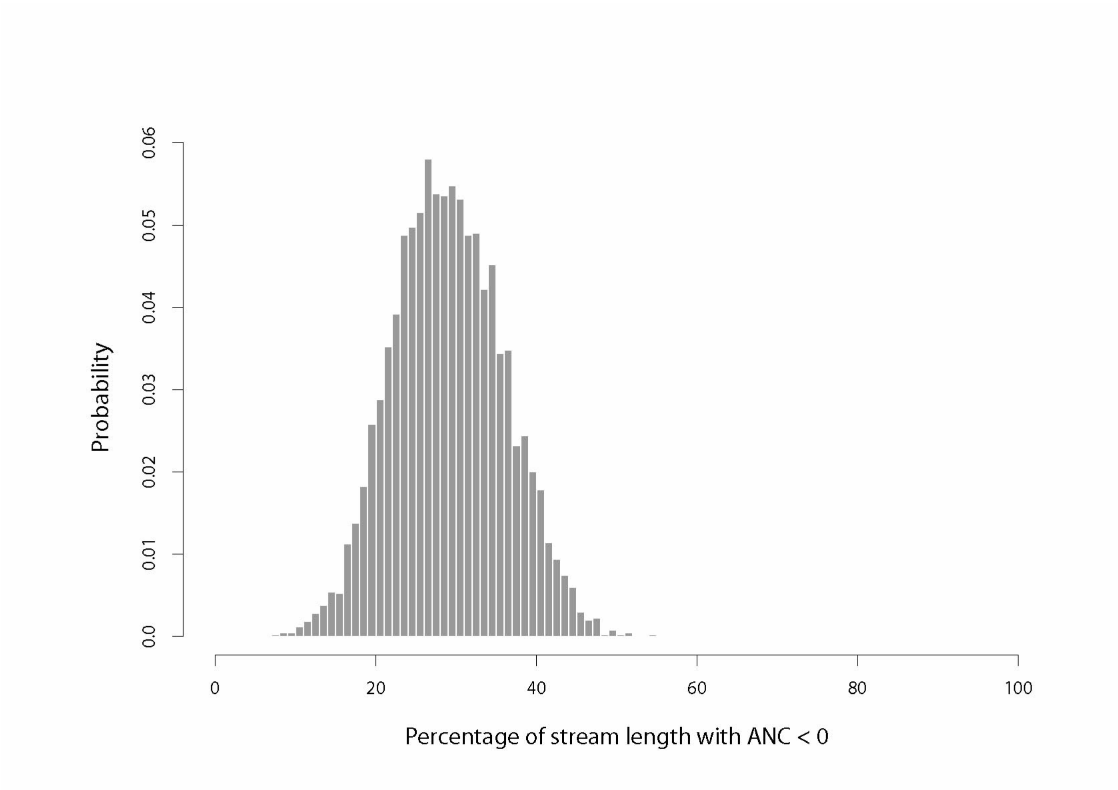


Figure 2.2.15: Distribution of stream length having ANC < 0 μeql^{-1}, January 2002 - Cree



Conwy

The PEARLS mixing model was applied to the Conwy using the methods described above, both for mean and January high-flow chemistry. These simulations were used to predict the probability of mean ANC falling below a threshold of 20 μeql^{-1} at all locations within the stream network for the January sampling (Figure 2.2.16) Results suggest that around 27% of the stream network has a current mean ANC < 20 μeql^{-1}, with acidified streams located in the higher, western part of the catchment, particularly where they drain peats or forested areas. The probability of streams having ANC < 20 μeql^{-1} in the eastern half of the catchment is low, due to the dominance of farmland and gley moorland landscapes in this area. In general, the probability of acid conditions is greatest in small headwater tributaries, above any farmland drainage

A comparison of mean and high flow probabilities is shown by Figures 2.2.17a and 2.2.17b. At high flow, the probability of streams becoming acidic increases substantially across the drainage network. Under these conditions around 45% of streams are predicted to have ANC < 20μeql^{-1}, again largely in the west of the catchment, but with the predicted acid conditions (ie probability > 0.5) extending into many larger streams; for example, ANC is predicted to remain below 20 μeql^{-1} for a considerable distance down the River Conwy (in the central southern part of the catchment) at high flow, despite mixing with runoff from farmland. These results illustrate the extent to which streamwaters which are circumneutral at low or mean flows may become acidic, and potentially damaging to the biota, at high flows.

Figure 2.2.16. ANC status of the Conwy using PEARLS, January 2003

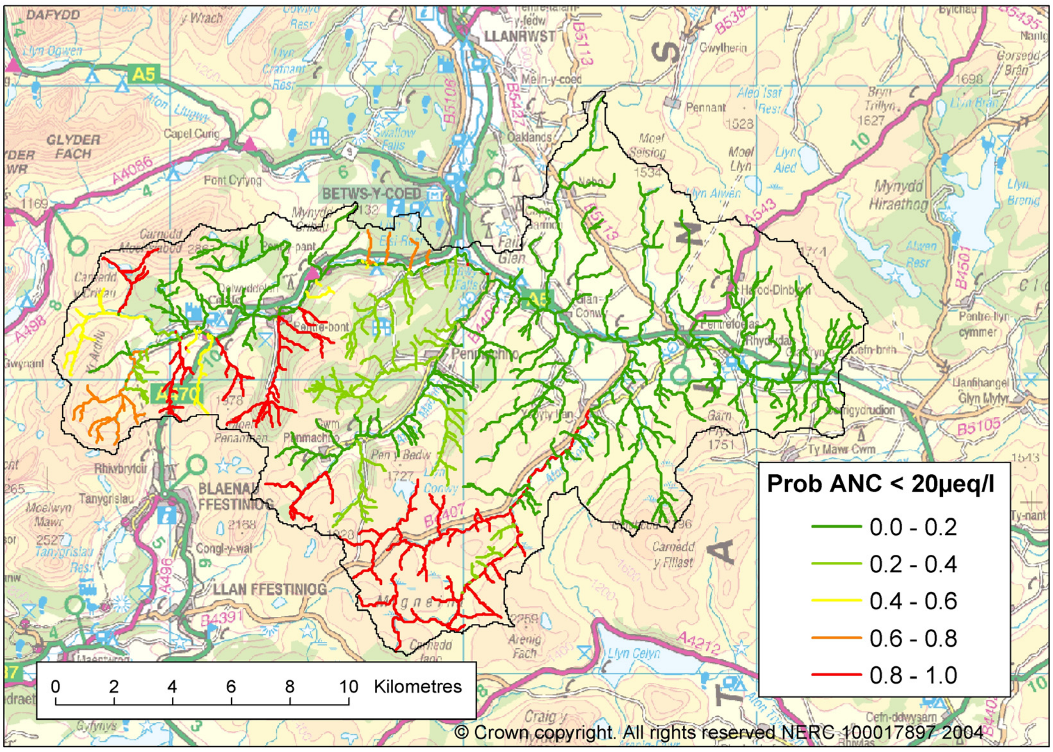
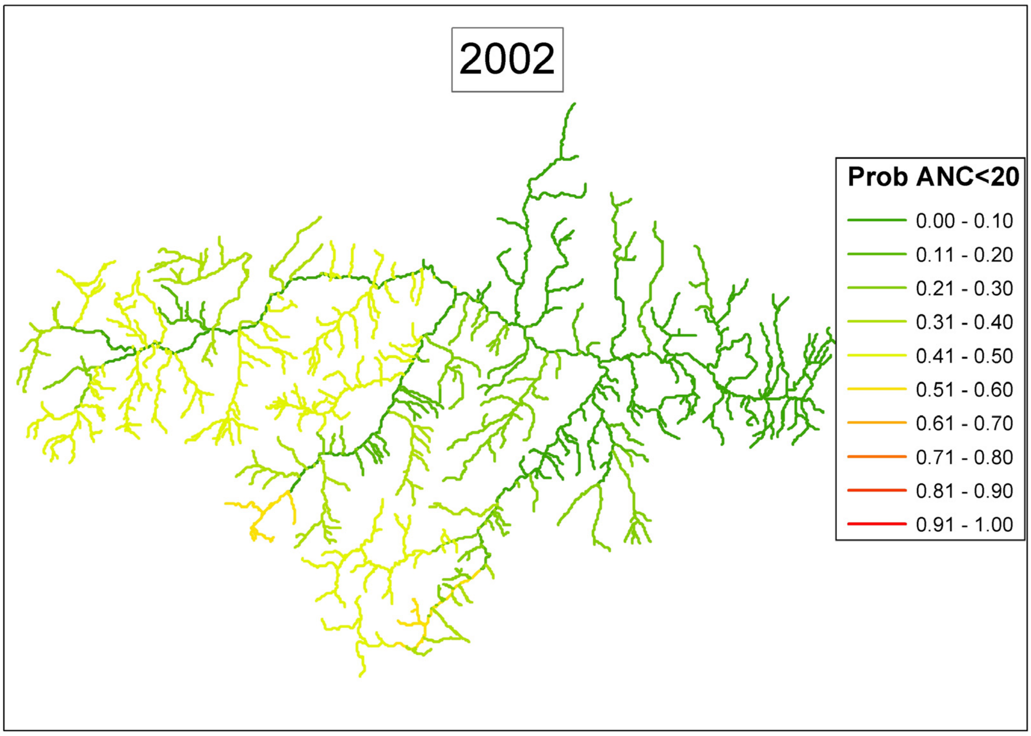
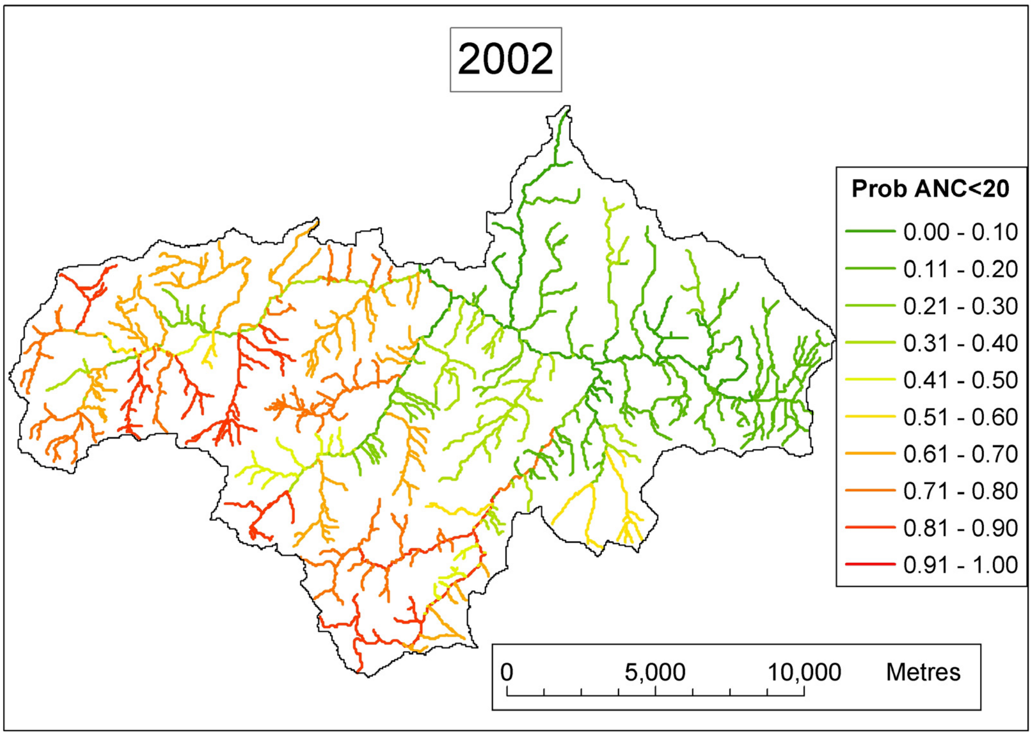


Figure 2.2.17: Probabilities of ANC <20 μeql^{-1} for the Conwy

a. Mean flow



b. High flow



Tywi/Irfon

The options for the use of PEARLS are limited, since the lower portion of the upper Tywi catchment is occupied by the Brianne reservoir. Nevertheless, subcatchments of the Tywi can be used to estimate ANC from the four landscape classes selected. PEARLS has then been run on the Irfon catchment. Probabilities of ANC less than 0 µeq l^{-1} throughout the stream network are shown in Figure 2.2.18 using February 2002 data. For this catchment, a comparison of probability distributions (Figure 2.2.19) suggests that most of the river network has ANC less than 20 µeql^{-1} and some 60% has ANC less than zero, though there is considerable uncertainty about this figure, because many streams have ANC close to zero.

Figure 2.2.18: ANC status of the Tywi/Irfon using PEARLS, February 2002

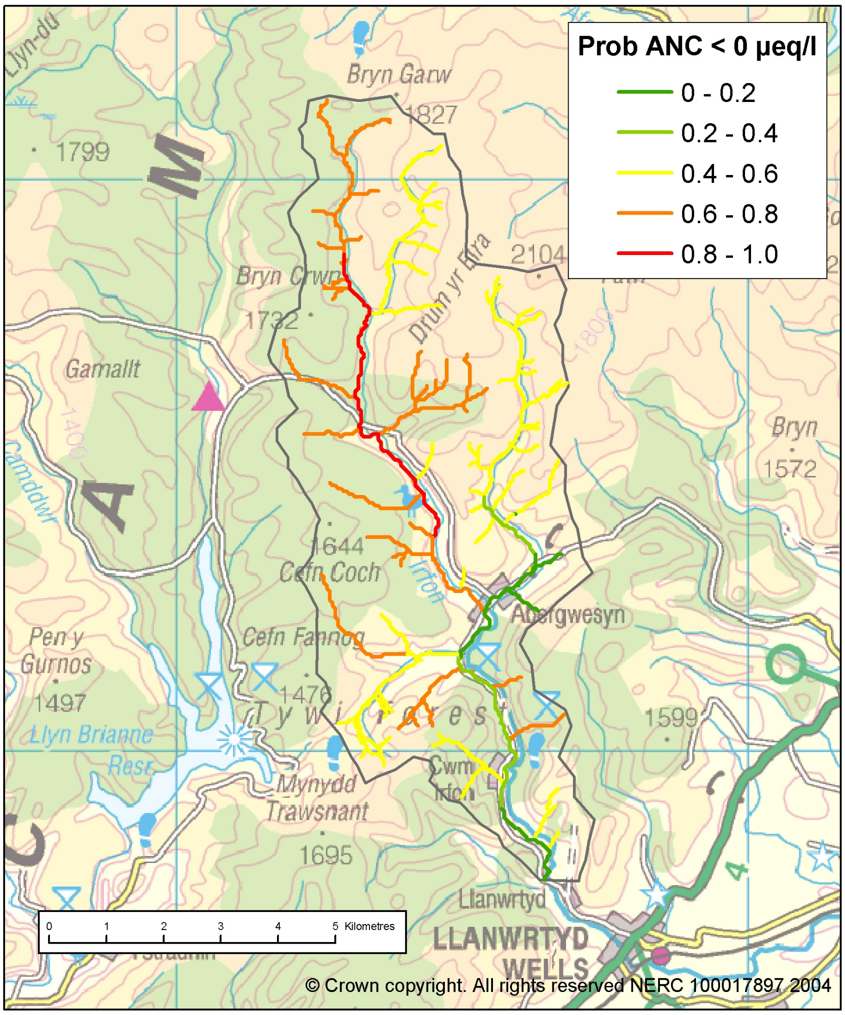
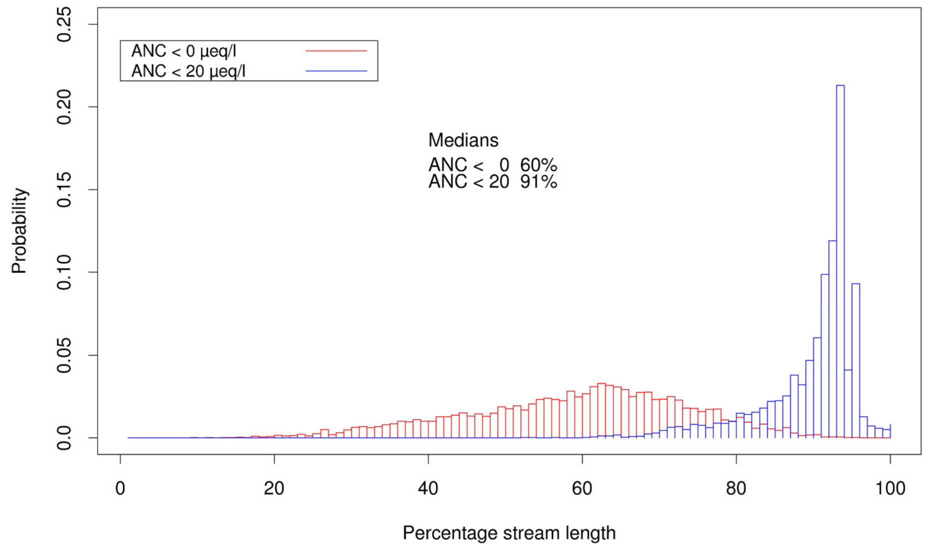


Figure 2.2.19: Histograms of ANC status of the Tywi/Irfon, February 2002



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Task 2.2.2. Sampling and analysis of chemistry and biology from streams in 3 regions at high and low flows

Task 2.2.4. Continue characterisation of high and low flow chemistry at Llyn Brianne and selected WAWS sites

Introduction

The physical and biological effects of acidification on freshwaters have now been well studied over a period of nearly 40 years (Donald & Gee, 1992; Gorham & McFee, 1980; Grant, 2003; Reynolds et al., 1999; Stoner et al., 1984; Weatherley & Ormerod, 1987; Weatherley et al., 1989). With reduced sulphur emissions over this period and the subsequent reduction in acidifying compounds interest has focused on the recovery of freshwaters from acidification. While evidence is increasing for chemical recovery, evidence for consistent biological recovery in the absence of mitigation such as liming is scarce (Fjellheim & Raddum, 1995; Masters, 2002; Raddum & Fjellheim, 1994; Weatherley, 1988; Weatherley et al., 1995). Work has developed to assess the reasons behind this apparent lag in response to recovery (Bradley & Ormerod, 2001). Two possible routes to biological recovery are first a response to natural chemical recovery by (re)colonisation, which may be slow, or mitigation by liming often with immediate but not necessarily sustainable results. Both these strategies can be influenced by episodic acidification, which may impede acid-sensitive species from re-establishing or colonising previously acidified freshwaters.

The effects of episodic acidification on the recovery of freshwaters is being investigated from a chemical and biological perspective. Chemical throughput in streams tends to be rapid due to the flow of water, increasing with rainfall events. Dramatic changes in pH and alkalinity can occur in a matter of hours (Davies et al., 1992) and endure from hours to days. There has been long interest in how communities of benthic invertebrates respond to such episodic acidification. More recently, questions have asked how response might vary across catchments or regions with contrasting character and deposition climate (Courtney & Clements, 1998).

To address the effect of variation in catchment character and benthic invertebrate assemblages, a large scale survey was completed during CLAM2 that covered acid-sensitive areas of Wales and Scotland. The northwest Highlands of Scotland (Figure 2.2.20) have been minimally impacted from anthropogenically influenced deposition (Evans & Monteith, 2001) and are therefore an interesting region with respect to the effects of episodic acidification. The Highlands are subject to enhanced orographic rainfall, as are the other regions, due to westerly winds blowing in from the Atlantic. However, the lack of adjacent industrial activity means wet and dry deposition is not particularly polluted. Nevertheless, the dilution effect of enhanced rainfall and the predominantly acid-sensitive geology result in streams that are vulnerable to acid episodes and risk of sea-salt deposition.

Galloway (Figure 2.2.20) on the other hand has been ecologically impacted by acidic deposition, while freshwaters here are influenced by extensive conifer plantations. Conifer forestry might retard recovery from acidification in Galloway (Helliwell et al., 2001), but with respect to recovery the high elevation loch areas of Galloway are in the best ecological status since the 1970's (Harriman et al., 2001). Similarly north and mid-Wales have been impacted from high levels of SOx deposition (Jenkins et al., 1996) but despite this the area is showing signs of chemical recovery (Juggins et al., 1996).

The objectives of this part of CLAM2 were to determine whether the relationship between invertebrates and chemistry reflect high-flow (episode) more than base-flow chemistry across the above regions of Wales and Scotland. The aims were to a) classify all sites in Wales and Scotland at low-flow as either acid, episodic or circumneutral, b) assess high-flow (episodic) trends across the sites, c) assess the factors (e.g. episodicity, base-flow chemistry) that explain the invertebrate patterns between the classified sites and d) quantify the relationship between episodes and invertebrate assemblage.

Methods

Site descriptions

The four regions (Figure 2.2.20), two in Scotland and two in Wales, are situated in the western UK and are subject to westerly airflows that bring relatively clean air from the Atlantic. They are also subject to high rainfall which leads to wet deposition of pollutants such as SOx and NOx. The sites were all second- or third-order upland streams, 24 in the Highlands of northwest Scotland, 25 in Galloway in the southwest of Scotland, 20 in Conwy, north Wales and 21 around the Llyn Brianne reservoir in mid Wales (Figure 2.2.20). Stream numbers, names (where applicable) and map grid references are given in Appendix 2.2.1. Preliminary streamwater pH and ANC were used to obtain a range of streams for sampling that might potentially be characterised from circumneutral to acid.

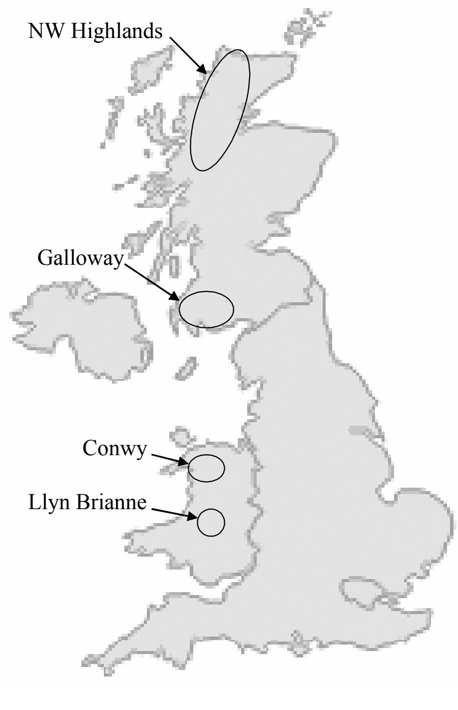

Figure 2.2.20. The regions in Scotland (NW Highlands and Galloway) and Wales (Conwy and Llyn Brianne).

Highlands, northwest Scotland. The underlying geology of this region consists of schists, gneisses, quartzites, granites and sandstones of limited buffering capacity and old red sandstone, limestones and shelly sands of medium buffering capacity. The overlying soils here are similar to Galloway with little neutralising capacity but in some areas the brown forest soils overlay basic limestone, offering some neutralising capacity.

Galloway, southwest Scotland. The underlying geology consists mainly of granites, greywackes, shales of limited buffering capacity and areas with the more basic basalt. The overlying soils range from those with little or no neutralising capacity such as podzols, non-calcareous gleys, basin and blanket peat, rankers, subalpine and brown forest.

Conwy, north Wales. The underlying geology consists of acid igneous, Ordovician and Silurian shales with low to medium buffering capacity and the more basic lava. The overlying soils are dominated by acid sensitive stagnopodzols (Hafren), stagnohumic gleys (Wilcocks) and brown podzols (Manod) and small areas of highly sensitive peat (Crowdy). In some areas stagnogleys (Cegin and BrE) offer some buffering capacity. The rankers present here can overly very variable geology and range from high to low sensitivity depending on location (C. Evans 2003, pers. comm.).

Llyn Brianne, mid Wales. The underlying geology of this region is based on Ordovician and Silurian shales, mudstones and grits. The overlying soils are podzols, stagnopodzols and peats. In general, upland streams have low buffering capacity.

Water chemistry

Water samples were taken from streams after rainfall (February 2002) and at base-flow (August 2002) to obtain high- and low-flow chemistry respectively. The water samples were analysed for ionic concentrations of sodium, potassium, calcium, magnesium, ammonium, chloride, nitrate, phosphate, sulphate, silica and aluminium (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Si^{4+}, Al). In addition pH, dissolved organic carbon (DOC) and charge balance acid neutralising capacity (CB ANC) were determined.

Macroinvertebrates

The semi-quantitative method of kick-sampling (standard net with 1 mm mesh size) was used to obtain macroinvertebrates during April 2002. Two minute riffle and one minute margin samples were taken at each stream in order to cover a range of habitats (Weatherly & Ormerod, 1989). The samples were preserved on site using 100% IMS (Industrial Methylated Spirit). The IMS was undiluted in order to prevent over dilution as the samples already contained a residue of water. Samples were sorted in the laboratory by initially rinsing through a 500 µm sieve, immersing in fresh water and removing the macroinvertebrates by hand. The sorted samples were preserved in a 70% solution of IMS. Identification was to species or genus level for the orders Plecoptera, Ephemeroptera, Trichoptera and Coleoptera and family level for some more difficult groups such as Limnephilidae, Simuliidae, Chironomidae and Tipulidae. The abundance of each taxon was recorded for both the riffle and margin samples taken at each stream.

Data analysis
All chemical variables were $\log_{10}$ transformed, with the exception of pH, to normalise distributions as far as possible. In the case of negative values such as may be present for CB ANC they were $\log_{10}(x + c)$ transformed, where c is a constant value chosen to increase the data to a positive value. Macroinvertebrate data were $\log_{10}(x + 1)$ transformed to accommodate cases of zero abundance.

The sites were classified using low-flow chemistry data by the multivariate technique of cluster analysis using Ward's linkage method and Euclidean distance measure. The cluster groups were chosen based on inspection of the dendrograms and the point at which the similarity level gave the most abrupt change between groups. The mean pH at high-flow for each cluster group was then used to describe them as either acid, episodic or circumneutral. Cluster groups were compared for each chemical variable at high-flow and for the abundance of the invertebrate orders Plecoptera, Ephemeroptera and Trichoptera using one-way analysis of variance (ANOVA $P<0.05$, confidence intervals by Tukey's method $P=0.05$).

The relationship between invertebrate assemblage and both episode and base-flow chemistry was examined by canonical correspondence analysis (CCA) using CANOCO (ter Braak & Smilauer, 1998). In order to test the significance ($P<0.05$) of the relationship between the environmental determinands and invertebrate composition, Monte Carlo permutation tests (499 permutations) were carried out. To determine the relative importance of high- or low-flow (episodicity), single variables (pH, CB ANC, DOC and Al) were compared at both flows along with a range of acid-tolerant to acid-sensitive invertebrate species from the orders Plecoptera, Trichoptera and Ephemeroptera. Only those species with a high degree of fit and weight (given with the figure legend) were displayed on the ordination diagrams.

Results

Welsh sites
In the majority (80%) of sites pH at low-flow was >5.5 (Figure 2.2.21a). However, during high-flow only 30% of sites had pH >5.5. Those sites with pH >7.0 during low-flow (15%) maintained pH >6.5 during high-flow with a difference between flows of around 0.5-1.0 pH unit (Figure 2.2.21e). The majority of streams (65%) that fell between pH 5.5-7.0 during low-flow dropped around 1.0-1.5 pH units so that 80% of those streams fell to pH <5.5. CB ANC in the majority of streams (76%) was >20 $\mu eq\ L^{-1}$ at low flow (Figure 2.2.21b). However, 72% dropped to <20 $\mu eq\ L^{-1}$ during high-flow, 57% of which were negative values. The difference between high- and low-flow was >100 $\mu eq\ L^{-1}$ in just over half the streams (Figure 2.2.21f). Al was below the detection limit (0.02 mg L^{-1}) in 74% of streams during low-flow (Figure 2.2.21c). During high-flow those streams with detectable Al (>0.03 mg L^{-1}) rose to 87%. Concentrations for 41% were >0.1 mg L^{-1}. DOC was low (<10 mg L^{-1}) in all the streams during high-flow and the majority (83%) of streams during low-flow (Figure 2.2.21d).

The Welsh sites were partitioned into 12 cluster groups (Figure 2.2.22). A number of clusters show similarities in site chemistry between Conwy and mid Wales (clusters 3, 5 and 7). However, the remaining clusters contained only sites from their respective regions i.e. clusters 1, 2, 4, 6, 8 and 9 were just Conwy sites and clusters 10, 11 and 12 were just mid Wales sites.

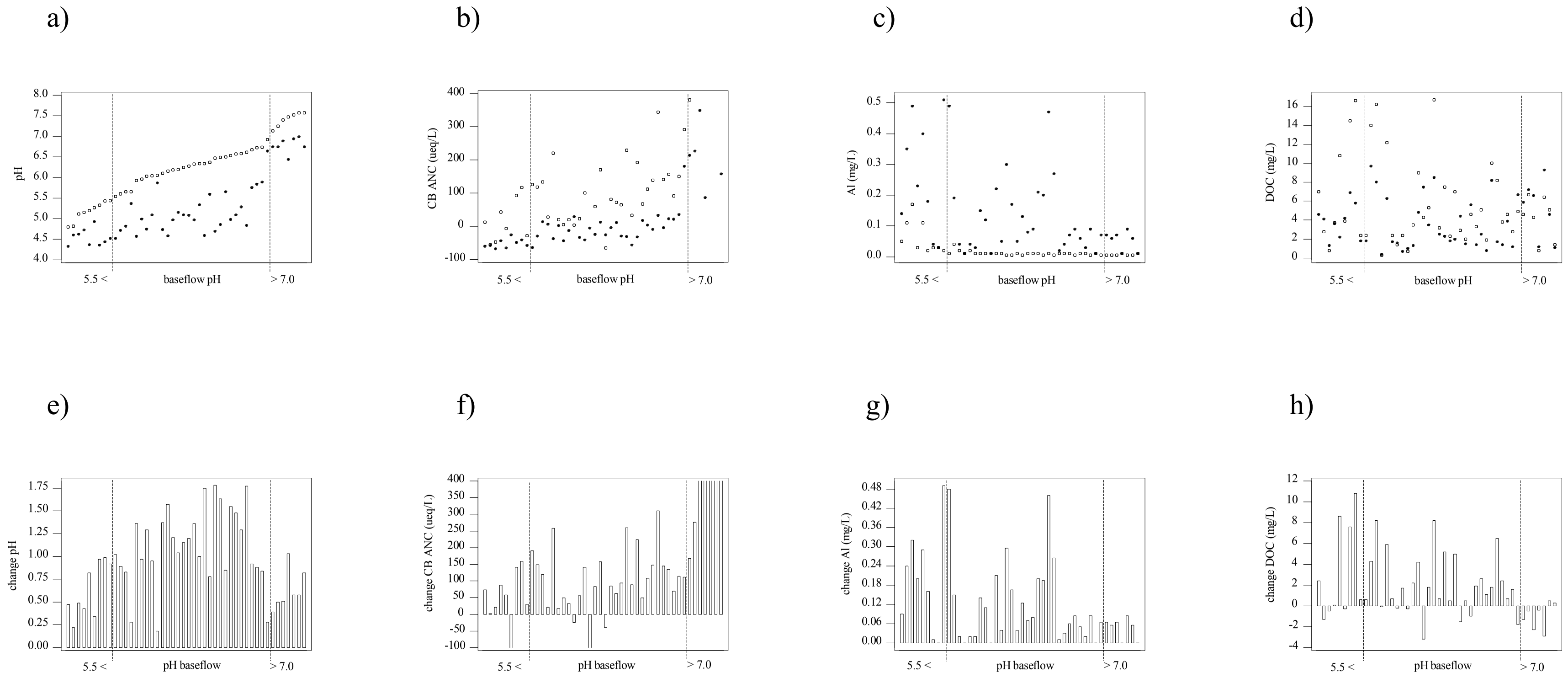

Figure 2.2.21: Stream chemistry for Welsh sites at high-flow (●) and low-flow (○), a) pH, c) CB ANC, f) Al and h) DOC) and the change between these flows b) pH, e) CB ANC, g) Al and i) DOC. Sites are arranged according to increasing (left to right) low-flow pH.

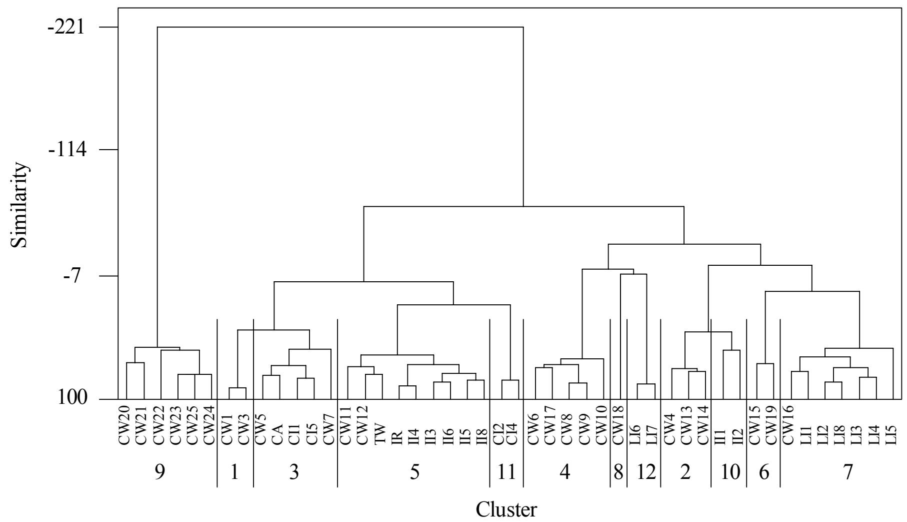

Figure 2.2.22:. Dendrogram of the Welsh cluster groups derived from low-flow chemistry with streams within each cluster labelled (CW = Conwy and all others mid Wales).

Scottish sites

The majority of sites (94%) had pH >5.5 during low-flow and just over half (53%) maintained this during high-flow (Figure 2.2.23a). Several streams showed a marked change between high- and low-flow (Figure 2.2.23e), and for example four streams with pH >7.0 during low-flow dropped as much as 1.5 – 2.0 pH units during high-flow. CB ANC during low-flow was >20 ueq L^{-1} in all streams. During high-flow 14% of sites dropped to <20 ueq L^{-1} and just under half of those (three sites) have negative values (Figure 2.2.23b). The loss in CB ANC between high-flow and low-flow was relatively high (Figure 2.2.23f) with the majority of streams being >100 ueq L^{-1}. Al concentrations (Figure 2.2.23c) during low-flow were below the detection limit (0.02 mg L^{-1}) in 41 % of the sites and only 16% had concentrations >0.1 mg L^{-1}. During high-flow 29% of the sites increased to >0.1 mg L^{-1} and half of those (seven streams) were >0.2 mg L^{-1}. The difference in concentration between high- and low-flow (Figure 2.2.23g) was >0.1 mg L^{-1} in a small number of streams (18%). DOC was low (<10 mg L^{-1}) in the majority of streams during both high- and low-flow (Figure 2.2.23d). For those streams with DOC >10 mg L^{-1} during high-flow (16%) all but two sites continued to maintain those concentrations during low-flow. The difference between high- and low-flow varied greatly among sites with 29% of streams increasing concentrations during low-flow. In streams with increased concentrations during high-flow the difference in 43% was <2 mg L^{-1}.

The Scottish sites were partitioned into 11 cluster groups (Figure 2.2.24). The clusters showed similarities in site chemistry between the Highlands and Galloway sites (clusters 2, 3, 6, 4, 7 and 8). However, a number of clusters were distinctly regional i.e. clusters 1 and 5 contain just Galloway sites and clusters 9-11 just Highland sites.

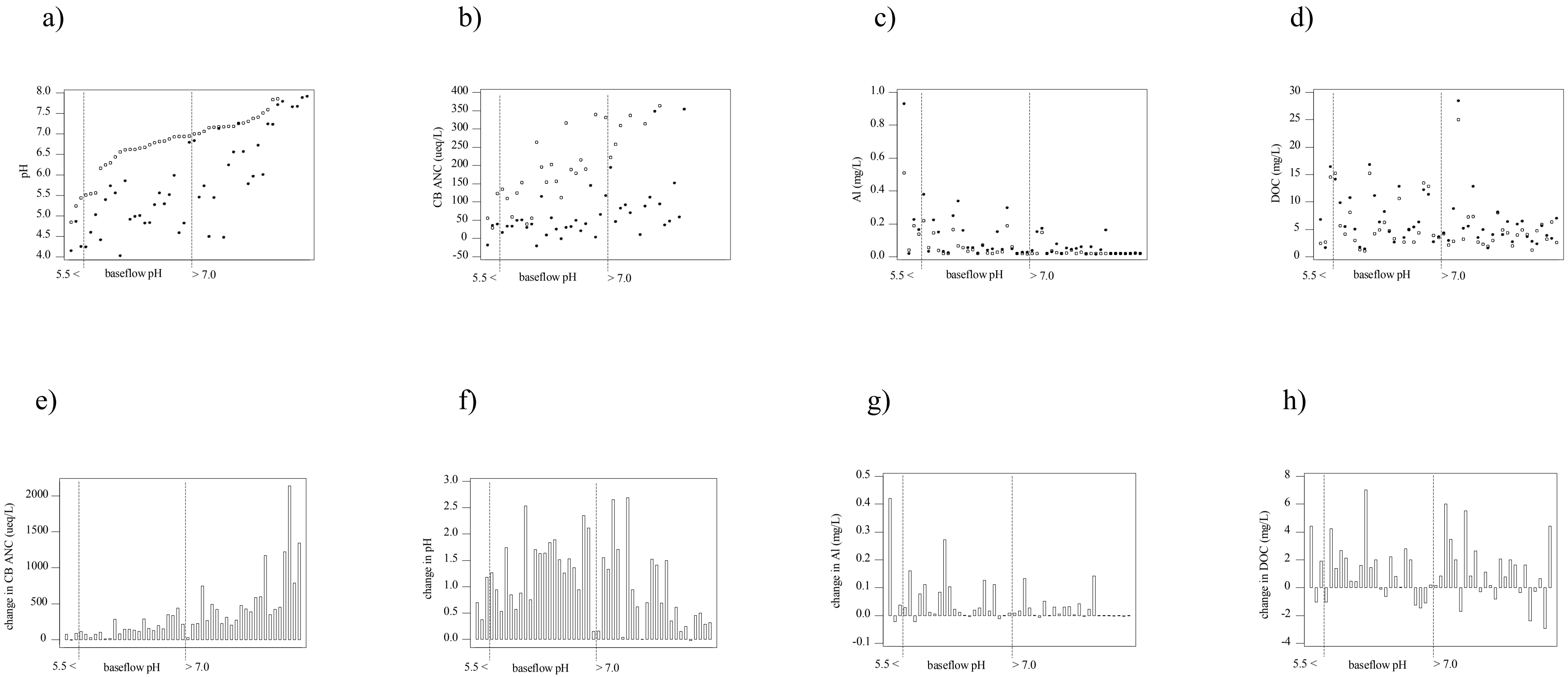

Figure 2.2.23: Scottish sites at high-flow (●) and low-flow (○), a) pH, c) CB ANC, e) Al and g) DOC) and the change between these flows b) pH, d) CB ANC, f) Al and h) DOC. Sites are arranged according to increasing (left to right) base-flow pH.

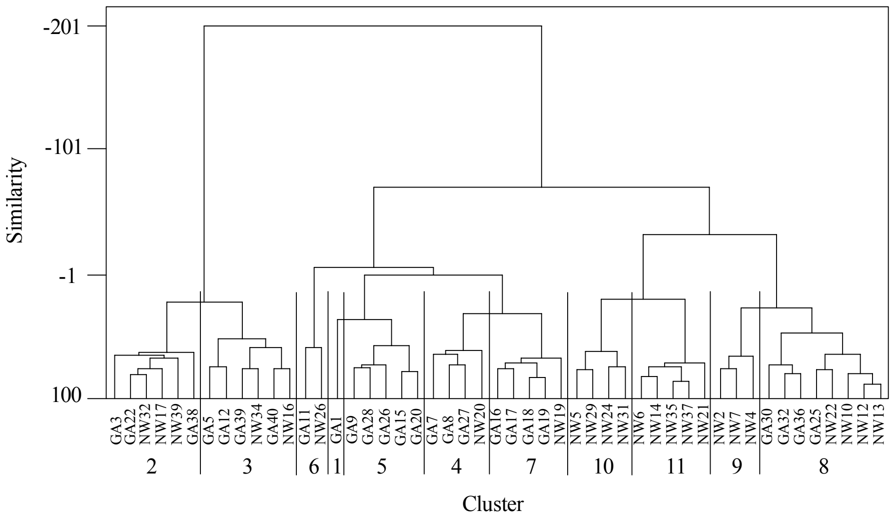

Figure 2.2.24: Dendrogram of the Scottish cluster groups derived from low-flow chemistry with streams within each cluster labelled (GA = Galloway and NW = northwest Highlands).

Episodic trends

Acid-base status at high-flow in both Wales and Scotland varied ($P< 0.05$) in chemistry across cluster groups (Table 2.2.6). The Welsh clusters 3, 4, 5, 6, 7, 8 and 11 were episodic and are labelled as such for the remaining analyses: the mean pH for these clusters during low-flow was >5.5 but during high-flow dropped to <5.5 (Figure 2.2.25a). In addition the mean ANC for these groups was >40 μeq L^{-1} at low-flow and <0 μeq L^{-1} during high-flow (Figure 2.2.25c). In addition to pH and ANC, DOC was a potential influencing factor in defining the clusters (Tukey's pairwise comparisons $P<0.05$). By contrast, clusters 1, 2 and 10 were categorised as acid with mean pH <5.5 at both high- and low-flow and ANC <0 μeq L^{-1} at high-flow. Clusters 9 and 12 are strongly defined by pH, ANC and Al (Tukey's pairwise comparisons $P<0.05$) with mean pH >6.5 and ANC >100 μeq L^{-1} at both high- and low-flow. These two clusters were therefore defined as circumneutral.

The Scottish clusters were not so well defined by episode chemistry, but clusters 4, 5, 6, 7, 8, 9 and 10 were potentially episodic as pH at high-flow drops to <5.5 and therefore were labelled as episodic for the remaining analyses (Figure 2.2.25b). However, CB ANC for these clusters did not drop below 25 μeq L^{-1} (Figure 2.2.25d). Cluster 1 was defined as acid as mean pH was <5.5 and during both high- and low-flow and CB ANC <0 μeq L^{-1} during high-flow. Clusters 2 and 3 were defined as circumneutral with mean pH >7.0 and mean CB ANC >400 μeq L^{-1} during both high- and low-flow.

Table 2.2.6: Results of one-way ANOVA (*P*<0.05*, *P*<0.01, *P*<0.001*** and Tukey's pairwise comparisons *P*=0.05) illustrate variation in high-flow chemistry across cluster groups (derived from base-flow chemistry).**

Var.	Wales $F_{11,45}$	Scotland $F_{10,48}$
pH	15.52***	16.75***
CB ANC	17.51***	17.15***
Al	2.59*	5.76***
DOC	8.83***	7.56***
Ca^{2+}	14.84***	13.31***
Mg^{2+}	6.75***	10.75***
Na^{+}	4.80***	3.85**
K^{+}	8.99***	3.30**
Cl^{-}	4.80***	3.33**
NH_4^{+}	4.23**	3.03**
NO_3^{-}	7.21***	5.23***
PO_4^{3-}	0.95ns	5.11***
SO_4^{2-}	5.72***	3.70**
Si^{4+}	5.53***	3.54**

Invertebrate variation

The variation in the abundance of invertebrate orders (Plecoptera, Ephemeroptera and Trichoptera) between the cluster groups was significant in both Wales and Scotland with the exception of Trichoptera from Scotland (Table 2.2.7). Acid-sensitive Ephemeroptera in Wales were highly abundant in the circumneutral clusters compared to the acid and episodic where they were either absent or very low in numbers (Figure 2.2.26c). Plecoptera and Trichoptera showed no overall pattern between clusters (Figure 2.2.26a and e). Ephemeroptera in Scotland were similar with higher abundance in the circumneutral clusters (Figure 2.2.26d). Plecoptera were more abundant in the acid cluster declining through episodic clusters to low abundance in the circumneutral clusters (Figure 2.2.26b).

Table 2.2.7: Results of one-way ANOVA (*P*<0.05*, *P*<0.01, *P*<0.001***, ns = no significant difference and Tukey's pairwise comparisons *P*=0.05) between abundances for the orders Plecoptera, Ephemeroptera, Trichoptera across cluster groups derived from low-flow chemistry (see Figure 2.2.26 for data).**

Invertebrate order	Wales $F_{11,39}$	Scotland $F_{10,48}$
Plecoptera	2.97**	3.38**
Ephemeroptera	3.72**	5.62***
Trichoptera	2.56*	1.95ns

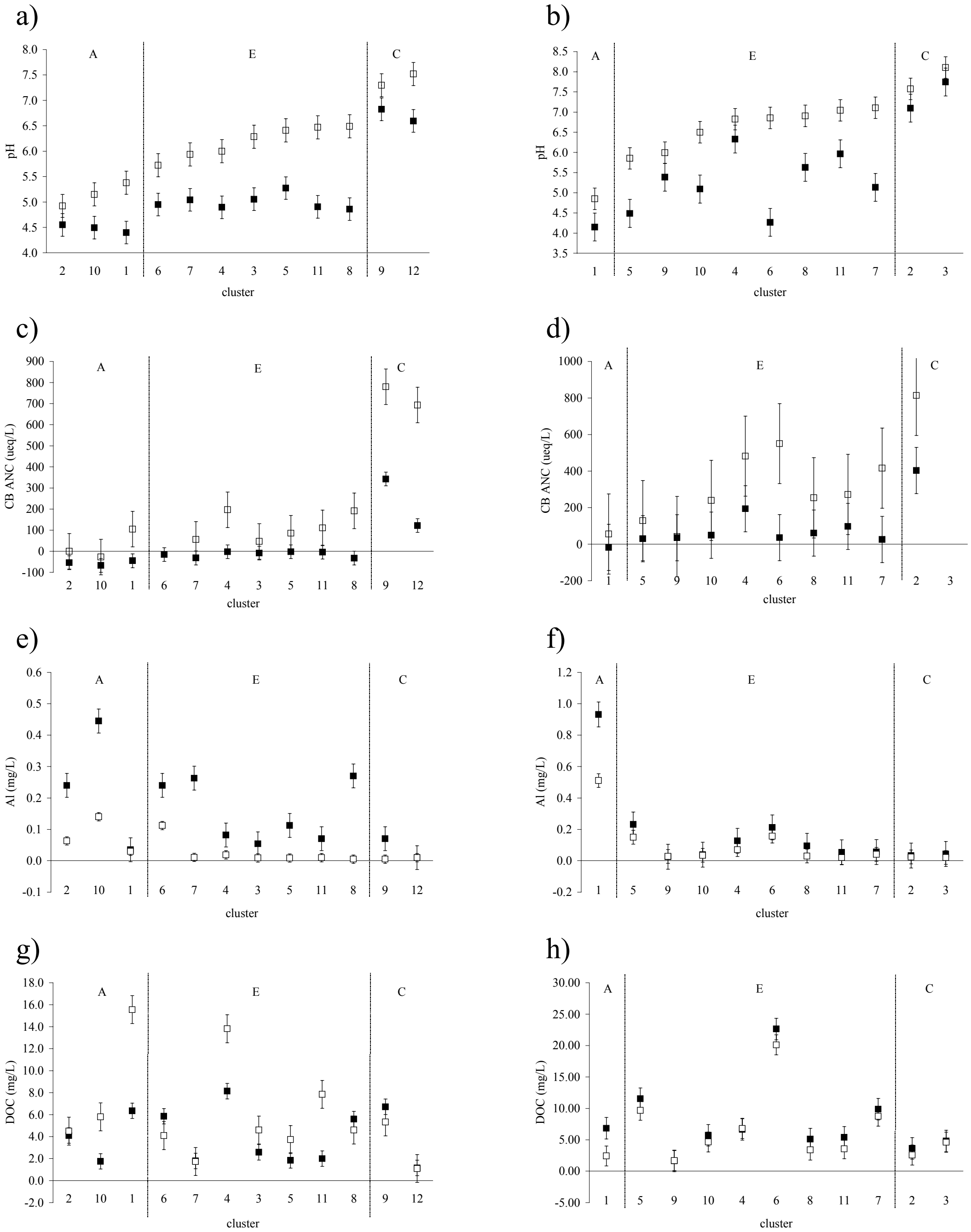

Figure 2.2.25: Cluster groups derived from low-flow chemistry with the mean for each cluster group at low-flow (□) and high-flow (■) ± SE. Groups are arranged according to increasing pH (left to right A=acid, E=episodic and C=circumneutral) at base-flow, Wales a) pH, c) CB ANC, e) Al, g) DOC and Scotland b) pH, d) CB ANC (cluster 3 means are not included as they exceed 1000 μeq L^{-1} at both high- and low-flow), f) Al and h) DOC.

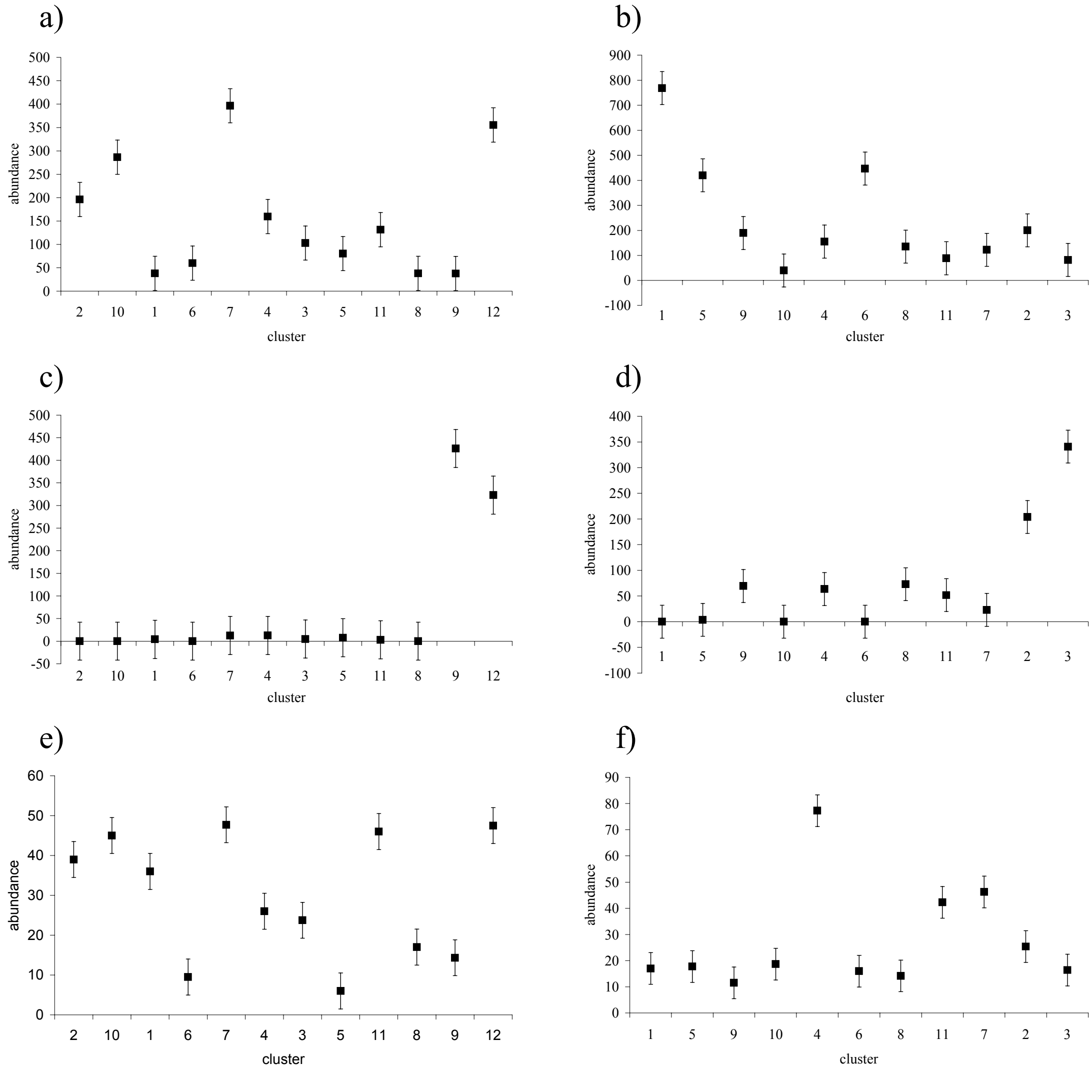

Figure 2.2.26: Mean abundance for invertebrates within each cluster derived from low-flow chemistry ± SE. Wales a) Plecoptera, c) Ephemeroptera, e) Trichoptera and Scotland b) Plecoptera, d) Ephemeroptera and f) Trichoptera. Clusters are arranged by increasing group mean base-flow pH (left to right).

Episodic effects
The first three axes of the Welsh CCA accounted for significant variation (maximum of 33.7%) in pH, CB ANC, Al and DOC at high- and low-flow, and species abundance patterns (Table 2.2.8). The eigenvalues for the first axis were between 0.075-0.230 but were all low for the second axis (maximum 0.055). However, the first canonical axis was significant ($P<0.05$) at both high- and low-flow for Al and high-flow for pH, CB ANC and DOC. The species with a high degree of weight and fit (>10%) in the models for each determinand were *Baetis rhodani*, *Heptagenia lateralis*, *Siphlonurus* spp., *Isoperla grammatica*, *Amphinemura sulcicollis*, *Chloroperla torrentium*, *Leuctra inermis*, *L. hippopus*, *L. nigra*, *Nemurella picteti*, *Nemoura cinerea*, *Protonemura meyeri* and *Plectrocnemia conspersa* (Figure 2.2.27a-d, first letter of genus and first four letters only of species name given in figure).

As in Wales the first three axes of the Scottish CCA accounted for significant variation (maximum of 26.9%) between pH, CB ANC, Al and DOC at high- and low-flow, as well as species abundance (Table 2.2.8). The eigenvalues for the first and second axes were all low (maximum 0.055) however, and the only variables that were significant ($P<0.05$) on the first canonical axis were Al at high-flow and DOC at low-flow. The species with weight and fit >5% in the models were *Baetis muticus*, *B. rhodani*, *Heptagenia lateralis*, *Rithrogena semicolorata*, *Paraleptophlebia cincta*, *Ecdyonurus* spp., *Isoperla grammatica*, *Brachyptera risi*, *Amphinemura sulcicollis*, *Chloroperla torrentium*, *Leuctra inermis*, *L. hippopus*, *L. nigra*, *Nemurella picteti*, *Nemoura* spp., *Protonemura meyeri*, *Hydropsyche siltalaii*, *H. instabilis* and *Plectrocnemia conspersa* (Figure 2.2.27e-h, first letter of genus and first four letters only of species name given in figure).

Table 2.2.8: Results of the CCA for a) Wales and b) Scotland. Eigenvalues and species variance (cumulative %) in parentheses are shown and F-statistics from the Monte Carlo permutation tests with significance (*P*<0.05*, *P*<0.01, ns=not significant).**

a)	1	2	3	4	F low-flow	F high-flow
pH	0.230 (15.6)	0.049 (18.9)	0.218 (33.7)	0.184 (46.2)	1.57ns	6.97**
CB ANC	0.218 (14.8)	0.028 (16.7)	0.230 (32.3)	0.188 (45.1)	0.94ns	6.48**
Al	0.147 (9.9)	0.044 (12.9)	0.231 (28.6)	0.197 (41.9)	3.26**	2.13*
DOC	0.075 (5.1)	0.055 (8.8)	0.288 (28.3)	0.181 (40.6)	1.77ns	1.78*

b)	1	2	3	4	F low-flow	F high-flow
pH	0.034 (2.4)	0.030 (4.6)	0.283 (24.7)	0.145 (35.0)	1.15ns	1.05ns
CB ANC	0.037 (2.7)	0.034 (5.1)	0.289 (25.7)	0.135 (35.3)	1.19ns	1.26ns
Al	0.055 (4.0)	0.023 (5.6)	0.280 (25.6)	0.135 (35.2)	0.84ns	1.90*
DOC	0.055 (3.9)	0.025 (5.7)	0.298 (26.9)	0.131 (36.2)	1.92*	0.86ns

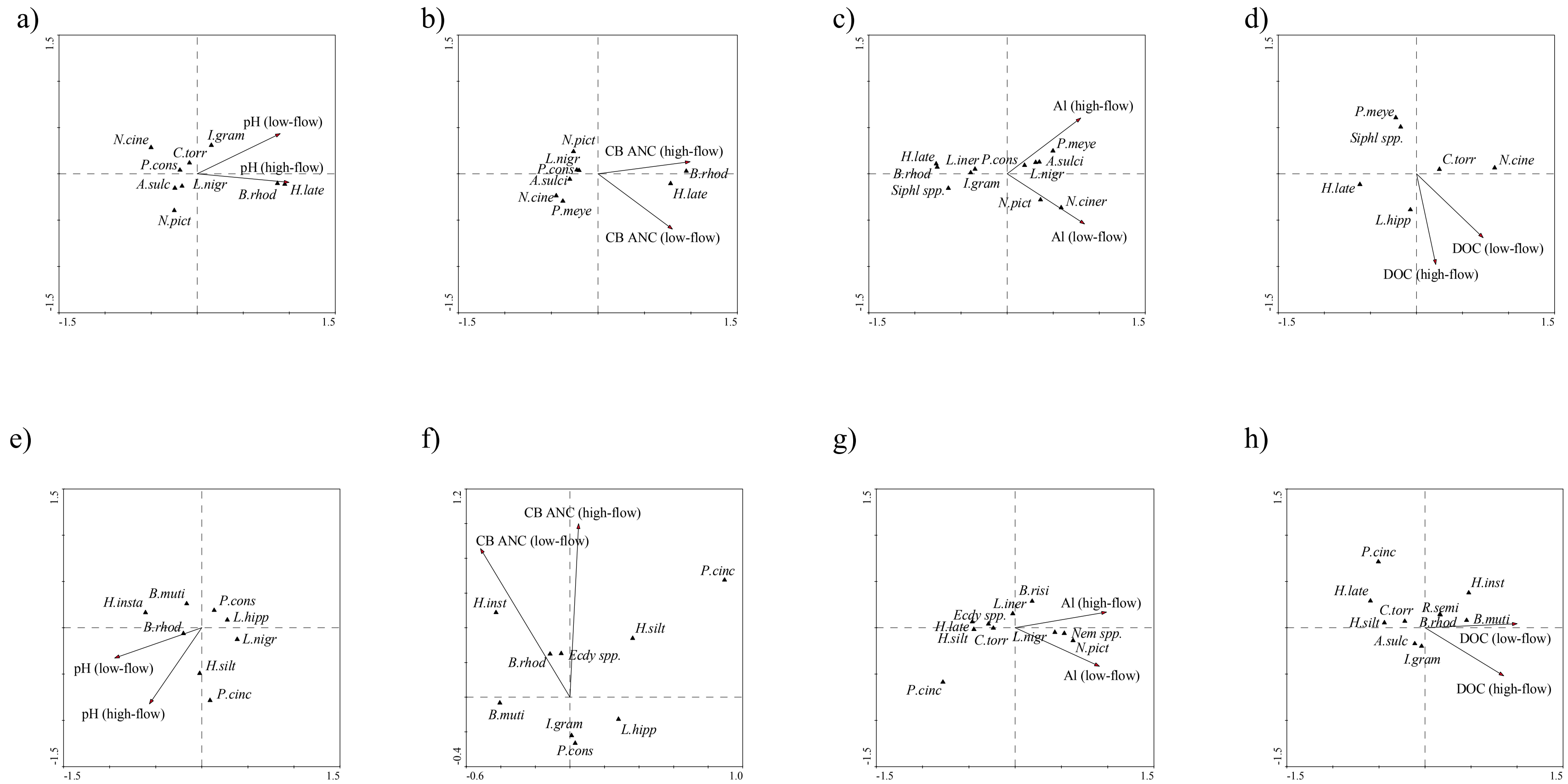

Figure 2.2.27: CCA ordination plots of species and high- and low-flow chemistry from Wales a) pH, b) CB ANC, c) Al and d) DOC and Scotland e) pH, f) CB ANC, g) Al and h) DOC. Only those species with >10% weight and fit are displayed in the Welsh plots a, b, c and d and >5% in the Scottish plots e, f, g and h.

Discussion

The overall aim of this study was to identify episodic acidification and its influence on invertebrate communities using water chemistry and invertebrate assemblage. The study was limited to a small set of streams within Wales and Scotland, with one set of example chemistry at base-flow and one at increased flow after rainfall, but still provided evidence for the influence of high-flow rather than base-flow chemistry on invertebrate assemblage.

Scotland and Wales are both susceptible and sensitive to episodic acidification (Davies et al., 1992; Fowler et al., 2001) but potentially have very different chemical and biological responses to enhanced rainfall. However, both regions appear to have streams of a predictable chemical nature so that at both base-flow and after storm events they can easily be identified as either having very little if any buffering capacity (acid) or highly buffered (circumneutral). Those streams susceptible to episodic acidification might also be identified in this way, being well-buffered during base-flow but not able to buffer against high rainfall. The initial method used here first took those streams that were well buffered during base-flow, i.e. showing relatively high pH and alkalinity and then secondly partitioned out those where declines during high-flow events indicated low or absence of buffering. In both Wales and Scotland the episodic sites that were designated in this way fell neatly within a declining pH and ANC during base-flow and then substantial losses in both these determinands i.e. reduced buffering capacity during high-flow (Figure 2.2.25). The strong influence of pH, ANC and Al in defining cluster groups was expected. In addition, Ca and DOC showed variation between groups, potentially influencing those defined as episodic or circumneutral.

Invertebrates have been used as indicator species in many studies of acidification and episodic acidification (Burton et al., 1985; Hopkins et al., 1989; Ormerod et al., 1987). In this study although all benthic invertebrates collected were available for investigation only the most dominant taxa were used at both species and order level. The choice of species was based on those already identified and studied in relation to episodicity (Merrett et al., 1991). The acid-sensitive Ephemeroptera were found to be particularly representative of the circumneutral streams in this study. In the Welsh sites they were absent from the acid streams and of very limited abundance in one or two of the episodic sites. In Scotland the pattern was similar for Ephemeroptera, with high abundance in the circumneutral streams, but abundance in the episodic streams was not as limited as the Welsh sites. Plecoptera and Trichoptera were present in streams over a wide range of chemistry. Plecoptera had very little difference in abundance over these streams while Trichoptera were varying in abundance, but there was no particular trend related to chemistry in either order.

There were close similarities throughout Wales and Scotland in species variation in response to episodic acidification. The acid-sensitive ephemeropterans Baetidae and Heptageniidae were good indicators of high pH and alkalinity during high-flow events and low levels of aluminium at either flow (Figure 2.2.27). The variation in these species was also explained by DOC which was significant (Monte Carlo permutation test $P<0.05$) during base-flow in the Scottish streams. In contrast to this the acid-tolerant plecopteran families Nemouridae and Leuctridae and the trichoptera *Plectrocnemia conspersa* reflected low pH and alkalinity. These findings are consistent with previous studies on episodic acidification (Hopkins et al., 1989; Merrett et al., 1991). The effect of episodic acidification on species assemblage may also be limited by catchment variation. Although there is evidence for similarities in invertebrate variation due to pH, ANC, Al, Ca and DOC these determinands appear to vary in effect between the Scottish and Welsh sites.

Appendix 2.2.1. Sampling sites in the four regions covering Scotland and Wales with label, stream name (where applicable) and OS grid reference.

NW Highlands			Galloway			Mid Wales			Conwy		
Stream	Name	OS Gridref	Stream	Name	OS Gridref	Stream	Name	OS Gridref	Stream	Name	OS Gridref
NW2	Allt an Tuill Bhain	NG920559	GA1	Glen Burn	NX888641	IR	Irfon	SN835555	CW1	Afon Ddu	SH769436
NW4	-	NH001642	GA3	Glen of Screel Burn	NX801545	II1	Nant y Cloddiad	SN821564	CW3	Nant y Brwyn	SH791449
NW5	River Erradale	NG744713	GA5	-	NX785661	II2	Nant y Rhiw	SN832556	CW4		
NW6	-	NG845811	GA7	Auchenvey Burn	NX729762	II3	Nant y Fedw	SN835556	CW5	Afon y Foel 2	SH763458
NW7	-	NH082883	GA8	-	NX651754	II4	-	SN843547	CW6	Aber Las	SH779445
NW10	-	NH205776	GA9	Mid Burn	NX614730	II5	Afon Aber	SN854525	CW8	Afon Nug	SH892541
NW12	-	NC138068	GA11	-	NX563662	II6	next to Nant y Brain	SN849517	CW9	Afon Cadnant	SH862546
NW13	-	NC108095	GA12	-	NX528528	II8	Nant y Walch	SN856459	CW10	Nant y Foel	SH875560
NW14	Allt lochan Sgeirich	NC022115	GA15	Pultayan Burn	NX291680	CA	Camddwr	SN774560	CW11	Afon Bwlch y Groes	SH747516
NW16	Abhainn a Chnocain	NC212110	GA16	Drumpail Burn	NX225622	CI1	Nant y Cwr	SN762576	CW12	Glasgwm 1	SH757498
NW17	-	NC268108	GA17	Laganabeastie Burn	NX128727	CI2	Nant Tyhelyg	SN763574	CW13	Glasgwm 2	SH755497
NW19	Allt na Cailliche	NC317102	GA18	Davenholme Burn	NX162711	CI3	Nant y Gelli	SN772568	CW14	Trib of Hafod-LlIan	SH719504
NW20	Allt Srath Seasgaich	NC332047	GA19	-	NX184736	CI4	Nant Gruffydd	SN770564	CW15	Trib of Wybrnant	SH767520
NW21	-	NC397009	GA20	Water of Tig	NX185815	CI5	Nant y Coeleth	SN774556	CW16	Iwerddon stream	SH798539
NW22	-	NC470032	GA22	-	NX133845	TW	Twyi	SN804572	CW17	Nant y Fflat Fawr	SH777506
NW24	-	NC407238	GA25	Pulniskie Burn	NX366745	LI1	-	SN809530	CW18	Trib of Ceunant y Garnedd	SH699524
NW26	-	NC533219	GA26	Low Mill Burn	NX365813	LI2	Nant y Fannog	SN810515	CW19	Trib of Oernant	SH796496
NW29	-	NC568585	GA27	Loan Burn	NX372833	LI3	Nant y Craflwyn	SN814507	CW20	Glasfryn stream	SH918497
NW31	-	NC503602	GA28	Butler Burn	NX362832	LI4	Nant Cwm-bys	SN816503	CW21	Pont Eidda stream 1	SH834504
NW32	-	NC412552	GA30	-	NX437941	LI5	Nant Gwrach	SN821497	CW22	Pont Eidda stream 2	SH835506
NW34	-	NC382646	GA32	-	NX475005	LI6	-	SN822496	CW23	Nant y Coed	SH849517
NW35	-	NC258524	GA36	Benloch Burn	NX561951	LI7	-	SN818493	CW24	Stream at Old Mill	SH829537
NW37	Allt an t-Srathain	NC179386	GA38	-	NX388031	LI8	Trawsnant	SN805489	CW25	Trib of Twrch	SH829557
NW39	Allt nan Uamh	NC253179	GA39	-	NX314039						
			GA40	-	NX288062						

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Task 2.2.5. Assess biological response to episodes using transplantation and intensive sampling

Task 2.2.6. Assess the effects of episodes on the survival of indicator species using experimental data

Introduction

Although long-implicated in the effects of acidification, acid episodes have more recently attracted interest because they might offset the recovery of invertebrate communities as mean pH increases (Bradley, 2002). Where acidification has altered the chemical and biological status of streams, evidence is now emerging for chemical recovery (Fölster & Wilander, 2002; Fowler et al., 2001; Harriman et al., 2001). However, biological recovery is limited and in most cases related to mitigation strategies such as liming. Invertebrate communities have responded to amelioration in streams treated with lime, although effects are sometimes modest (Bradley & Ormerod, 2002). Nevertheless, some acid-sensitive species do occur in recovering streams, albeit sporadically. Moreover, acid-sensitive species such as *Baetis rhodani* can disperse over catchments of differing acidity and overcome barriers to stream habitats such as forestry (Masters, 2002; Williams, 2003). This information together indicates that acid-sensitive species might be reaching acid-sensitive streams but failing to persist, perhaps because of acid episodes.

Transplantation and *in situ* toxicity testing is being utilised increasingly to evaluate responses of a range of organisms to ecological changes, both natural and anthropogenic, in freshwaters. In order to assess the effects of acidification on freshwater organisms some of the earliest designs used experimentally acidified streams, mimicking acidification and short acid-episodes through reduced pH and increased metal concentrations (Allard & Moreau, 1987; Burton et al., 1985; Hall et al., 1980; Ormerod et al., 1987). However, hydrological and chemical artifacts might have resulted. Transplantation, on the other hand, allows organisms to be exposed to more 'natural' episode chemistry, possibly incorporating changes in physicochemical conditions such as lowered pH with increased flow (Hall et al., 1988; MacNeil et al., 2000).

Detailed sampling of invertebrates through time also allows an assessment of how their distribution changes seasonally (Brewin et al., 2000; Furse et al., 1984; Ormerod, 1987), for example in response to episodic effects. Episodic acidification can affect acid-sensitive taxa in a range of ways. Episodicity may cause direct mortality or affect life cycles and reproduction through toxic effects of increased metals at low pH (VanSickle et al., 1996). Episodes may also influence the behaviour of acid-sensitive species preventing (re)colonisation or dispersal (Iivonen et al., 1995). Intensive sampling spanning the seasons encompasses a range of episodic effects, but has rarely been done in such detail.

This part of the CLAM2 project uses a blend of intensive sampling and transplantation in streams at Llyn Brianne to begin to evaluate episodic effects. We hypothesised that strong seasonal variation in the episodic streams would indicate possible episodic effects, and then used transplantation to mimic short-term acid episodes. The streams were classified according to their physicochemical characteristics (acidic, episodic and circumneutral) and invertebrate populations within the resulting groups described.

Methods

The method for this part of CLAM2 involves a blend of intensive sampling coupled with transplantation experiments undertaken at base-flow and high-flow (i.e. episodic).

Site descriptions

The sites were situated in the catchments of the rivers Camddwr and Tywi feeding the Llyn Brianne reservoir in mid Wales (52°8'N, 3°45'W). A full description of the geology, topography, and soil types can be found in Task 2.2.2/4, Merrett et al. (1991), Rutt et al. (1989), Stoner (1984) and Stoner et al. (1984). The Camddwr catchment supports moorland vegetation and parts of it were artificially limed during 1987/88. The streams in this catchment, CI 2 (SN765575) and CI 5 (SN775557), are now considered representative of episodic chemistry (Bradley & Ormerod, 2002). The streams of the Tywi catchment, LI 1 (SN809530) and LI 2 (SN881516) are situated in a long established conifer forest and have acidic water chemistry. The two moorland streams, LI 6 (SN822496) and LI 7 (SN818493), are circumneutral. Each pair of streams (acidic, episodic and circumneutral) are considered replicate sites. For the transplantation studies, the acidic streams LI 1 and LI 2 were the test sites and episodic CI 2 and CI 5 and circumneutral streams LI 6 and LI 7 the reference sites.

Intensive sampling

Benthic invertebrates were sampled over a 20 month period between February 2002 and September 2003 from LI 1, LI 2, LI 6, LI 7, CI 2 and CI 5. Sampling was at approximately four week intervals with a gap of two sampling periods between May and June 2003. Invertebrates were sampled quantitatively using a Surber sampler (HMSO, 1982). Five replicate samples were taken from each stream on each occasion from the riffles where possible, which were disturbed up to a depth of 10 cm. The samples were preserved, sorted and identified as described in the methods in report Task 2.2.2/4.

Water chemistry

Stream chemistry was monitored prior to the invertebrate samples being taken using a hand-held combined pH, EC and TDS meter (Hanna Instruments HI 991300). Chemistry data were also available to represent base-flow (low-flow August 2002) and episodic conditions (high-flow February 2003), and details can be found in the water sampling for Task 2.2.2/4. The data used here include ionic concentrations of sodium, potassium, calcium, magnesium, chloride, nitrate, sulphate and total monomeric aluminium (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, Al), plus dissolved organic carbon (DOC) and charge balance acid neutralising capacity (CB ANC).

Transplantation experimental design

Transplantation experiments were carried out on two occasions respectively at low- and high-flow in September 2003 and April 2004. In the first stage of the transplantation experiment (Figure 2.2.28a) the animals were left in the reference and acid streams for four days and monitored for mortality and emergence every 24 hours. On day four, the second stage of the experiment, four cages and animals were removed from the acid stream and placed back in the reference stream (Figure 2.2.28b). These animals had then been subjected to a short acid episode. All the cages were then monitored every 48 hours. On day eight the four cages that had been transferred from the test stream to the reference stream were move back to the test stream (Figure 2.2.8c). This pattern of maintaining four static cages in the reference and test streams and repeatedly moving four cages every four days was continued for 16 days. The four cages that remained in the test stream were used to determine response to an extended period of episodic acidification and the four moved to determine response to a series of short acid episodes.

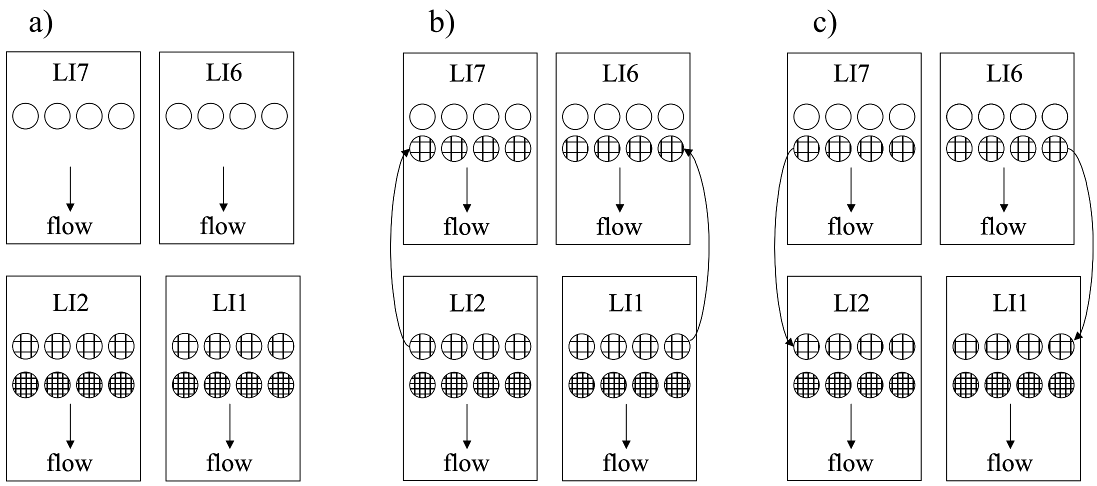

Figure 2.2.28: Experimental design for the transplantation of *Baetis* spp. from reference streams (LI 6 and LI 7) to test streams (LI 1 and LI 2). First stage a) 8 test cages were placed in each acid stream, 4 episodic (hatched circles) and 4 chronic (shaded circles) and 4 controls (clear circles) in each reference stream; second stage b) after day 4, 4 cages from each acid stream were transferred to the reference stream for a further 4 days; third stage c) after day 8, the cages from the second stage were moved back to the acid streams. This was repeated twice covering a 16 day period.

Test animals

The test animals for the transplantation were ephemeroptera nymphs *Baetis rhodani*, an acid-sensitive species used in many acidification effects studies. *B. rhodani* are abundant in the circumneutral sites LI 6 and LI 7. However, it is not possible to distinguish between *B. rhodani*, *B. muticus* and *B. vernus* in the field, all of which may be found in these streams. *B. rhodani* is the more abundant species and it was expected that they would make up the majority during random selection for test animals based on the intensive sampling in this study and Masters (2002). All animals that died or emerged during the experiment and those remaining at the end of the experiment were preserved in 70% IMS for formal identification on completion of the experiment.

Transplantation set-up

The test cages used to house the mayfly nymphs were cylindrical with a plastic base, mesh (560 µm) sides and lid. They were 10 cm in height and had a 16 cm diameter base. The cages were placed in the streams two days prior to commencement of transplantation to allow them to settle through stream movement and check for free movement of water through them. Metal stakes were hammered into the substrate and cages were attached with clips to enable them to be moved during the course of the experiment. Four cages were placed in each of the reference streams and eight in each of the test streams.

The animals were selected by gently disturbing the substrate and holding a standard kick net downstream to retain drifting animals. The contents of the net were emptied into a tray containing streamwater and *Baetis* spp. were selected from the tray using a wide mouth plastic pipette to prevent damaging the animals. A total of 160 test animals were placed straight into eight containers holding streamwater in batches of 20. They were then ready to be placed in the test cages preventing further stress by handling. These containers were then placed inside a further container holding streamwater to insulate during transportation to the test site. These test animals were moved first and placed in the cages in the acid streams. A total of 80 reference animals were then selected and placed in batches of 20 into the cages in the reference stream. The reference animals were sampled by the same method and treated to the same transportation conditions as the test animals at all stages of the experiment to ensure they were subject to a comparable level of stress. Also, during transportation the animals were kept in water from the stream they were removed from at each stage of the experiment.

In addition pH, electrical conductivity (EC) and temperature were recorded using a hand-held combined pH/EC/TDS meter (Hanna Instruments, HI 991300). These measurements were taken at the beginning of the experiment and each day the cages were checked. The combined pH/EC meter was calibrated several hours prior to use in the field with standard buffer solutions (pH 4 and 7 and EC 1014 $\mu S\ cm^{-1}$) at room temperature (~21°C). The experiment was carried out in September 2003 during what was considered base-flow conditions (low-flow) and again in April 2004 during increased rainfall (high-flow). The differentiation between high- and low-flow was based on the change in pH dropping circa 1-2 pH units from low- to high-flow.

Data analysis

Prior to any analysis invertebrate abundances and chemical variables were $\log_{10}$ transformed or in the case of zero abundance values $\log_{10} + 1$ to normalise distributions as far as possible and where necessary.

Intensive sampling. Pearson product moment correlations were performed to assess the relatedness of pH, EC and temperature. In order to determine possible episodic effects significant changes in pH between replicate, reference and test streams over the sampling period were assessed using one-way ANOVA ($P<0.05$). The monthly abundance of each acid-sensitive mayfly species was standardised by subtracting the mean and dividing by the standard deviation and variation assessed over the sampling period. Species suitable for the transplantation experiment were selected based on abundance and availability during periods when base-flow and high-flow conditions might be expected.

Transplantation. Final survival, mortality and emergence of the test species were assessed using the data collected from each replicate cage in the experiment. Paired T-tests were performed in order to determine any significant increase or decrease in pH, EC and temperature over the two transplantation experiments (September 2003 low-flow and April 2004 high-flow). One-way analysis of variance (ANOVA) was used to determine any significant difference in chemistry between the reference and test sites during high- and low-flow.

Two-way ANOVA were used to assess any variation in test species between the reference streams (LI6 and LI7) and type of bioassay (control, episodic and chronic) for both transplantation experiments (low- and high-flow). Any significant increase or decrease in survival, mortality and emergence between low- and high-flow was assessed using paired T-tests. In addition, any significant difference between survival, mortality and emergence in the control and test cages was assessed using one-way ANOVA at both low- and high-flow.

<u>Results</u>

Chemical character

The monthly changes in pH, EC and temperature were not related (Pearson correlations $P<0.05$) but chemistry generally differed between low- and high-flow (Table 2.2.9). pH, ANC and Ca^{2+} dropped in all sites during high-flow and Al was noticeably higher in the acidic streams. There was very little change in SO_4^{2-} but NO_3^- increased slightly during high-flow. The variation in pH between the test and both sets of reference streams was highly significantly different (ANOVA $F_{5,93}=41.30$, Tukey's pairwise comparisons $P=0.05$). The difference in pH between replicate streams, however, was not significant (Tukey's pairwise comparisons $P=0.05$). Figure 2.2.29 demonstrates the similarity between replicate streams and the unrelatedness of changes in monthly measured pH and EC.

Variation in acid-sensitive mayfly species

Acid-sensitive mayfly species were present in all reference streams (Figure 2.2.30). However, the only acid-sensitive mayfly found in CI 2 and CI 5 was *B. rhodani*. Abundance of *B. rhodani* in these two streams increased from late spring (May) onwards with around 300 to >600 m^{-2} and declined around autumn (October). By contrast the mayflies in the circumneutral streams LI 6 and LI 7 were *Ephemerella ignita*, *B. rhodani*, *B. muticus*, *B. vernus*, *Rithrogena semicolorata*, *Ecdyonurus* spp. and *Heptagenia lateralis*. Species low in numbers (<200 m^{-2}) were *E. ignita*, *Ecdyonurus* spp., *B. vernus* and *H. lateralis*. In addition, *E. ignita* and *B. vernus* were only present during July/August, and *Ecdyonurus* spp. in the spring around April. *R. semicolorata* and *B. muticus* were also low in numbers during the spring and summer months, but increased in abundance (*R. semicolorata* >500 m^{-2} and *B. muticus* >200 m^{-2}) during autumn/winter months (October onwards). *B. rhodani* had the highest numbers between spring and autumn (April-November) in these two streams, around 400-3000 m^{-2} depending on the month of sampling. In general, variation in density across streams in each pair were highly synchronous (Figure 2.2.30).

Table 2.2.9: Base-flow chemistry for the six streams with high-flow in parentheses. All concentrations in mg L^{-1}, except ANC (μeq L^{-1}) and pH.

	Acidic		Circumneutral		Episodic	
	LI1	LI2	LI6	LI7	CI2	CI5
pH	5.5 (4.5)	5.4 (4.5)	7.5 (6.4)	7.6 (6.8)	6.3 (5.0)	6.5 (5.7)
Al	<0.01 (0.49)	0.02 (0.51)	<0.01 (<0.01)	<0.01 (<0.01)	<0.01 (0.08)	<0.01 (0.02)
Na	6.9 (4.6)	5.0 (4.8)	4.1 (3.3)	3.4 (3.5)	3.3 (3.3)	2.9 (3.2)
K	0.19 (0.25)	0.11 (0.16)	0.19 (0.28)	0.14 (0.25)	0.17 (0.20)	0.07 (0.20)
Ca	2.9 (0.7)	1.5 (0.8)	8.8 (1.8)	8.7 (3.0)	1.6 (0.9)	1.7 (2.1)
Mg	1.3 (0.6)	0.8 (0.7)	4.4 (1.2)	3.3 (1.3)	0.8 (0.5)	0.6 (0.6)
Cl	10.2 (8.0)	9.9 (8.3)	5.4 (6.0)	4.9 (6.3)	6.0 (6.3)	4.4 (6.0)
NO3-N	0.34 (0.51)	0.10 (0.37)	0.01 (0.13)	0.05 (0.15)	0.10 (0.25)	0.08 (0.45)
SO4	5.8 (4.7)	5.2 (5.1)	3.4 (3.4)	4.7 (3.5)	2.0 (2.3)	3.3 (3.7)
DOC	2.4 (1.8)	2.4 (1.8)	0.8 (1.2)	1.4 (1.1)	7.5 (2.3)	3.3 (1.4)
ANC	126.4 (-64.8)	-29.1 (-58.5)	767.3 (86.5)	619.5 (157.6)	81.0 (-3.8)	66.7 (17.8)

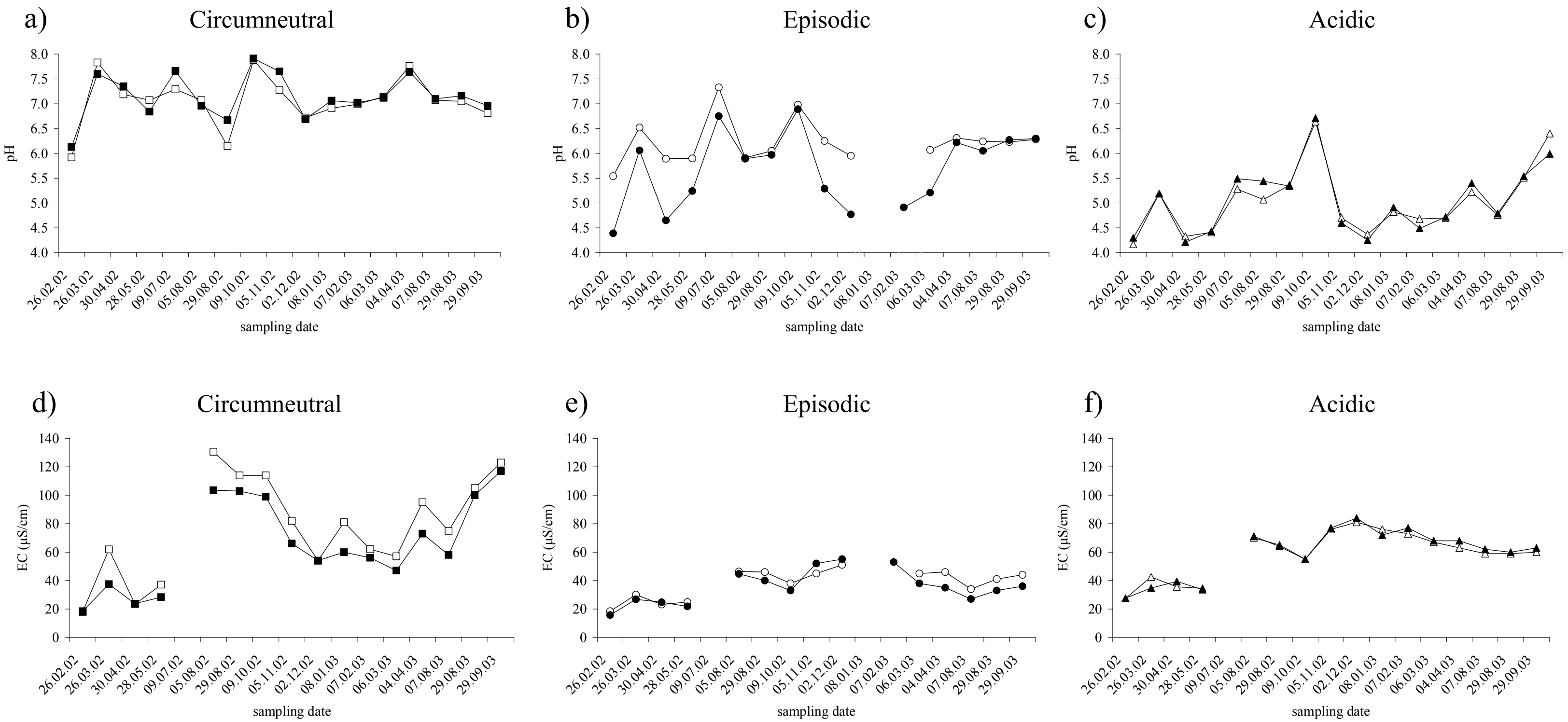

Figure 2.2.29: Change in pH and EC over a 20 month period for circumneutral streams LI 6 (■) and LI 7 (□), episodic streams CI 2 (●) and CI 5 (○) and acidic streams LI 1 (▲) and LI 2 (Δ).

Stream chemistry during transplantation

Variation between high- and low-flow. pH, EC and temperature were highly significantly lower (*P*<0.001) during high-flow than low-flow with the exception of EC in the test streams LI 1 and LI 2 (Table 2.2.10 and Figure 2.2.31). EC in LI 2 was significantly increased (*P*<0.001) during high-flow, but in LI 1 there was no significant change between the flows.

Variation between reference and test sites. Difference in pH was highly significant (*P*<0.001) between reference and test sites during both high- and low-flow (low-flow $F_{3,24}$=185.84, high-flow $F_{3,24}$=140.56, Tukey's pairwise comparisons *P*=0.05). During low-flow the difference in EC between the reference and test streams was also highly significant, but not during high-flow ($F_{3,24}$=375.16, Tukey's pairwise comparisons *P*=0.05). The difference in temperature between the reference and test streams during high- and low-flow was not significant, with the exception of LI 1 and LI 6 during low-flow (low-flow $F_{3,24}$=13.32, high-flow $F_{3,24}$=2.17, Tukey's pairwise comparisons *P*=0.05).

Table 2.2.10 Paired T-test for chemical variables comparing low- to high-flow. T value is shown with significance level (P<0.001* and ns=not significant). Mean difference test statistic = 0 vs. < or > 0 and N=7.**

	LI7	LI6	LI2	LI1
pH	9.06***	15.54***	10.69***	10.68***
EC	7.89***	11.41***	6.27***	0.28ns
temperature	9.12***	8.74***	8.44***	8.52***

Transplantation effects: species survival, mortality and emergence

Survival was high in all the control cages during transplantation experiments, ranging between 90-100% during low-flow and 80-100% during high-flow. Those animals that reached emergence were included in the survival data. The number of mortalities during low-flow was slightly higher in the episodic exposure (LI 2 = 5-25%, LI 1 = 5-30%) and in the chronic exposure (LI 2 = 20-35%, LI 1 = 10-30%) compared to the control cages (LI 6 = 5-10% and LI 7 = 0-5%) (Figure 2.2.32).

During the high-flow experiment overall mortality increased significantly (N=24, T-value =5.21, *P*<0.001) and emergence was significantly reduced (N=24, T-value =6.95, *P*<0.001). There was a slight increase in mortality in the control cages during high-flow (LI 6 = 5-10%, LI 7 = 0-20%) but the number of mortalities was still low. However, mortality in the test cages was considerably higher in the episodic exposure (LI 2 = 15-40%, LI 1 = 30-55%) and markedly higher in the chronic exposure (LI 2 = 75-100%, LI 1 = 65-90%) during high-flow compared to low-flow (Figure 2.2.32).

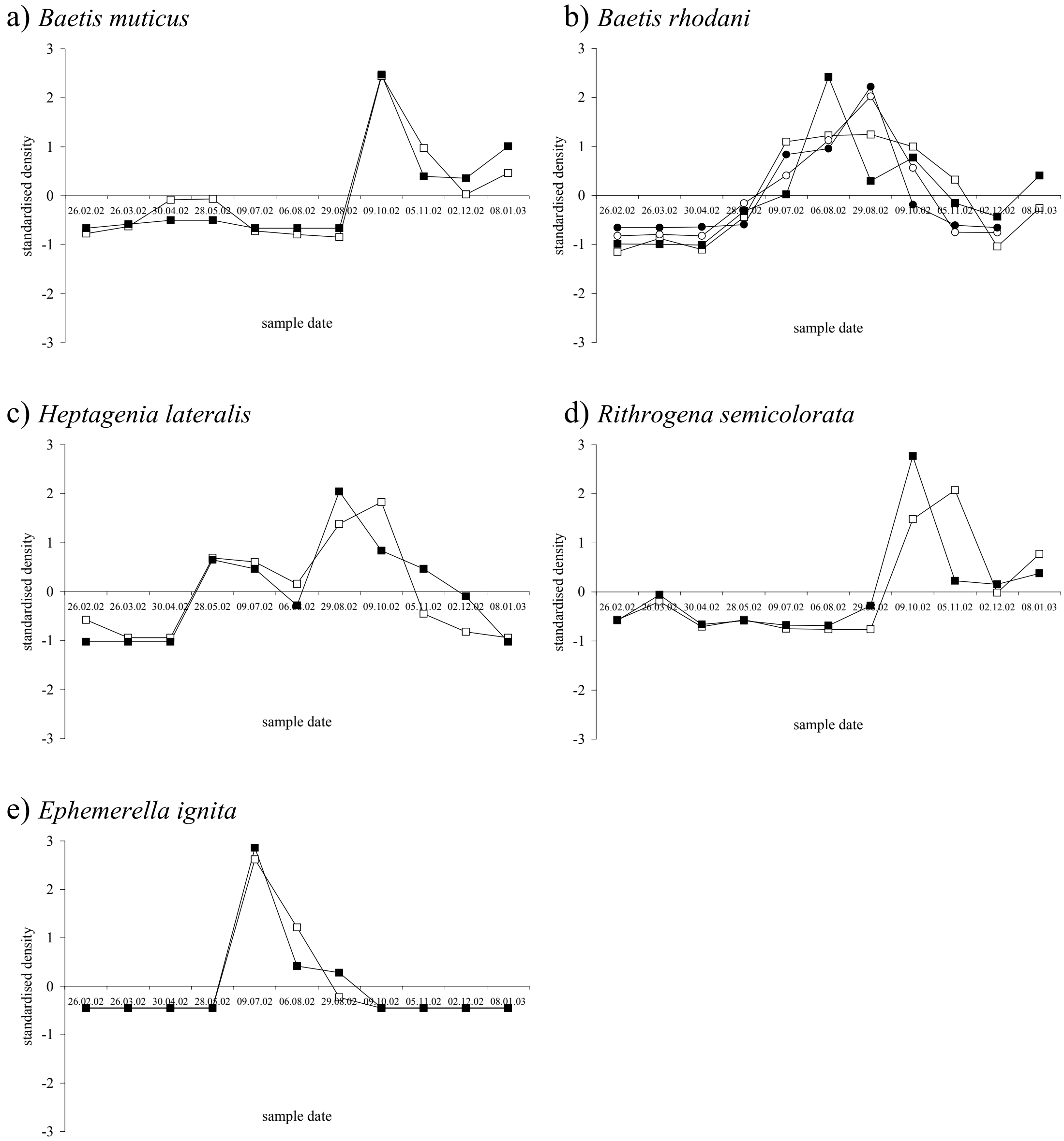

Figure 2.2.30: Acid-sensitive mayfly species presence over a 20 month period in LI 6 (■), LI 7 (□), CI 2 (●) and CI 5 (○). *Baetis vernus* and *Ecdyonurus* spp. are not shown as abundance levels were so low. Densities for each month sampled have been standardised by subtraction of the mean and division by the standard deviation.

Species location and treatment effect.
Two-way ANOVA determined no difference (P<0.05) in species response based on the sites they were sampled from (low-flow $F_{1,18}$=0.87 and high-flow $F_{1,18}$=0.92). However, there was a highly significant difference (low-flow $F_{2,18}$=12.82 and high-flow $F_{2,18}$=46.15) in response to treatment (control, chronic and episodic). That is to say, during low-flow survival was much greater in the controls than chronic or episodic exposure and during high-flow much higher in the controls and episodic than chronic. The sites the animals were collected from made no difference to the overall results of experimental treatment (control, chronic or episodic) during either flow (low-flow $F_{2,18}$=2.44, high-flow $F_{2,18}$=2.06).

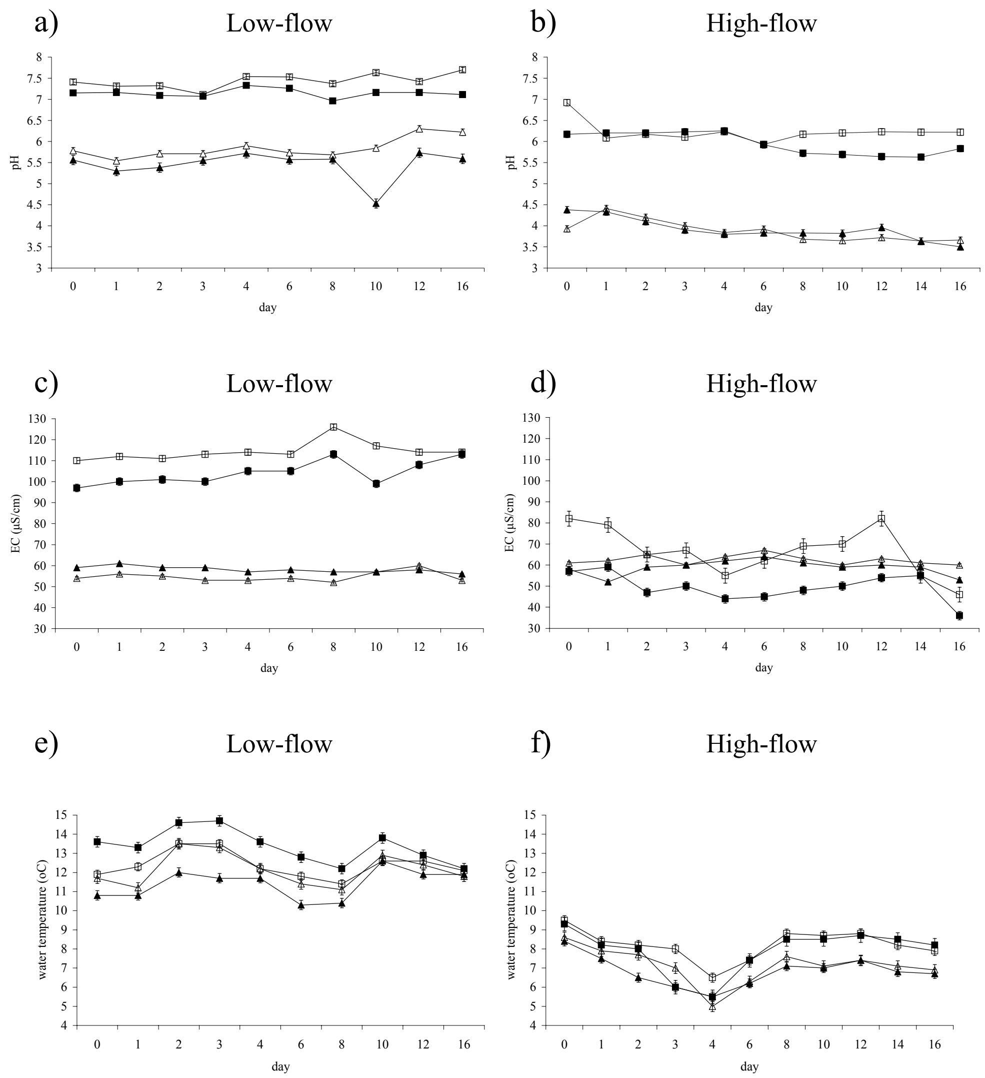

Figure 2.2.31: Physicochemical changes in pH (a-b), EC (c-d) and temperature (e-f) during the transplantation experiment at low-flow and high-flow in LI 7 (□), LI 6 (■), LI 2 (Δ) and LI 1 (▲).

Discussion

It is only recently that research has started to look at acid episodes as a possible influencing factor offsetting biological recovery from acidification (Bradley & Ormerod, 2002; Gibbins et al., 2001; Laudon & Hemond, 2002; Masters, 2002). Transplantation experiments carried out here have been used to identify possible influences of seasonal episodicity. In the experiments *B. rhodani* were held in cages and tested for their tolerance to acid conditions. In their natural habitat they may evade an acid episode through drift response (Allard & Moreau, 1987; Kratz et al., 1994; Ormerod et al., 1987), or the use of refugia, but no provisions were made for these responses in this experimental design. The animals were subjected to mild and severe acidic conditions, and survival vs. mortality observed. The response to acid conditions was varied in *B. rhodani*, and appears to be influenced by the intensity of pH decline (acid episode).

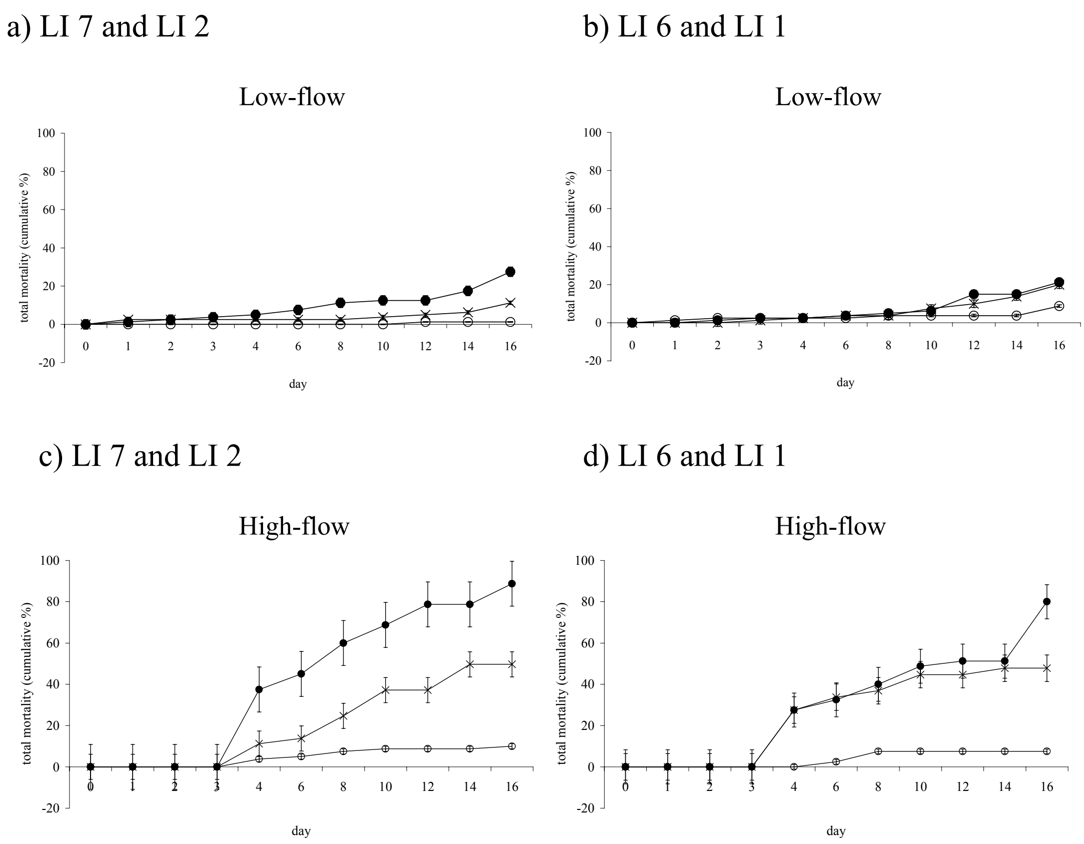

Figure 2.2.32: Cumulative (%) mortality of *Baetis* spp. using the combined data from four cages in each of the transplantation experimental types: chronic (●); episodic (x); and control (○).

Although all six sites were selected for the transplantation experiment only the two acidic (LI 1 and LI 2) and two circumneutral (LI 6 and LI 7) streams were chosen for this experiment. The physicochemical conditions in these streams were ideal and the invertebrate abundance in LI 6 and LI 7 more than sufficient, with availability extending over conditions (base-flow and high-flow) required for the experiment. The episodic sites (CI 2 and CI 5) would also have been ideal in comparing acid-sensitive species that may have evolved or adapted to episodic conditions and the chemical conditions found in a set of streams that are distinctly episodic. However, it was not possible to incorporate these two streams in the transplantation at this stage and further work using these sites would be advantageous in understanding the response of acid-sensitive species colonising recovering streams susceptible to episodic acidification.

The acid sensitive species *B. rhodani* was the only animal selected for transplantation. This was due to its presence and abundance during months that were potentially suitable for the experiment to run, incorporating a high- and low-flow event. There is also potential for using acid-sensitive species such as *R. semicolorata* and *H. lateralis*, but the timescale for setting up the experiment would have to be more flexible in order to accommodate fluctuations in population numbers and the vagary of the weather. In addition, the use of acid-tolerant species, such as *Chloroperla* spp. and *Leuctra* spp., might help to further identify experimental artifacts. Only *B. rhodani* from the circumneutral streams LI 6 and LI 7 were used for this experiment. It was considered that adequate numbers for sampling were restricted in the episodic streams CI 2 and CI 5, so their use would jeopardise replication of the experiment during a high- or low-flow event. In addition, preliminary sampling immediately prior to the first transplantation failed to find adequate numbers of animals.

Overall survival rate during base-flow was considered high, with the majority of animals surviving over the 16 day experiment. These populations of *B. rhodani* flourish in a circumneutral environment, but the streams, although extremely well buffered, can experience episodes close to pH 5.5 (Kowalik 2003, unpublished data) suggesting pH levels below this are possible. This also suggests that acid-sensitive *B. rhodani* have either adapted or evolved with the conditions, which may explain the high survival rate in acid streams during base-flow conditions. In addition, although *Baetis* spp. are considered acid-sensitive, it has been suggested they have a tolerance to acidic conditions (Engblom & Lingdell, 1984).

During the high-flow experiment, survival in *B. rhodani* was considerably lower in the test cages, and in some cases 100% mortality was observed by the end of the experiment. pH levels during the high-flow experiment were considerably lower than those recorded during any episode in the reference streams suggesting that the animals were experiencing conditions not previously encountered. The animals that were moved between the reference and acid sites every four days, simulating short acid episodes, had a higher survival rate than those left in the acid streams for the length of the experiment (chronic exposure). This may buffer them against the full effects of the episode, but there was still significant mortality during high-flow. The effects of the simulated acid episodes presented here are consistent with previous research using similar field sites and acid pulsing *in situ* (Kratz et al., 1994; Merrett et al., 1991).

Transplantation has been used in freshwater systems to determine a variety of ecological information (Claveri et al., 1995; Hall et al., 1988; Hirst et al., in draft; MacNeil et al., 2000; Masters, 2002; Rosemond et al., 1992; Valdovinos et al., 1998) and particular to this study further the understanding of acidification and acid episodes. Hirst et al. (in draft) and Masters (2002) presented similar results with regards to the intensity of acid episodes. A stream with low buffering capacity and in spate offers an unfavourable habitat to acid-sensitive species, but the temporal conditions may ameliorate the toxic effects of major depressions in pH as shown here.

In conclusion, these data confirm that episodic exposure to low pH at high-flow can be detrimental to mayfly survival. Density data, by contrast, were equivocal. Seasonal variations in *B. rhodani* were similar across circumneutral and episodic streams, but only this mayfly species occurred in the latter, indicating possible episodic effects on mayfly assemblage composition. Further work is still required on the field effect of acid episodes on species other than *B. rhodani*.

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Job 2.2.7. Develop biological 'episode response' model

Methods

Data

The data comprise macroinvertebrate species abundance and ionic concentrations of the chemical variables sodium, potassium, calcium, magnesium, ammonium, chloride, nitrate, phosphate, sulphate, silica and Al (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Si^{4+} and Al). In addition pH, electrical conductivity (EC), dissolved organic carbon (DOC) and charge balance acid neutralising capacity (ANC) were determined. The data were obtained from a range of freshwater streams and catchments in four regions, two in Scotland and two in Wales. The data used here were sampled from a high- (episodic) and low-flow. Information relating to the sites, flow types, sampling techniques and dates are described in the reports Task 2.2.2/4.

Data analysis

All chemical variables were $\log_{10}$ transformed, with the exception of pH, to normalise distributions as far as possible. In the case of negative values such as may be present for ANC they were $\log_{10}(x + c)$ transformed, where c is a constant value chosen to increase the data to a positive value. Macroinvertebrate data were $\log_{10}(x + 1)$ transformed to accommodate cases of zero abundance.

Linear and multiple linear regression analysis was used to describe the relationship between species community composition and selected chemical variables using Minitab v.13.32. Invertebrate and chemistry data covering Scotland and Wales were combined giving a total of 89 sites. Sixty-seven sites (75%) were randomly selected to use in the regression analyses leaving 22 sites to test the final regression models. Principle components analysis (PCA) reduced the number of invertebrate variables and the first PC axis scores used in the regression. A combination of chemical variables were selected to develop the optimum equation for prediction purposes, based on the final results of the regression equation, *a priori* selection, stepwise regression and preliminary assessment of Mallows' C*p*, coefficient of determination R^2(adj) and multicollinearity (Iles, 1993). To test for the significance of the final predicted values to observed, Chi^2 was performed.

Results

Results are presented in Table 2.2.11 and Figs. 2.2.33-34. PCA site scores describe each stream based on invertebrate species community composition, which can be interpreted from the principle component (PC) species scores. The first PC scores explain the majority of the variation (22.0%) and were used in the regression. The first PC scores were strongly representative of acid-sensitive crustacea *Gammarus pulex*, ephemeroptera *Baetis muticus*, *B. rhodani* and *Rithrogena semicolorata*; plecoptera *Brachyptera risi*; coleoptera *Elmis aenea*, *Limnius volckmari* and various larvae; acid-tolerant plecoptera *Isoperla grammatica*, *Leuctra inermis*, *Nemoura cinerea*, *Nemurella picteti* and trichoptera Hydropsychidae and *Plectronemia* spp. (Appendix 2.2.2).

The predictor variables chosen for both linear and multiple linear regression were pH, CB ANC, Al and DOC. Al appears to most significant during high-flow. In most cases concentrations were below detection limit (<0.02 mg L^{-1}) during low-flow, so this variable was only used in models developed for high-flow. The predictor variables were identified as constructing the best fitted regression models with high

R^2(adj) values and C*p* values roughly equal to *q*+1=*p*', where *p*' is the number of constants in the regression equation (Iles, 1993). In addition, *a priori* selection determined these variables to be biologically significant.

Regression models using combinations of pH, aluminium, DOC and charge-balance alkalinity always explained 40-60% of the variance in invertebrate score (Table 2.2.11). While determinands measured at high flow on average explained more variance (49-59%) than at low flow (42-57%), differences were modest and in no case statistically significant. All models gave invertebrate scores for the 22 test sites that were highly significantly related to observed scores (r = 0.71-0.88), although there was a moderate tendency in all cases to underestimate acidification effects at the most acid sites.

Comparison across determinands illustrated that pH at high flow either alone (r^2 = 0.58) or in combination with aluminium (r^2 = 0.59) gave the best overall fit to both calibration and test data. Charge-balance ANC performed worst, particularly at low flow (r^2 = 0.42).

Overall, these data indicate that, for the purposes of modelling invertebrate assemblages in acid-sensitive streams, combinations of pH and aluminium at high-flow offer the most accurate outcome. However, base-flow chemistry can offers a valuable approximation to biological effects at more extreme flows, although losses in accuracy will be greatest using base-flow ANC as a sole predictor.

Table 2.2.11: Results of regression analysis on predictor variables (pH, Al, DOC and CB ANC) and independent variable (first principle component scores for invertebrate species community composition). ±SE is given in parentheses with the intercept and slope (a_1, a_2, a_3), R^2(adj) is the % value, F-statistic ($P<0.001$) (n=66, 1-2 df depending on number of predictor variables) and r (Pearsons correlation coefficient).

a) High flow

Intercept	a_1	a_2	a_3	R^2	F	r
4.59(0.67)	-1.14(0.12)pH	-	-	58.4	93.56	0.86
4.56(0.80)	-2.87(0.36)ANC	-	-	48.8	63.84	0.81
4.56(0.66)	0.395(0.32)Al	-1.05(0.14)pH	-	58.7	47.87	0.88
4.97(0.73)	-1.15(0.12)pH	-0.434(0.36)DOC	-	58.7	47.85	0.86

b) Low flow

Intercept	a_1	a_2	a_3	R^2	F	r
8.06(1.11)	-1.48(0.17) pH	-	-	54.3	79.44	0.82
7.47(1.14)	-1.45(0.16)pH	0.668(0.39)DOC	-	55.7	42.41	0.84
8.32(1.21)	-1.05(0.27)pH	0.847(0.39)DOC	-1.32(0.71)ANC	57.3	30.48	0.85
7.72(1.36)	-3.42(0.49)ANC			41.9	48.60	0.71

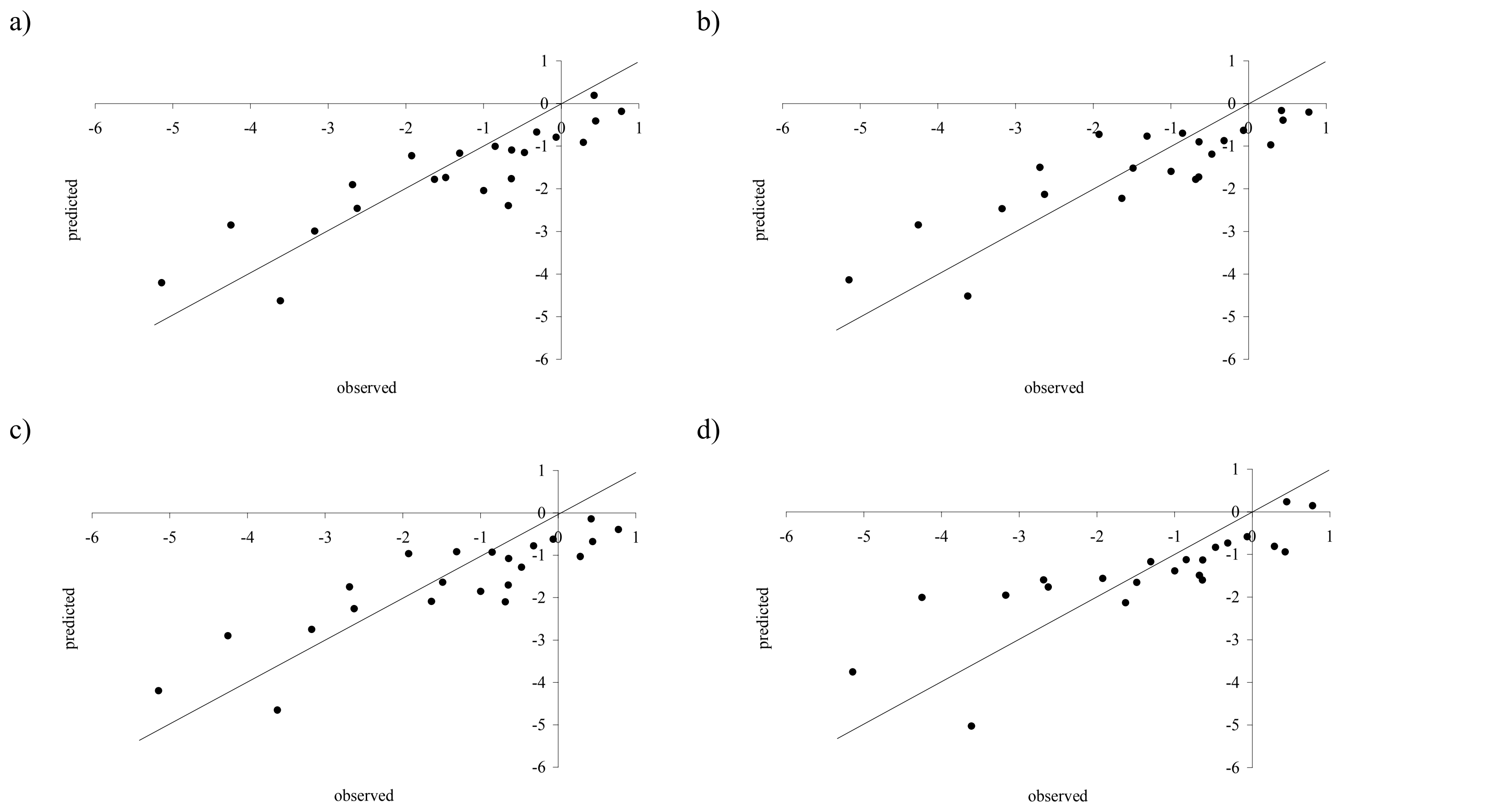


Figure 2.2.33: Regression analysis results for high-flow chemistry, a) pH and Al, b) pH and DOC, c) pH and d) ANC, and invertebrate community composition (represented by PC1 species scores).

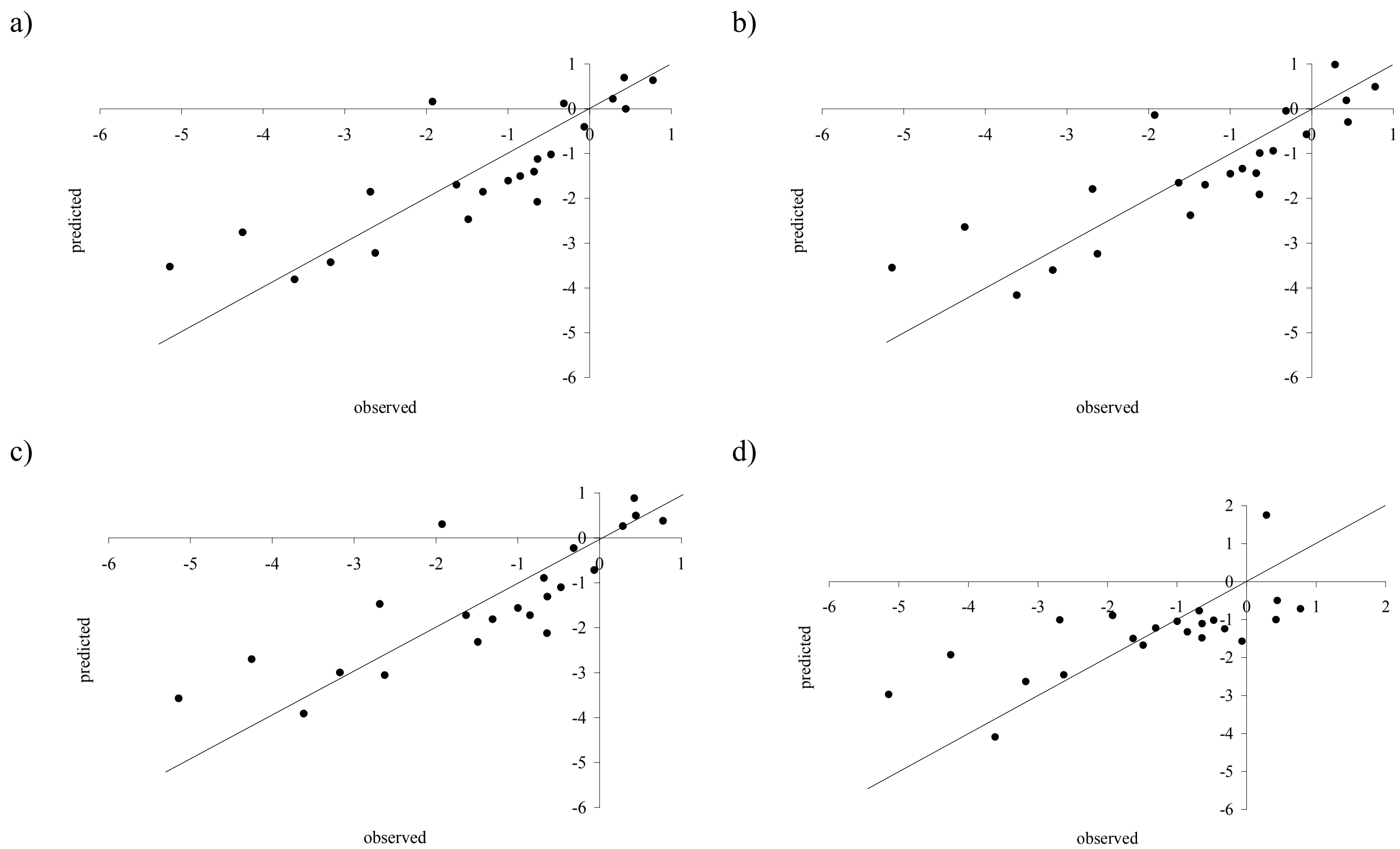


Figure 2.2.34: Regression analysis results for low-flow chemistry, a) pH and DOC, b) pH, ANC and DOC, c) pH and d) ANC, and invertebrate community composition (represented by PC1 species scores).

Appendices

Appendix 2.2.2: Principle components analysis of invertebrate species community composition, showing the first PC species scores. Eigenvalues for the first three axes and cumulative percentage variance (in parentheses) are respectively 2.48(22.0), 1.37(34.3) and 0.92(42.5).

Species	PC 1	Species	PC 1	Species	PC 1
Brachyptera risi	-0.149	*Baetis digitatus*	-0.003	Limnephilidae	0.012
Chloroperla torrentium	-0.061	*B. muticus*	-0.314	Psychomyiidae	-0.011
C. tripunctata	-0.050	*B. nigra*	-0.000	*Silo* spp	-0.031
Dinocras cephalotes	-0.056	*B. rhodani*	-0.478	Hydropsychidae	-0.224
Diura bicaudata	-0.000	*Caenis rivulorum*	-0.033	*Plectrocnemia* spp.	0.130
Isoperla grammatica	-0.222	*Ecdyonurus* spp.	-0.187	*Rhyacophila dorsalis*	-0.049
Leuctra hippopus	0.010	*Heptagenia lateralis*	-0.118	*Wormaldia* spp.	-0.02
L. inermis	-0.247	*Rithrogena semicolorata*	-0.358	*Philopotamus montanus*	-0.033
L. nigra	0.092	*Leptophlebia* spp.	0.035	*Cordulegaster boltonii*	0.001
Nemoura cambrica	0.020	*Paraleptophlebia* spp.	-0.038	Pyralidae	0.012
N. cinerea	0.134	*Agabus didymus*	0.024	*Ancylus fluviatus*	-0.019
Nemoura spp.	0.010	Dytiscidae	-0.004	*Polycelis* spp.	-0.017
Nemurell picteti	0.143	*Oreodyte sanmarkii*	-0.019	*Phagocata* spp.	0.007
Amphinemura sulcicollis	0.032	*Anacaena globulus*	0.014	*Pisidium* spp.	0.004
Protonemura meyeri	-0.017	*Hydraena gracilis*	-0.175	*Sialis fuliginosa*	0.010
Chironomidae	-0.162	Helophorus spp.	0.004	Oligochaeta	-0.068
Psychodidae	-0.038	*Elmis aenea*	-0.137	Hydracarina	0.006
Ptychopteridae	-0.007	*Esolus parallelepipedus*	-0.064	Collembolla	0.022
Simuliidae	0.052	*Oulimnius* spp.	-0.052	Glossiphoniidae	-0.027
Tipulidae	-0.068	*Limnius volckmari*	-0.108	*Asellus* spp.	-0.015
Siphlonurus armatus	-0.020	Coleoptera larvae	-0.300	*Gammarus pulex*	-0.163
S. lacustris	0.014	*Agapetus fuscipes*	-0.022		

Job 2.2.8. Predict and model the risk to biology and chemical signature of episodes from catchment character

Methods

Data

The data comprise macroinvertebrate species abundance and ionic concentrations of base cations sodium, potassium, calcium, magnesium (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) and acid anions chloride, nitrate and sulphate (Cl^{-}, NO_3^{-}, SO_4^{2-}). In addition pH and charge balance acid neutralising capacity (ANC) were determined. The data were obtained from a range of freshwater streams and catchments in four regions, two in Scotland and two in Wales. The data used here were sampled from a high- (episodic) and low-flow. Information relating to the sites, flow types, sampling techniques and dates are described in the reports for Task 2.2.2/4.

Data analysis

Acid episodes can be described as the loss of pH and alkalinity due to the input of acids (titration) and the effects of dilution. Initial analysis characterised the streams in Wales and Scotland through the loss in alkalinity, which was identified as either dilution or titration. Dilution and titration were determined in relation to the decline in base cations and the contribution of acid anions to titration also assessed after Kahl et al. (1992). Dilution or titration is based on the ratio of change in base cations (Na, K, Ca and Mg) at baseflow (BC_{low}), at a flow where loss in ANC is at its greatest (BC_{high}) and the ratio of change in ANC during both flow types: base flow (ANC_{low}) and high flow with the greatest change (ANC_{high}). Dilution less than 100% indicates the addition of acids through precipitation or catchment processes and therefore a loss in alkalinity due to titration not dilution.

$$\% \text{ ANC dilution} = ((((\Sigma BC_{low}-\Sigma BC_{high})/\Sigma BC_{low})ANC_{low})/(ANC_{low}-ANC_{high})) \times 100$$

The effect of titration during a high-flow event was evaluated by comparing the ratios of ANC to the sum of base cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) and anion contribution (anion fraction) to the sum of anions (SO_4^{2-}, NO_3^{-} and Cl^{-}) relative to the previous ratio.

$$\text{ANC/base cation ratio} = \text{ANC}/\sum \text{BC}$$

$$\text{Anion fraction} = \text{anion}/\sum \text{anions}$$

For the remaining analyses all chemical variables were $\log_{10}$ transformed, except pH, to normalise distributions as far as possible. In the case of negative values such as may be present for ANC they were $\log_{10}(x + c)$ transformed, where c is a constant value chosen to increase the data to a positive value. Macroinvertebrate data were $\log_{10}(x + 1)$ transformed to accommodate cases of zero abundance. The streams were grouped according to pH at high-flow i.e. <5.0 (acidic), >5.0 - <5.7 (episodic) and >5.7 (circumneutral). One-way ANOVA and Tukey's pairwise comparisons were performed on these groupings to determine any significant (P<0.05) variation between streams and the loss in ANC through dilution or titration (i.e. anion addition). The presence of selected acid-sensitive and acid-tolerant invertebrate species were assessed with one-way ANOVA and Tukey's pairwise comparisons to determine any significant (P<0.05) variation in density between stream groups.

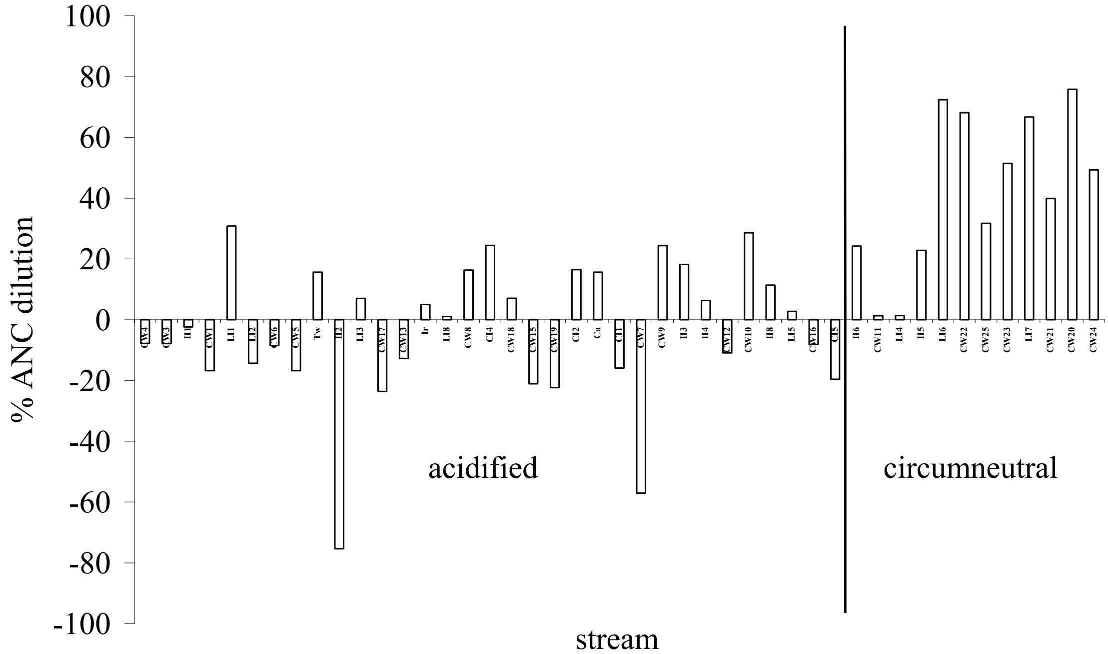
Results

Results are presented in Figs. 2.2.35-37. ANC in some streams increased at high flow over low flow for the events measured (3/48 in Scotland, 17/45 in Wales) - presumably because of increased base cation release. In Wales, contributions to episodic acidification by base cation dilution differed highly significantly ($P < 0.001$) between circumneutral streams (mean = 42%), intermediate (0%) and strongly acidified streams (0%), where strong acid addition was the dominant source of acidification at high flow. By contrast, in Scotland, episodic acidification reflected greater contributions by dilution in all stream types (circumneutral = 58%; intermediate = 26% and strongly acidified 44%; N.S. at $P < 0.1$). As a result, strong acid additions during high flow events were a much greater source of episodic acidification in Wales than in Scotland, even for strongly acidified and intermediate sites ($P < 0.001$).

Contributions to anion loading at high flow due to sulphate were significantly greater in Wales (16-24%) than at the Scottish sites (3-5%). Similarly, anion contributions due to nitrate were significantly greater in Wales (4-7% on average) than in Scotland (2-4%). Chloride made up the bulk of the remaining anion loading at high flow, particularly in Scotland.

The apparent consequences of these chemical effects for invertebrates differed between species. Acid tolerant organisms such as *Chloroperla torrentium* (Plecoptera) and *Plectrocnemia conspersa* (Trichoptera) were at least as abundant in streams that were intermediate or strongly acidified at high flow as they were at circumneutral sites. By contrast, acid sensitive species such as *Baetis rhodani* (Ephemeroptera), *Heptagenia lateralis* (Ephemeroptera; Wales only) and *Isoperla grammatica* (Plecoptera; Scotland only) were significantly reduced in abundance or absent at strongly acidified and intermediate sites by contrast with those that remained circumneutral at high flow ($P = 0.05$-0.001).
Together, these data indicate that acid anions – and still dominantly sulphate over nitrate – drive episodic acidification more in acid-sensitive areas of Wales than in Galloway and NW Scotland. Nevertheless, strong acid additions still contribute significantly to acid episodes at some episodically acidified sites in all regions, which in turn have markedly different invertebrates than those where pH remains over $pH > 5.7$ at high flow.

a) Wales



b) Scotland

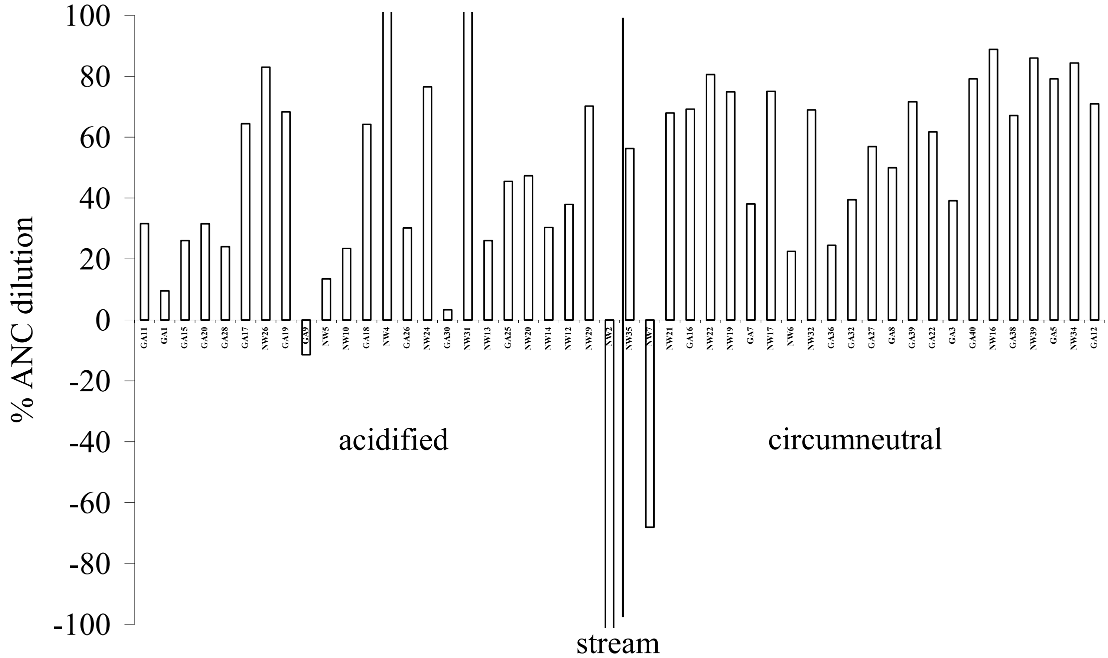
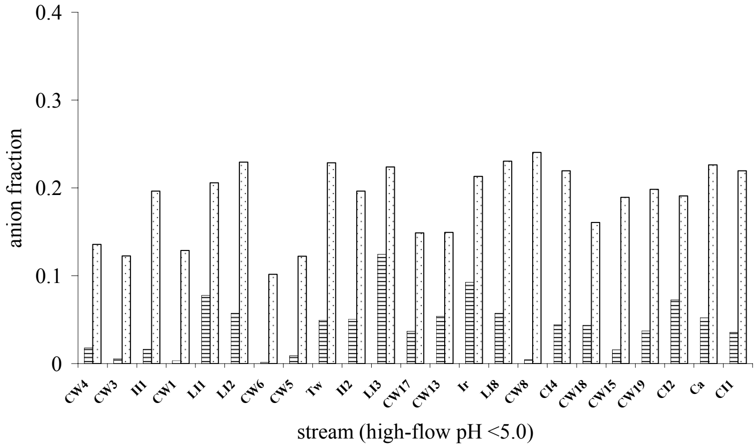
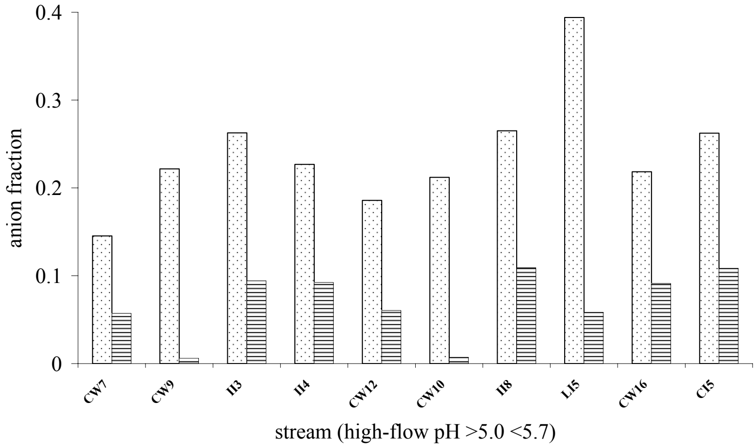


Figure 2.2.35: % ANC loss attributed to dilution or titration in streams from a)Wales and b) Scotland. The higher percentage value the higher the influence of dilution i.e. a low percentage indicates the addition of acid anions. Streams are arranged according to increasing pH during high-flow (acidified =< 5.7, circumneutral > 5.7). The axis only shows values ±100%, in Scotland NW31=116%, NW4=128% and NW2=-166%.

a)



b)



c)

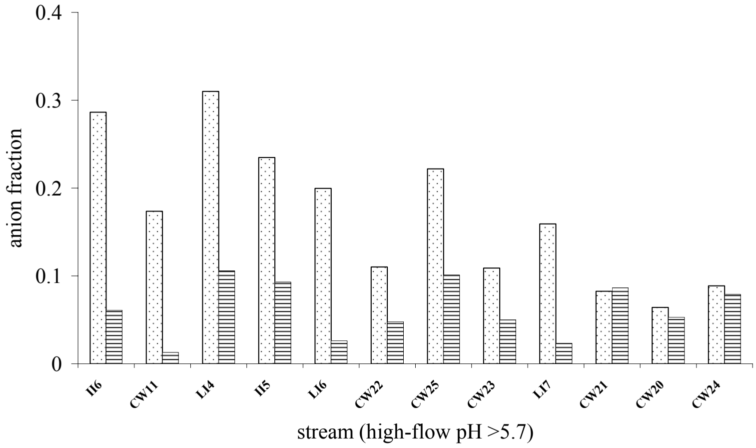
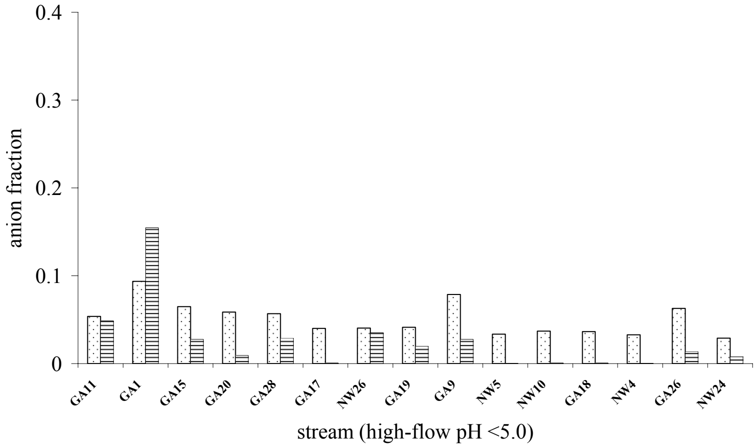
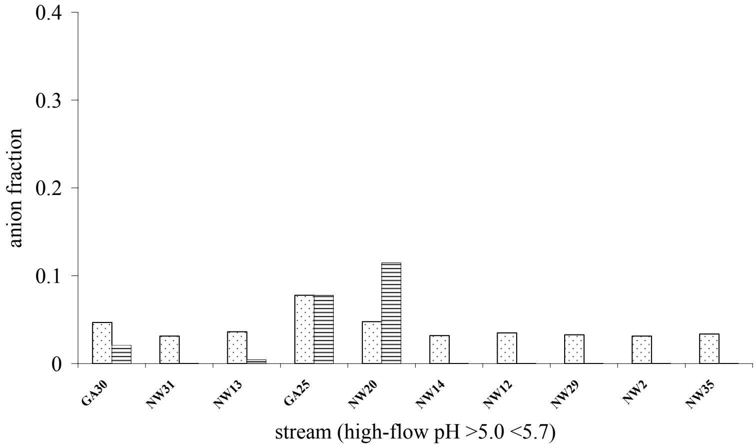


Figure 2.2.36: The contribution of acid anion fractions with a) pH <5.0, b) pH >5.0, <5.7 and c) pH >5.7, at high-flow in the Welsh streams (SO_4^{2-}=dotted and NO_3^-=bars).

a)



b)



c)

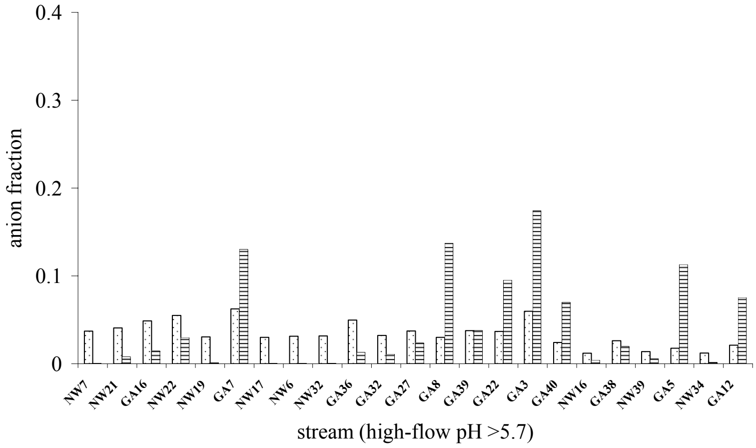


Figure 2.2.37: The contribution of acid anion fractions with a) pH <5.0, b) pH >5.0, <5.7 and c) pH >5.7, at high-flow in the Scottish streams (SO_4^{2-}=dotted and NO_3^-=bars).

2.2.9 Validate outputs from HRU/biological modelling

The PEARLS methodology is a simple approach to interpolating of water quality in stream networks from limited samples. It is natural to base such extrapolation on the upstream catchment characteristics which influence concentrations. Similar approaches are used in other areas of hydrology, where they are referred to as "regionalised variable" analysis. There are a number of issues with the approach:

- It is only suitable for conservative species since it takes no account of in-stream processes other than mixing. While it might be straightforward to allow a simple loss or gain function within each reach to account for these processes, this would need to be supported by a field program to determine the relative importance of a number of processes
- The assumption that landscape class is the major determinant of water quality, in the sense that it explains most of the variability, may be reasonable. However, it may be appropriate to include continuous as well as classification variables as explanatory.
- In past applications of PEARLS, landscape class has been defined by region. There is a case for pursuing a unified landscape classification for the UK for the purpose of predicting water quality. This is attractive, but would be a major undertaking.
- Then lack of temporal variability is a limitation. A natural extension of the model would be to include a hydrochemical response function for each landscape class, related primarily to flow. This would require a significant field programme but is conceptually and computationally straightforward if the mixing assumption is retained.
- The influence of each landscape class is assumed to be additive and scale-independent. Under field conditions, water quality draining a given landscape may vary according to the area drained. For example, a small drainage channel in peat may be uninfluenced by underlying mineral soils or geology, while a stream draining several km^2 of peat is likely to have had some contact with underlying material, under UK conditions.
- The probabilistic assumptions in PEARLS are simple and represent a realistic attempt to account for natural variability in drainage response. There is scope for improved representation of the sources of uncertainty.
- HRUs are used to generate water quality estimates throughout a stream network. This is now less essential since GIS software can now efficiently perform the same function for every cell in a fine catchment grid. However, GIS software does not have ready capability to generate the Monte Carlo simulations used to estimate stream network recovery.

Then PEARLS approach has generated new and useful catchment-wide estimates of stream water quality. The use of field measurements made at small catchment scale is a move away from fine scale modelling, while retaining support from field measurements. This would seem a promising approach for large-scale regional modelling. There are clear lines forward for this scale of modelling, some of them outlined above, which have application in water quality areas other than acidification

Job 2.2.10. Continue to evaluate and review evidence that recovery processes might be affected by dispersal and colonisation dynamics.

SUMMARY

In the 3 years of CLAM2 (2001-2004), almost 100 additional papers have been published in peer-reviewed international journals on the theme of recovery from acidification in lakes, rivers or streams. They include experimental studies, for example by liming, modelling studies and empirical observation of trends. The vast majority of work has focussed on hydrochemistry, although a significant proportion has addressed biological trends, mostly in lakes. Collections of papers have formed themed special issues of journals such as *Ambio*, *Water, Air and Soil Pollution* and *Hydrology and Earth-Systems Sciences*.

Chemical trends towards recovery from acidification are now widespread in Europe and N. America. While trends in N are not consistent across sites, reduction in sulphate concentrations in surface waters have generally mirrored reduction in S deposition. In turn, these patterns appear to be engendering increased pH and increased ANC, but also reduced base-cation concentrations in some locations. Trends towards chemical recovery vary between regions or individual locations for reasons that are not always clearly explained. Moreover, chemical trends are slow, and often of the order 0.01 pH units increase per year at recovering sites in Europe.

Documented physico- chemical factors that can offset or confuse recovery processes include S mineralisation, past S accumulation into the soil sulphur pool, metal remobilisation during brief periods of re-acidification, non-linearity between sulphur release and alkalinity, reduced output of base cations, retarded internal alkalinity generation in lakes, and large scale climatic effects in both Europe and N. America.

Evidence on the links between episodic acidification and recovery is conflicting, incomplete and poorly understood. Some studies in Scandinavia indicate declining severity of acid episodes with declining S deposition, while other work suggests that acid episodes will persist beyond the timescale required for recovery from chronic acidification. Interactions between episodicity and climatic variations are also increasingly clear.

Land use affects chemical recovery from acidification, for example through forest harvesting, forest presence and forest regrowth. Interactions with deposition, catchment sensitivity and N immobilisation are all complex.

By comparison with data on chemical recovery, evidence on biological recovery from acidification is still weak, patchy and partial. So far, most data indicating recovery have arisen from lakes and involve small organisms with short life cycles such as diatoms, rotifers and microcrustaceans. In a smaller number of instances, individual species of larger organisms such as macrophytes, invertebrates and fish have also recovered – sometimes completely.

Increasing evidence reveals that biological trajectories during recovery will not be a direct reversal of those apparent during acidification. Well-rehearsed complications affecting biological recovery from acidification include the strong likelihood of the

effects of continued acid episodes, climatic variation or land use effects, all of which are clearly demonstrated. Other limits on biological recovery might arise, for example, where species changes lead to competitive exclusion, where there are intrinsic demographic limits on rates of recovery, where there are food-web effects, or where species losses during acidification might have reduced resilience to new stressors (climate warming, stratospheric ozone depletion, invasive species).

Limits on dispersal into recovering sites that might be considered geographically isolated have received specific research attention. While some instances of recovery have involved individuals developing from dormant or background sources within ecosystems, other cases can only have involved dispersal along river systems, across river catchments or between lakes. Genetic data, specialist marking methods and direct observations have all provided direct evidence that such dispersal movements might be widespread. Nevertheless, the required times scales required for recolonisation (as distinct from dispersal alone) vary from small numbers of years to > 20 years, and limits imposed by the abundance and behaviour of dispersing colonists are still poorly understood.

Together, the data reviewed here indicate that biological recovery can, and does, sometimes follow chemical recovery from acidification. Nevertheless climate, the chemical dynamics of acid-sensitive systems, ecological process within and between species, and the onset of new stressors will continue to affect biological responses to deposition reduction in future. These issues should not be overlooked as research priorities.

Task 3.1: Recovery in lakes

Task 3.1: Recovery in lakes

Job 3.1.1: Calibrate MAGIC using 'best' and 'worst' case N scenarios

Just as the damage to biota was delayed beyond the onset of acid deposition, so the recovery from acidification will also be delayed. In the chain of events from the deposition of strong acids to the damage to key indicator organisms there are two major factors that can give rise to time delays. Biogeochemical processes can delay the chemical response in the catchment soils and consequently surface waters and biological processes can further delay the response of indicator organisms, such as damage to fish. The static models to determine critical loads consider only the steady-state condition, in which the chemical and biological response to a change in deposition is complete. Dynamic models, on the other hand, attempt to estimate the time required for a new state to be achieved. This report describes the possibilities and limitations of using dynamic models to better define the limits and timescales of the recovery processes. Dynamic models have a key role to play in the review of the latest (Gothenburg) Protocol for emission reductions and can provide a new effects driven basis to underpin any further negotiations in the future.

Dynamic model applications are to a certain extent limited by the availability of suitable data to describe the physico-chemical characteristics of surface waters and their terrestrial catchment areas, especially soil chemistry. Given this requirement, it is clear that the focus of dynamic model applications should be on areas that are considered to be acidified or acid 'sensitive'. This makes sense within the framework of the Convention since emissions across Europe are declining and will continue to decline into the foreseeable future under the Gothenburg Protocol and so the speed of recovery from acidification is the key question.

For this study the MAGIC model has been applied to freshwater sites focused in 8 regions of the UK; Cairngorms (NE Scotland), Galloway (SW Scotland), Trossachs (C Scotland), Lake District (NW England), S Pennines (N England), Dartmoor (SW England), Mournes (N Ireland) and Wales. All regions are identified as being sensitive to acidification on the basis of calculated steady-state critical loads and current exceedance (Figure 3.1.1).

The regions comprise different numbers and types of waterbodies (Figure 3.1.2). In the S pennines the surveyed population comprises mainly old, currently unused, water supply reservoirs, used extensively for sport fishing. In Wales, the Welsh Acid Waters Survey sampled 102 headwater streams identified mainly on the basis of their accessibility. In the Lake District, small lakes mainly located on acid sensitive geology were sampled. In Dartmoor, the survey comprised a mixture of headwater streams and standing waters. In Galloway, the Mournes, the Trossachs and the Cairngorms all standing waters located on the acid sensitive geology and without agriculture influence other than plantation forestry were sampled. As a result, the sampled population in each region does not always fully represent the characteristics of all waters in the region and the representivity is not consistent between regions. Nevertheless, this database provides for the most extensive dynamic modeling assessment possible in the UK and provides a unique tool for assessing the likely impact of the Gothenburg Protocol and potentially for calculating further emission reductions targets.

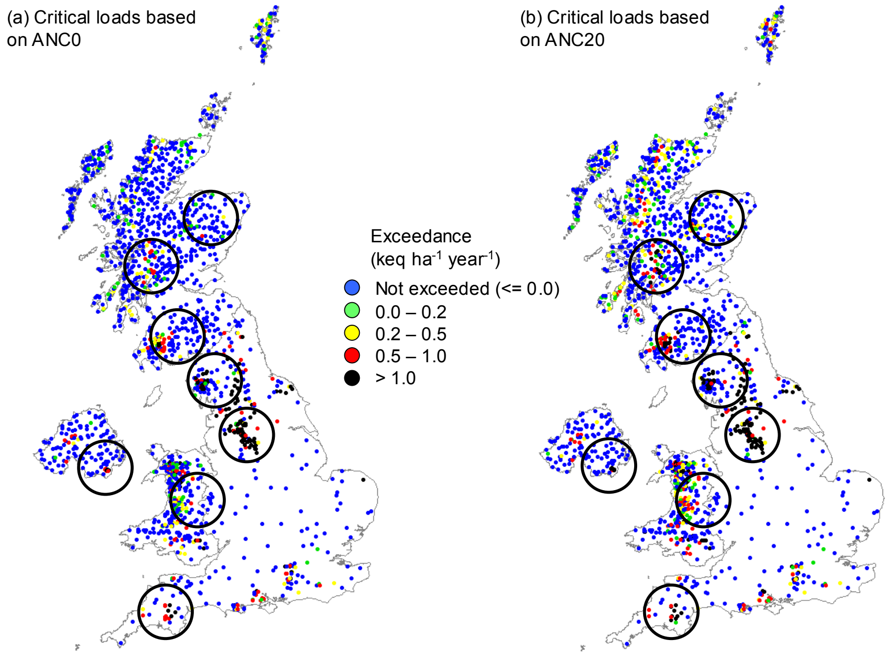


Figure 3.1.1: Exceedance of acidity critical loads for freshwaters by acid deposition for 1998-2000 based on ANC zero and 20 ueq l^{-1}. Dynamic model assessment is focused on the most sensitive regions circled.

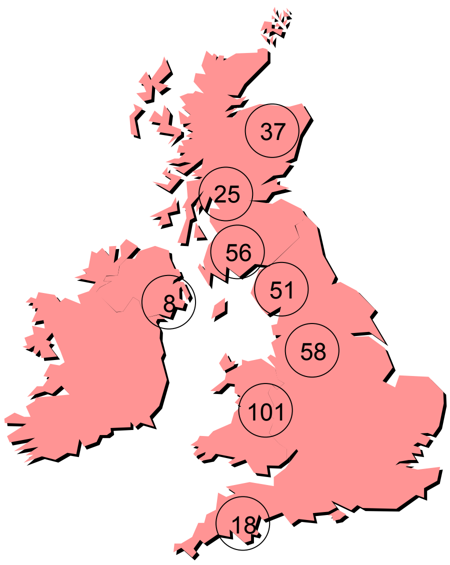


Figure 3.1.2: Numbers of freshwater sites used in each regional modelling assessment.

MAGIC (**M**odel of **A**cidification of **G**roundwater **I**n **C**atchments) is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soils and surface water chemistry (Cosby *et al*. 2001).

The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in lakes and streams. MAGIC represents the catchment with aggregated, uniform soil compartments (one or two) and a surface water compartment that can be either a lake or a stream. MAGIC consists of (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution-precipitation-speciation of aluminium and dissolution-speciation of inorganic and organic carbon, and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change in surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

The soil layers can be arranged vertically or horizontally to represent important vertical or horizontal flowpaths through the soils. If a lake is simulated, seasonal stratification of the lake can be implemented. Time steps are monthly or yearly. Time series inputs to the model include annual or monthly estimates of (1) deposition of ions from the atmosphere (wet plus dry deposition; (2) discharge volumes and flow routing within the catchment; (3) biological production, removal and transformation of ions; (4) internal sources and sinks of ions from weathering or precipitation reactions; and (5) climate data. Constant parameters in the model include physical and chemical characteristics of the soils and surface waters, and thermodynamic constants. The model is calibrated using observed values of surface water and soil chemistry for a specific period. The basic output from the model is a simulation of the changes in chemical concentration/fluxes through time from pre-acidification conditions to present and on into the future under some assumption of change in atmospheric deposition of S and N.

An earlier version of the model (MAGIC5) lacked any process-based mechanisms for N retention in soil and first order uptake coefficients were calibrated to represent catchment immobilization such that input matched output at present day levels. These uptake coefficients were then assumed constant into the future. This model represents the ‘best case’ of N leakage because catchments that do not currently leak N will not leak as N deposition is reduced in the future and for those where N does leak, the loss will be reduced in proportion to the reduction in N deposition.

More recently, the model has been elaborated to incorporate N dynamics (MAGIC7). MAGIC7 embraces the N saturation concept (Stoddard, 1994) with the inclusion of dynamic equations for N cycling. The introduction of a soil inorganic matter compartment controls NO_3^- leakage from the soil, based conceptually on an empirical model described by Gundersen *et al*. (1998). Major processes affecting NO_3^- and NH_4^+ concentrations in surface water have been represented in the model; the most significant are nitrification (biological conversion of NH_4^+ to NO_3^-) and immobilization. Nitrification is modelled as a first order process and immobilization of inorganic N into the soil organic matter is controlled by the C/N ratio (Gundersen *et al*., 1998; Jenkins *et al*., 2001). When the C/N of the soil is above an upper threshold, immobilization of N in soil solution is 100%, while at low C/N when the ratio is below a lower threshold, immobilization becomes incomplete and N leaks from the soil to the surface water. The percentage of inorganic N immobilised is assumed to be a linear function from 100% to 0%. This model represents the 'worst case' for future N leaching since NO_3^- leaching will occur even with reduced inorganic N deposition as a result of continued input to the soil organic N pool.

The regional model applications utilized the best available surface water, soil physical and chemical and land use data. Soil physical and chemical characteristics were spatially and vertically aggregated at a catchment scale from national soil maps and characteristic profiles. Spatial extent and planting dates of forestry were determined where relevant and most recent assessments of net uptake were used. Current and future deposition data were derived from the UK database. At forested sites, a scenario of felling stands at 50 years and immediate re-planting of the same area was used (Helliwell *et al*., 2003).

The MAGIC calibration procedure followed is that documented by Jenkins *et al*. (1998) and Evans *et al*. (2001) and a detailed account of the calibration with N dynamics (MAGIC7) is given in Cosby *et al*. (2001) and Jenkins *et al.* (2001).

The input data required by MAGIC includes annual rainfall and runoff volumes, deposition chemistry and catchment aggregated soil physico-chemical parameters including soil depth, bulk density, cation exchange capacity, carbon pool and C/N ratio of the organic soil compartment. The model is calibrated to surface water concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+), SO_4^{2-}, Cl^-, NO_3^- and NH_4^+ and soil exchangeable fractions of Ca^{2+}, Mg^{2+}, Na^+, K^+. Soil physico-chemical data were aggregated using a catchment-based weighting technique (Helliwell *et al*., 1998).

Deposition data for each site in each region were derived by overlaying the catchment outline onto the most up-to-date UK deposition data at a 5 km x 5 km grid scale. A mean value was calculated for each catchment by averaging the values for the relevant squares and proportioning the deposition from partial squares. The UK deposition data incorporate variations in deposition resulting from orographic enhancement (Fowler *et al*., 1988). Rainfall volumes were obtained from the same database using the same averaging methodology. Base cation deposition was calculated from Cl^- assuming no anthropogenic contribution.

The historical trend in wet deposited non-marine SO_4^{2-} was assumed to follow the sequence described by the Warren Springs Laboratory (1983), adjusted regionally to take account of observations since 1980. Other ions in deposition are assumed to remain constant throughout the simulation unless the catchment has undergone a change in land use. In the British uplands, large scale commercial afforestation is the main land management practice. Conifer plantations significantly exacerbate the acidification status of soils and surface waters and, given that forest uptake, dry deposition and runoff are influenced by the age and forest cover at a site, historical sequences and future forecasts are constructed for the key driving variables.

Evapotranspiration was assumed to vary between 10% for a moorland catchment to 20% for a fully forested catchment. At forested sites, runoff yield is assumed to decrease linearly with increasing area of mature canopy cover. The enhancement of acid input through dry deposition mechanisms increased deposition in forested catchments. Net uptake of ions in biomass was modelled relative to the age and spatial coverage of forest within the catchment during the historical reconstruction and forecast simulation (Ferrier *et al*., 1995).

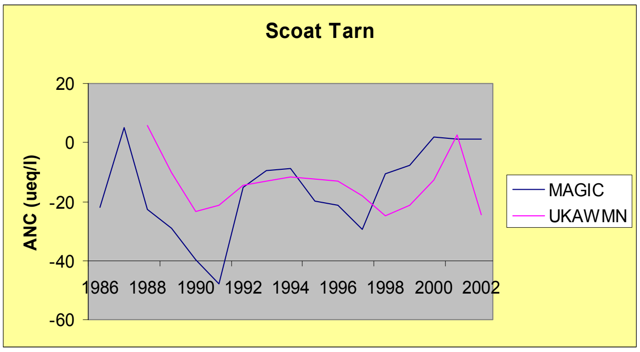
Job 3.1.2: Test model simulations using reconstructed reference conditions and present day chemistry

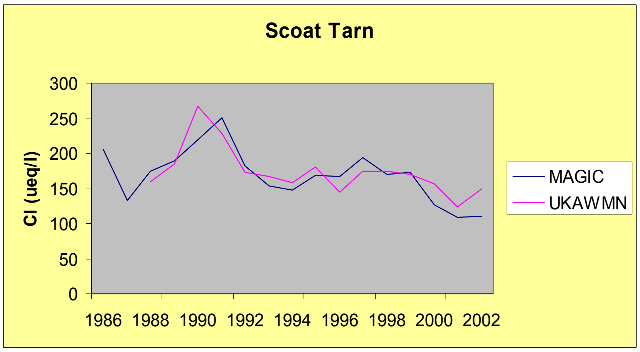
The MAGIC model has been tested against the 15 year time series of chemistry data at 7 lake sites of the UK Acid Waters Monitoring Network; Lochnagar, Round Loch of Glenhead, Loch Grannoch, Loch Tinker, Scoat Tarn, Llyn Llagi and Blue Lough (Monteith, 2004). The AWMN documents trends in chemistry in response to a general decline in S deposition across the UK (Cooper and Jenkins, 2003). If the model is capable of matching the observed trends this provides confidence that the process representation within the model, the data supporting its calibration and the calibration procedure are appropriate to the problem. Further, this provides greater confidence in the future predictions of the model. Superimposed on the longer term trends at the UKAWMN sites is considerable year to year variation caused by annual variation in input chemistry, rainfall and weather conditions. Matching this variation represents a significant test of the model structure.

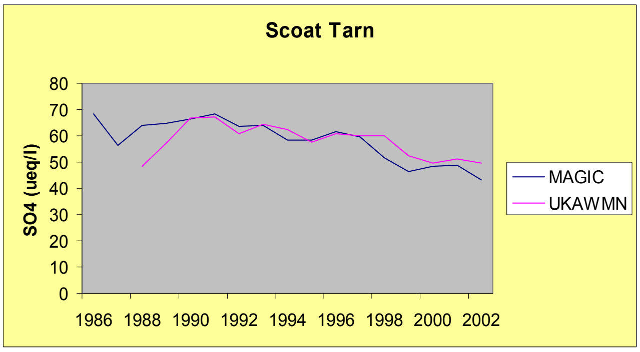
Each model application utilized detailed soil information available for each site. The model was calibrated to match the observed water chemistry in 1988. Because of the annual variation in chemistry this was calculated as the mean of the first 5 years of data, a period in which no trend was observed. The deposition chemistry for 1988 was calculated as the mean of 1988 – 93 from the nearest located deposition collector in the UK Acid Deposition Monitoring Network (Jenkins *et al*., 1998). Annual deposition chemistry from the co-located collector was then used as input to drive the model from 1988 to 2002. Because the deposition collector is not directly co-located at the monitoring site and also since wet deposition does not accurately reflect dry and occult deposition inputs, the annual wet deposition concentrations at each site are corrected to match the observed Cl and SO4 in surface water. This is calculated for the 5 year mean data used in the initial calibration and the same adjustment is then applied to the marine ions and SO4 for each year of record.

At Scoat Tarn (Figure 3.1.3) there is a close match between observed and predicted concentrations. The model is able to match the declining trend in SO4 concentration and also captures the annual variability in Cl. As a result the slight improvement in pH is well simulated although the ANC is very variable. This is the same situation at Round Loch of Glenhead (Figure 3.1.4) although at this site the slope of decline in SO4 is less well matched and yet there is a closer match between observed and simulated ANC. The model shows these same characteristics at Llyn Llagi (Figure 3.1.5).

At Loch Tinker (Figure 3.1.6) no strong trends are evident in the observed data although the recent decline in SO4 concentration is not well captured by the model. This implies that the deposition observations do not reflect those at the catchment or that catchment processes are occurring which are not included in the model such as sulphate adsorption/desorption. It must also be noted that in some catchments SO4 concentrations may be influenced by rainfall variability. Nevertheless, the annual variation in Cl is well captured by the model which implies that the rainfall observations are representative.







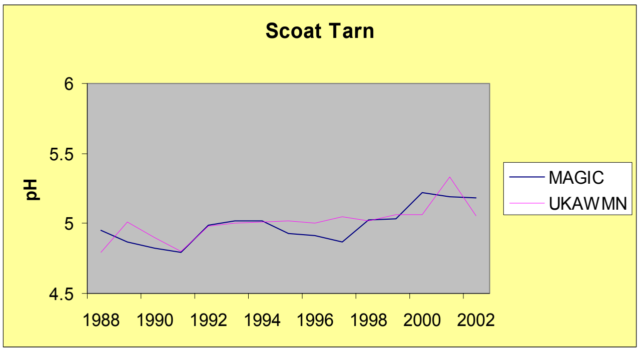
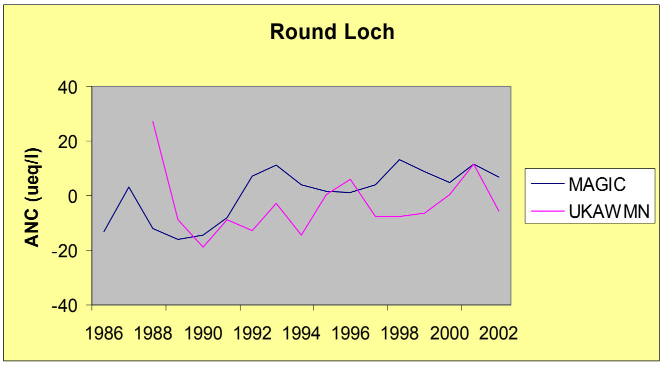
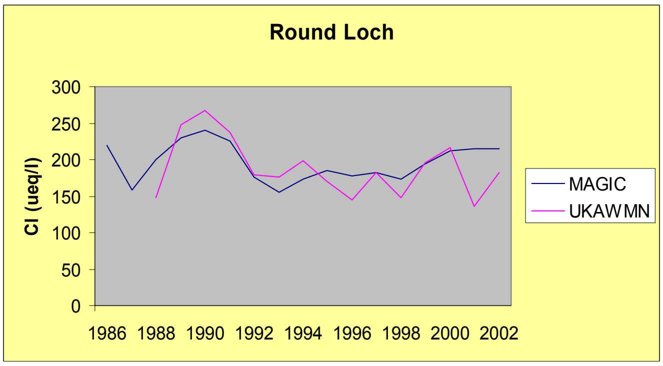
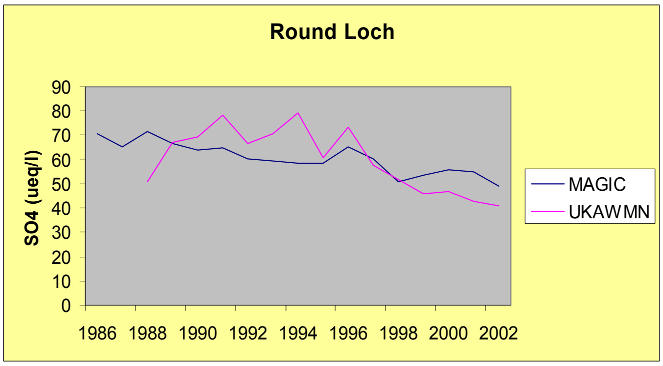


Figure 3.1.3: Comparison of MAGIC and 15 years observed water chemistry at Scoat Tarn (UKAWMN site 10).







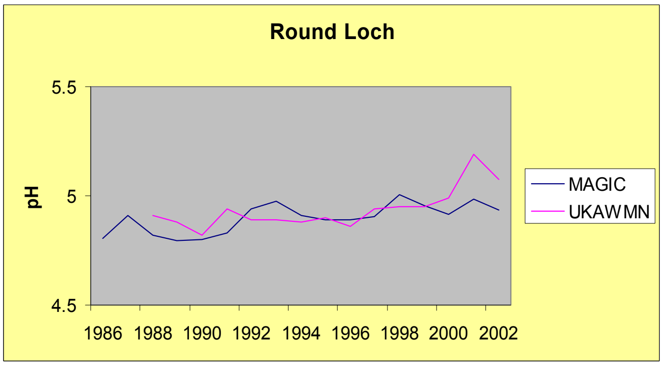


Figure 3.1.4: Comparison of MAGIC and 15 years observed water chemistry at Round Loch of Glenhead (UKAWMN site 7).

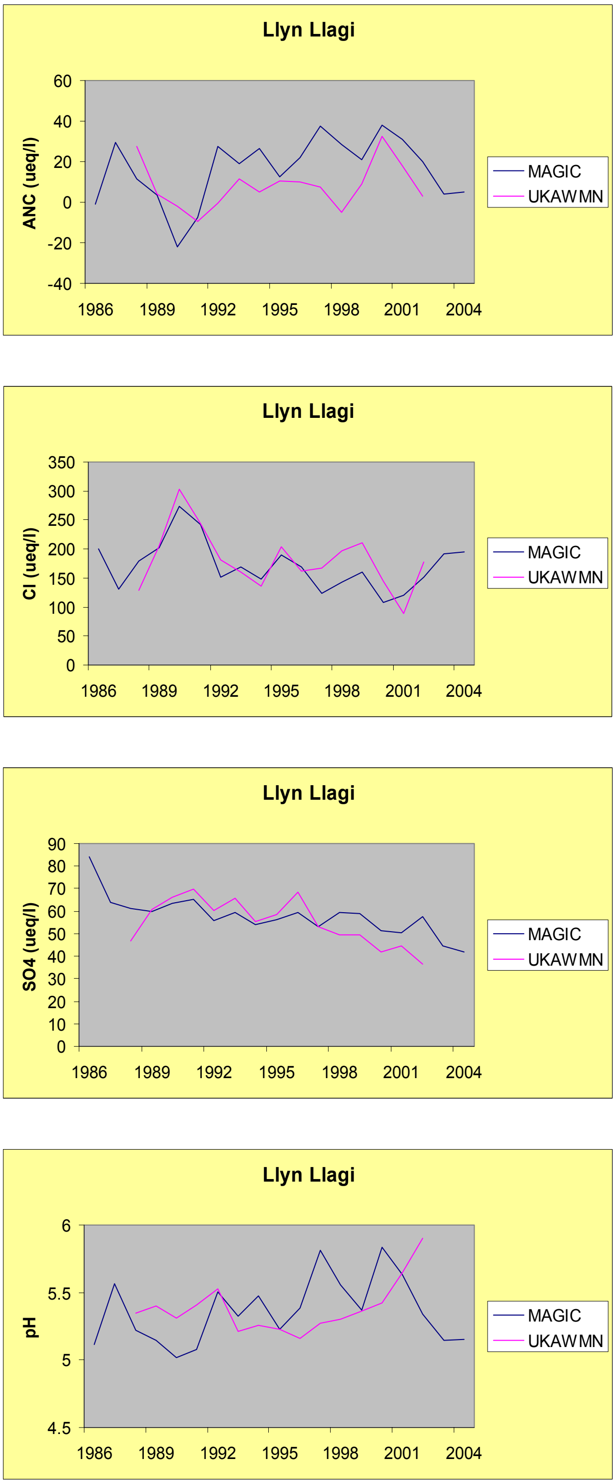


Figure 3.1.5: Comparison of MAGIC and 15 years observed water chemistry at Llyn Llagi (UKAWMN site 15).

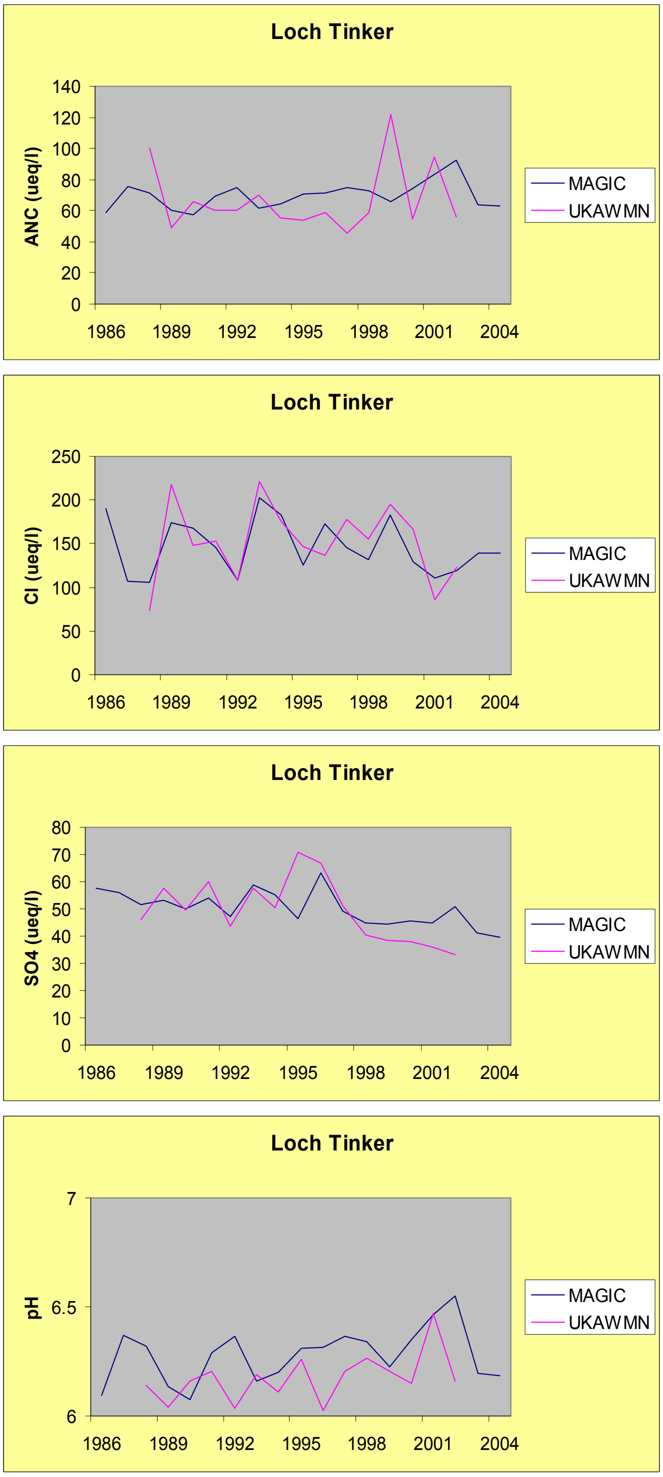


Figure 3.1.6: Comparison of MAGIC and 15 years observed water chemistry at Loch Tinker (UKAWMN site 6).

At Lochnagar (Figure 3.1.7), the decline in SO4 and variability in Cl are well matched by the model simulation. ANC and pH show a close match until recently when the model predicts a sharp increase in ANC and pH which is not evident in the observations. In this case, the implication is that SO4, which is declining in the observations, is not promoting any observed recovery from acidification. Likely causes are rainfall and temperature impacts, especially on DOC. At Loch Grannoch (Figure 3.1.8), there is a similar mismatch in the observed and simulated pH although here, the recent sharp decline in SO4 is not so well matched by the simulation. ANC concentrations are not well simulated throughout the period. At this site plantation forestry through the 1970s and 1980s complicates the assessment of deposition inputs to the catchment.

The simulation at Blue Lough (Figure 3.1.9) is the least convincing as a test of the model capabilities. Both the recent trends towards declining SO4 and the annual variation in Cl are not well captured by the model implying that the rainfall data is not representative of the site. ANC is not well matched with observations throughout the period.

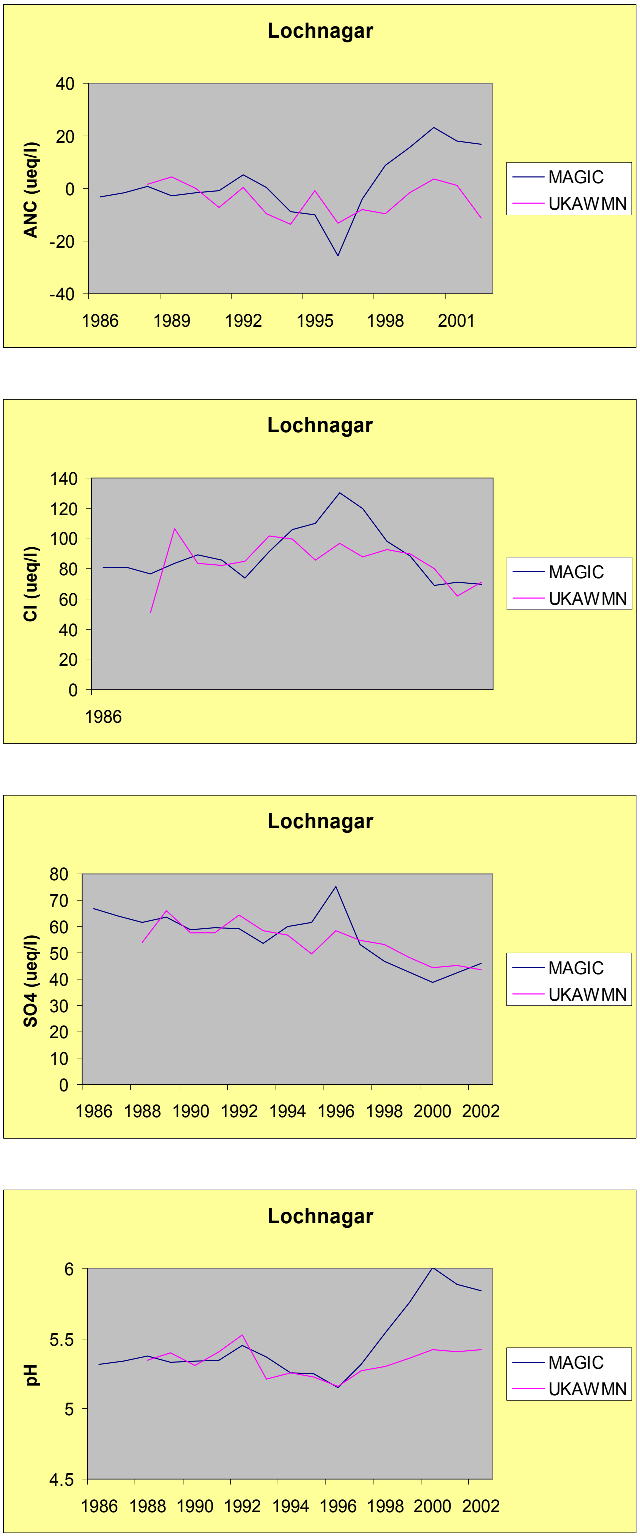
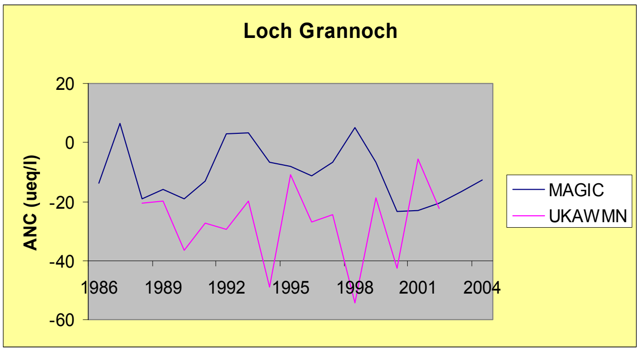
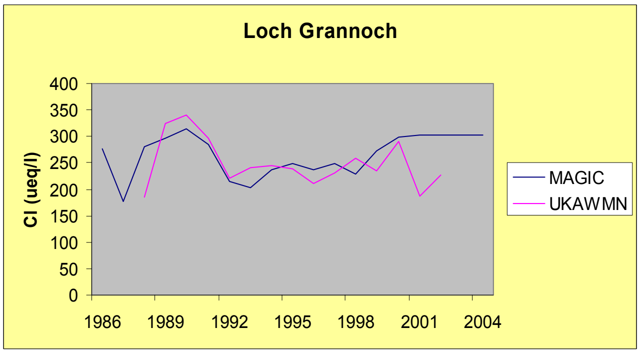
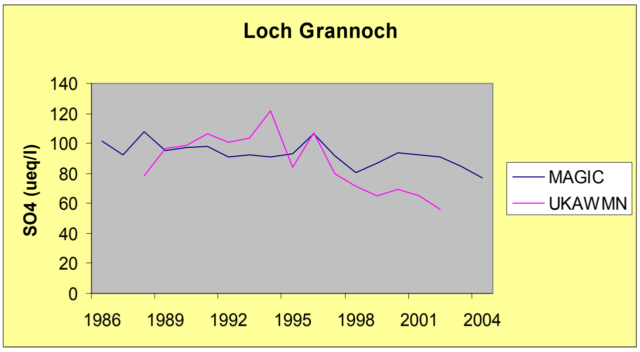


Figure 3.1.7: Comparison of MAGIC and 15 years observed water chemistry at Lochnagar (UKAWMN site 4).







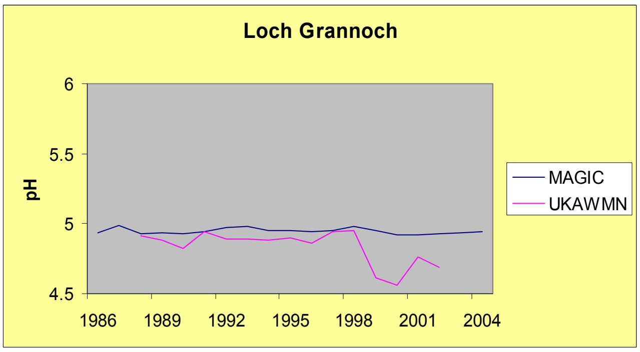


Figure 3.1.8: Comparison of MAGIC and 15 years observed water chemistry at Loch Grannoch (UKAWMN site 8).

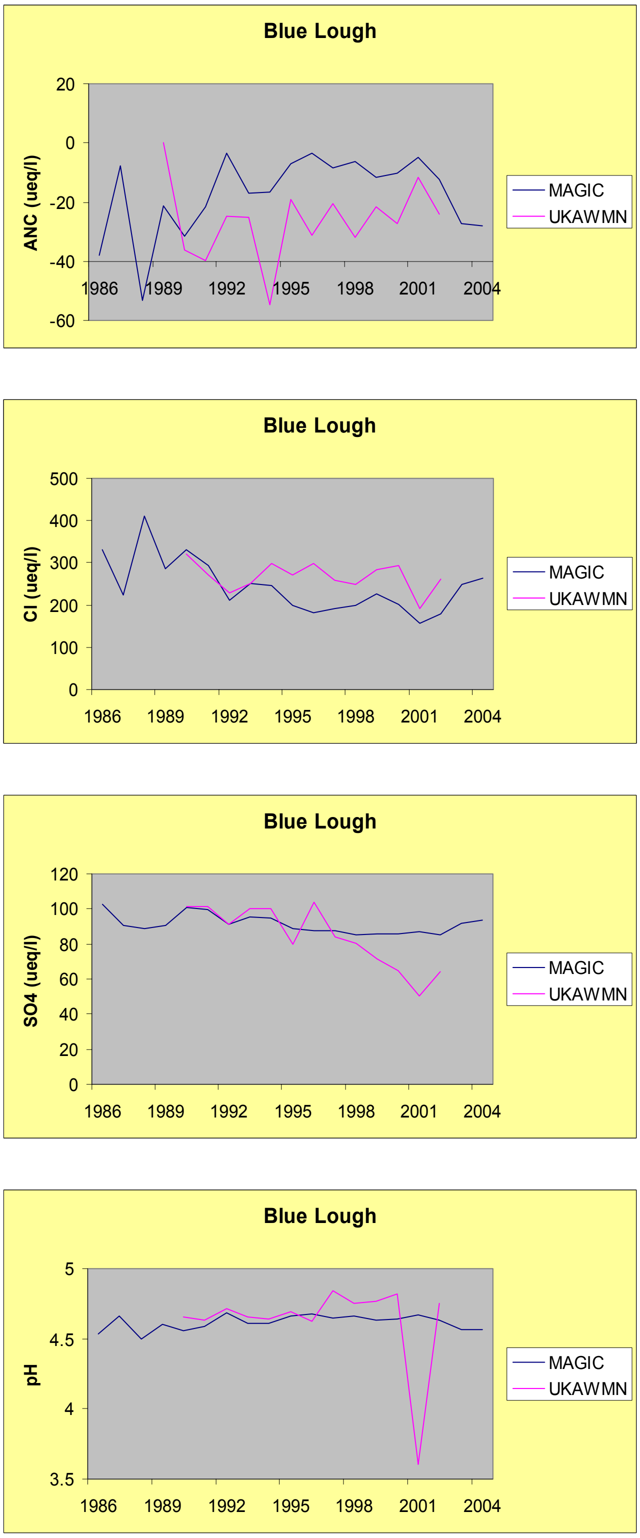


Figure 3.1.9: Comparison of MAGIC and 15 years observed water chemistry at Blue Lough (UKAWMN site 21).

The linkage of chemical and biological predictions is described under Jobs 3.1.5-3.1.6 below. Comparisons of model performance relative to palaeolimnological reconstructions are described in the report for Task 3.3 below.

Overall, the model effectively matches observed trends in major ions, including those driven by marine influence. Where a mis-match occurs, only at Blue Lough can this be attributed to the data from the nearest rainfall collector being un-representative of the actual deposition to the site. At other sites, mismatches between observed and predicted are likely to result from chemical and physical processes which are not included in the model. These include SO4 adsorption/desorption, variation in annual rainfall inputs and climatic effects.

Job 3.1.3: Assess Gothenburg Protocol in relation to time to reach ANC targets and reference conditions

Job 3.1.4: Assess water chemistry following Gothenburg Protocol up to 2050

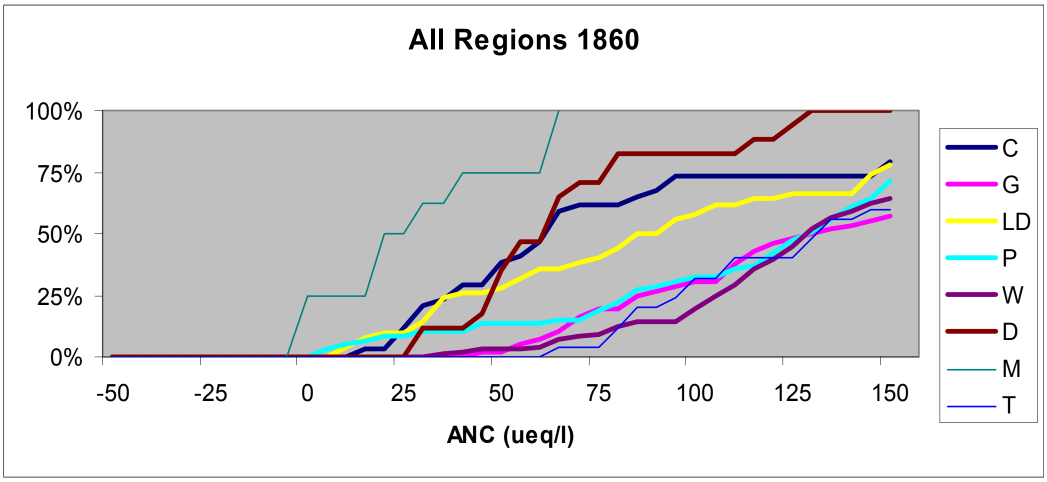
The calibrated model for each regional set of lakes can be used to predict future response to reductions in S and N deposition. Estimates of the deposition across the UK in response to the agreed emission reductions under the Gothenburg Protocol have been calculated using the FRAME model. These regional deposition loadings are comparable with those calculated at European scale using the EMEP model. The regional deposition in 2010, assuming a linear decline from the present level of deposition, is used as input to drive the model to make predictions. Beyond 2010 the deposition is assumed to remain constant at that level.

Reconstructed reference conditions (pre-acidification 1860) are significantly different between the regions (Figure 3.1.10). The Mournes have the most acidic reconstructed background conditions but note that this region comprises only 8 sites and so the percentages are misleading. The reason for the low simulated background ANC, below zero, is unknown and requires further investigation. ANC is also generally lower in the Cairngorms, Dartmoor and the Lake District. In these regions mineral weathering in the model provides the main source of base cation buffering whereas in the Pennines, Wales and Galloway the soil base cation pool provides a significant contribution. Nevertheless, background simulated ANC at all sites in all regions is above zero and is predominantly above 20 ueq l^{-1}.

Predictions for 2010 indicate that significant acidification problems remain in the Mournes, S Pennines and Lake District where ANC in c.15% - 50% of lakes remains below zero (Figure 3.1.10). In all other regions ANC is greater than zero although some regions are predicted to have a significant percentage of lakes with ANC below 20 ueq l^{-1}.

In each region the model reconstructions indicate a significant acidification from baseline conditions to a peak of surface water acidity (lowest ANC) in c.1970 which coincides with the peak of S deposition in the UK (Figure 3.1.11). Since 1970, reductions in S deposition have led to increased ANC by 2000. Further improvements are predicted by 2010 in response to further reductions in S and some smaller reductions in N deposition but recovery beyond 2010 to 2100 is extremely slow as the deposition is held constant at the 2010 level. In all regions the predicted ANC in 2010 remains significantly lower than the pre-acidification baseline.

Worst case scenarios invoking the best current understanding of N dynamics in catchments were undertaken at 4 regions; Wales, S Pennines, Galloway and the Mournes. All other regions currently lack appropriate data to calibrate the soil C and N pools. In all 4 regions the worst case model predicts significantly increased NO3 concentrations relative to the best case model in 2050 (Figures 3.1.12-3.1.15). In all 4 regions this promotes lower ANC in 2050, however, this has little potential ecological impact as few sites in any region move between the biologically relevant ANC classes (Figures 3.1.12-3.1.15). It must be considered, however, that the significantly increased NO3 concentrations will have an impact with respect to surface water eutrophication.



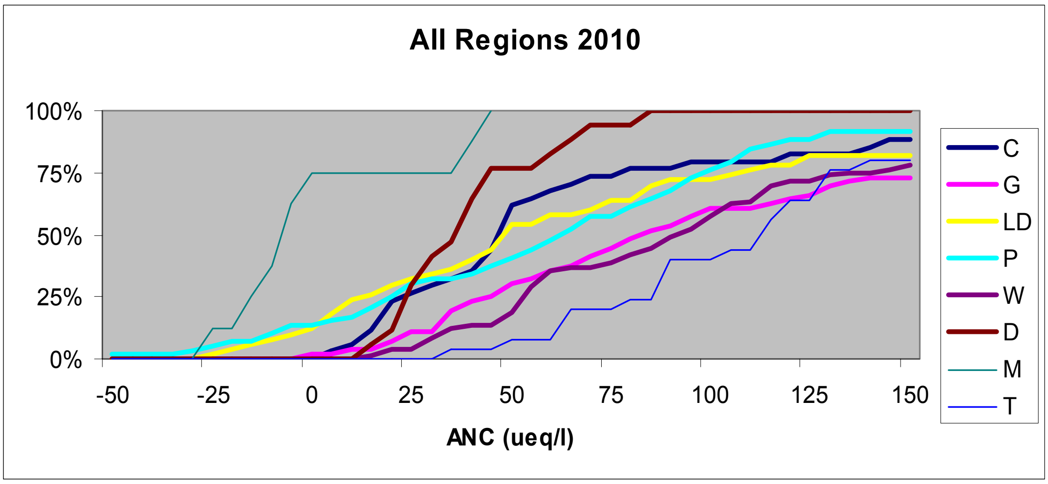
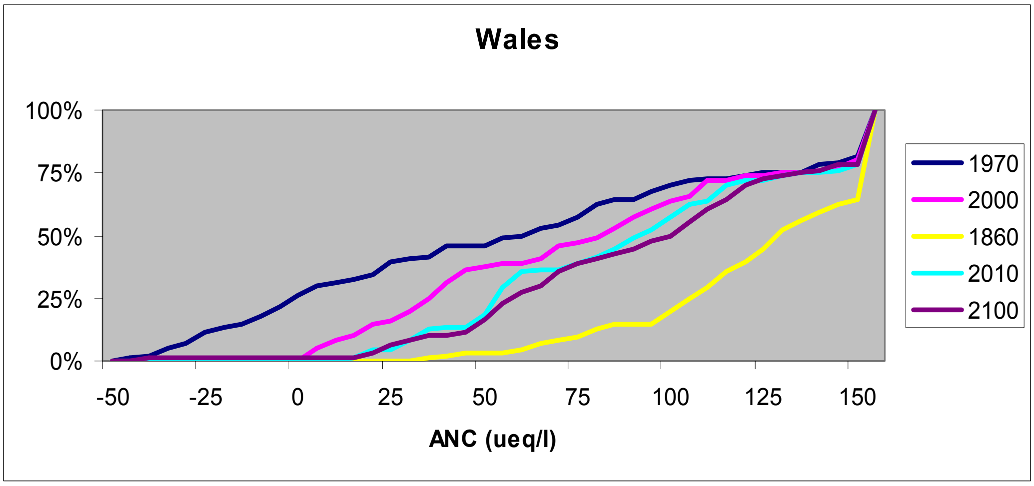


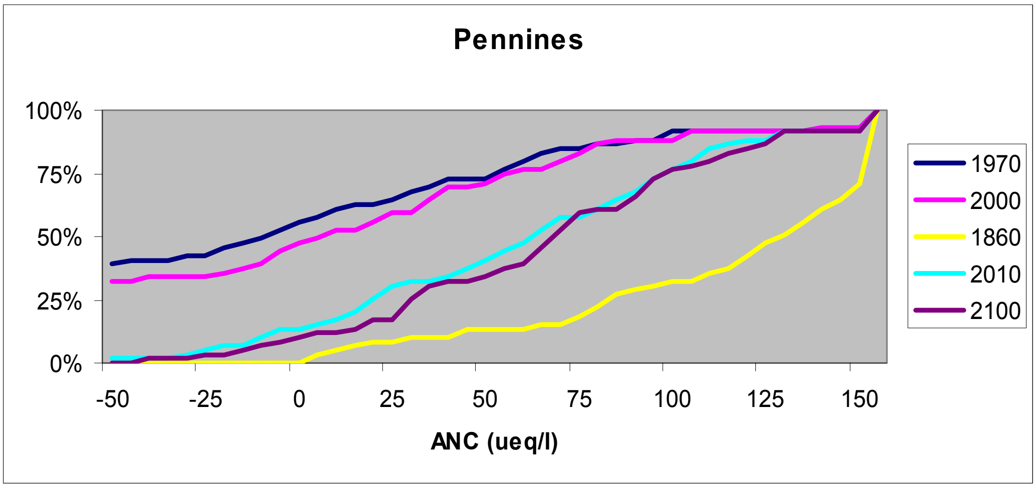
Figure 3.1.10: Cumulative frequency distributions of ANC for all regions in reconstructed reference conditions (1860) and future predictions under the

Gothenburg Protocol deposition scenario (2010). (Note that the Mournes includes only 8 lakes).

The biological relevance of these predictions can be assessed with reference to threshold ANC concentrations; zero, 20 and 40 μeql^{-1} (Figure 3.1.16). In all regions the impact of achieving the Gothenburg Protocol emission reductions by 2010 is stabilized by 2030. With respect to ANC zero, all regions achieve their pre-acidification status by 2030 except for the S Pennines, the Mournes and the Lake District. For ANC of 20 μeql^{-1}, none of the regions return to their pre-acidification level in 2030 and for ANC of 40 μeql^{-1}, there remains a significant difference from pre-acidification levels in Dartmoor, Galloway and the S Pennines. This implies that for organisms with a high sensitivity to acidity further deposition reductions beyond those agreed under the Gothenburg Protocol will be required to return to their background biological status.

For UK freshwaters critical loads are calculated using an ANC crit of zero or 20 μeql^{-1} depending on estimated background reference conditions. An assessment of predicted recovery in relation to these thresholds at the UK scale shows that if the agreed emission reductions are achieved by 2010, most surface waters will return to their background status by 2020 (Figure 3.1.17), the exceptions being the South Pennines, the Mournes and the Lake District. Further reductions will be required to produce complete recovery and these would need to be targeted especially to the Mournes, S Pennines and Lake District regions. These UK results have been set in a European context through participation in the European scale RECOVER:2010 and EMERGE projects and the results indicate that the acidity problems that persist in the Lake District and S Pennines are comparable with those remaining in 2016 in Sweden, Slovakia and N Italy (Figure 3.1.18). A more significant problem remains in the Mournes, comparable to the prediction for S Norway (Jenkins *et al.*, 2003).





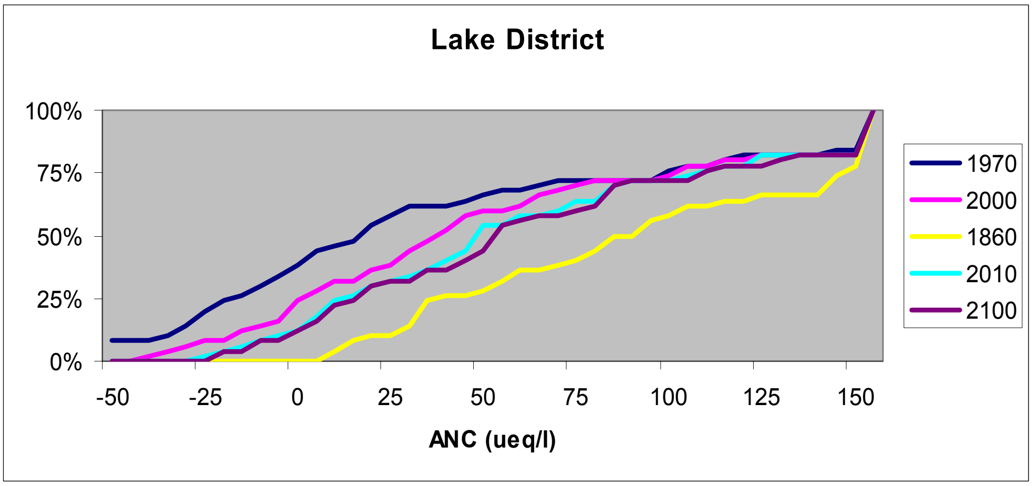


Figure 3.1.11: ANC cumulative frequency distributions by region.

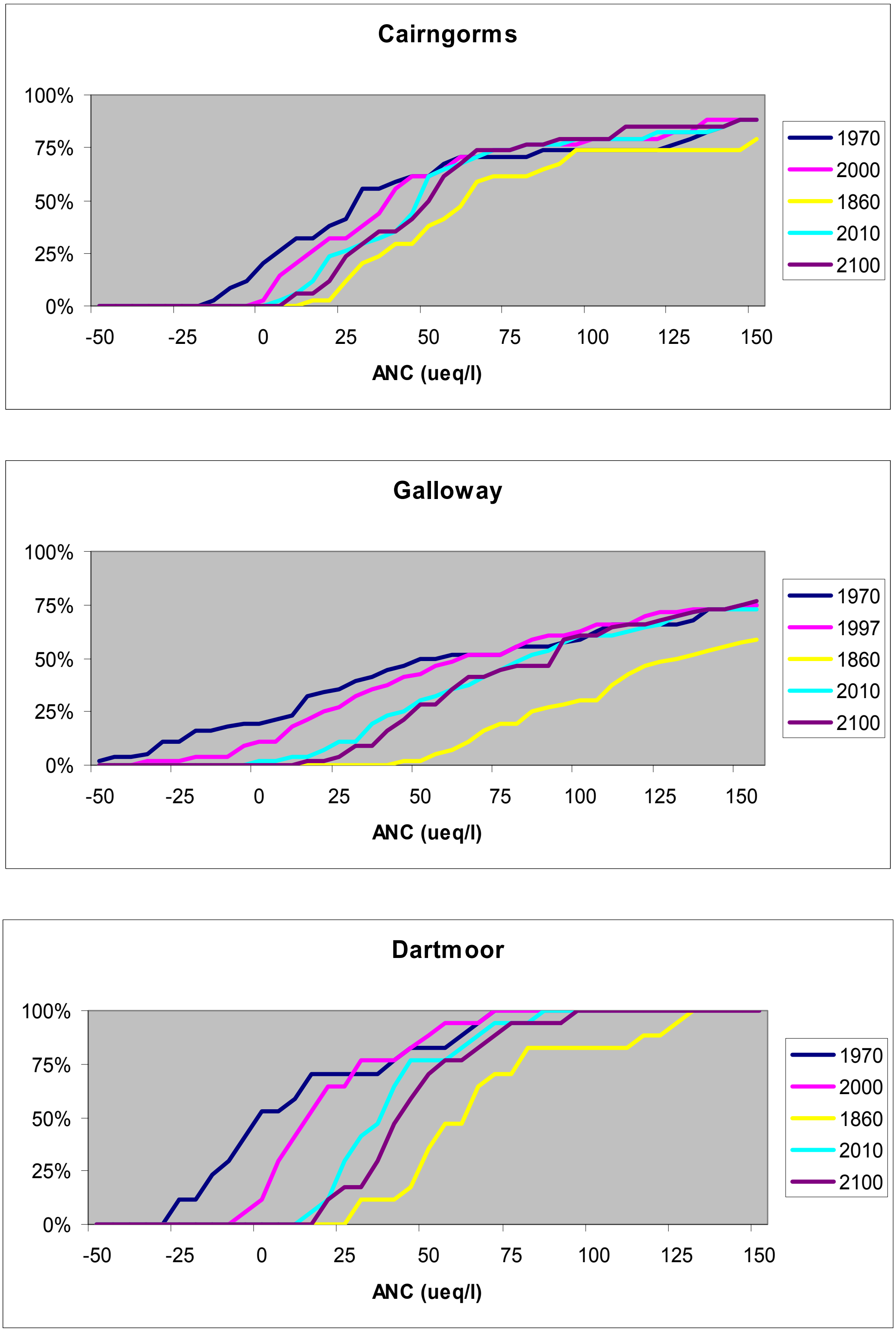
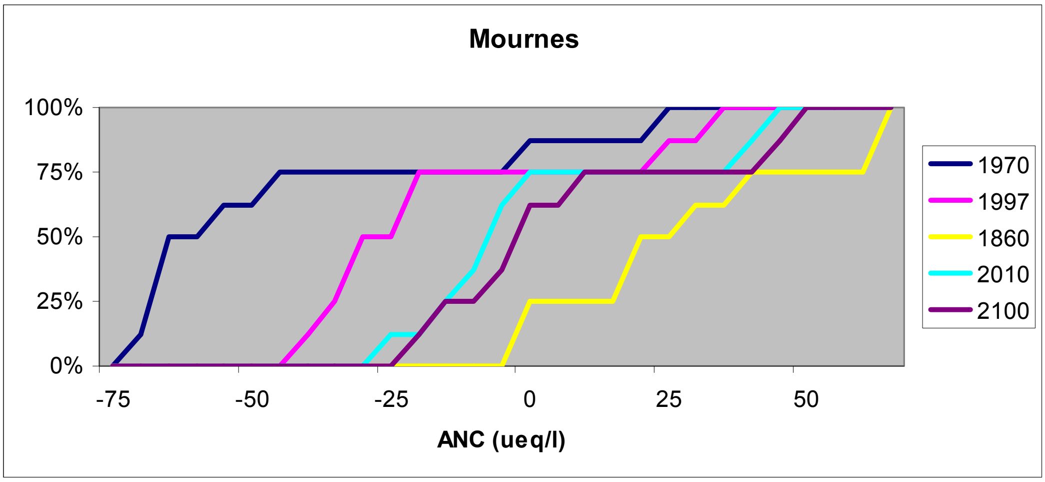


Figure 3.1.11 (Contd.): ANC cumulative frequency distributions by region.



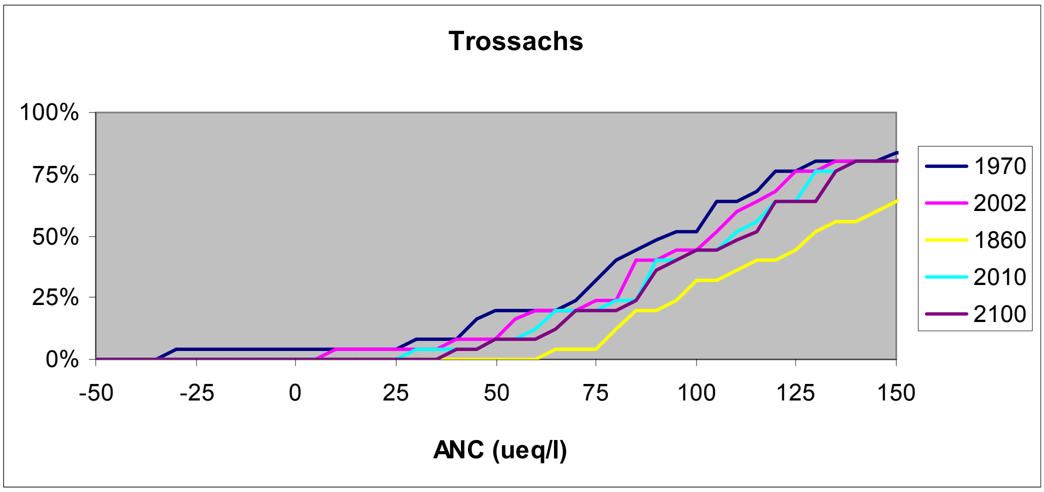


Figure 3.1.11 (contd.): ANC cumulative frequency distributions by region (NB. Different ANC scale for the Mournes).

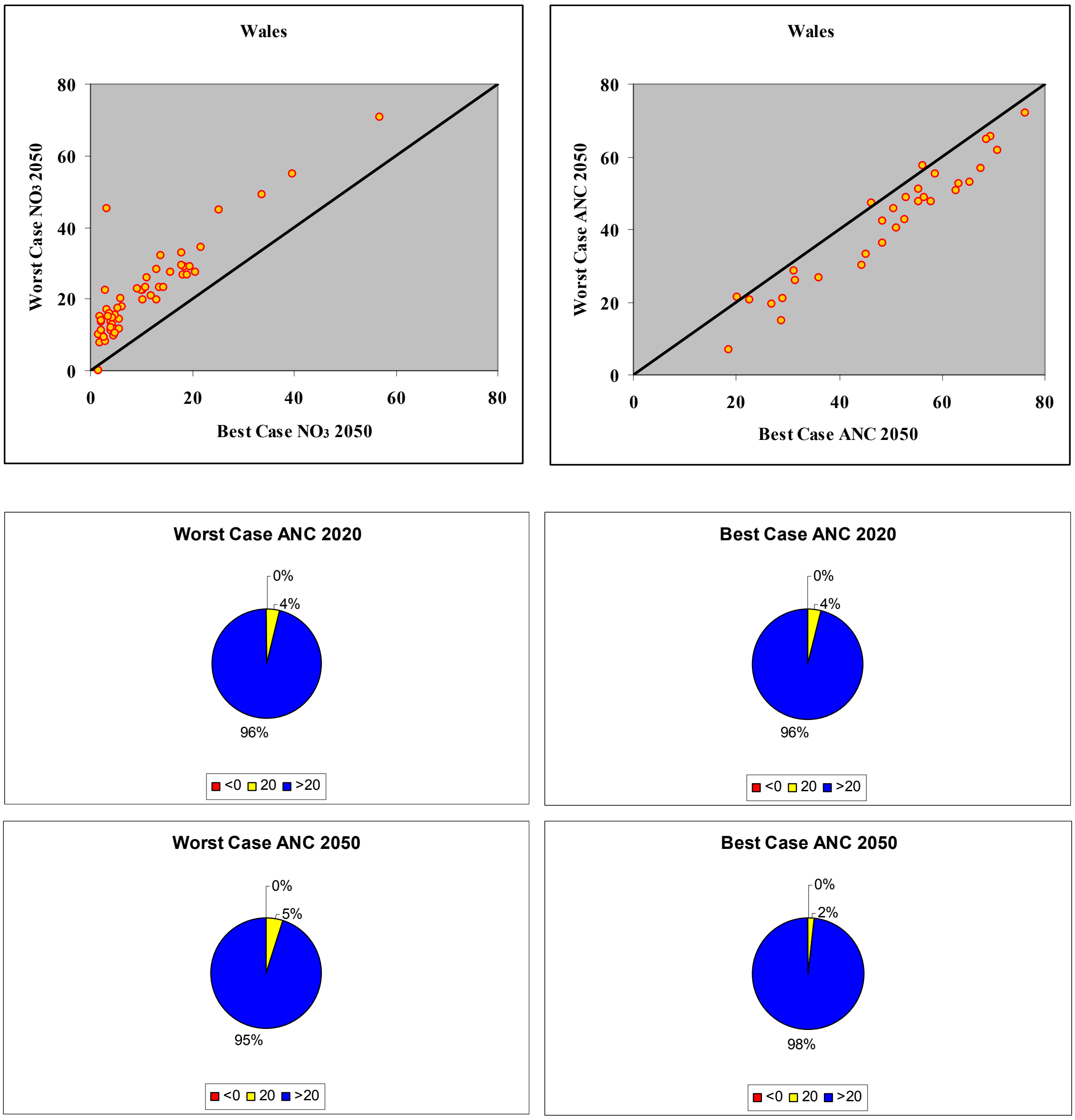
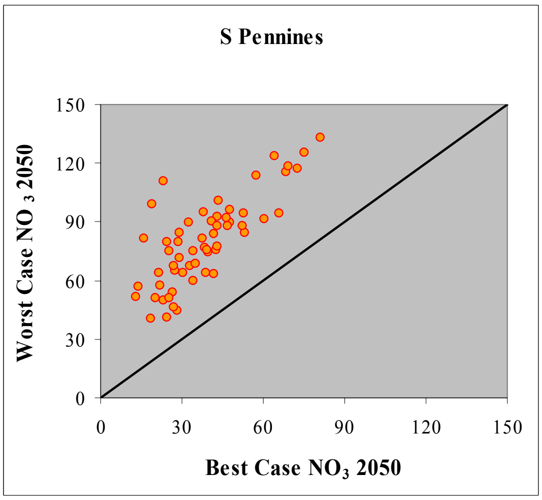
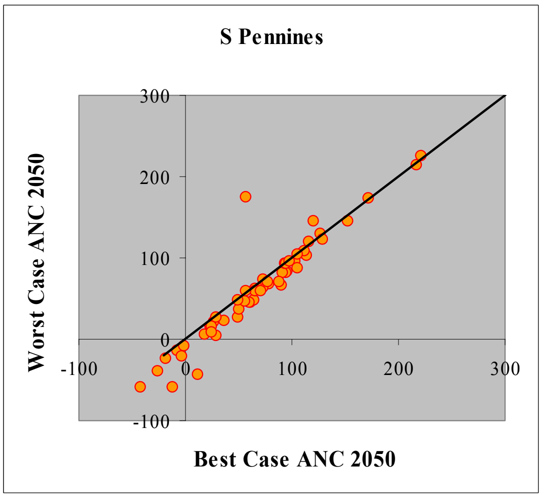
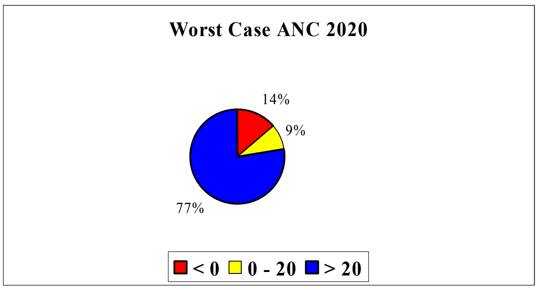
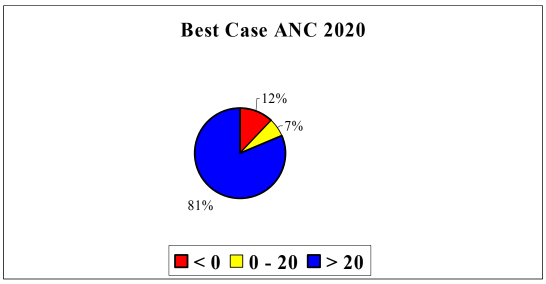


Figure 3.1.12: Comparison of the best and worst case N scenarios for Wales. Upper panels show absolute differences at all sites. Middle and lower panels (pie charts) show variation between the biologically relevant ANC classes.


S Pennines
Worst Case NO 3 2050
Best Case NO3 2050
0
30
60
90
120
150


S Pennines
Worst Case ANC 2050
Best Case ANC 2050
300
200
100
0
-100
-100
0
100
200
300


Worst Case ANC 2020
14%
9%
77%
< 0
0 - 20
> 20


Best Case ANC 2020
12%
7%
81%
< 0
0 - 20
> 20

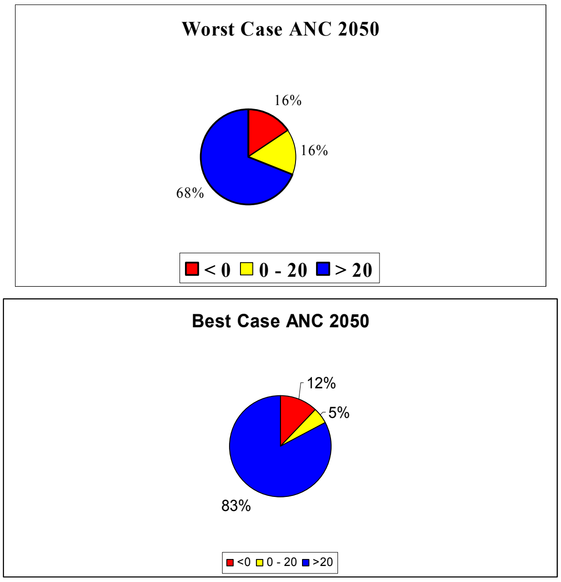
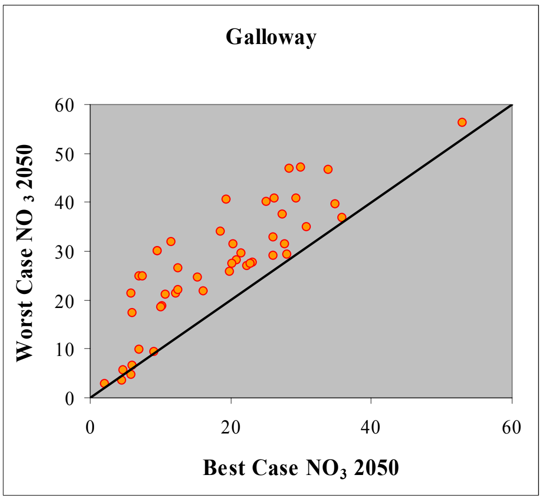
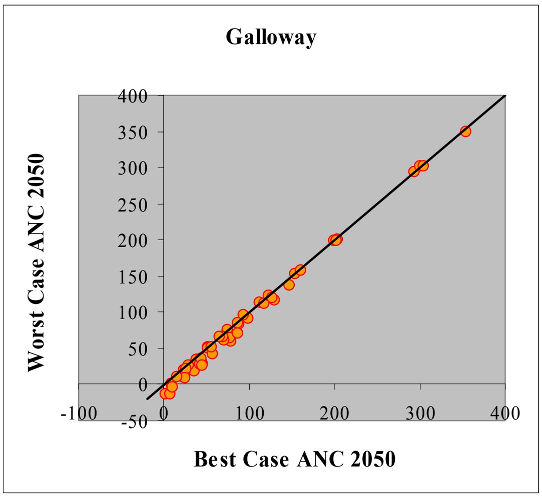
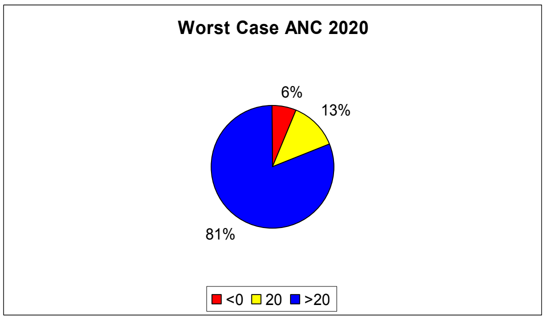
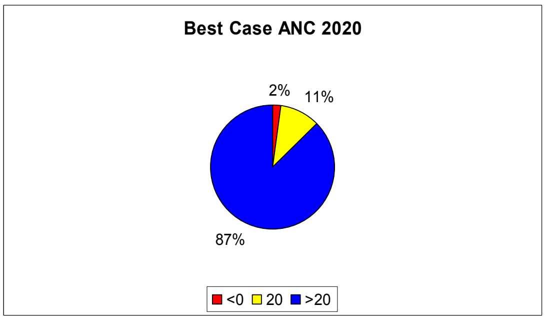


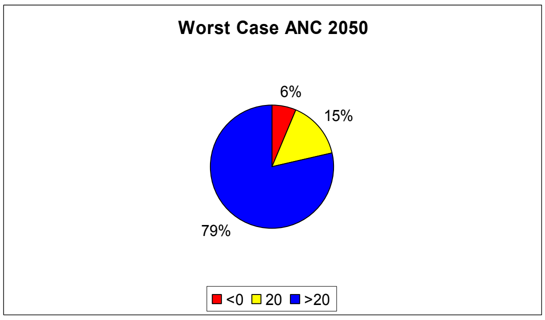
Figure 3.1.13: Comparison of the best and worst case N scenarios for the S Pennines. Upper panels show absolute differences at all sites. Middle and lower panels (pie charts) show variation between the biologically relevant ANC classes.


Galloway
Worst Case NO 3 2050
Best Case NO_3 2050
0
10
20
30
40
50
60
0
20
40
60


Galloway
Worst Case ANC 2050
Best Case ANC 2050
400
350
300
250
200
150
100
50
0
-50
-100
0
100
200
300
400


Worst Case ANC 2020
6%
13%
81%
<0
20
>20


Best Case ANC 2020
2%
11%
87%
<0
20
>20



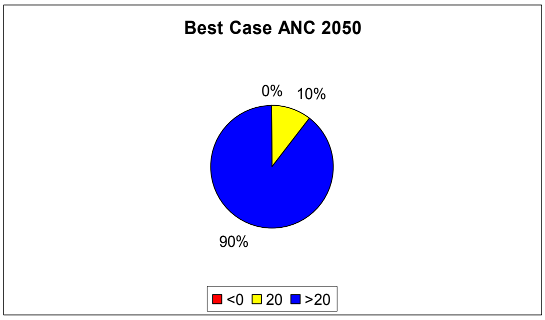
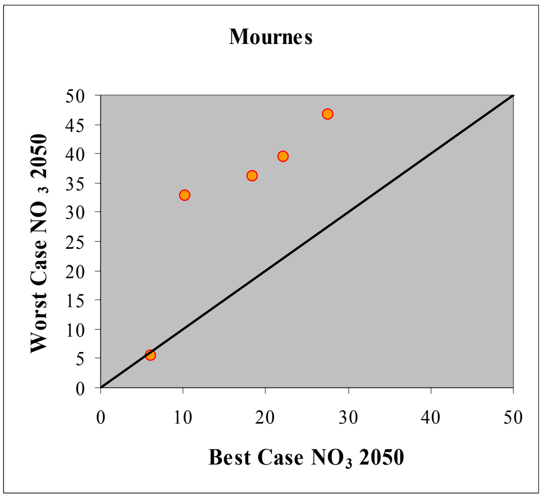
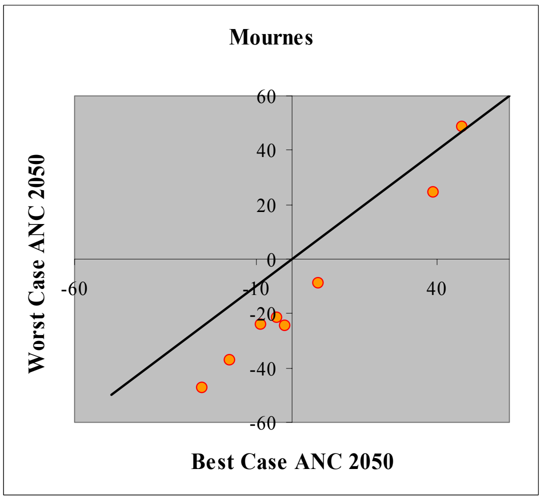
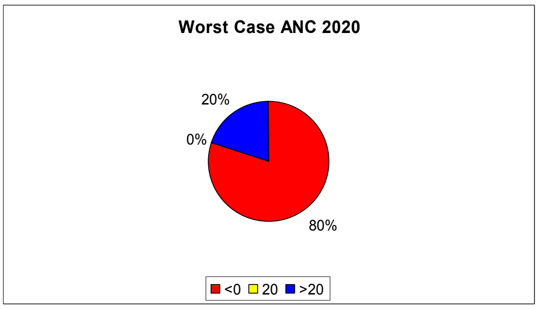
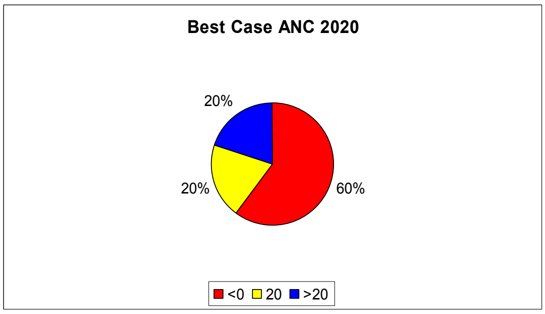


Figure 3.1.14: Comparison of the best and worst case N scenarios for Galloway. Upper panels show absolute differences at all sites. Middle and lower panels (pie charts) show variation between the biologically relevant ANC classes.


Mournes
Worst Case NO 3 2050
Best Case NO3 2050
0
5
10
15
20
25
30
35
40
45
50
0
10
20
30
40
50


Mournes
Worst Case ANC 2050
Best Case ANC 2050
60
40
20
0
-20
-40
-60
-60
-10
40


Worst Case ANC 2020
20%
0%
80%
<0
20
>20


Best Case ANC 2020
20%
20%
60%
<0
20
>20

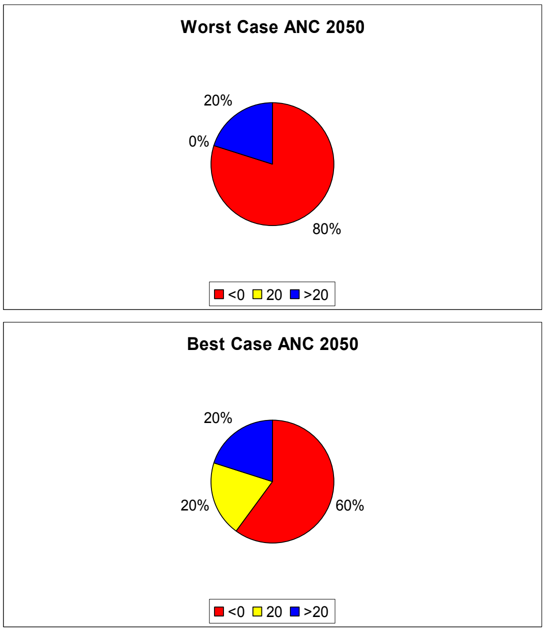


Figure 3.1.15: Comparison of the best and worst case N scenarios for the Mournes. Upper panels show absolute differences at all sites. Middle and lower panels (pie charts) show variation between the biologically relevant ANC classes.

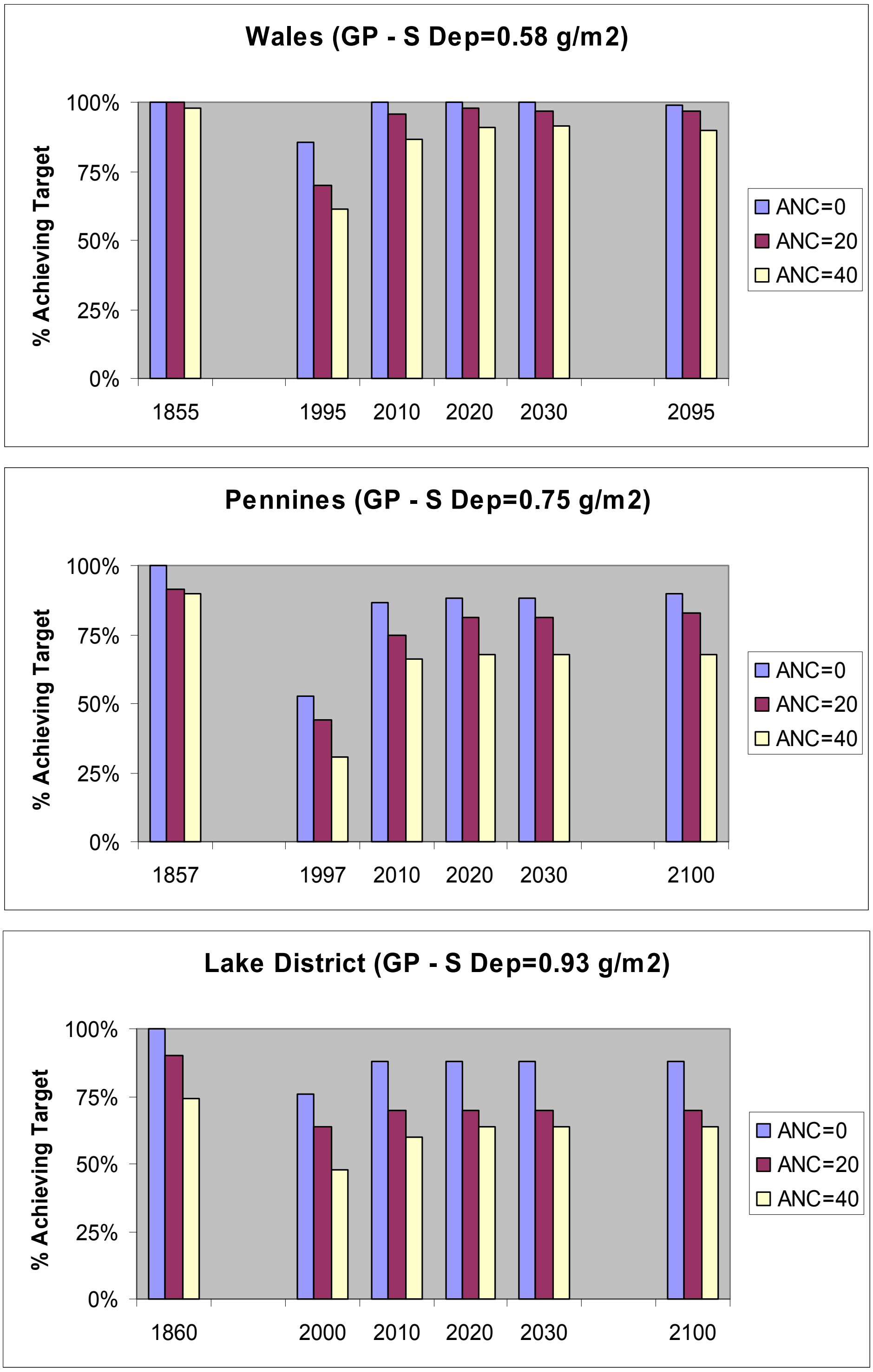
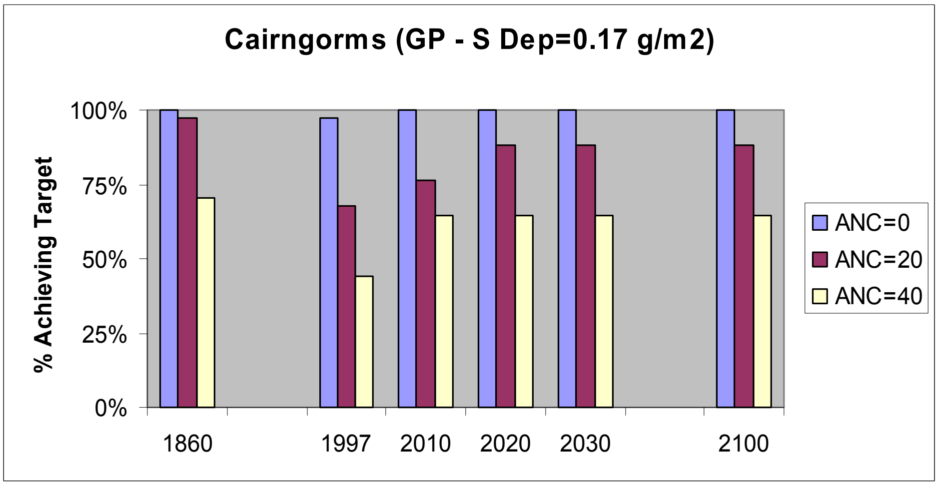
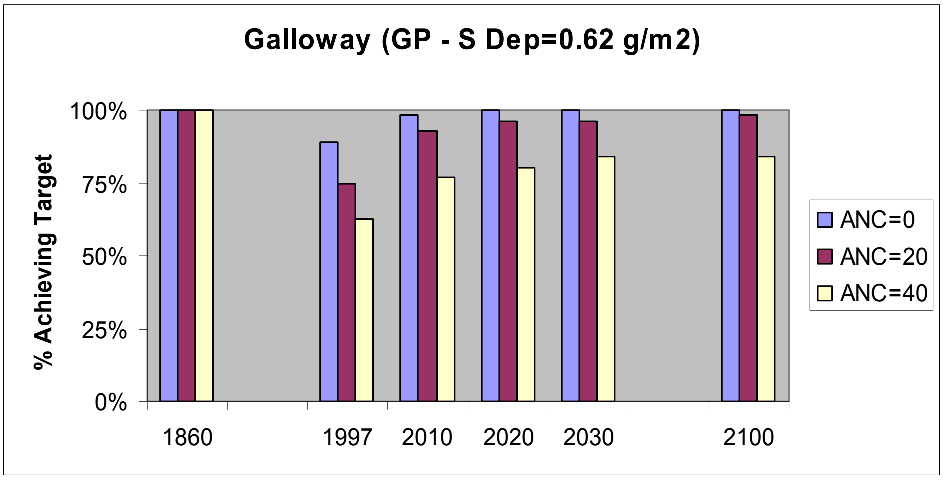


Figure 3.1.16: Percent of sites achieving critical ANC thresholds, zero, 20 and 40 μeql^{-1} in each region under the Gothenburg Protocol deposition scenario. Regional S deposition used in the model for 2010 is given.





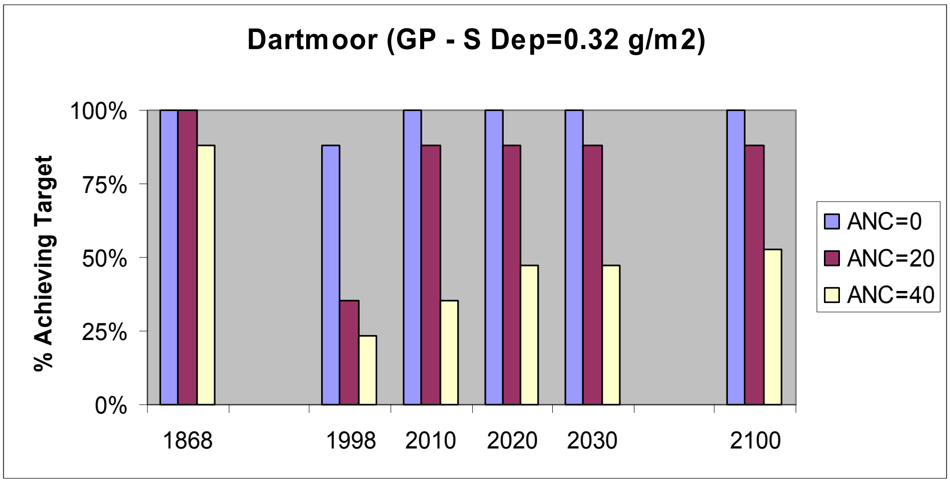
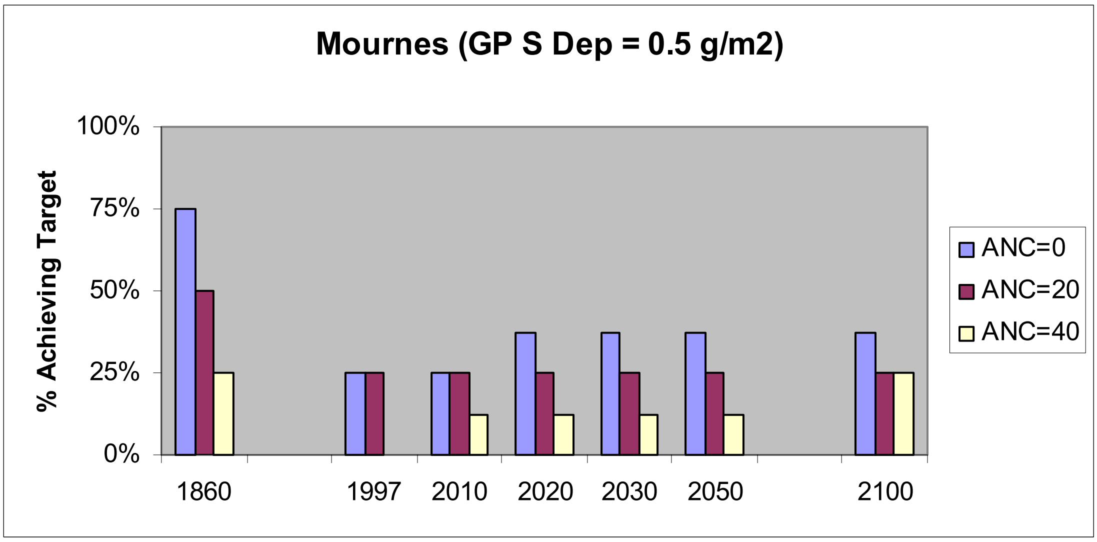


Figure 3.1.16 (Cont'd): Percent of sites achieving critical ANC thresholds, zero, 20 and 40 μeql^{-1} in each region under the Gothenburg Protocol deposition scenario. Regional S deposition used in the model for 2010 is given.



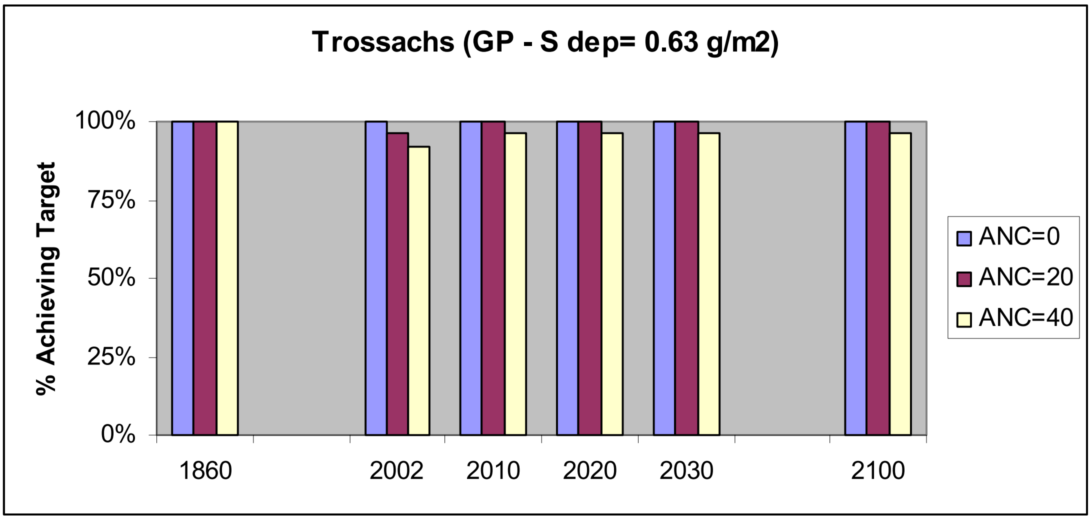


Figure 3.1.16 (Cont'd): Percent of sites achieving critical ANC thresholds, zero, 20 and 40 μeql^{-1} in each region under the Gothenburg Protocol deposition scenario. Regional S deposition used in the model for 2010 is given.

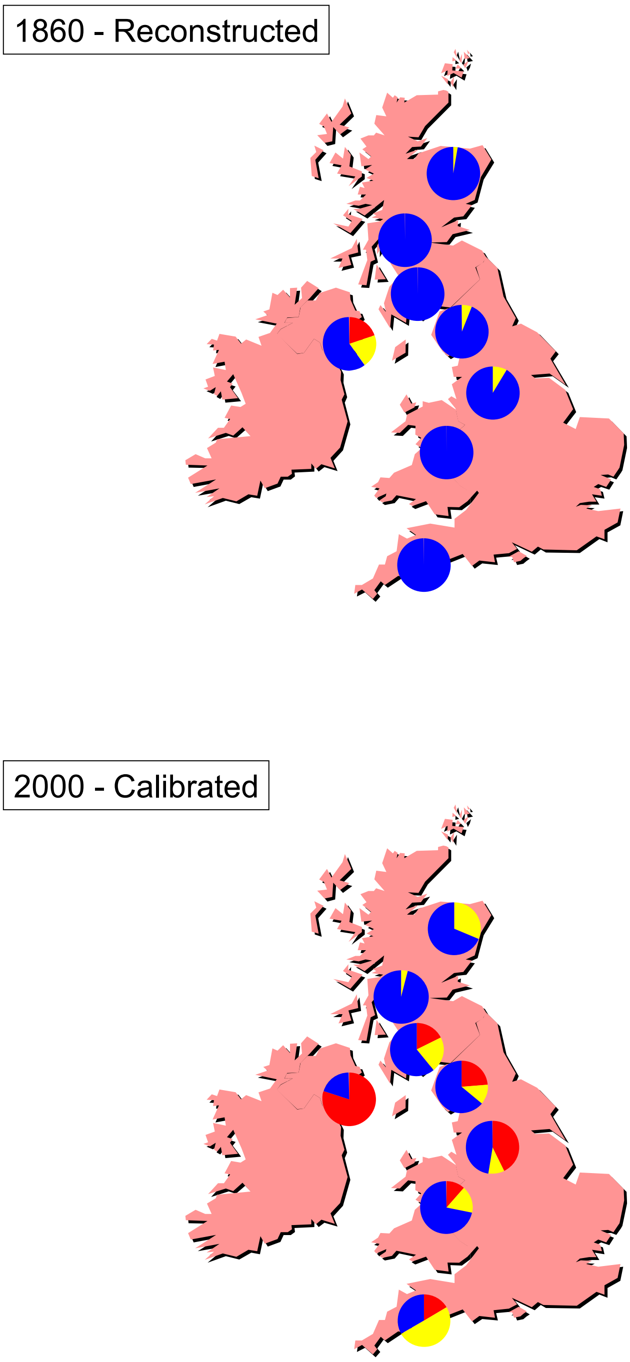


Figure 3.1.17: Regional ANC reconstructions for 1860 (top) and calibrated present day (bottom) as percentages in 3 biologically relevant ANC classes.

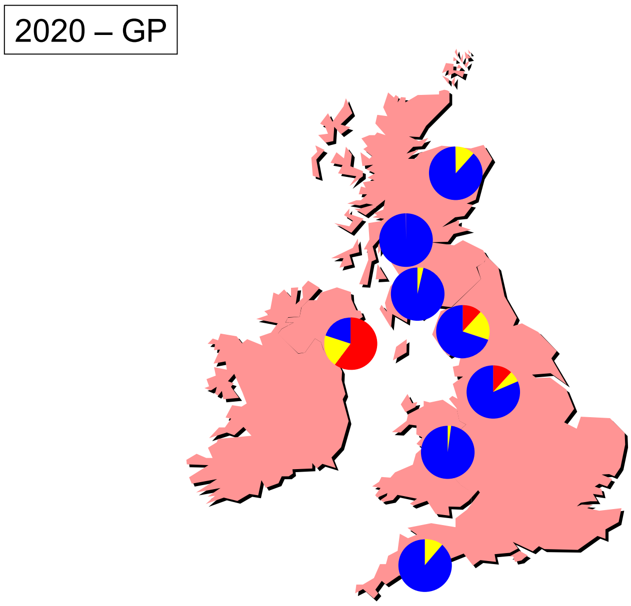


Figure 3.1.17 (Cont'd): Regional ANC predictions in 2020 as percentages in 3 biologically relevant ANC classes in response to the Gothenburg Protocol.

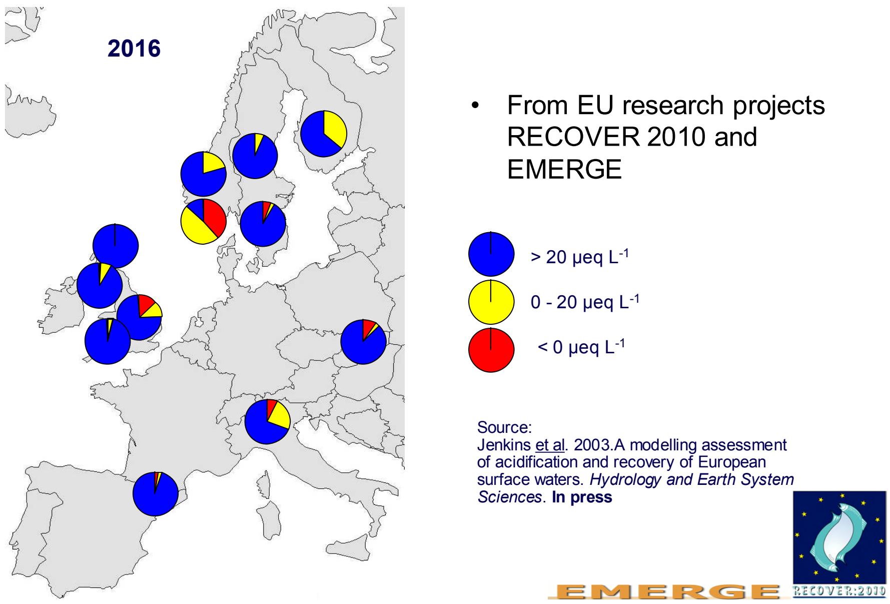


Figure 3.1.18: Comparison of selected UK regional results with other regions with sensitive surface waters in Europe. This was a contribution to the RECOVER:2010 and EMERGE projects part funded by the European Commission under FP5.

Job 3.1.5 Link chemical simulations with biological status at lake sites

Job 3.1.6 Assess time-scale to biological gap closure using MAGIC

Introduction

In this section we link output from the regional MAGIC predictions developed in Task 3.1 Jobs 3 and 4 to the biological models developed in Task 1.2 Job 2. As discussed in Task 2.1 we use two aggregate indicators – the sum of acid sensitive diatoms and invertebrates as these fulfil the requirements of an indicator taxon in that they are sensitive to the impact of increased acidity and they are widespread in nature.

We apply these two biological models to six MAGIC regional datasets: the Cairngorms (N=34), Galloway (N=56), the English Lake District (N=50), the Pennines (N=59), Dartmoor (N=17) and Wales (N=96).

Predicted biological status

Biological predictions for the MAGIC regional datasets are shown in Figures 3.1.19-3.1.24. These figures show cumulative frequency plots of probabilities of occurrence for each biological target for three time periods; 1850 or baseline, present (1997) and 2050 under the Gothenburg scenario.

All regions exhibit significant biological change between baseline and present conditions, although the magnitude of change varies greatly between regions. Results indicate that the Cairngorms are the least impacted, with acid sensitive diatoms and invertebrates lost from a relatively small proportion of sites since the onset of acidification. The Pennines have undergone most change, with the probability of occurrence of acid sensitive species reduced to less than 0.5 at over 40% of sites.

Time-scale to biological gap closure

Figures 3.1.25-3.1.26 present results for the timescale to gap closure for the sum of acid sensitive diatoms and invertebrates respectively under the target of probability of occurrence of at least 0.5. Gap closure is reported as the percentage of sites in each region meeting the target. Also shown in the figures is the percentage of sites meeting the target under baseline (pre-acidification) conditions.

Results indicate that all sites except for a few in the Pennines are predicted to have supported the target organisms at a probability of at least 0.5 under baseline conditions. Simulations for the Cairngorms suggest that this region can still support this target today. Almost all sites in Dartmoor and Galloway, and 90% of sites in Wales can also support this target, and in these regions the models predict that gap closure will occur by 2010. For the Pennines the models predict that only 50-60% of sites support the biological targets at present but that gap closure will also occur at most of these sites by 2010. The Lake District is the only region where a significant percentage (15-30%) of sites fail to support the targets today and also has a significant number (20% for invertebrates, 10% for diatoms) not meeting the targets under Gothenburg conditions, at least within the next 100 years.

Figures 3.1.27-28 repeat this analysis using more stringent biological targets of probability of occurrence of at least 0.75. In this case none of the regions achieve complete gap closure although the Cairngorms, Galloway and Wales achieve approximately 90% closure by 2010. Predictions are rather different for Dartmoor for the two organisms: closure is reached for diatoms for the majority of sites after 2050 but only 50% of sites reach closure for invertebrates. For the Pennines and the Lake District the models suggest that 10 – 20% of sites that previously supported these biological targets will not reach closure by 2100.

Conclusions

The models used to predict biological status from MAGIC ANC simulations are essentially steady state models - they take no account of additional chemical, habitat or other biotic factors that influence biological distributions, nor do they allow for hysteresis or lags in recolonisation. Despite these limitations the models provide a useful means of predicting the likely or potential occurrence of key organisms from simple hydrochemical data. As such the models provide a convenient way of converting MAGIC hindcasts and forecasts into measures of biological change.

Application of the models to six MAGIC regional datasets shows that biological damage and future recovery is regionally variable, with the Cairngorms least impacted, Galloway and Wales showing recovery and gap closure at the majority of sites, and the Pennines and the Lake District having 10-20% of sites failing to reach gap closure by 2100.

Figure 3.1.19: Predicted biological status of the Cairngorms regional MAGIC dataset (N=56) under baseline (1850), present (1997) and Gothenburg (2050) ANC scenarios.

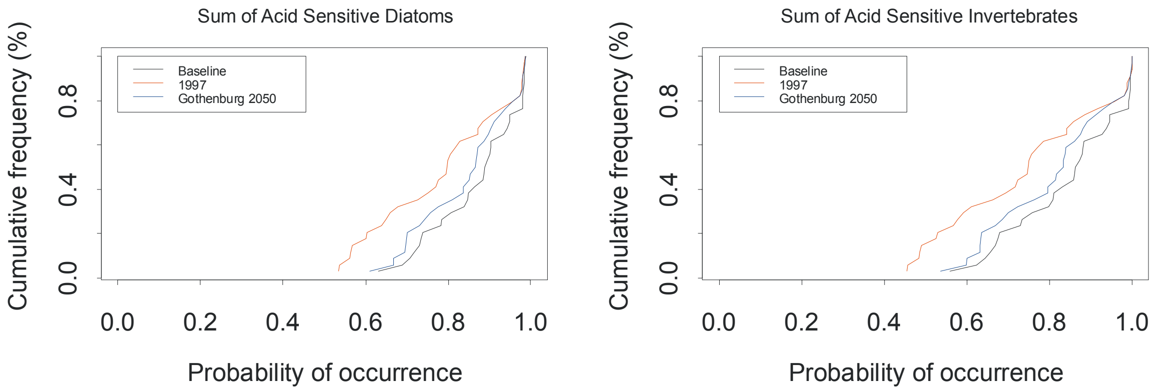


Figure 3.1.20: Predicted biological status of the Dartmoor regional MAGIC dataset (N=17) under baseline (1850), present (1997) and Gothenburg (2050) ANC scenarios.

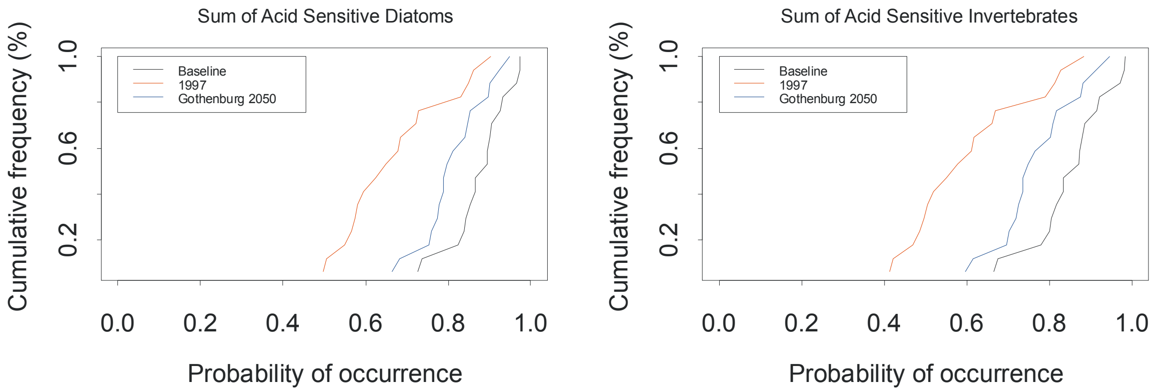


Figure 3.1.21: Predicted biological status of the Galloway regional MAGIC dataset (N=56) under baseline (1850), present (1997) and Gothenburg (2050) ANC scenarios.

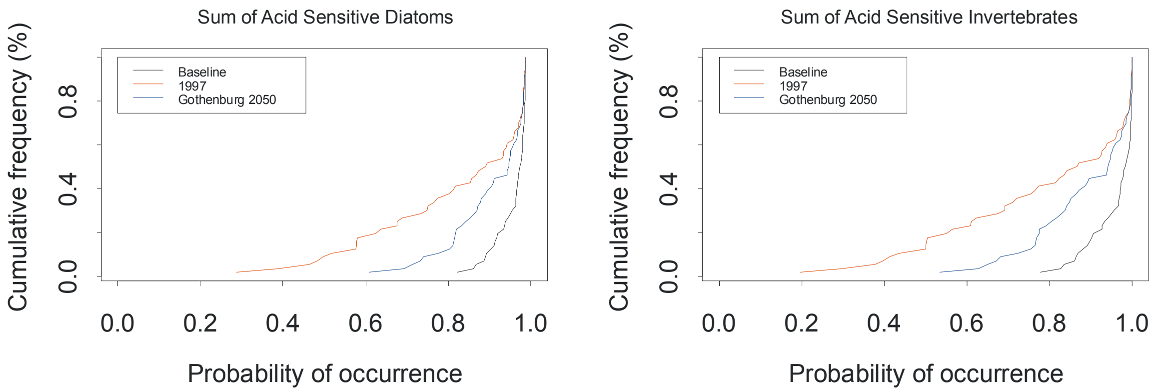


Figure 3.1.22: Predicted biological status of the Lake District regional MAGIC dataset (N=50) under baseline (1850), present (1997) and Gothenburg (2050) ANC scenarios.

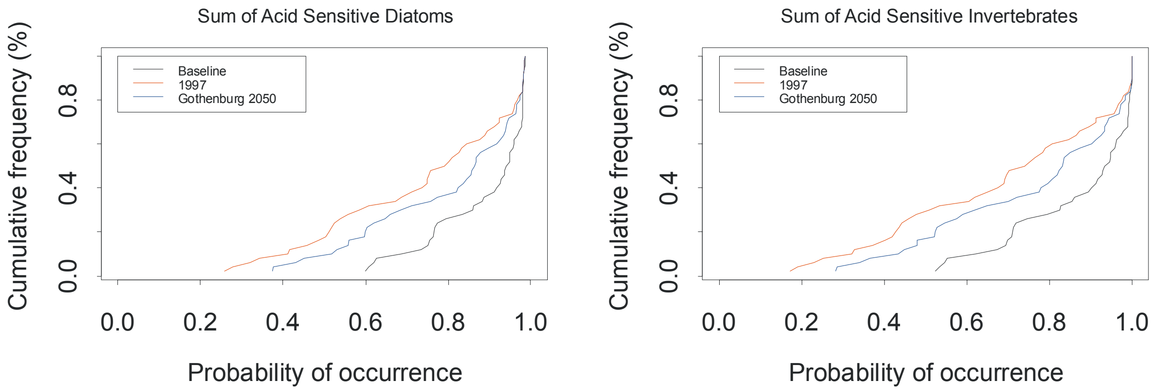


Figure 3.1.23: Predicted biological status of the Pennines regional MAGIC dataset (N=59) under baseline (1850), present (1997) and Gothenburg (2050) ANC scenarios.

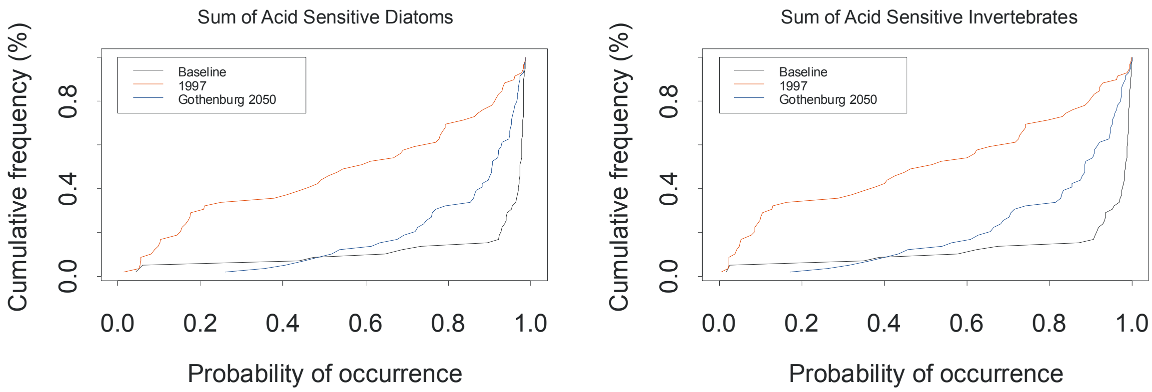


Figure 3.1.24: Predicted biological status of the Welsh regional MAGIC dataset (N=96) under baseline (1850), present (1997) and Gothenburg (2050) ANC scenarios.

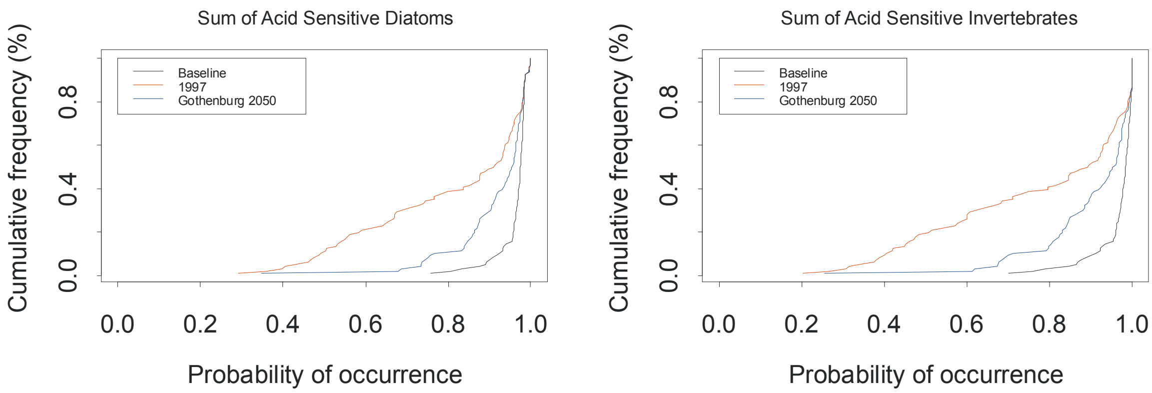


Figure 3.1.25: Timescale to gap closure using target of 0.5 probability of occurrence for the sum of acid sensitive diatom taxa. (Horizontal line shows percentage of sites achieving target under baseline conditions).

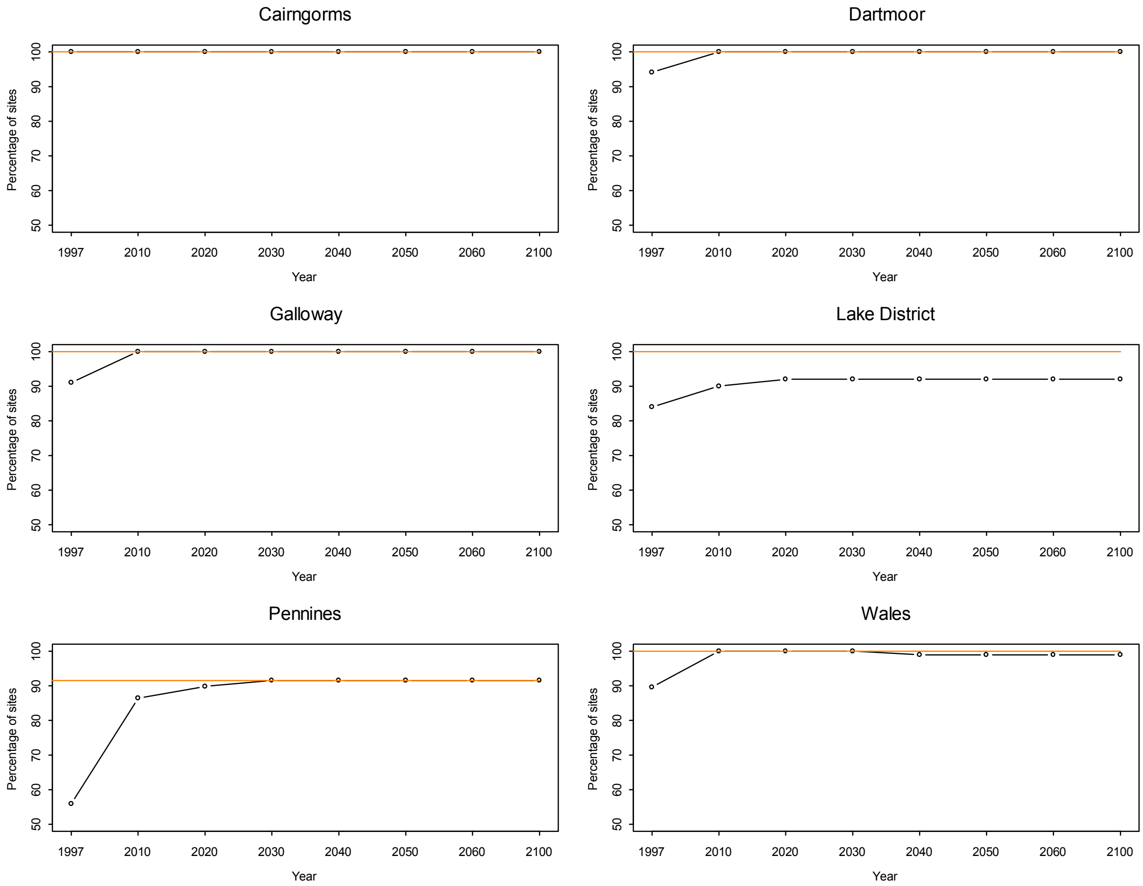


Figure 3.1.26: Timescale to gap closure using target of 0.5 probability of occurrence for the sum of acid sensitive invertebrate taxa. (Horizontal line shows percentage of sites achieving target under baseline conditions).

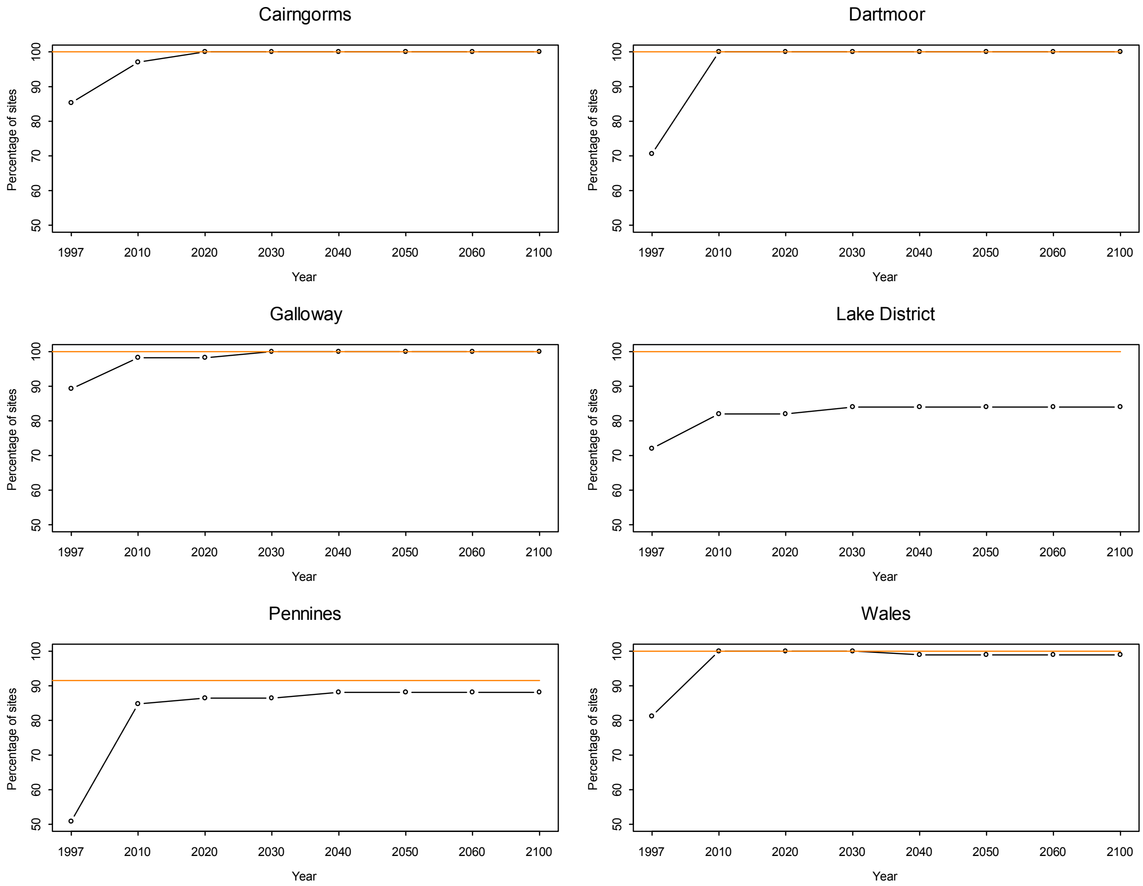


Figure 3.1.27: Timescale to gap closure using target of 0.75 probability of occurrence for the sum of acid sensitive diatom taxa. (Horizontal line shows percentage of sites achieving target under baseline conditions).

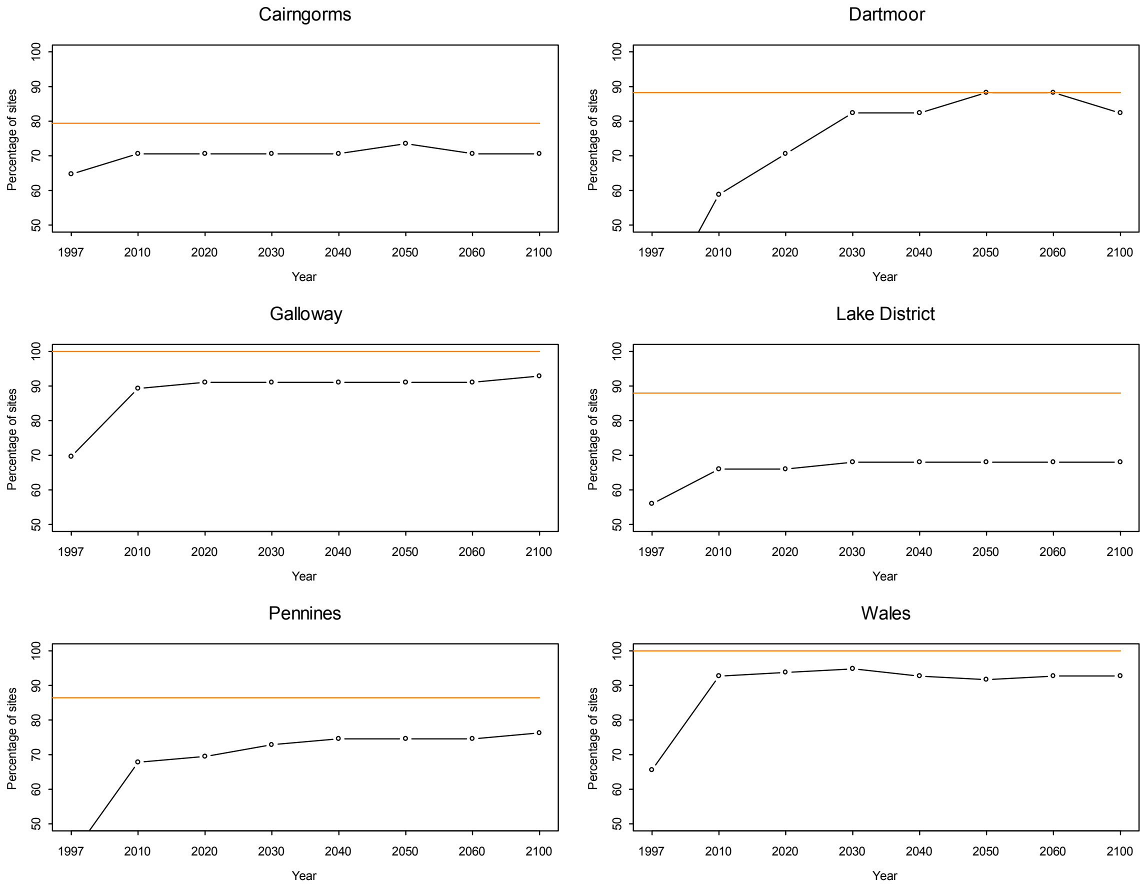
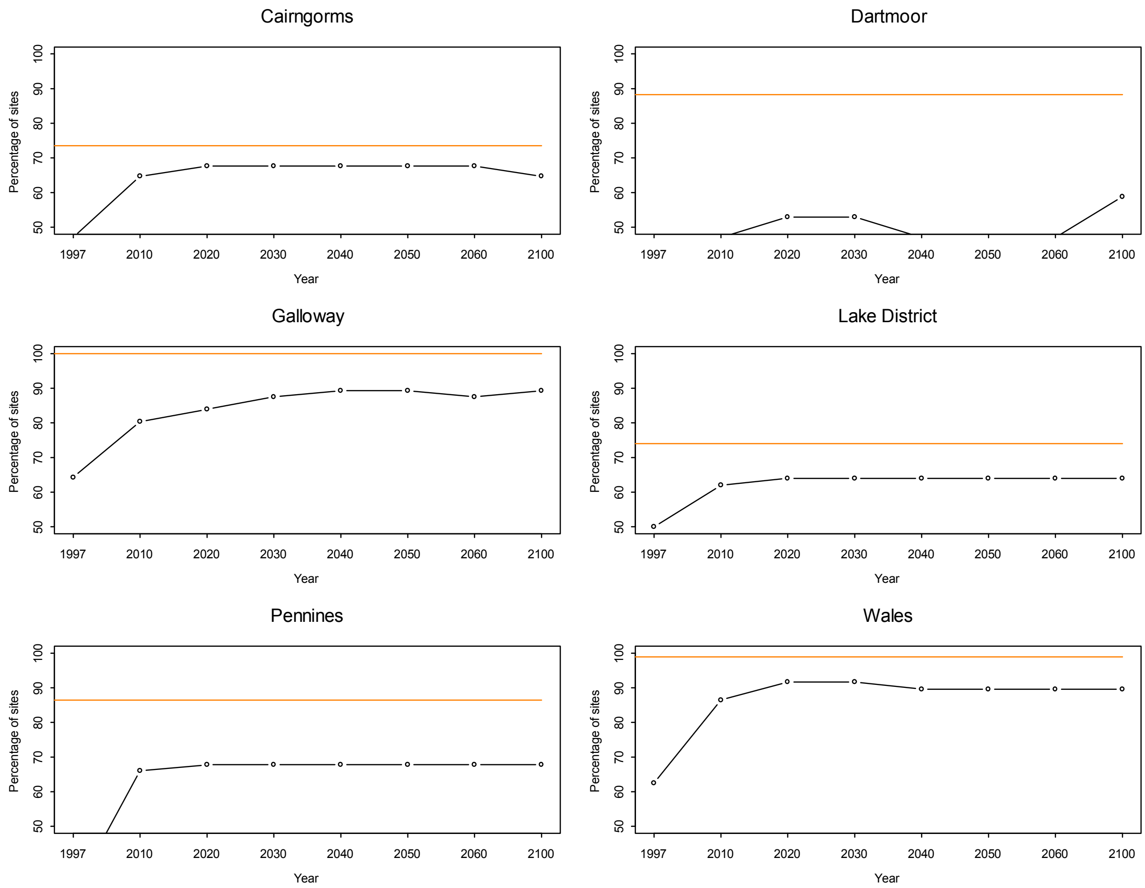


Figure 3.1.28: Timescale to gap closure using target of 0.75 probability of occurrence for the sum of acid sensitive invertebrate taxa. (Horizontal line shows percentage of sites achieving target under baseline conditions).



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Task 3.2: Recovery in streams

Task 3.2: Recovery in streams

Job 3.2.1 Calibrate MAGIC model to regional HRUs

For the Cree catchment MAGIC has been applied to the 5 merged landscape classes defined on the basis of runoff chemistry (Section 2.2.3). The model output was then used in the same manner as specified earlier for each HRU and routed using the PEARLS procedure. Soil characteristics were assessed for the 13 original landscape types and weighted on the basis of depth and bulk density to define soil chemical characteristics for the 5 merged landscape classes. MAGIC was applied using the standard methodology for regional applications described by Evans et al. (2001) and in Section 3.1 using the 'best case' nitrogen model, ie. with N dynamics switched off. Generalised forest uptake and dry deposition sequences were used for the forested landscape types. The model was calibrated to the chemistry data from the Trip 2 samples which represented the most acid conditions of the four samplings.

The MAGIC reconstructed ANC for each landscape type (Table 3.2.1) shows that the drainage water chemistry was consistently above 20 μeq l^{-1}. With the onset and intensification of acid deposition, drainage from the two most acid landscape types acidified and at the peak of deposition around 1970 were significantly below zero ANC. Predictions into the future show a rapid recovery in the two most acid classes although they remain below ANC 20 μeq l^{-1} in 2050.

For the Conwy catchment, a variation to the method used in previous PEARLS applications (and for Galloway in this study) was tested. Instead of first calculating mean landscape type water and soil chemistry, and applying MAGIC to these conceptual systems, the model was applied directly to individual catchments. This increases the number of calibrations required, but has the advantage that the model is applied to real catchments, which allows (for example) site-specific rather than generic forest uptake sequences to be applied. Site-based model outputs were then used as input data to calculate landscape type chemistry for a given year, providing inputs to the PEARLS mixing model. MAGIC was applied using the standard methodology for regional applications described by Evans et al. (2001), with N dynamics switched off. Soil chemistry data for each landscape type were derived from analyses of representative soil series in Snowdonia, undertaken for a recent NERC GANE project (Davies et al., in prep). The model was calibrated to mean stream chemistry for the three surveys.

MAGIC simulated ANC for each landscape type is shown in Table 3.2.2 for 1850 (pre-industrial), 1970 (approximate peak of acid deposition), present day and 2050. As noted earlier, three of the landscape types (peat moorland, mountain, forest) are acid sensitive, with present-day modelled mean ANC in the range 21 to 31 μeq l^{-1}. MAGIC indicates that, in pre-industrial conditions, all landscape types had a mean ANC of 45 or higher, with the lowest background ANC in streams draining peats as expected. Note that, since the majority of conifer forests were planted during the last 60 years, the 'forest' landscape type for 1850 represents the moorland that existed pre-afforestation, and a pre-industrial mean ANC of 90 μeq l^{-1} appears reasonable for the intermediate-quality soils on which many of the forests were planted. Simulated

1970 ANC is negative for all of these landscape types, suggesting widespread chronic acidification at this time.

Table 3.2.1: Cree MAGIC simulated mean ANC for each landscape class, by year

Class	1862	1970	2002 (Observed)	2010	2050
1. Forest I	30	-88	-35	-14	-8
2. Farmland	1865	1630	1622	1690	1762
3. Moor I	28	-10	-1	14	16
4. Forest II	363	325	327	329	328
5. Moor II	679	635	636	639	638

Table 3.2.2: Conwy MAGIC simulated mean ANC for each landscape class, by year.

Class	1850	1970	2002	2050
1. Peat moorland	44.8	-4.9	24.9	37.1
2. Montane	67.4	-6.3	20.9	43.6
3. Peaty gley moorland	177.9	123.1	131.0	150.1
4. Forest	90.3	-18.8	30.8	50.1
5. Farmland	683.2	600.6	609.2	631.0

3.2.2 Develop and calibrate the dynamic mixing model for streams

Prediction of recovery throughout a stream network uses MAGIC, followed by PEARLS. MAGIC provides estimates of the drainage chemistry for each landscape class, and PEARLS provides spatial interpolation for selected years, giving expected acidification status throughout the stream network. In applying PEARLS as a spatial interpolator only, the main sources of variability are identified in the model. Application of PEARLS with MAGIC introduces two major additional sources of uncertainty which are not quantified in the combined model. MAGIC is defined at an annual time step, and works with annual losses. The estimation of these from a very small number of samples taken at each sampling point is a major source of additional uncertainty. There is also uncertainty in the process representation in MAGIC. Both these sources of uncertainty are likely to be significant. While addressing the issue of uncertainty, the PEARLS-estimated uncertainty used after MAGIC simulations, in contrast to the spatial simulations, should not be considered as realistic estimates of the entirety of the uncertainty in hindcasts or forecasts of water quality.

A combination of PEARLS and MAGIC has been run for the Cree and Conwy, taking the MAGIC simulations for 2002 to 2050 for the Cree, and for 1850, 1970, 2002 and 2050 for the Conwy.

PEARLS simulations for the Conwy based on mean MAGIC-simulated landscape type chemistry in 1850 and 1970 (Figures 3.2.1-3.2.2) show, as would be expected, low probabilities that ANC fell below 20 μeql^{-1} anywhere in the Conwy catchment in 1850. In 1970, by contrast (Figures 3.2.1-3.2.2), a large part of the drainage network (around 42%) is predicted to have had a mean ANC below this threshold value.

For the Conwy, MAGIC was applied only to mean stream chemistry, and episodic minima were predicted statistically on the basis of currently observed relationships between mean and episode chemistry in the 24 survey catchments. Analysis of mean vs January high flow ANC (Figure 3.2.3) gives a high correlation ($r^2 = 0.98$) and the regression equation:

$$ANC_{episodic} = 0.62ANC_{mean} - 35 \qquad (1)$$

This relationship implies i) despite the differences in mechanism described earlier, the overall extent of episodic acidification is reasonably predictable across the catchment; ii) that ANC depressions are largest at high mean ANC, but iii) that biologically-damaging negative episodic ANC is most likely to be observed at a stream with an already low mean ANC. Making a space-for-time substitution (i.e. assuming that current mean-versus-episodic ANC relationships operate at all times) allows minimum stream ANC to be predicted from MAGIC-simulated means at each timestep. These stream ANC minima were then used as input to PEARLS in order to simulate episodic ANC throughout the stream network at each point in time, as for mean ANC.

Predicted ANC minima by landscape type, predicted from mean ANC using equation 1, are shown in Figure 3.2.4. In 1850, this simulation suggests that while episodes would have been associated with ANC decreases (for example due to natural dilution processes) this would rarely have led to negative ANC. The slightly negative ANC predicted for the peat landscape type may well simply reflect the limitations of equation 1, which for example cannot account for the loss of episodic buffering by cation exchange that has occurred since 1850. On the basis of these simulations, PEARLS-modelled probability of episodic ANC < 20 μeql^{-1} is low through most of the catchment at this time, but somewhat higher in the peat and montane areas.

By 1970, chronic acidification (negative mean ANC) is simulated for streams draining peat, forest and montane landscape types, with conditions most severe under forestry. Consequently, PEARLS predicts a substantial proportion (42%) of stream length with ANC < 20 μeql^{-1} at this time, rising to 56% as streams acidify further during episodes. At this time, much of upper Conwy, and almost the entire Lledr catchment in the northwest, are predicted to be episodically acidic.

Figure 3.2.1: MAGIC & PEARLS simulations of ANC for the Conwy river network under mean flow conditions

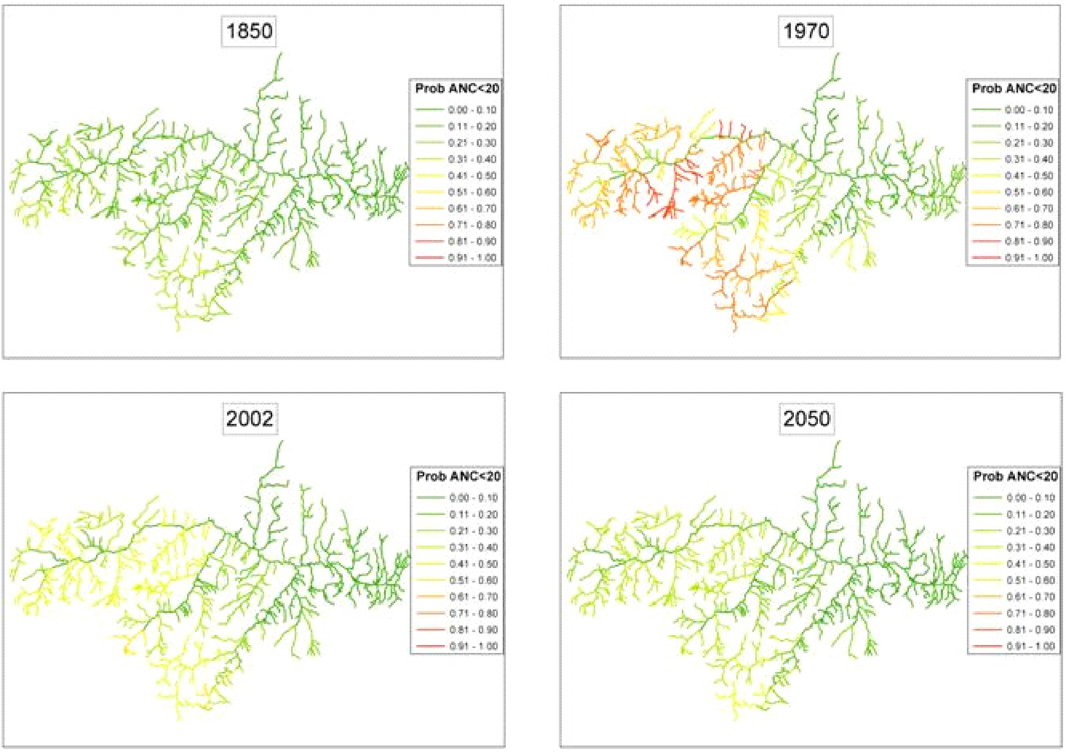


Figure 3.2.2: MAGIC & PEARLS probability distributions of ANC status for the Conwy

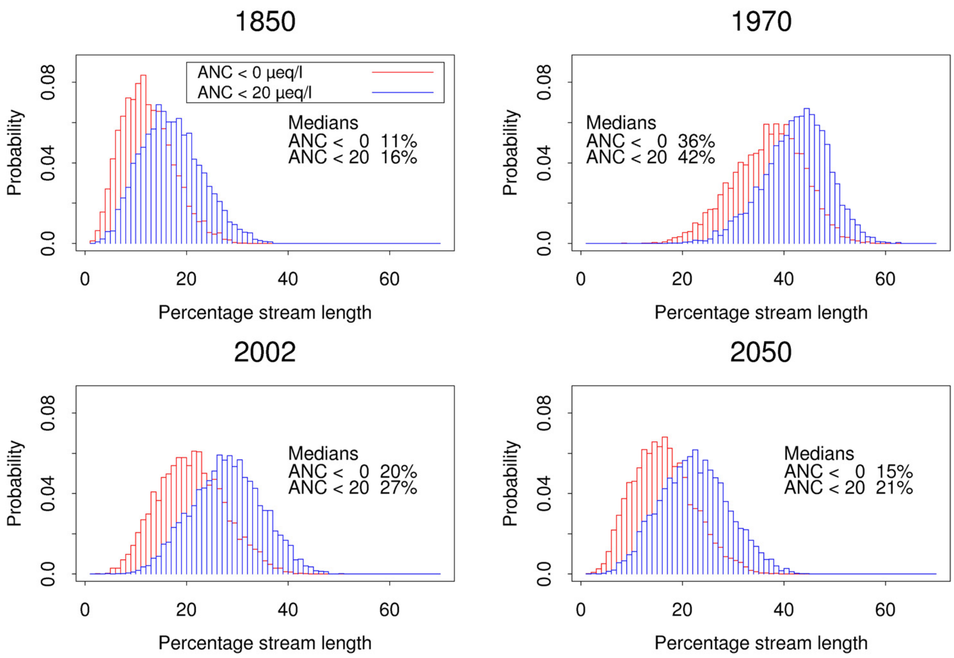


Figure 3.2.3: January 2003 against mean ANC for the Conwy sampling sites

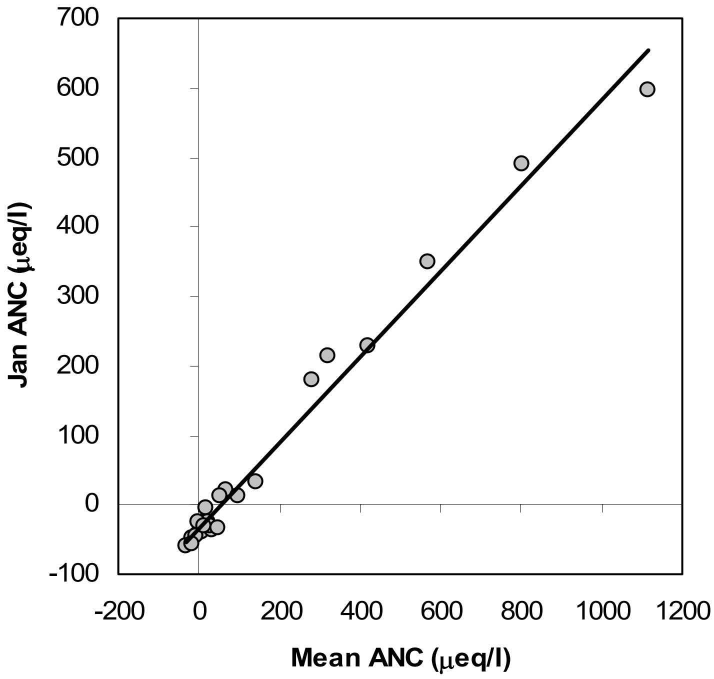
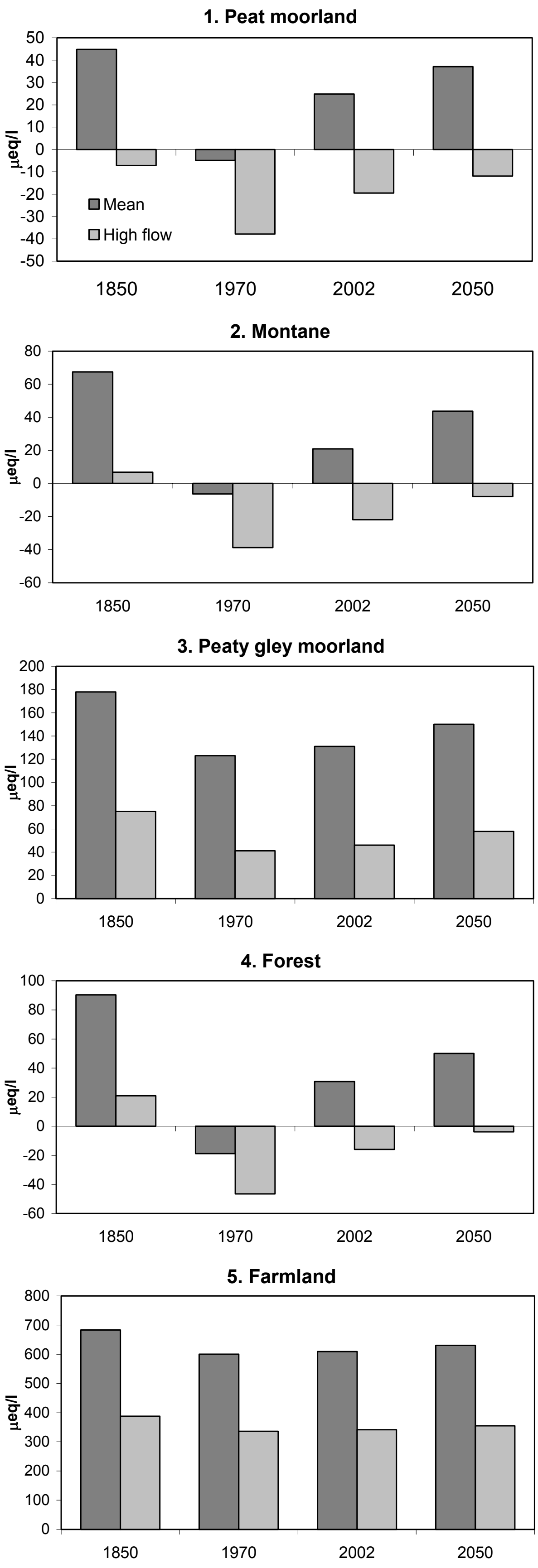


Figure 3.2.4: Estimated ANC by landscape class at high and mean flow for the Conwy



3.2.3 & 3.2.4 Assessment of Gothenburg Protocol in relation to timing of stream recovery targets; Assessment of stream chemistry in 2050

Simulations for the Cree under the Gothenburg Protocol are presented in Figures 3.2.5-3.2.6 for average and high flow conditions defined by the MAGIC runs described under Job 3.2.1. The analysis gives probabilities of ANC less than 0 and less than 20 $\mu eq\ l^{-1}$ throughout the stream network in 2002 and 2050. Figure 3.2.5 does not show obvious dramatic future improvement in acidification status, with the probability of ANC less than 0 or 20 declining by about 0.1 by 2050. Figure 3.2.7 shows probability distributions of the proportion of streams having ANC less than the two threshold values of 0 and 20 $\mu eq\ l^{-1}$ in 2002 and 2050. These also suggest a modest recovery, with about 5% greater length of streams moving from ANC<0 status to ANC<20, and 5% moving above ANC<20 status at high flows, but only 2% at average flows. These small expected changes are consistent with the simulated changes in landscape class drainage generated by the MAGIC model, coupled with uncertainty in the distribution of actual ANC values about the mean value for each landscape.

Future MAGIC simulations for the Conwy suggest a significant further recovery in the ANC of streams draining all landscape types in response to the Gothenburg protocol (Table 3.2.2), with mean ANC > 20 μeql^{-1} for all landscapes, and > 40 μeql^{-1} for all except for the (naturally low-ANC) peat. Extending the simulation to the whole catchment (Figures 3.2.1-3.2.2) suggests that only around 20% of stream length will have a mean ANC < 20 μeql^{-1}. However, based on equation 1, the peat, montane and forest landscape types are predicted to remain episodically acidic, falling to a negative ANC at high flows (Figure 3.2.4). Consequently, a significantly higher proportion (42%) of the stream length is predicted by PEARLS to have an ANC < 20 μeql^{-1} at high flow. Compared to the modelled 1850 reference state, therefore, it appears that parts of the Conwy catchment may remain acid-impacted in 2050, despite emissions reductions under the Gothenburg protocol. To a large extent, this impact will be due to the persistence of acid episodes in future, rather than to widespread chronic acidification.

Figure 3.2.5: MAGIC & PEARLS simulations of ANC for the Cree river network under mean flow conditions

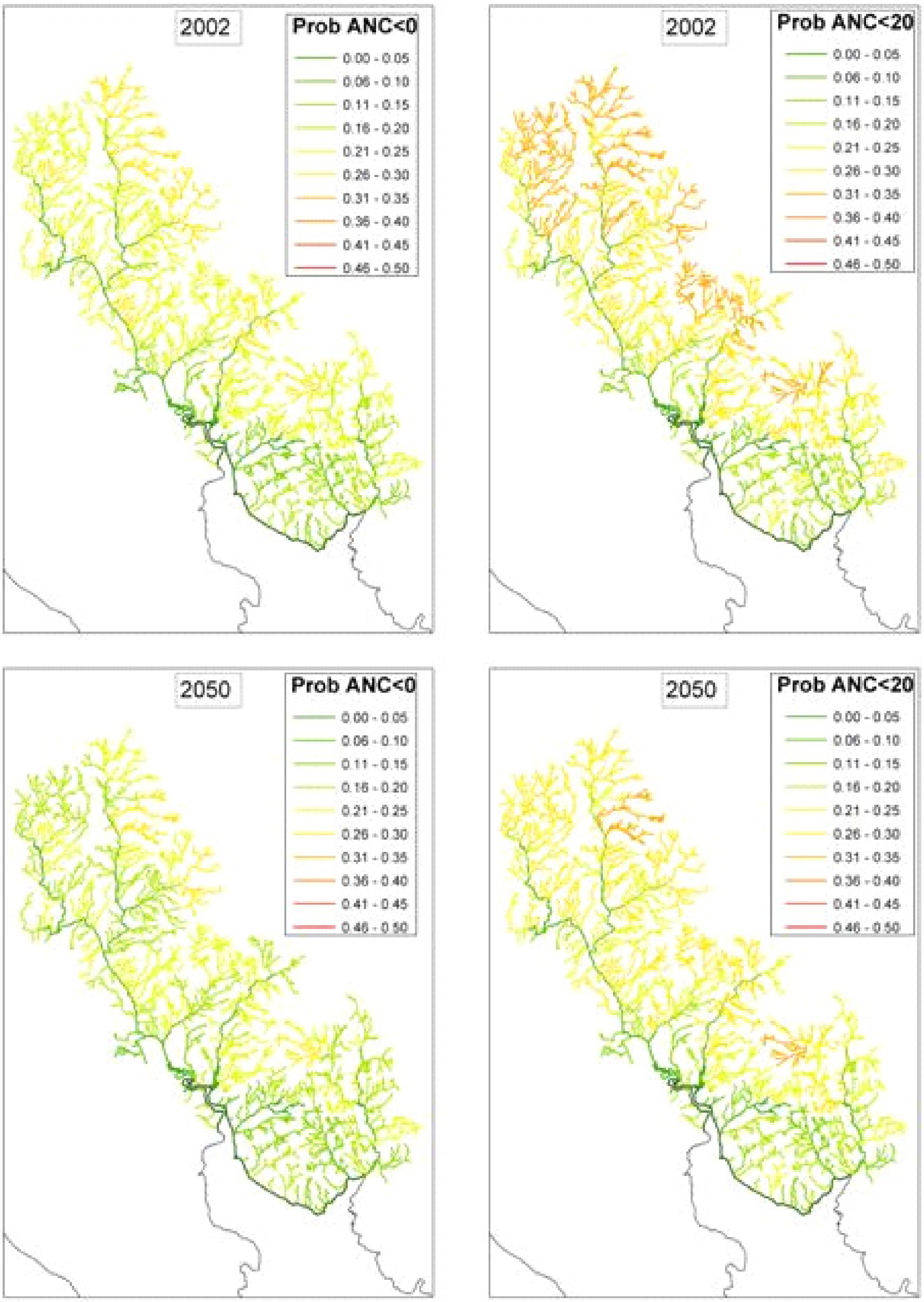


Figure 3.2.6: MAGIC & PEARLS simulations of ANC for the Cree river network under high flow conditions

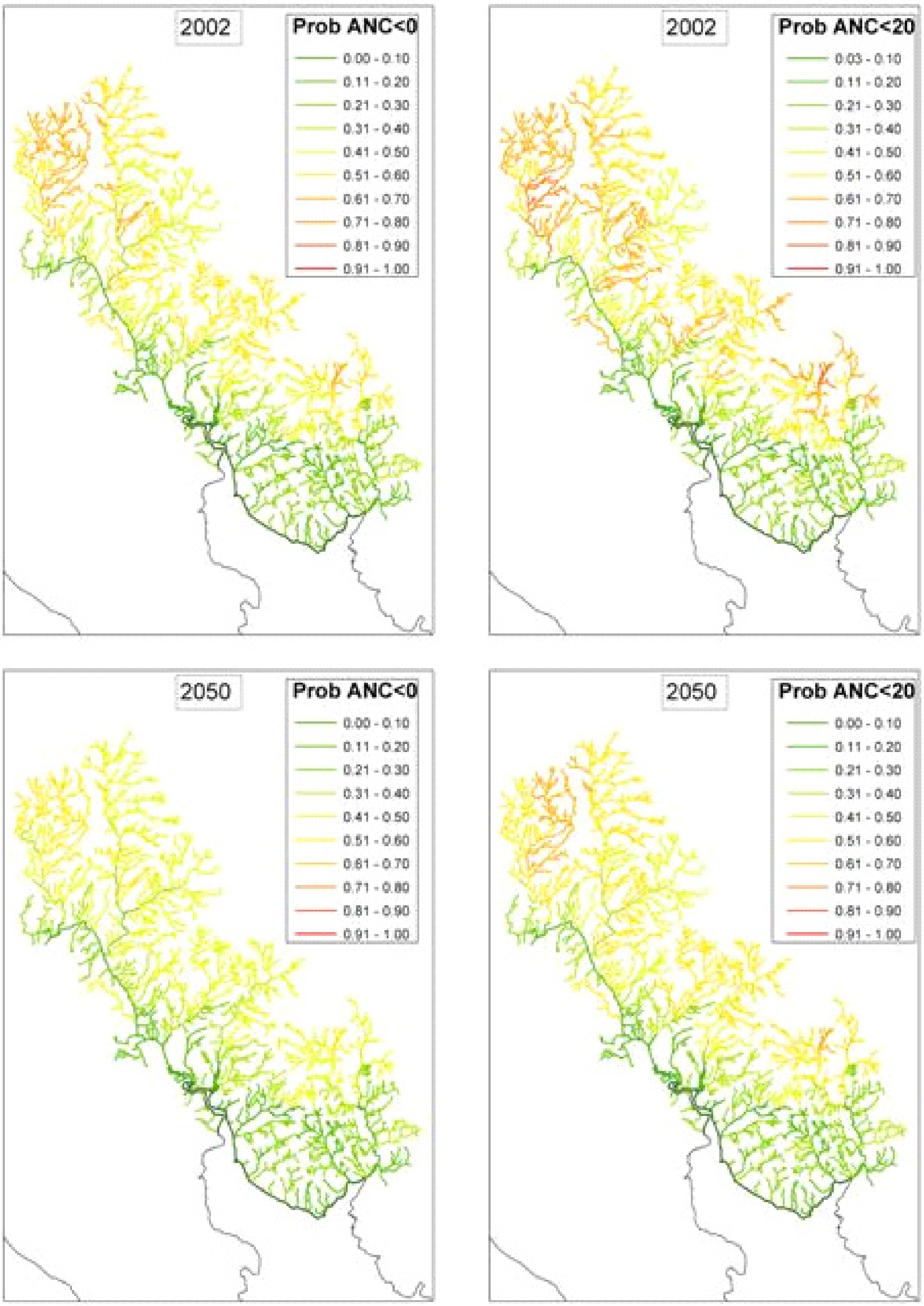
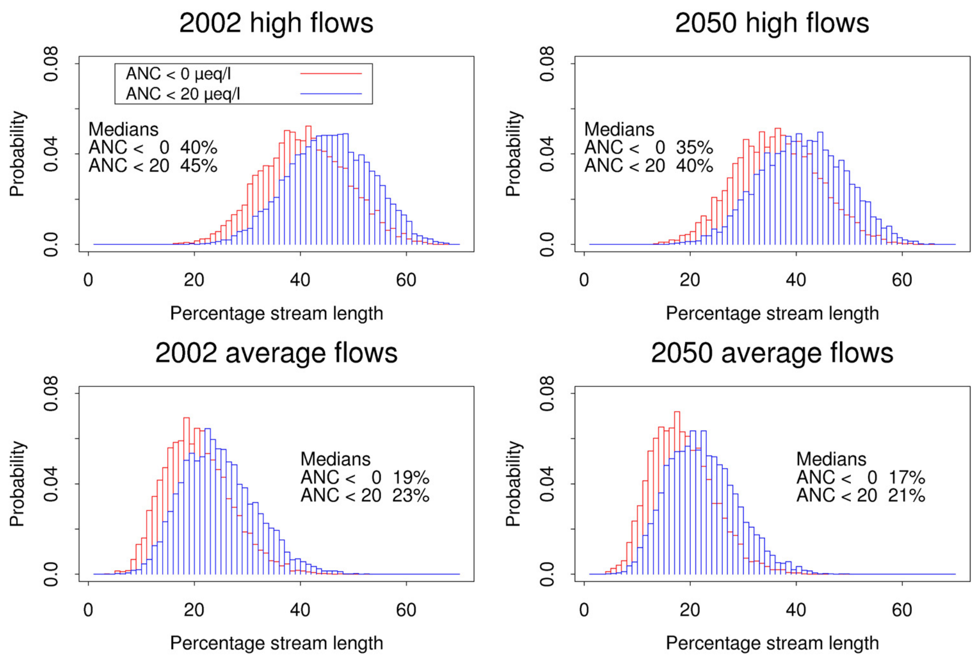


Figure 3.2.7: MAGIC & PEARLS probability distributions of ANC status for the Cree

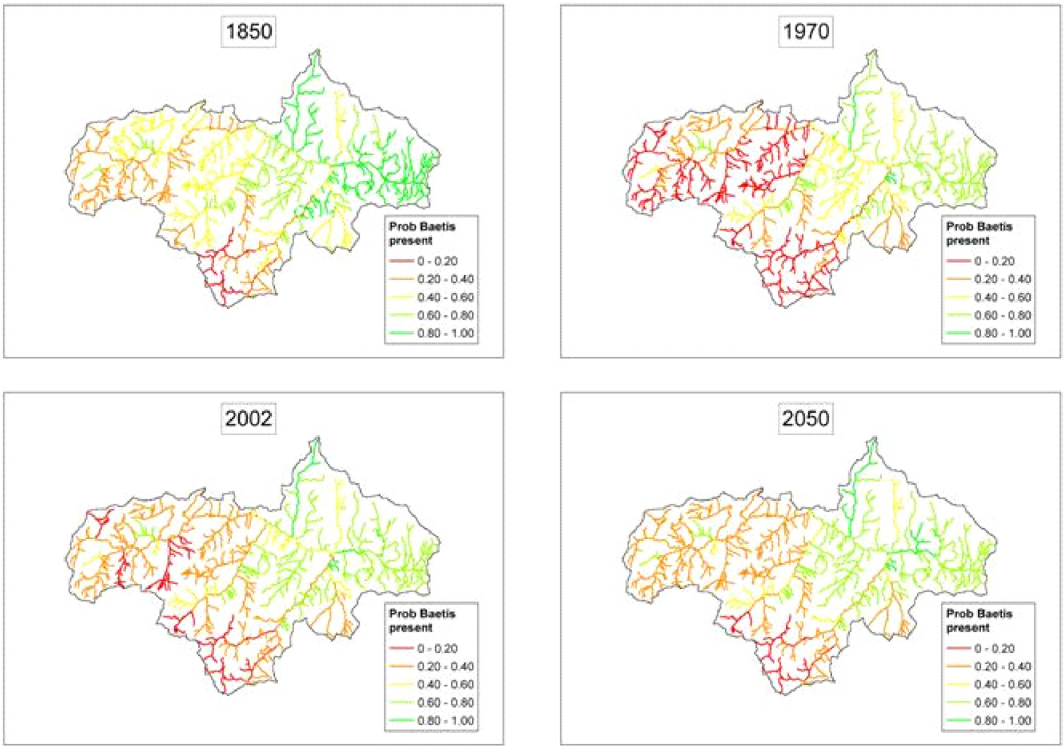


3.2.5 Link chemical simulation with biological status for streams

An exploratory attempt to use the outputs from chemistry models to predict catchment-scale biological status was made for the Conwy catchment, based on logistic regression equations for the probability of occurrence of the indicator species *Baetis rhodani* as a function of mean stream ANC (See 1.2.2). This equation was applied to PEARLS-MAGIC outputs for 1850, 1970, 2000 and 2050 (Figure 3.2.8). Results show less obvious temporal variability than the ANC simulations, since it appears that even pre-industrial ANCs in the upper Conwy catchment may have been too low for *Baetis* occurrence. Nevertheless the simulations do clearly suggest a marked decrease in probability of occurrence across much of the catchment between 1850 and 1970, followed by a gradual, but incomplete, return towards reference conditions.

It should be noted that, by combining a dynamic model with a (static) empirical prediction of biological status, these results effectively show the *suitability* of chemical conditions for *Baetis* in each year, rather than an actual prediction of species occurrence in that year; further model development is required in order to simulate the dynamics in biological recovery following improvements in chemistry. In this respect, the ability of PEARLS to identify areas of higher ANC in which relic populations may have persisted (e.g. an isolated stream in the northwest of the Conwy catchment which is predicted to have retained an ANC > 20 μeql^{-1} through the simulation period) may provide a valuable tool for modelling biological recovery.

Figure 3.2.8: Suitability for *Baetis rhodani* based on ANC limitation - Conwy



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Task 3.3: Model Uncertainty

Task 3.3 Model Uncertainty

Job 3.3.1: Develop transfer functions for hindcasting ANC from sediment core diatom assemblages and cross-validate.

Introduction

In the absence of long-term instrumental data the remains of diatoms and other microfossils preserved in lake sediments provide a powerful means of reconstructing, or hindcasting, limnological change prior to the start of biological or chemical monitoring programs (Smol 2002). In particular, recent advances in sediment dating (Appleby 1993) and in the development of quantitative microfossil-based transfer functions (Birks 1995) have allowed palaeolimnologists to use this technique to investigate the causes and consequences a range of environmental impacts. Indeed, palaeolimnological evidence has provided crucial evidence on the timing, rate and magnitude of lake acidification in the UK and elsewhere (Battarbee *et al.* 1999).

Diatom based transfer functions are an important component of this approach as they allow the biological changes in species composition observed in sediment cores through time to be interpreted quantitatively in terms of the key driving hydrochemical parameter. For acid lakes this has usually been pH: the transfer function is derived using a training set of modern lake surface sediments and associated mean pH measurements. Statistical relationships between diatom taxa and pH in this training set, the so-called “transfer functions”, are then applied to the fossil diatoms in the dated sediment core to “reconstruct” past pH levels.

Following international agreements on S and N abatement much of the current emphasis is on the application of dynamic models to evaluate different emission reduction scenarios. While this emphasis is on future change the palaeolimnological record remains essential to evaluate the performance of dynamic models across a range of sites and chemistries, and to identify the pre-acidification or baseline chemical and biological status of the ecosystem. Thus, comparison of dynamic model and palaeolimnological hindcasts of water chemistry provide an opportunity for assessing the uncertainty in these two approaches.

In part, the accuracy and applicability of the palaeolimnological transfer function approach is determined by the availability of an appropriate training set. At present transfer functions have been developed for predicting pH from sediment diatoms (e.g. Birks *et al*. 1990) and although MAGIC can be used to hindcast pH there is additional uncertainty in this parameter. In this Job we therefore use recently developed and expanded diatom training sets to develop and evaluate transfer functions for reconstructing ANC for direct comparison with MAGIC hindcasts.

ANC training-set development

Recently diatomists have collaborated in an EU-funded project to combine and extend the training sets used for pH and other hydrochemical transfer functions. The results of this collaboration are available in the European Diatom Database (EDDI: Battarbee *et al*. 1998). Although EDDI has so far only been used to develop new pH transfer functions it also contains other chemical data, including alkalinity and DOC. We have therefore used the EDDI database to select surface samples that could be used to develop a new transfer function for hindcasting ANC.

Diatom and chemical data were selected from EDDI using the criteria below. Reliable aluminium determinations were only available for a small percentage of the EDDI sites so ANC has been calculated as Gran alkalinity + DOC following McCartney *et al*. (2003).

i. Each sample should have at least 4 independent alkalinity and DOC determinations for calculation of an annual mean value.

ii. Samples should, where possible, come from impacted and un-impacted parts of the country and span both pH and ANC gradients to enable the independence of pH and ANC models.

The resulting dataset contains 163 samples that meet the above criteria. Figure 3.3.1 shows the distribution of pH and ANC values in the training set, and Figure 3.3.2 shows the spatial distribution of sites.

The dataset has good geographical coverage and includes lakes from all the main softwater areas of the UK. Importantly, the dataset includes lakes from heavily impacted areas in Wales, the Lake District and Galloway and more pristine waters of NW Scotland: the latter are important in providing coverage of likely species distributions under pre-acidification conditions. The dataset also covers a fairly even spread of pH values between 4.8 and 7.0, although there are relatively few acidified sites with pH less than 4.6 and ANC less than zero.

ANC transfer function development

Although most transfer functions in acidification research have been developed for pH, these are largely justified on the basis of their empirical predictive ability, as there is evidence for the physiological effect of pH for only a few diatom taxa. There is no reason, *a priori*, therefore, that transfer functions for other measures of acidity, such as ANC, cannot be developed. pH and ANC are directly correlated in soft waters so a transfer function for ANC might simply reflect the correlation of this parameter with pH. In developing an ANC transfer function we should therefore require that pH and ANC explain, in a statistical sense, independent and significant components of variation in the diatom distributional data. That is, that the relationship between diatom distribution and ANC does not just reflect its correlation with pH.

To test this requirement we used canonical correspondence analysis (CCA) and partial CCA of the diatom and pH / ANC data to partition the variance in the diatom data into components explained by (1) pH, (2) ANC, (3) the joint distribution of pH and ANC, and (4) unexplained variation (c.f. Jones & Juggins 1995). The statistical significance of the first three of these components was assessed using a Monte Carlo permutation test (999 permutations).

Results of this analysis are presented in Table 3.3.1. pH and ANC together explain only 8.4% of the variance in the diatom data: such small amounts of explained variance are common in this kind of large, diverse dataset that contains many rare species present in a small number of sites (Birks 1995). However, this explained variance is highly significant (p = 0.001). Furthermore, results of the variance partitioning demonstrate that approximately 2/3 of the pH or ANC "signal" in the diatom data is a response to the common pH / ANC gradient, but that pH and ANC both explain unique and statistically significant components of the diatom data. Thus, as expected, although ANC reconstructions cannot be considered totally independent of pH, there is a sufficiently strong unique influence of ANC on the diatom assemblages in this dataset to justify the reconstruction of ANC independently from pH.

Table 3.3.1 Variance partitioning of the ANC diatom training set.

	Variance accounted for (%)	
Variable	**Total**	**Unique**
pH	**6.4% (p = 0.001)**	**2.4 % (p = 0.001)**
ANC	**6.0 % (p = 0.001)**	**2.0 % (p = 0.001)**
pH | ANC	**4.0 % (p = 0.001)**	**N/A**
Total explained	**8.4 % (p = 0.001)**	
Unexplained	**91.6 % (p = 0.001)**	

On the basis of the variance partitioning we developed a predictive ANC transfer function using the method of weighted-averaging with classical deshrinking (Birks *et al*. 1990). The performance of the transfer function was assessed by comparing observed ANC with model predicted ANC for the training set lakes, and reported in terms of (1) the squared correlation between observed and predicted, and (2) the root mean squared error of prediction RMSEP (Birks, 1995). To provide a more rigorous test of performance we also carried out an internal cross-validation using a bootstrap technique (1000 bootstrap cycles). Table 3.3.2 reports the performance of the transfer function, and, for comparison, also the performance of a transfer function derived for pH using the same dataset. Figure 3.3.3 shows the relationship between observed and inferred ANC and pH for the model and under cross-validation.

Table 3.3.2: Performance statistics for the ANC and pH transfer functions

Variable	Model		Cross-validation	
	r-squared	**RMSEP**	**r-squared**	**RMSEP**
ANC	**0.49**	**37**	**0.40**	**43**
pH	**0.80**	**0.36**	**0.76**	**0.38**

Compared with other transfer functions (e.g. Birks *et al*. 1990) the model for ANC is relatively weak, with only 49% of the variation observed in the training set ANC accounted for by the model. This compares with a figure of 80% for pH using the same dataset. Plots of the relationship between observed and diatom-inferred chemistry suggest that the model is able to predict ANC well at values below 10 μeql^{-1}. Above this value there is considerable scatter in the residuals and a number of sites are overestimated by the model. Under cross-validation the overall RMSEP is about 43 μeql^{-1}.

The model for pH developed from the same training set shows significantly better performance with a squared correlation between observed and predicted pH of 0.8 and a cross-validation RMSEP of 0.38 pH units.

Although ANC explains a unique and significant component of variation in the diatom data which is only slightly smaller than that for pH (2.0% compared to 2.4%), the transfer function developed for ANC performs poorly in comparison to the pH transfer function developed from the same dataset and those developed elsewhere (e.g. Birks *et al*. 1990, Battarbee *et al*. 1998).

Job 3.3.2: Compare MAGIC and diatom inferences models and instrumental data for pH and ANC for UKAWMN sites.

In this section we apply the ANC transfer function derived above, and a pH transfer derived from the larger EDDI database, to cores from seven of the UK Acid Waters Monitoring Network sites for which MAGIC hindcasts are available.

In inferring past water chemistry from fossil diatoms using a transfer function we make the assumption that the training dataset fully encompasses the chemical and biological conditions represented by the fossil assemblages: that is, the modern training set contains analogues for the fossil assemblages. This assumption is tested by calculating the squared Chi-square dissimilarity between each fossil sample and its closest analogue in the ANC training set (c.f. Jones & Juggins 1995). Results of this analysis are shown in Figure 3.3.4. Analysis of between samples dissimilarities in the modern training set suggest fossil samples with a dissimilarity of greater than 0.4 and 0.5 lack “close” and “good” modern analogues in the modern dataset respectively. Analogue analysis suggests that only the Round Loch of Glenhead has close analogues for the whole sequence. Loch Grannoch possesses close analogues for most of the core, except for the most recent surface samples, where the presence of *Asterionella ralfsii*, a taxon that is rare in the modern training set, has increased at this site in response to forest fertilization rather than acidity changes. Llyn Llagi, Scoat Tarn and Lochnagar have close analogues for the upper parts of the core but the latter two sites lack analogues for the period prior to 1920. Loch Tinker has good analogues for most of the core except for a few samples in the early 1900s that are characterised by high numbers of a small *Cyclotella* species that is not so abundant at sites in the training set. Finally, Blue Lough lacks good analogues for its whole history: this site is characterised by the presence of *Melosira arentii*, a diatom not recorded in the training set.

While a number of sites appear to have good or close analogues in the modern training set the lack of analogues for Blue Lough and for the earlier parts of the Scoat

Tarn and Lochnagar cores suggest that reconstructions for these sites and periods should be treated with additional caution.

Comparisons between MAGIC and diatom hindcasts for pH and ANC for the UK Acid Waters Monitoring Network lake sites are shown in Figures 3.3.5 – 3.3.11. The comparisons are summarised below:

Blue Lough: MAGIC hindcasts agree well with the instrumental record for pH although they overestimate ANC values by 10 - 20 μeql^{-1}. Diatom reconstructions suggest a relatively stable pH of c. 5.0 and an ANC of 5 μeql^{-1} for the last 150 years but should be treated with caution due to the no-analogue problems in the reconstructions discussed above.

Loch Grannoch: Diatom, MAGIC and instrumental pH show good agreement and indicate a slight acidification from c. pH 5.2-5.3 in 1850 to c. 5.0 at present, except for the diatom hindcasts for the surface samples which underestimate measured pH. This is again due to no-analogue problems in the reconstruction caused by the unusual diatom response to recent forest fertilisation as discussed above. For ANC the diatom and MAGIC predictions overestimate instrumental values by c. 10 – 20 μeql^{-1} for the late 1980s – early 1990s. Diatom hindcasts are consistently lower than MAGIC for 1850 (c. 20 μeql^{-1} vs. c. 55 μeql^{-1}).

Llyn Llagi: Diatom and MAGIC agree well with measured pH for the instrumental period and both consistently track the acidification at this site from c. pH 6.0 in 1850 to pH 5.1-5.2 in the late 1980s. Similarly Diatom and MAGIC predictions agree well with the recent measured ANC record from this site and diatom and MAGIC hindcasts both suggest an ANC of c. 40 μeql^{-1} for 1850, although the earlier levels in the sediment core suggest a possibly higher pre-acidification ANC.

Lochnagar: Diatom and MAGIC hindcasts agree well with measured pH and ANC at this site for the late 1980s although MAGIC predicts a rapid increase in both parameters in the 1990s not observed in the instrumental record. For earlier periods MAGIC consistently predicts higher pH and ANC: MAGIC hindcasts for 1850 are 6.5 pH units and ANC c. 50 μeql^{-1} compared with pH 5.8 and ANC 20 μeql^{-1} for diatoms. There are some no-analogue problems in the quantitative diatom reconstructions for the pre-1900 sediment levels at this site although a qualitative assessment of the diatom taxa in the lower part of the core suggests a pH of around 6.0.

Round Loch of Glenhead: Diatom and MAGIC predictions agree well with measured pH for the instrumental record although MAGIC predicts slightly higher pH for 1850 (pH 6.0 for MAGIC compared to pH 5.5 for the diatom hindcast). For ANC MAGIC agrees well with measured values although the diatom reconstructions overestimate the late 1980s values by c. 10 μeql^{-1}. For 1850 MAGIC again hindcasts higher values at 40 μeql^{-1} compared to diatom predictions of 20 μeql^{-1}.

Scoat Tarn: Diatom and MAGIC predictions agree well with the measured pH at this site for the late 1980s although for earlier periods the diatom hindcasts are consistently lower, suggesting a value of c. pH 6.0 for 1850, compared to a MAGIC prediction of 6.5 for this time. Similarly, the MAGIC and diatom predictions are consistent with the measured ANC values for the late 1980s although MAGIC predicts a much greater inter-annual variability than that seen in the instrumental record. For the mid-1800s MAGIC hindcasts are consistently higher than diatom reconstructions for pH and ANC, and there is a large discrepancy between the very low ANC values predicted by MAGIC for the period 1940-1980 (< 40 μeql^{-1}) and the values of c. 0 μeql^{-1} suggested by the diatom reconstructions for this period. Although there are some no-analogue problems in the diatom reconstructions for the lower parts of the core at this site a qualitative assessment of the diatom taxa in the 1850 levels are more consistent with the reconstructed value of pH 6.0 rather than the MAGIC hindcast of pH 6.5.

Loch Tinker: MAGIC agrees well with the instrumental record for this site for both pH and ANC and predicts only a slight acidification for this site, from c. pH 6.3 in 1850 to pH 6.2 in 1970 (or a drop in ANC from 70 to 60 μeql^{-1} for the same period). Diatom reconstructions consistently underestimate measured pH and ANC by c. 0.7 pH units and c. 30 μeql^{-1} ANC respectively. However, diatom and MAGIC hindcasts are in reasonable agreement for 1850, predicting a pre-acidification pH of c. 6.3 and ANC of c. 70 μeql^{-1}.

Comparisons between diatom, MAGIC and instrumental records have highlighted no-analogue problems in the diatom reconstructions at some sites (e.g. Blue Lough) and for parts of the record at others (e.g. Loch Grannoch). However, given these problems, and the relatively large errors in the diatom-ANC predictions, both diatom and MAGIC predictions agree well with measured chemistry at 4 of the five sites with no no-analogue problems in the uppermost core levels (Llyn Llagi, Round Loch of Glenhead, Scoat Tarn and Lochnagar). For 1850 diatom and MAGIC pH hindcasts agree well at Llyn Llagi, Loch Grannoch, and Loch Tinker. At the other three sites (Lochnagar, Round Loch of Glenhead, and Scoat Tarn) MAGIC pH hindcasts are consistently higher by c. 0.5 pH units than the diatom-based reconstructions. Similarly, MAGIC ANC hindcasts are consistently higher than diatom-based reconstructions at all sites except Loch Tinker and Llyn Llagi. These discrepancies are further explored in the next section.

Job 3.3.3: Compare diatom, MAGIC and F-factor ANC hindcasts and identify systematic differences between models.

This section extends the analysis of Job 3.3.2 and compares ANC hindcasts for baseline (1850) conditions predicted by diatom, MAGIC and F-factor models. The analysis is carried out on the seven UK Acid Waters Monitoring Network sites discussed above and an additional 20 lakes for which diatom and F-factor hindcasts are available. MAGIC hindcasts are only available for six of these additional sites, giving a total of 27 sites for diatom – F-factor comparisons, and 13 for diatom-MAGIC comparisons. pH hindcasts are not compared because these are not available for the F-factor model, and they are only available for the seven UK Acid Waters Monitoring Network sites. Summary chemistry, ANC hindcasts, critical load exceedance and sulphur deposition for each site is listed in Table 3.3.3.

Relationships between baseline ANC hindcasts for the three methods are shown in Figure 3.3.12. The figures show that there is considerable discrepancy between the three methods: F-factor and diatom ANC exhibit a significant linear correlation (p <

0.01) but MAGIC hindcast ANC is not significantly related to either diatom or F-factor ANC. Furthermore, it is clear from the figures that for the majority of sites the diatom reconstructions consistently predict a lower baseline ANC than either the F-factor or MAGIC models, and that MAGIC predicts higher baseline ANCs than the F-factor model. That is, there is a systematic bias in the methods towards higher ANC predictions in the diatom, F-factor and MAGIC models respectively.

There is considerable uncertainty in F-factor hindcasts (Task 2.1), and in the diatom reconstructions (Job 3.3.1 above), and there is some bias towards over-prediction for the latter model at ANC values > 20 μeql^{-1}. However, this bias cannot explain the observation that the diatom reconstructions, and to some extent, the F-factor hindcasts, are consistently lower than the MAGIC hindcasts across the majority of sites examined here. Further patterns in these discrepancies are explored in the next section.

Job 3.3.4: Use exploratory regression analysis to relate differences in hindcasts to differences in deposition, chemistry and site characteristics.

Multiple linear regression is used to identify site variables (deposition, chemistry, catchment characteristics) that explain, in a statistical sense, the differences in ANC hindcasts between the different models with the hope that variables identified as significant may offer some insights into the mechanisms responsible for the discrepancies.

Results of the regression analysis showed that only one relationship was significant ($p < 0.05$): that of the difference between diatom and MAGIC hindcast ANC and site alkalinity ($p = 0.0045$). The relationship between diatom ANC – MAGIC ANC and alkalinity is plotted in Figure 3.3.13 and suggests a trend towards increasingly high MAGIC ANCs compared with diatom reconstructions at the more sensitive sites that are today acutely acidified and have very low alkalinities.

Job 3.3.5: Determine the impact of uncertainties on chemical and biological predictions.

There are considerable errors in the F-factor, MAGIC and diatom models and these have been estimated for the latter in Job 3.3.1. The comparisons have also only been carried out at a small number of sites. Nevertheless, they do revealed systematic differences between models that cannot be explained by the errors associated with an individual methodology. Differences between the diatom reconstructions and F-factor hindcasts do not appear to be systematically related to site characteristics making it difficult to offer an explanation for the discrepancies, or to quantify the magnitude of uncertainty in the F-factor predictions. Differences between diatom and MAGIC hindcasts do have a significant relationship with alkalinity: MAGIC consistently predicts higher baseline ANC at sites with low present day alkalinity. However, although there is a systematic difference between diatom and MAGIC hindcast ANCs, the magnitude of the error in the diatom model makes it difficult to quantify the uncertainty in the MAGIC hindcasts. Thus it is not possible with the small number of sites with diatom, F-factor and MAGIC data to derive quantitative estimates of the uncertainties in the chemical, and by inference, the biological predictions at individual sites or regionally. However, the data do indicate systematic differences between methods that need further investigation.

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Table 3.3.3 Diatom, MAGIC and F-factor hindcasts for 1850 for UK Acid Waters Monitoring Network Sites. Units are μeql^{-1} (Alk., Ca, ANC) and keq ha^{-1} yr^{-1} (critical load exceedance and sulphur deposition).

Site Name	Site Code	Sq	E	N	pH	Alk.	Ca	TOC (mgl^{-1})	F-factor ANC	Diatom ANC	MAGIC ANC	CL Ex	S Dep.
Llyn Berwyn	BER	SN	743	568	4.3	1.5	41.1	3.0	39	26			1.0
Burnmoor Tarn	BURNMT	NY	184	44	6.5	38.6	91.3	1.8	90	100	99	1.2	1.3
Llynoedd Ieuan	CE45A	SN	794	812	4.9	-11.0	45.0	2.2	39	47		0.7	0.9
Loch Chon	CHN	NN	421	51	5.2	13.5	78.5	2.3	43	80	66	1.1	1.2
Llyn Clyd	CLYD	SH	635	597	6.1	62.4	55.9	0.5	55	135		2.4	1.5
Llyn Conwy	CON	SH	780	463	4.8	12.5	41.8	2.1	20	87		1.9	1.5
Loch Coire an Lochan	COR	NH	943	4	5.3	21.8	28.8	0.2	12	52	35	0.4	0.4
Dubh Loch	DUH	NO	238	828	5.2	10.3	30.0	1.4	27	16	40	0.6	0.6
Llyn Dulyn	DUL	SH	662	244	5.2	24.4	48.8	1.6	31	54		1.1	1.2
Llyn Eiddew Bach	EIB	SH	646	345	4.8	27.0	48.9	1.2	27	154		1.5	1.2
Loch Enoch	ENO	NX	446	853	4.5	0.5	12.5	1.1	-7	6	43	1.7	1.3
Loch nan Eun	EUN	NO	230	854	5.0	3.0	29.7	0.5	27	189		0.8	0.6
Llyn Glas	GLAS	SH	601	547	6.3	61.9	71.3	0.5	74	162		1.7	1.5
Llyn Gynon	GYN	SN	800	647	5.2	32.4	41.4	3.6	31	58		0.9	1.2
Llyn Irddyn	IRD	SH	630	220	5.3	30.5	60.4	1.0	56	92		1.0	1.2
Llyn Llagi	LAG	SH	649	483	5.2	19.1	60.5	2.4	33	47	45	2.0	1.5
Loch Grannoch	LGR	NX	541	691	4.6	-28.0	48.9	3.9	17	16	54	1.4	1.2
Lochan Dubh	LOD	NM	895	710	5.6	16.2	33.2	2.8	17	21	40	1.0	1.1
Lochnagar	NAGA	NO	252	859	5.0	5.7	29.8	0.8	37	19	19	0.7	0.6
Loch Narroch	NARR	NX	453	816	5.0	-17.5	26.0	3.3	2	0	61		1.3
Round Loch of Glenhead	RLGH	NX	450	804	4.7	-1.3	20.8	2.5	0	25	46	1.5	1.3
Scoat Tarn	SCOATT	NY	159	104	5.0	-9.0	38.0	0.5	19	29	48	2.3	1.3
Loch Tanna	TANN	NR	921	428	5.0	5.0	35.2	1.8	55	6		1.1	0.9
Lochan Uaine	UAI	NO	1	981	5.8	22.7	69.0	0.4	51	8		0.2	0.6
Loch Urr	URR	NX	760	845	6.8	80.7	166.5	0.4	142	135		0.1	1.0
Loch Valley	VAL	NX	445	817	4.7	1.3	17.7	2.6	-5	21	61	1.8	1.3
Llyn y Bi	YBI	SH	670	265	5.1	19.0	53.1	1.2	29	38		1.1	1.2

Figure 3.3.1: Frequency distribution of pH and ANC in the UK-ANC transfer function training dataset.

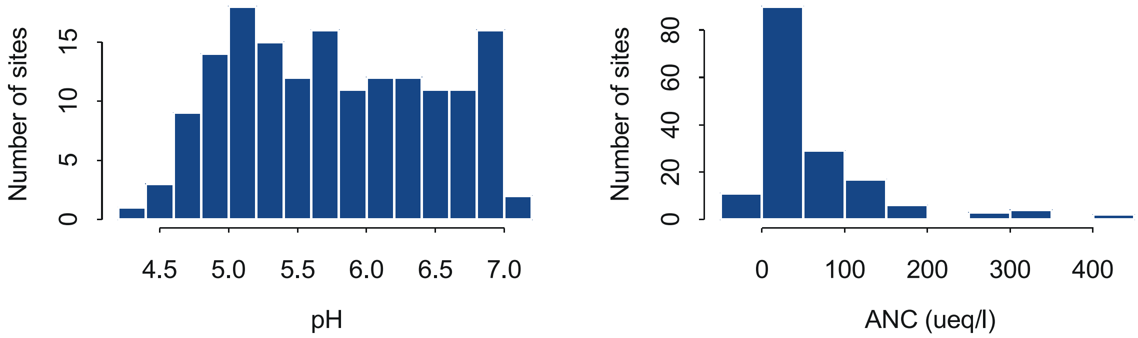


Figure 3.3.2: Spatial distribution of sites in the UK-ANC transfer function training dataset (N = 163).

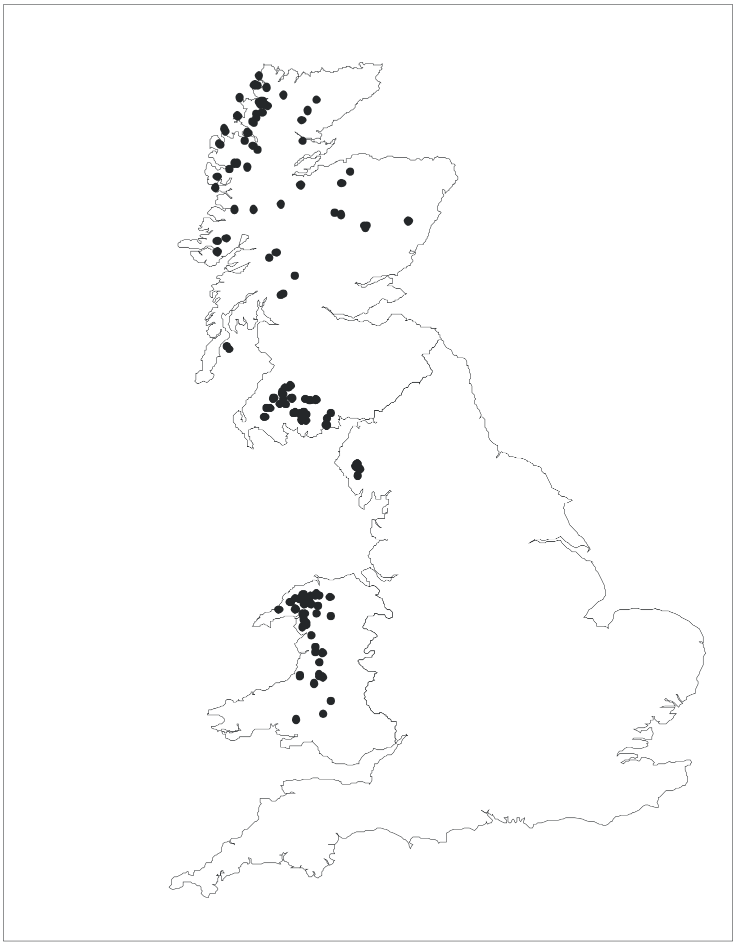


Figure 3.3.3: Plot of observed ANC vs. diatom-inferred ANC (upper) and observed pH vs. diatom-inferred pH (lower) for transfer functions derived from the 163-sample ANC training set. Left-hand plots show model predictions, right-hand plots show bootstrap cross-validation results.

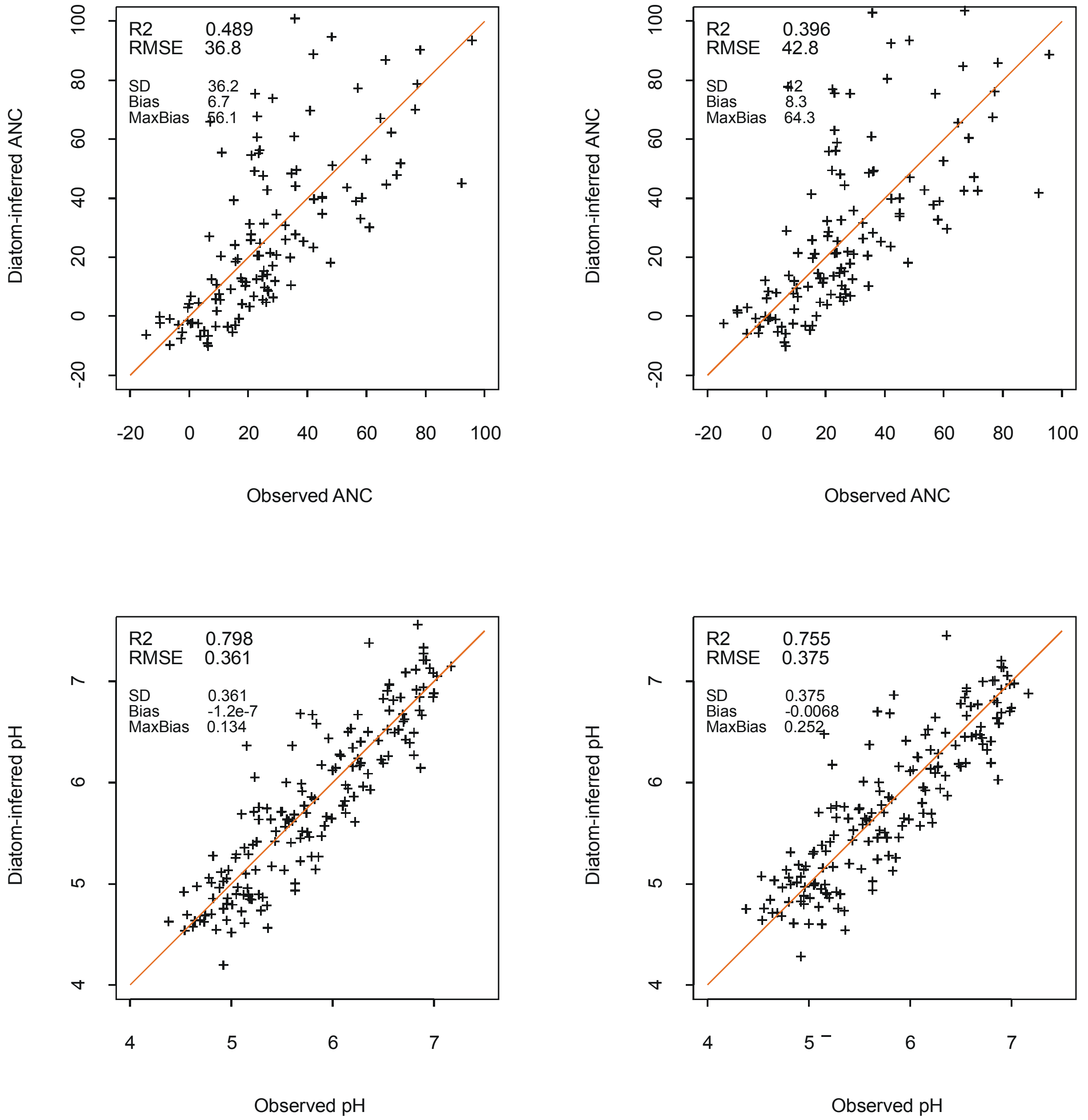


Figure 3.3.4: Plot of Squared Chi-square dissimilarity between each fossil diatom sample and its nearest analogue in the ANC training set for the UK Acid Waters Monitoring Network core sites. Horizontal lines indicate cut-offs for good (0.5) and close (0.4) analogues respectively.

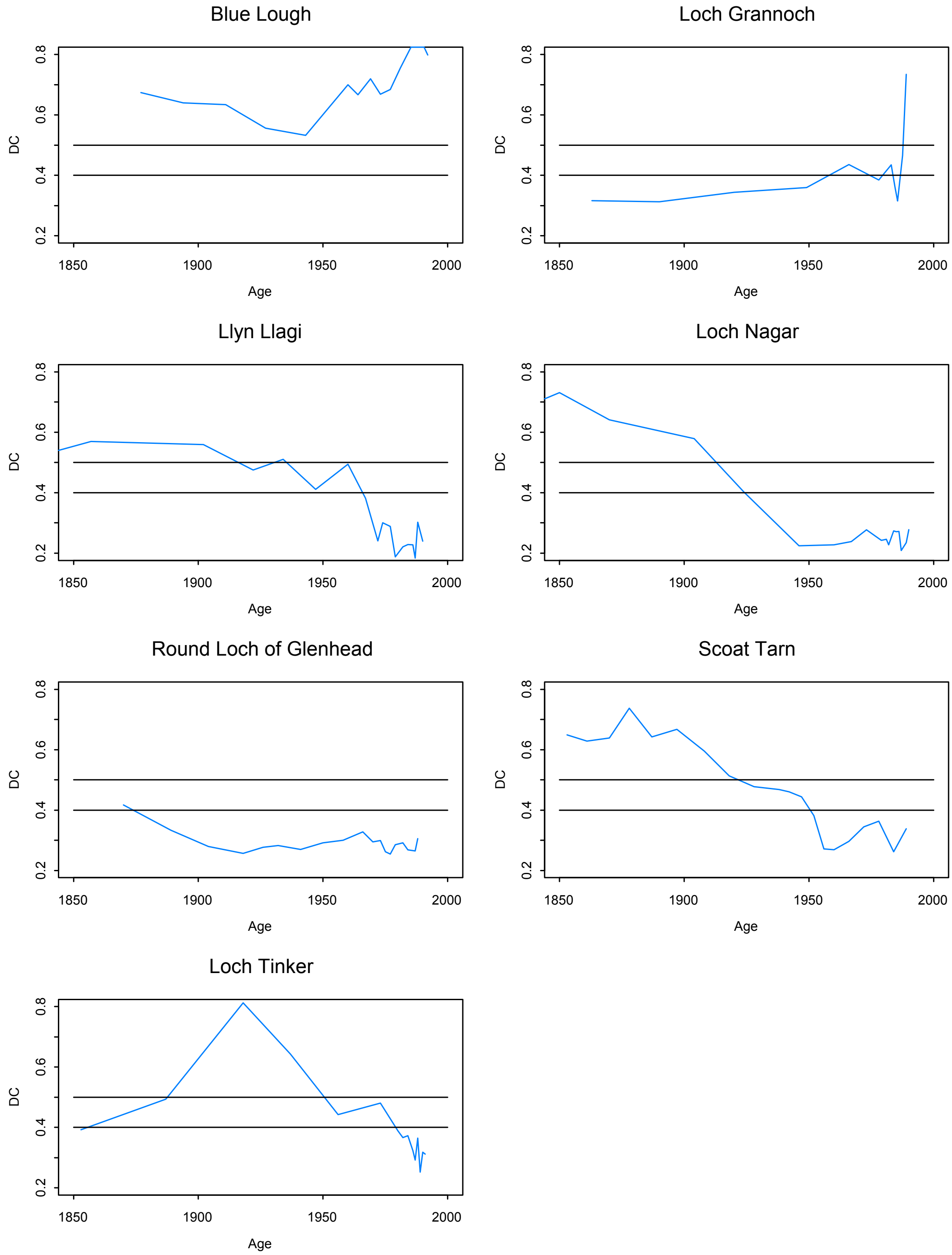


Figure 3.3.5: Blue Lough pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

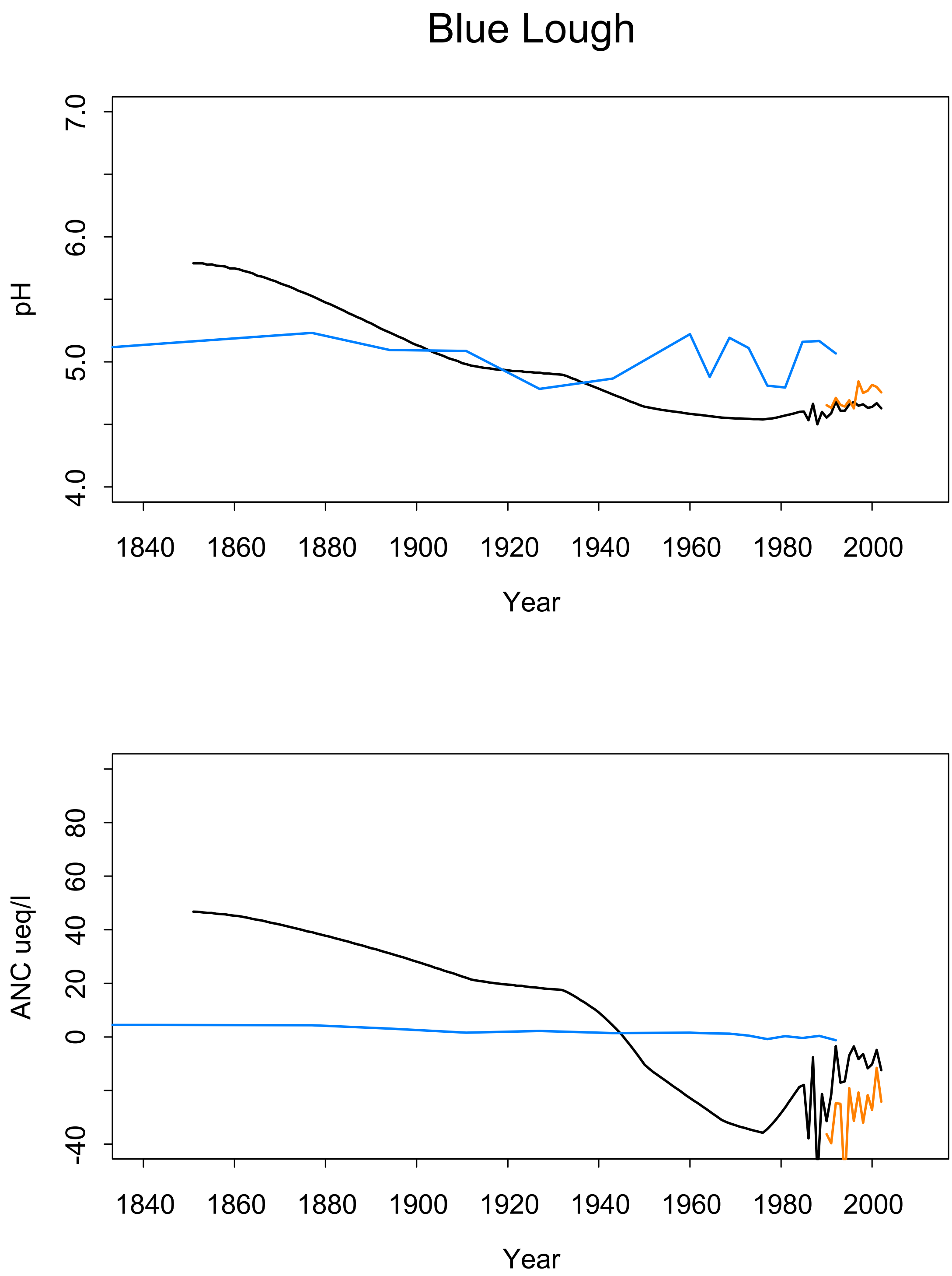


Figure 3.3.6: Loch Grannoch pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

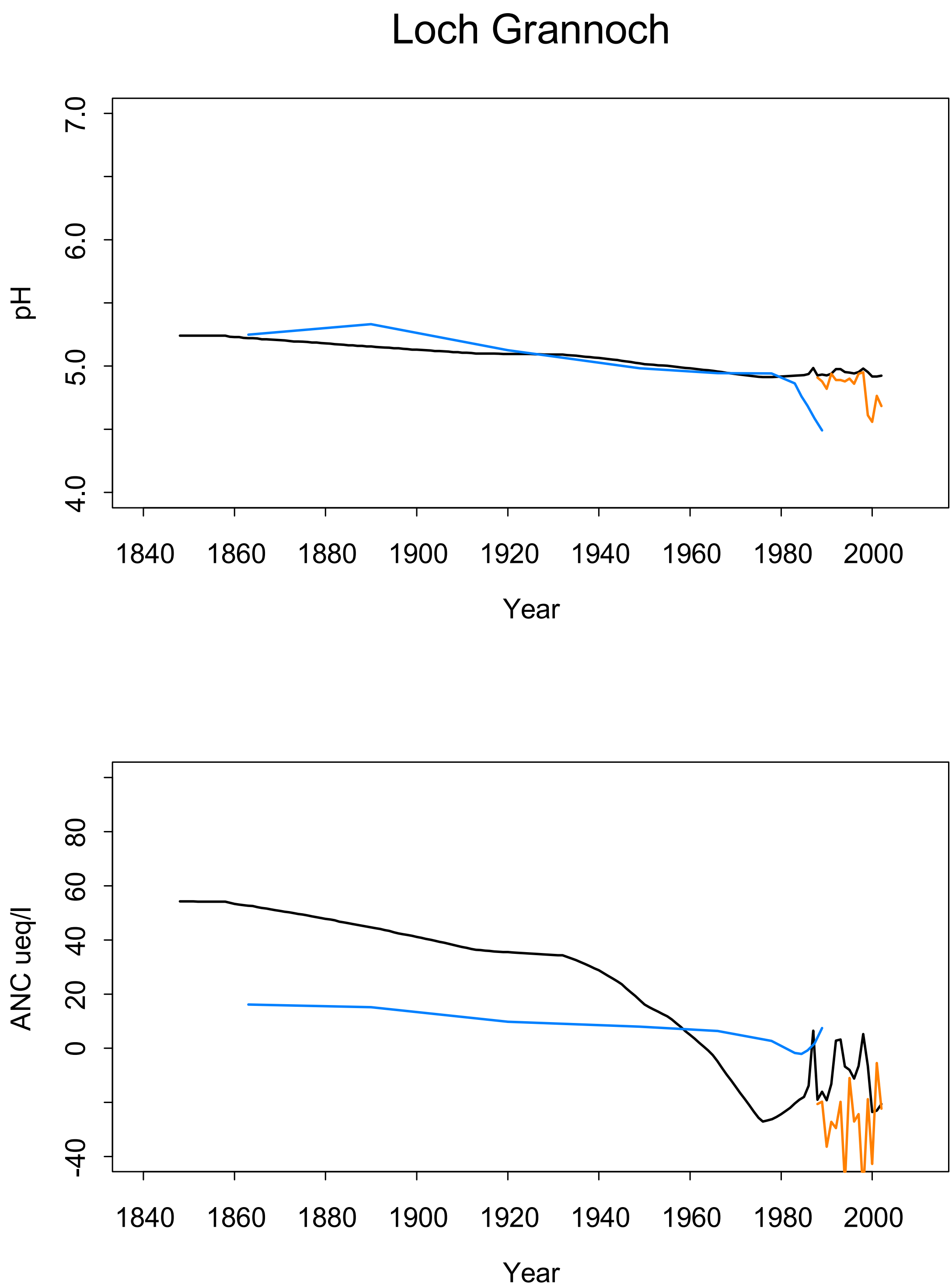


Figure 3.3.7: Llyn Llagi pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

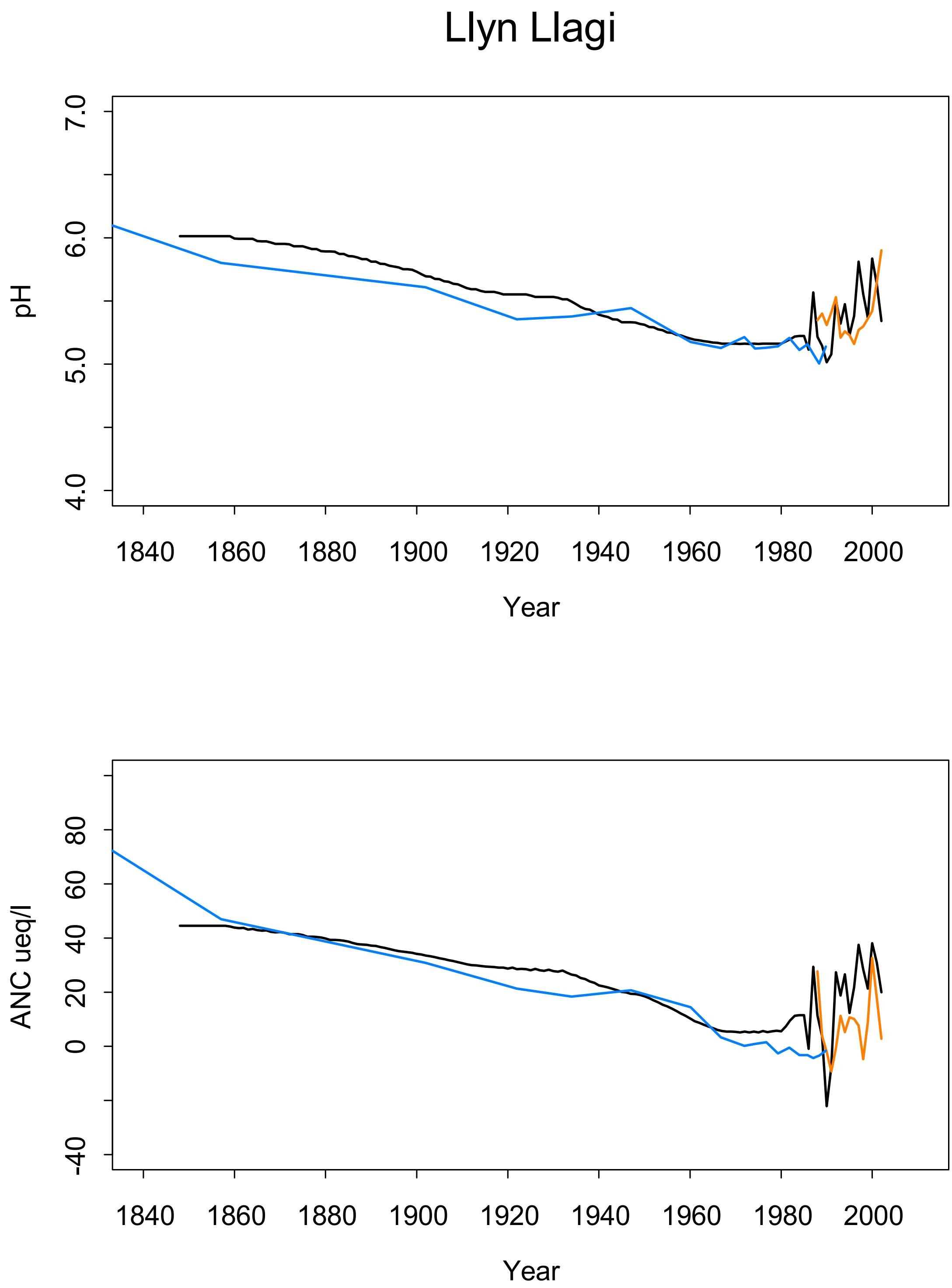


Figure 3.3.8: Lochnagar pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

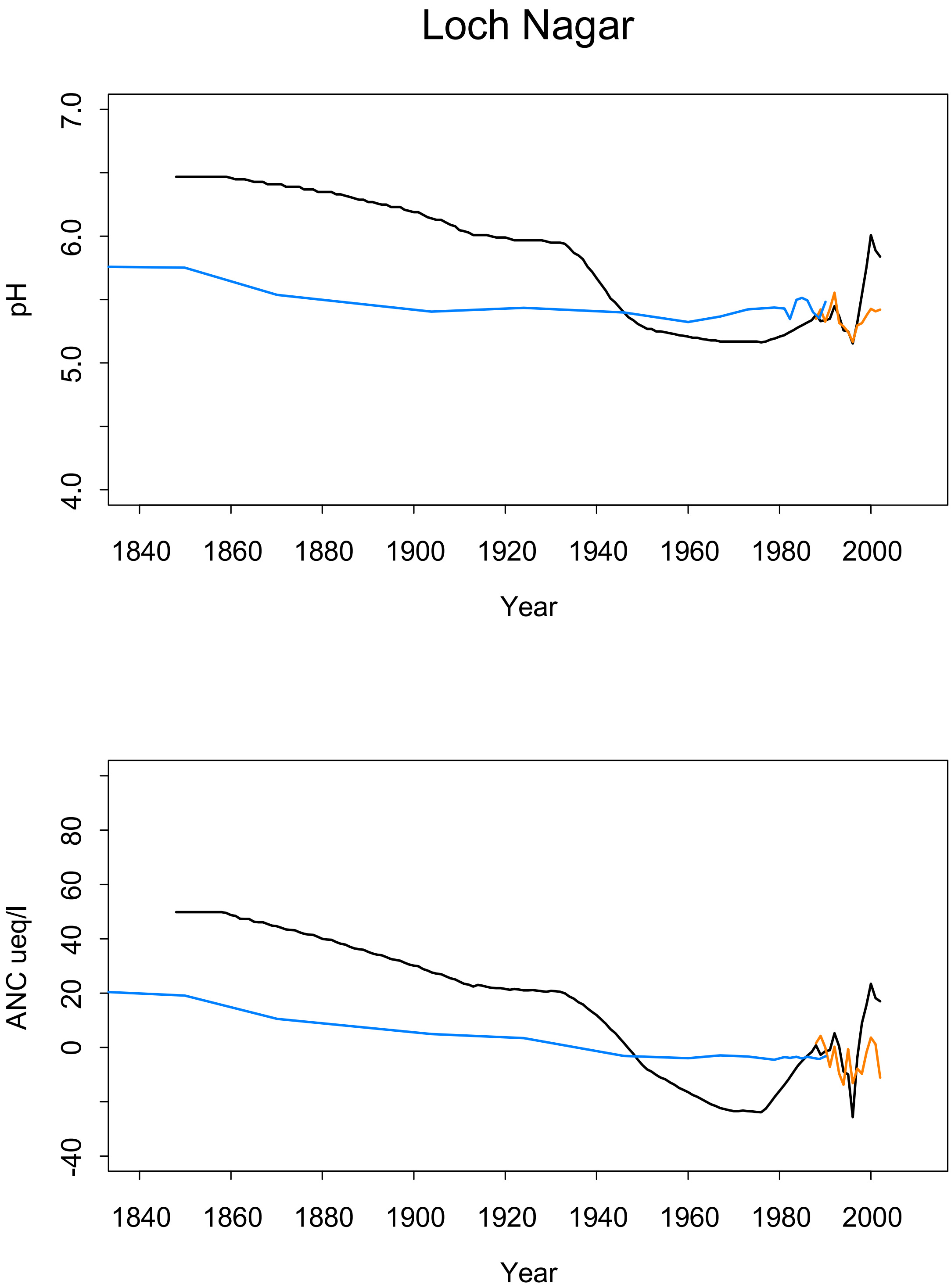


Figure 3.3.9: Round Loch of Glenhead pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

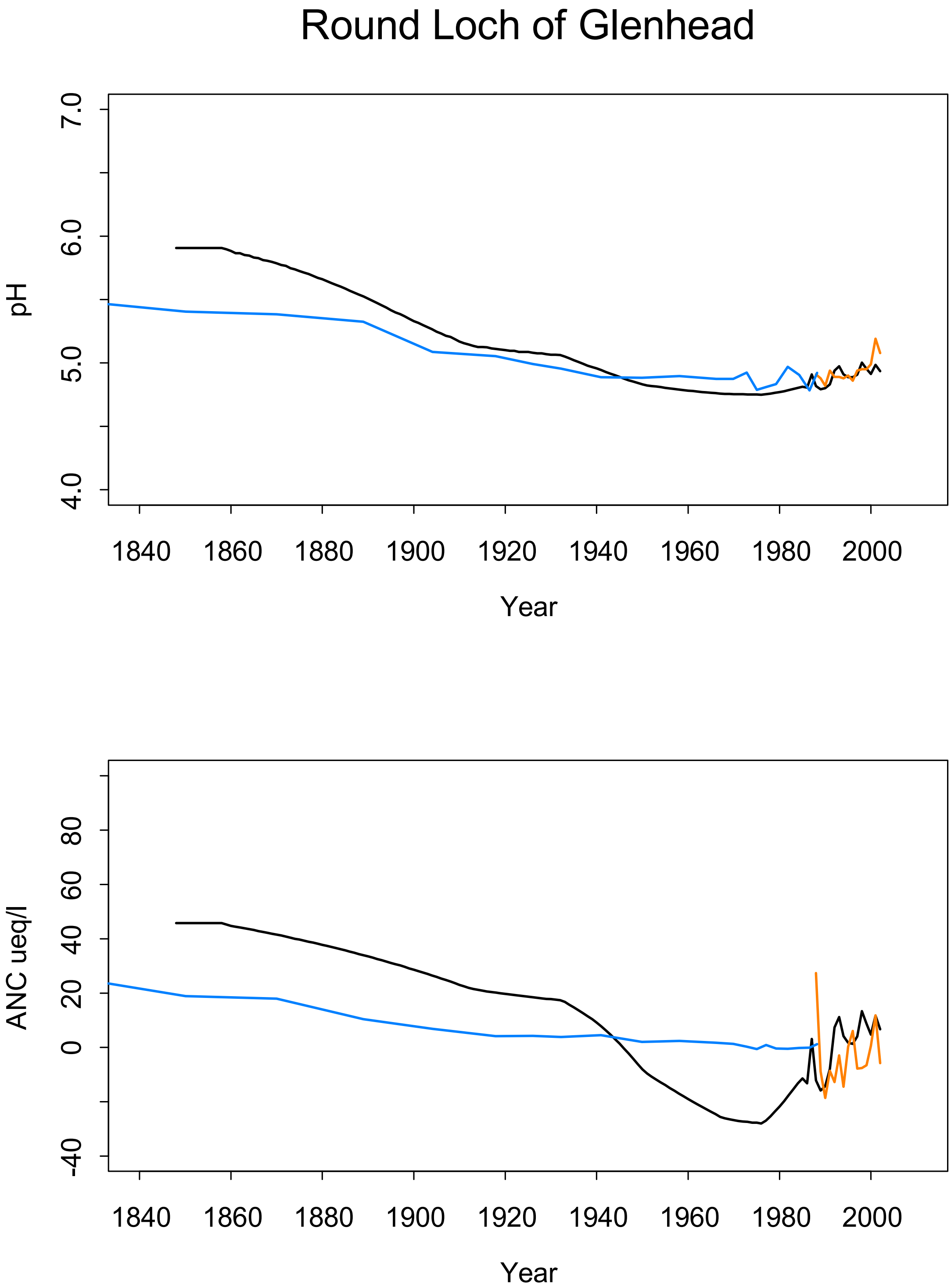


Figure 3.3.10: Scoat Tarn pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

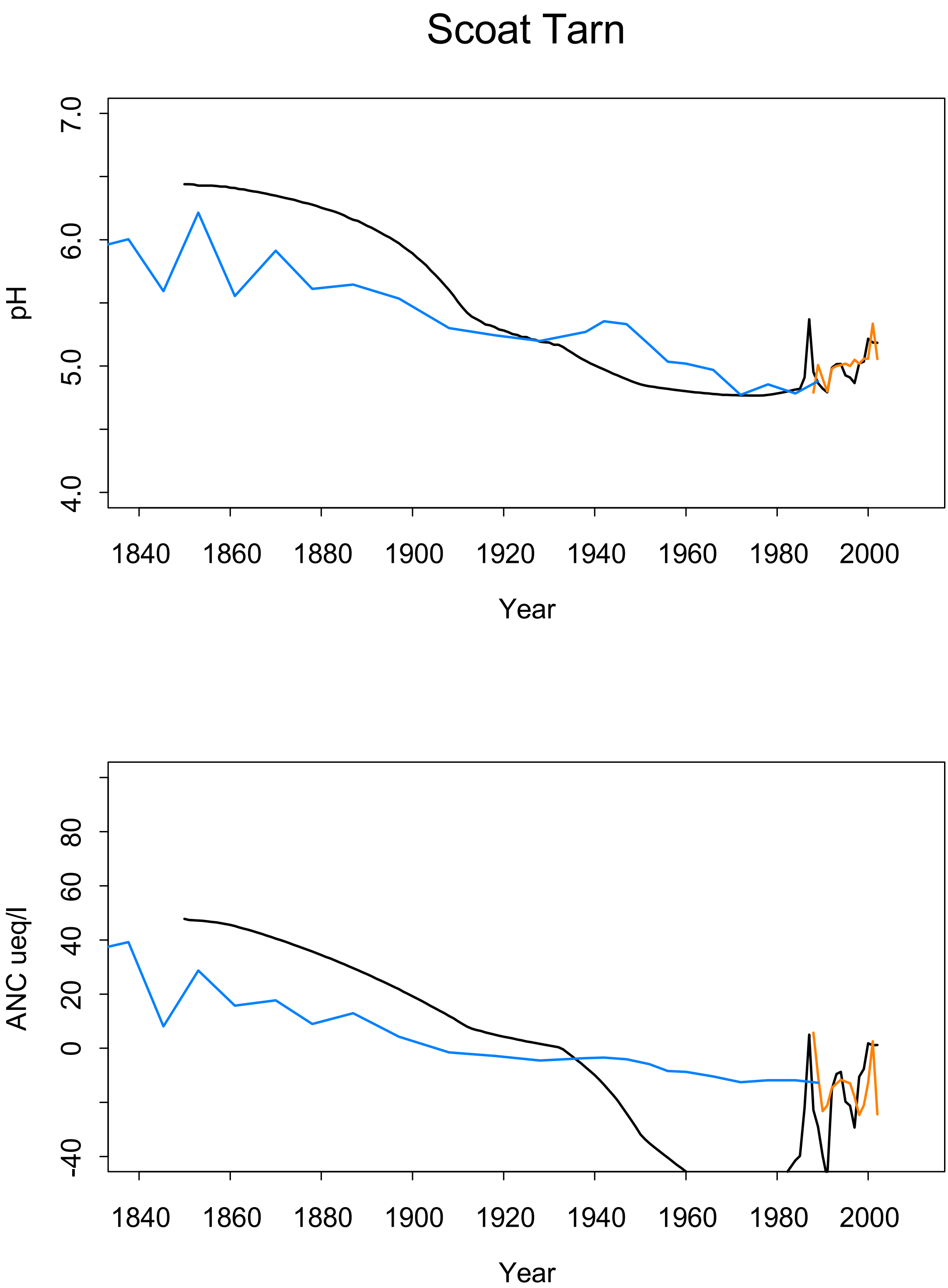


Figure 3.3.11: Loch Tinker pH (top) and ANC (bottom) historic chemistry time-series showing diatom-based reconstructions (blue), MAGIC hindcasts (black) and mean annual instrumental chemistry (orange).

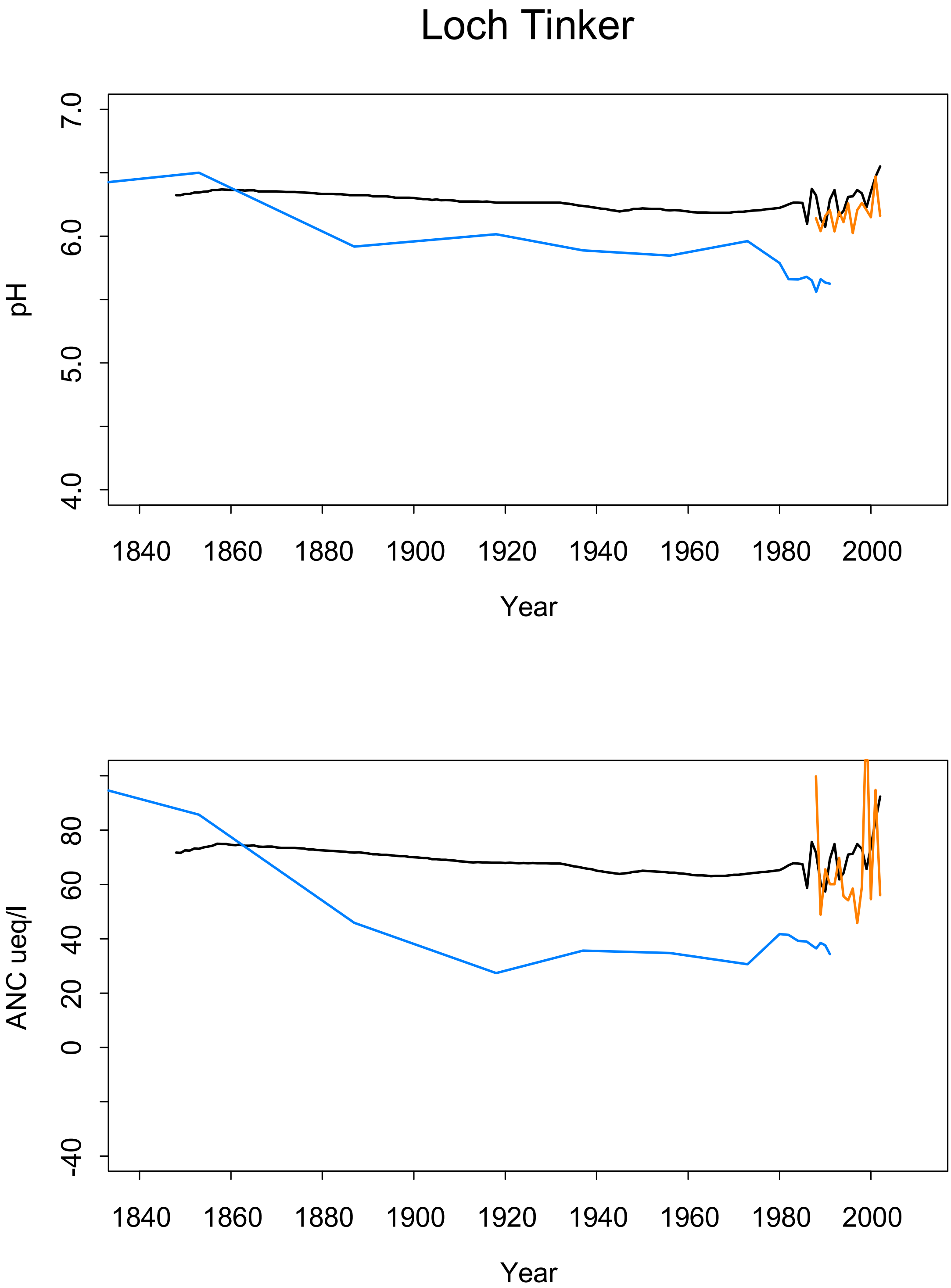


Figure 3.3.12: Relationship between Baseline (1850) ANC hindcasts using diatom, MAGIC and F-factor models.

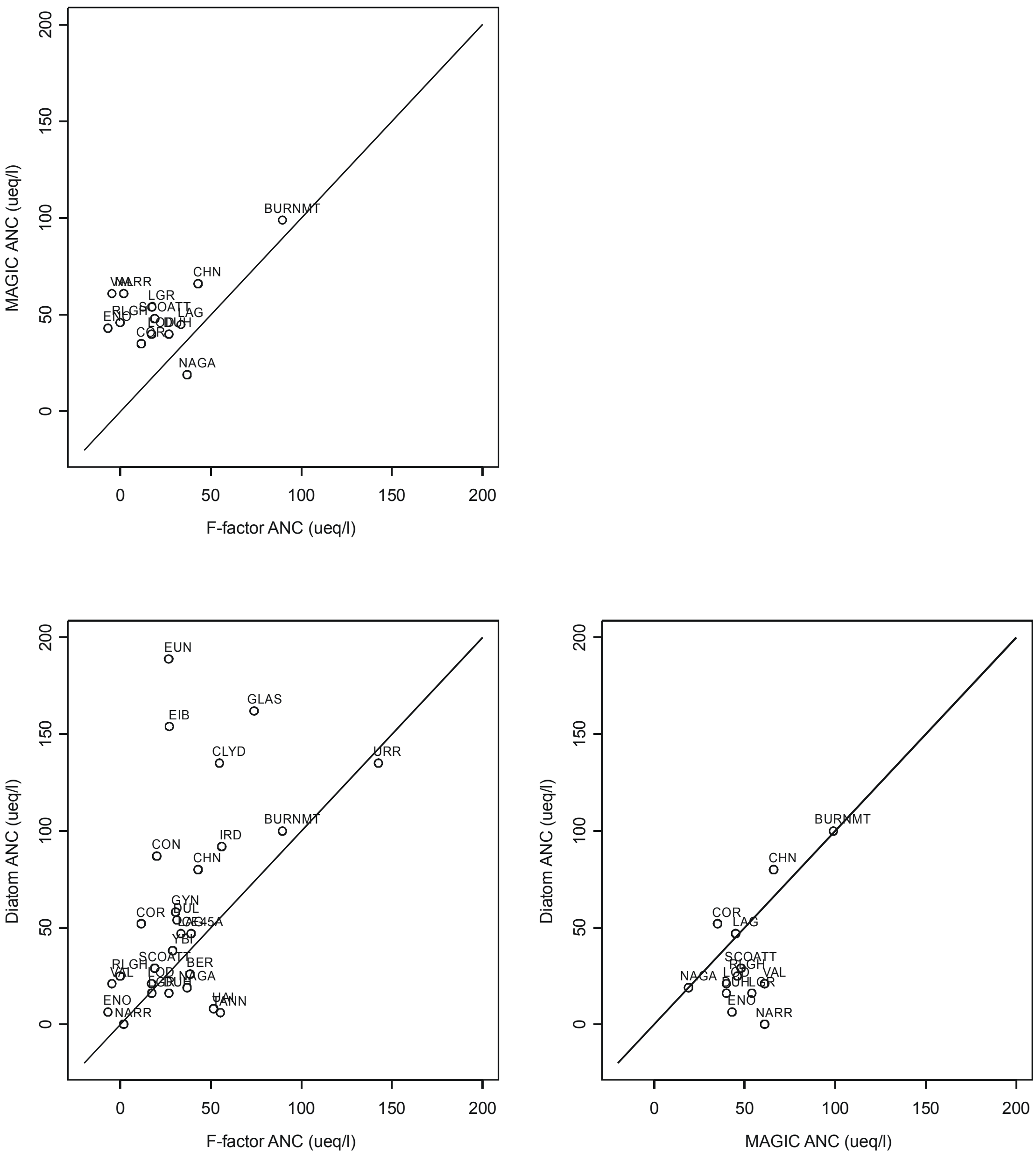
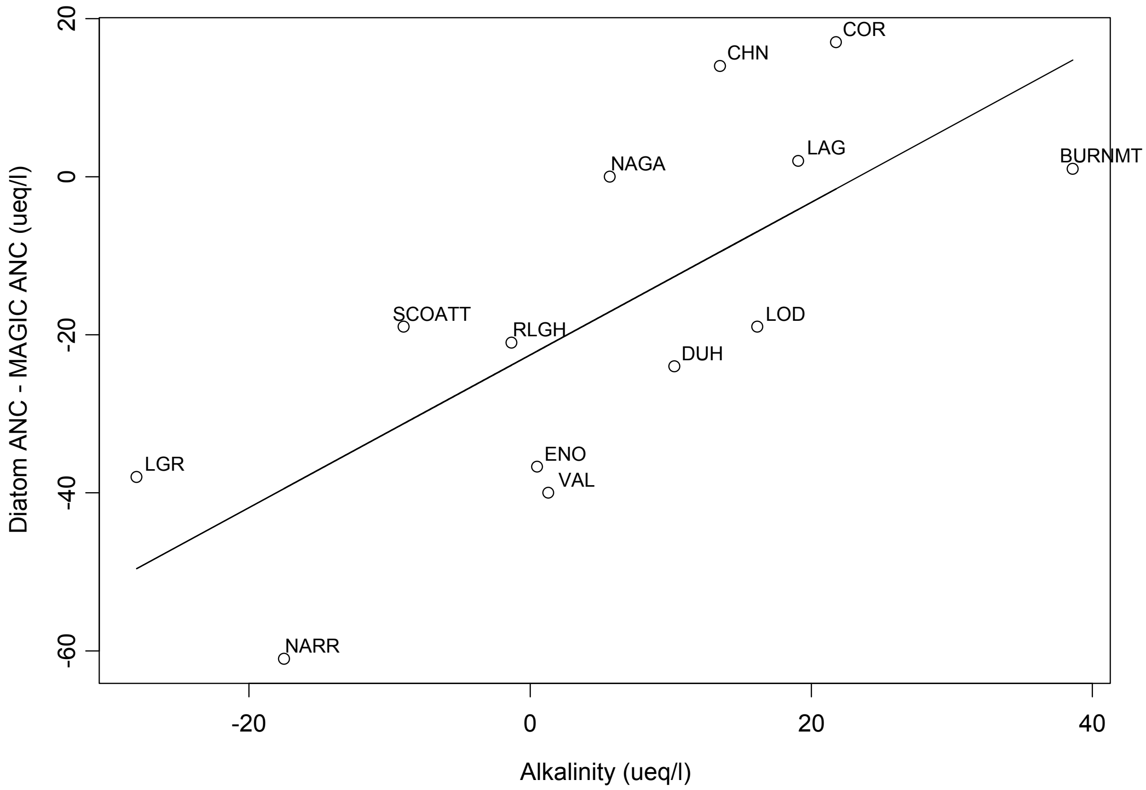


Figure 3.3.13 Relationship between diatom hindcast ANC minus MAGIC hindcast ANC and alkalinity. Line shows fitted regression model: correlation coefficient is 0.73).



Task 4: Metal deposition and cycling at Lochnagar

Work Package 4: Metal deposition and cycling at Lochnagar

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Introduction

Trace metal analyses were first undertaken at Lochnagar in 1986 when a palaeoecological investigation was undertaken by the ECRC as part of a Department of the Environment (Air Quality) funded study into the causes of surface water acidification in the UK. In 1988, Lochnagar was selected as one of the sites in the newly established Acid Waters Monitoring Network (AWMN) and chemical and biological data from the site have since contributed to both national (Environmental Change Network; Acid Deposition Monitoring Network) and international (UNECE International Co-operative Programme for Assessment and Monitoring of Acidification and Rivers and Lakes) monitoring networks. Furthermore, the loch has been one of the flag-ship sites in the EU funded European mountain lakes research programmes AL:PE and AL:PE II (1991 – 1996), MOLAR (1997 – 1999) and EMERGE (2000 – 2003) and more recently, the EU 6th Framework European freshwaters research project EUROLIMPACS.

Monitoring of trace metals at Lochnagar began in 1996, with a sampling programme established for the EU MOLAR project and a linked PhD study by Handong Yang (Yang, 2000). The combined aims of these studies was to try and link depositional fluxes of metals at Lochnagar to the lake sediment record in such a way that historical deposition could more accurately and quantitatively be determined. Further, sampling of many ecological compartments including not only atmospheric deposition and lake waters, but also lake sediments, suspended sediments, catchment soils, various terrestrial plant and aquatic macrophyte species, epilithic diatoms and zooplankton were undertaken and analysed for a range of metals in order that a mass balance for the lake system could be obtained. This study also showed, for the first time, the major input of metals from the catchment of an upland UK lake, at Lochnagar thought to be mainly the result of increased peat erosion.

After MOLAR, the monitoring of trace metals in bulk deposition, lake waters, sediment traps and aquatic and catchment biota continued with support from the DETR under the ‘Critical Load of Acidity and Metals’ (CLAM) project. The aims of this work were:

- To provide data on inter- and intra-annual variability in deposition of metals and identify any temporal trends that might become apparent;
- To assess the role that catchment and lake biota and sediment trapping could play in the monitoring of metal deposition and / or lake water metal concentrations;
- To produce data on Hg in the various ecological compartments of an upland lake site as these data were particularly rare in the UK.

Analysis of lake water and deposition samples for the trace metals, other than Hg, caused some problems during the CLAM project. High and erratic values were

observed in a number of samples and, after a number of 'blank' test analyses, were attributed to sample filters used in one of the laboratories. Consequently, these data, prior to May 1999, are considered of doubtful quality. All other analyses were completed without any problems producing a dataset, especially for Hg, unique within the UK and possibly within Europe.
Whilst this dataset was not of sufficient length to allow any significant temporal trends to be identified, possible declines were observed for most of the measured metals in both lake water and deposition. Further, metal concentrations for most of the terrestrial plant species appeared to show a reasonable agreement with depositional trends whilst data from some reed and grass species (e.g. *Nardus stricta* and *Juncus sp.*) were considered of little further monitoring value. This was also found to be the case for epilithic diatoms on artificial substrates, but only because of the low productivity in the loch meant that insufficient sample was obtained. In a more productive lake epilithic diatoms may yet prove to be a useful metal monitoring tool.

The conclusions of CLAM were, therefore, that this work should be continued in order to maintain and extend this high value dataset, but that the number of individual 'biomonitors' could be reduced without loss of monitoring, or data, quality. It was also recommended that the work be extended to other sites in order to provide supporting data for the observed trends. Whilst the recommended expansion to other sites was not included in the current DEFRA 'Freshwater Umbrella' project, the continued monitoring at Lochnagar was. Therefore, the aims of this current study were:

- To continue the monitoring for Cd, Pb, Zn, Cu, Ni and Hg, in a range of aquatic and terrestrial biota, sediment traps, bulk deposition and lake water taking into account the conclusions of CLAM;
- To investigate the possibility of including further groups/species to provide more information on trace metals through the food-web;
- To identify any trends in depositional fluxes and how these relate to measured lake water concentrations; catchment and aquatic biota concentrations;
- To provide trace metal data for catchment / lake modelling work;
- To provide recommendations for the extension of similar monitoring to other upland sites under the auspices of the UK AWMN.

The data required to address these aims were collected under three distinct 'Jobs'.

Job 4.1: Fortnightly sampling of lake water and deposition for Cd, Pb, Zn, Cu and Ni.

Sampling
Bulk deposition was collected in a NILU (Norwegian Institute of Air Research) -type bulk deposition collector (P.no. 9713, RS1; NILU, 2001) deployed about 50m from the north-east loch shore. Samples were collected fortnightly and acidified to 1% Aristar HNO_3.

Lake water samples were collected by submerging a rigorously acid leached 250 ml Teflon bottle approximately 20 cm beneath the surface of the water near the outflow where the lake water is well mixed. The bottles were completely filled; the lids tightened by gloved hands underwater and then the bottles double bagged. Samples were taken fortnightly and sample treatment was the same as for the deposition samples.

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

Cd	Pb	Zn	Cu	Ni
0.02	0.01	0.20	0.18	0.11

Results
Details of the monitoring of these trace metals in lake waters and bulk deposition up to 2000 are given in the previous CLAM report and, apart from a few samples lost due to bad weather, this work has continued uninterrupted to the present. As mentioned above, and recorded in more detail in this earlier report, samples prior to May 1999 were affected by the leaching of metals by filtering, however, measurements after this time are considered accurate and reliable and this reliability has continued throughout the current project.

Figure 4.1.1 shows the full dataset for the selected trace metals in Lochnagar lake water since 1997, with the data from the current study highlighted. Whilst the elevated levels resulting from the leaching prior to May 1999 are obvious in elements such as Cd, Ni and possibly Cu, the other elements do not appear to have been so affected. However, since this period, trends between the elements seem to have been quite similar with a period of low concentrations (resulting in the decline observed in CLAM) followed by an increase to the present. In most cases this has resulted in recent concentrations reaching levels as high as any observed throughout the monitoring period, including those samples thought to be affected by leaching from the filters. This increase is most marked in Cu and Ni, where periods of concentrations below detection limit in 2001 and 2002 respectively appear as gaps on the Figure followed by periods of elevated concentration, and in Zn where concentrations appear to have been steadily increasing over a number of years.

Figure 4.1.2 shows the concentrations for the same trace elements in Lochnagar bulk deposition over the full monitoring period. Whilst the pre-May 1999 samples affected by the leaching appear to be more obvious in these bulk deposition samples, the recent trend towards increased concentrations does not appear to be so apparent as in the lake water samples. However, occasional recent samples still show concentrations for most elements elevated to levels as high as any observed throughout the monitoring period.

The recent high concentrations lead to some ambiguity when considering trends in annual data. Lake water data are shown as annual mean concentrations in Figure 4.1.3

whilst the bulk deposition concentrations are combined with rainfall data to produce annual depositional fluxes in Figure 4.1.4a. Initially, there would appear to be evidence for increasing trends in both sets of data but in all cases the 2003 values are highest and this may be biasing this observation. Indeed, if the 2003 data are removed, the trend would appear to be a decline in annual mean lake concentration for Zn and no change for Cd, Ni and Cu, whilst for annual depositional fluxes, removal of the 2003 data would appear to show declining trends in Cd and Ni and no change in Zn and Cu. Only Pb seems to be showing a consistent ‘trend’: an increase across most of the monitoring period. Without doubt a longer period of monitoring is required to confirm these observations.

Figure 4.1.1. Trace element concentrations in Lochnagar lake water 1997 – 2003. Sampling period covered by the current project is shown in red.

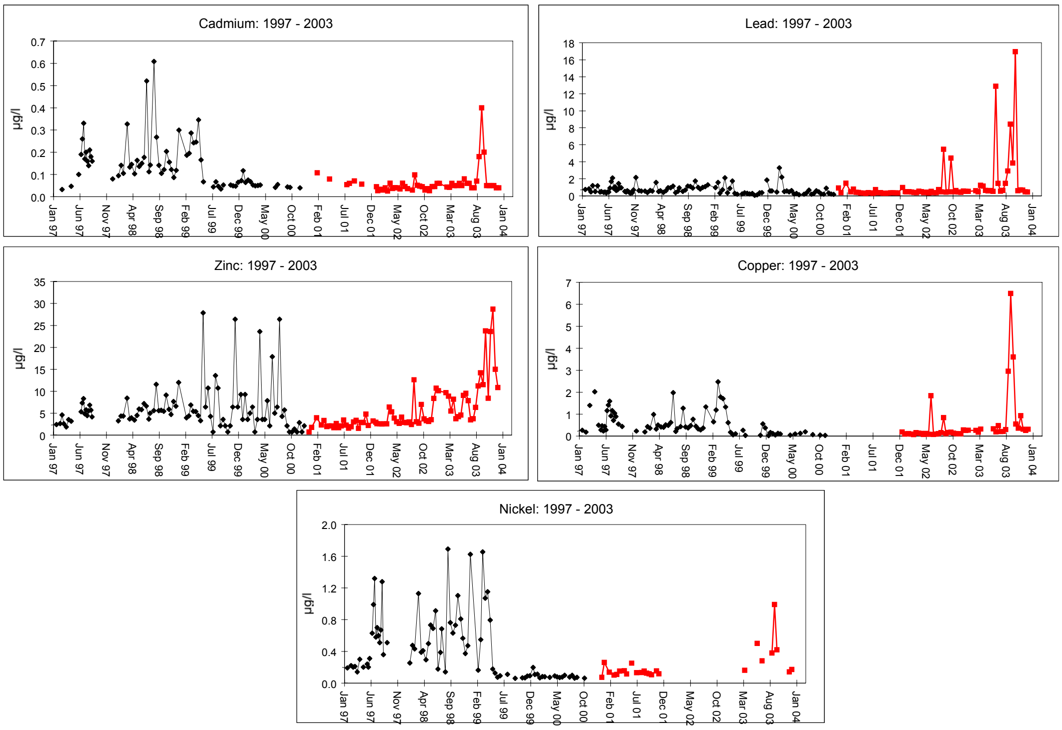


Figure 4.1.2. Trace element concentrations in Lochnagar bulk deposition 1997 – 2003. Sampling period covered by the current project shown in red.

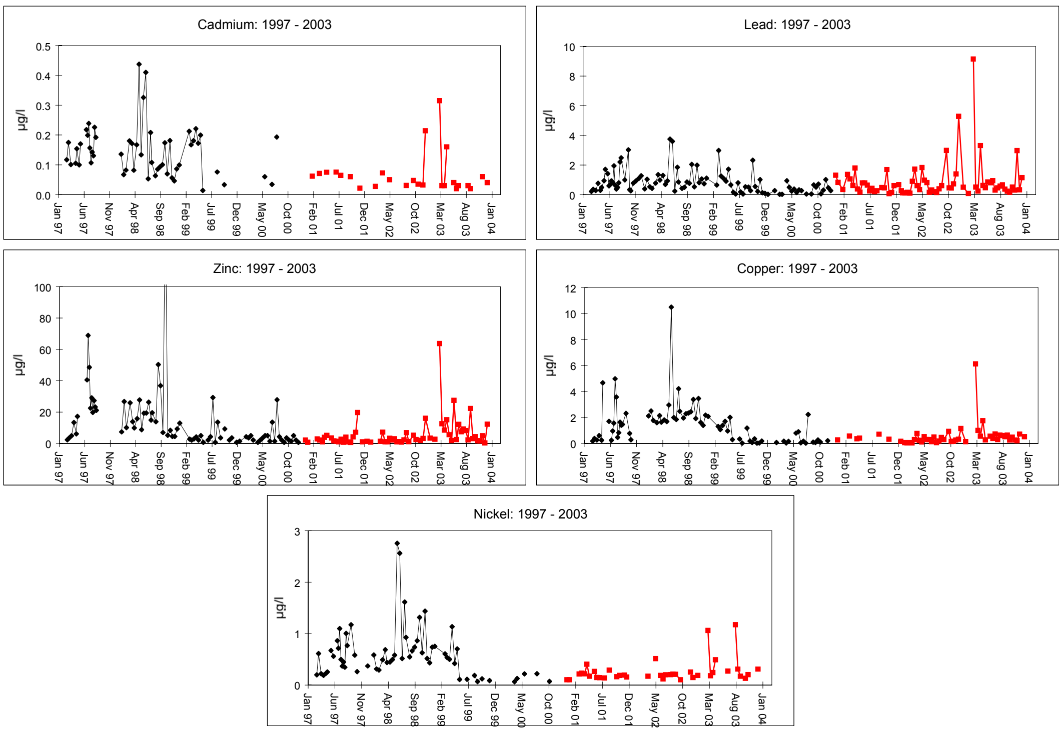
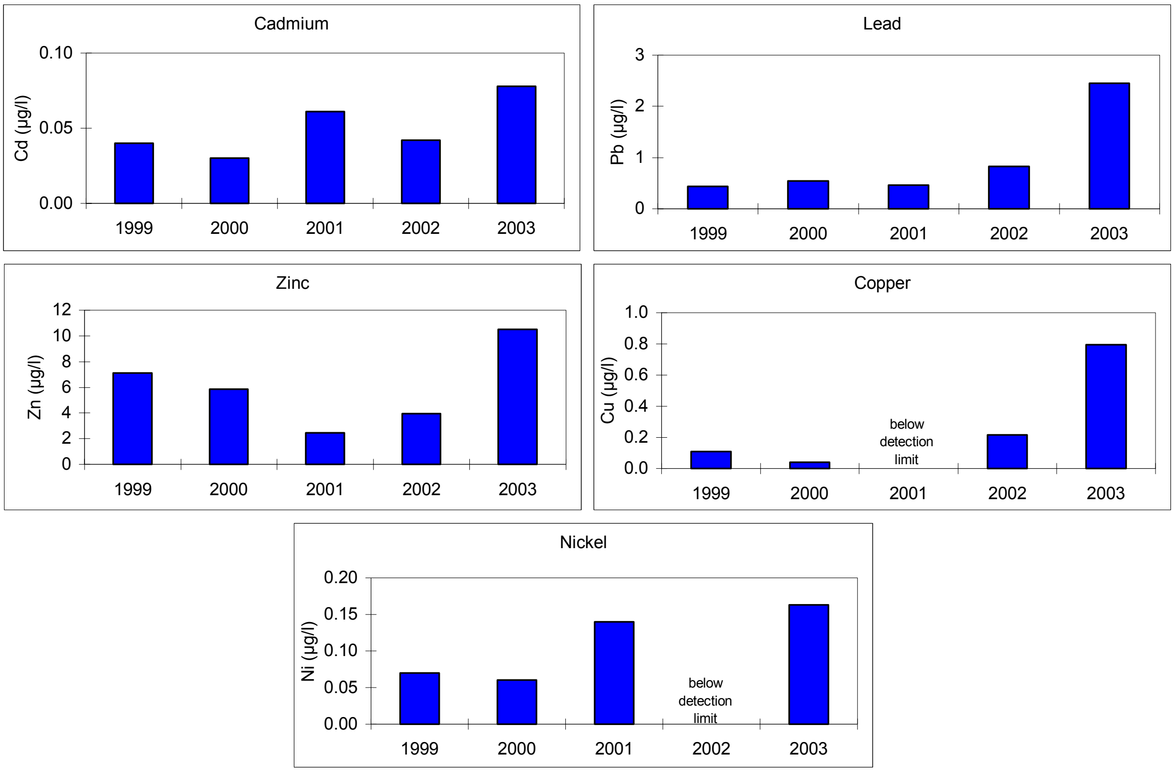


Figure 4.1.3. Mean annual (calendar year) lake water concentrations for Lochnagar trace metals.



The reason for the increasing trend in Pb and for the high 2003 values for all metals is uncertain, but 2003 could be an anomaly superimposed on a longer declining trend. As fluxes are the product of concentration and rainfall data, high fluxes could be the result of elevated rainfall at Lochnagar. However, as Figure 4.1.4b shows this is not the case as annual rainfall at the site shows little trend over the period 1997 – 2003 and indeed, rainfall was at its lowest for at least seven years in 2003. If rainfall has not increased it would appear that the increasing depositional Pb flux is due to increasing metal concentrations. However, whether the increasing depositional flux is solely responsible for the elevated lake water concentrations of Pb is uncertain, as there could also be a catchment input.

Figure 4.1.4a. Annual (calendar year) bulk deposition trace metal fluxes for Lochnagar. (<LoD = too many individual sample concentrations below the analytical limit of detection within the year to calculate a meaningful annual flux)

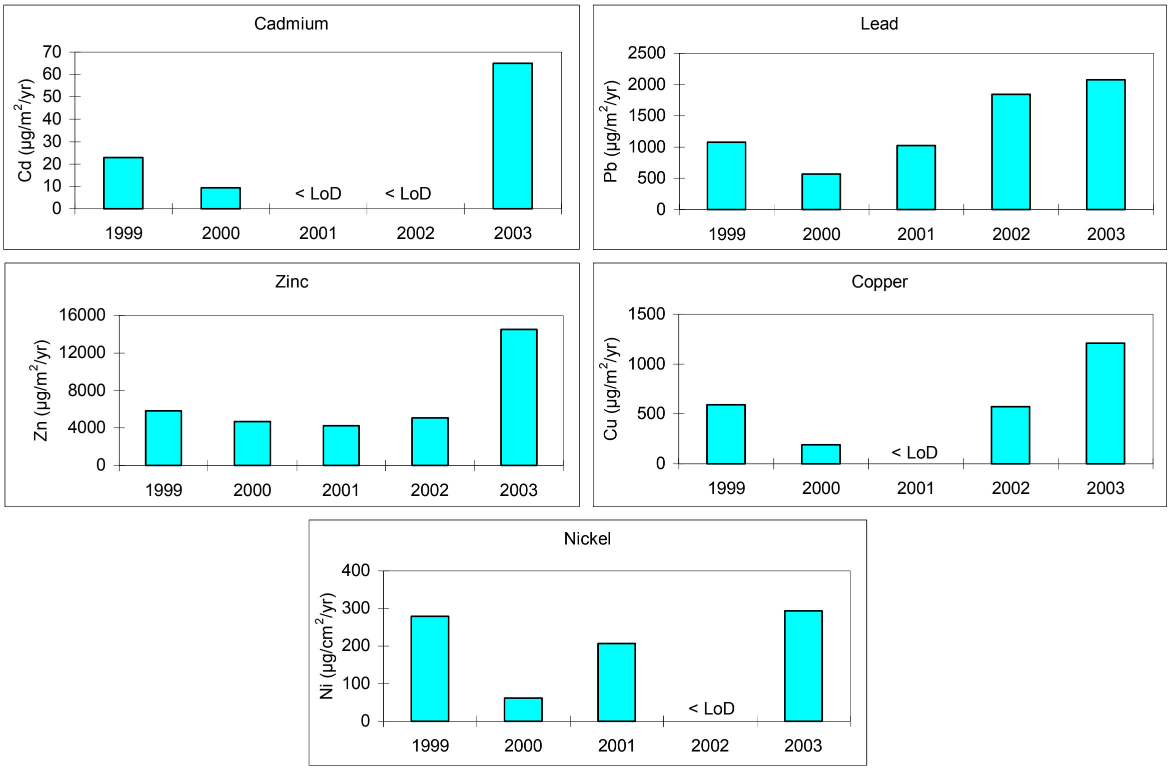
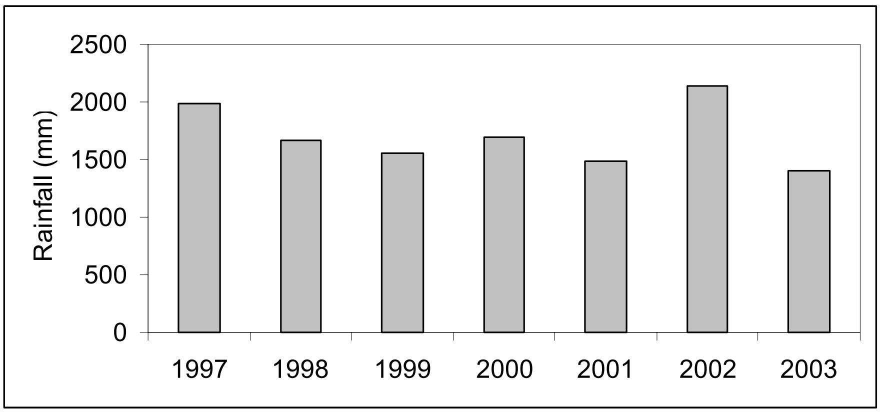


Figure 4.1.4b. Annual rainfall at Lochnagar.



Job 4.2: Monthly sampling of deposition and lake water for Hg

This work continued the monitoring of total mercury in bulk deposition and lake water samples begun in 1997. However, from October 2001, we also introduced the measurement of methyl mercury (MeHg) to this sampling programme. MeHg is the biologically available and most toxic form of Hg and hence is of considerable interest. Despite this, there are remarkably few MeHg data for the UK and these monitoring data for lake waters and deposition are a unique dataset in this country.

Sampling

Bulk deposition samples for Hg analysis was undertaken using an IVL (Institutet för Vatten-och Luftvårdsforskning – Swedish Environmental Research Institute) –type sampler (Lindqvist et al., 1991; Jensen and Iverfeldt, 1994). 5ml concentrated Aristar HCl was placed in the sample collection bottle before fitting to the collector in order that the collected samples were immediately acidified. Samples were collected monthly and sent to the Norwegian Institute of Air Research (NILU) for analysis by cold vapour – atomic fluorescence spectroscopy (CV-AFS).

Lake water samples were collected in the same way as for the other trace metals (see above) except on a monthly basis. Sample treatment was the same as for the Hg deposition samples.

Analytical methods

All Hg analyses on water and bulk deposition samples were undertaken at the Norwegian Institute of Air Research (NILU). Samples prior to 4th June 2003 were analysed using the PS-Analytical system. Samples after this date were analysed with the Tekran 2600. This move to a new system has significantly improved the limits of detection for the Hg analysis.

Samples were stored in the dark at +5°C for up to 3 months. Before analysis the samples were oxidised with BrCl, converting stable mercury forms to water soluble species, which in turn were reduced to Hg° with $SnCl_2$. Analysis was performed using Cold Vapour Atomic Fluorescence Spectroscopy (CV-AFS) (PS-Analytical). Using the PS-system, the Hg° is passed through a drying column before being detected in the AFS detector. The detection limits had been about 5 ng Hg L^{-1}, but towards the end of its use, the detection limits had been getting higher. With the Tekran 2600 system, the Hg° is concentrated on a gold trap before being detected in the AFS detector. The detection limits are 0.5 ng Hg L^{-1}.

Methylmercury analytical procedures

Methylmercury (MeHg) was analysed using a procedure similar to those described by Liang et al. (1994) and Bloom (1989). Prior to analysis a chelating agent APDC (Ammonium salt of Pyrrolidine-1-dithiocarboxylic acid) was added to 45 ml of the water sample and the sample distilled. A detailed description of the distillation procedure using APDC can be found in Horvat et al. (1993). The distillate is treated with sodium tetraethylborate to form methylethylmercury ($CH_3HgC_2H_5$). Inorganic Hg (II) species, that also may be present in the solution, are simultaneously converted to diethylmercury. The ethylated mercury species are volatile and are stripped of the solution by purging with N_2 and adsorbed on a graphitic carbon column. The Hg-species are then thermally desorbed from the carbon column in a stream of He and separated by means of iso-thermal gas chromatography. Finally, by heating to 700 - 800°C in a pyrolysis column the methyl/ethylated Hg species are decomposed to elemental mercury and detected using Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). The detection limit is 0.06 ng L^{-1}.

Results

Figures 4.2.1 and 4.2.2 show the full dataset for Hg in Lochnagar lake water and bulk deposition respectively, since 1997. The data from the current study are highlighted in red and show clear declines in Hg concentration, especially in lake waters, over the project period. This is in contrast to the dataset at the end of the CLAM project (in black on the Figures) which would appear to have been showing little change in lake water concentration and possibly an increase in bulk deposition concentration. This highlights the value of maintaining a monitoring programme over the long-term.

Figure 4.2.1. Mercury concentrations in Lochnagar lake water 1997 – 2003. Sampling period covered by the current project is shown in red.

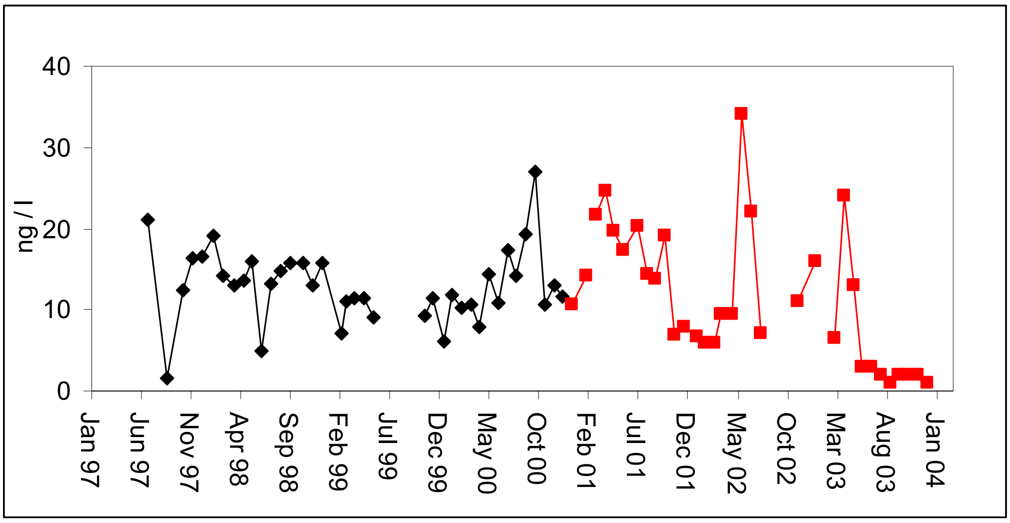
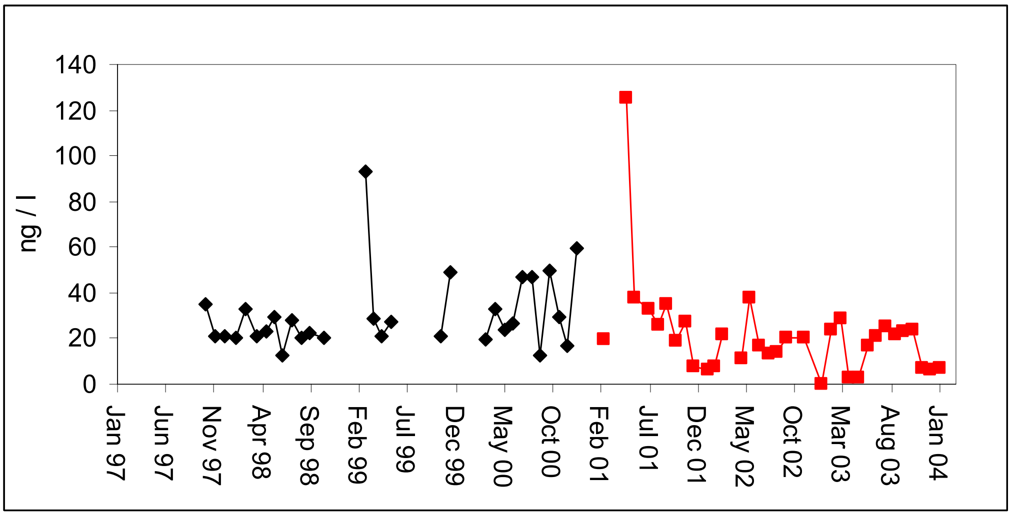


Figure 4.2.2. Mercury concentrations in Lochnagar bulk deposition 1997 – 2003. Sampling period covered by the current project is shown in red.



Converting the lake water concentrations to an annual mean (Figure 4.2.3) and the bulk deposition concentrations to an annual Hg depositional flux (Figure 4.2.4), emphasises these declining trends and, in contrast to the data from the other trace metals, shows 2003 had the lowest annual values, rather than the highest. As the rainfall data used in the flux calculations for both Hg and the other trace metals are the same; this difference must be due to the metal concentration data. Similarly, the exceptionally high Hg flux in 2000 does not correspond to a high rainfall year and also must be due to the concentration data. In summary, deposition and lake waters show good agreement in declining Hg trends since 2000.

The methyl mercury (MeHg) bulk deposition data (Figure 4.2.5), whilst only available for 2½ years, shows the start of an intriguing temporal trend. Concentrations are only elevated above the limit of detection during the winter, whilst peak concentrations seem to be occurring in February. Whilst this trend has only been repeated for the two years of monitoring, the data for the winter of 2003/4 also seem to be starting to show this pattern. Lake water concentrations show no elevation above detection limit at any time of year. Only in the most recent sample for which we have data (February 2004) has MeHg concentration increased to the detectable limit (0.06 ng L^{-1}). Currently, the reason for this seasonal trend in MeHg deposition is uncertain but has not been observed at other monitoring sites across Europe (John Munthe, IVL pers. comm.; Matti Verta SYKE (Finnish Environment Institute), pers. comm.). No comparable data exist within the UK with which to compare these trends and therefore whether such trends are unique to Lochnagar or typical of UK uplands is unknown. Further work, including continued monitoring, is therefore essential in order to more fully understand the depositional pathways of this most toxic component of Hg to upland UK freshwaters.

Figure 4.2.3. Mean annual (calendar year) lake water mercury concentrations for

Lochnagar.

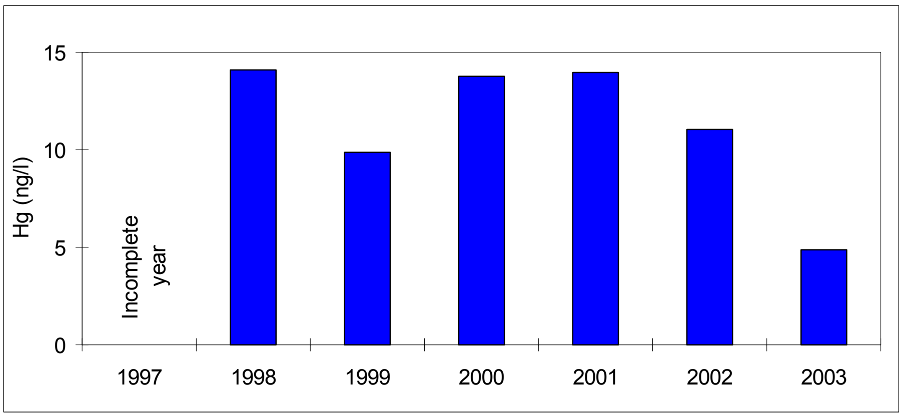


Figure 4.2.4. Annual (calendar year) bulk deposition mercury flux for Lochnagar.

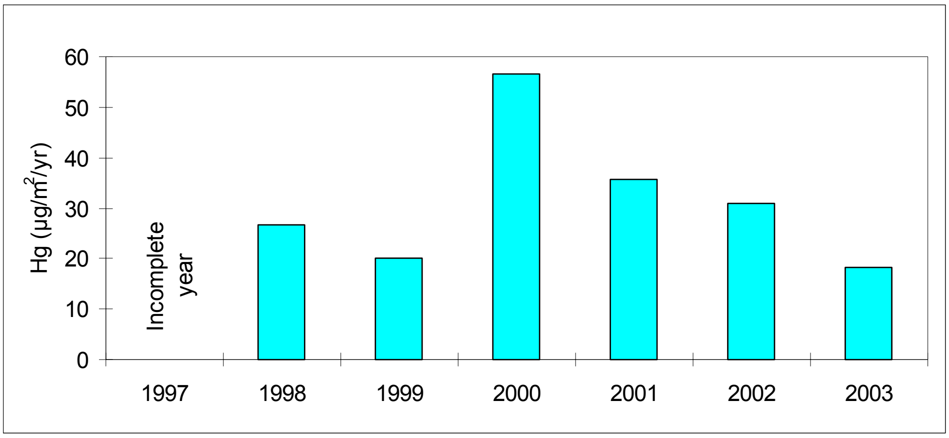
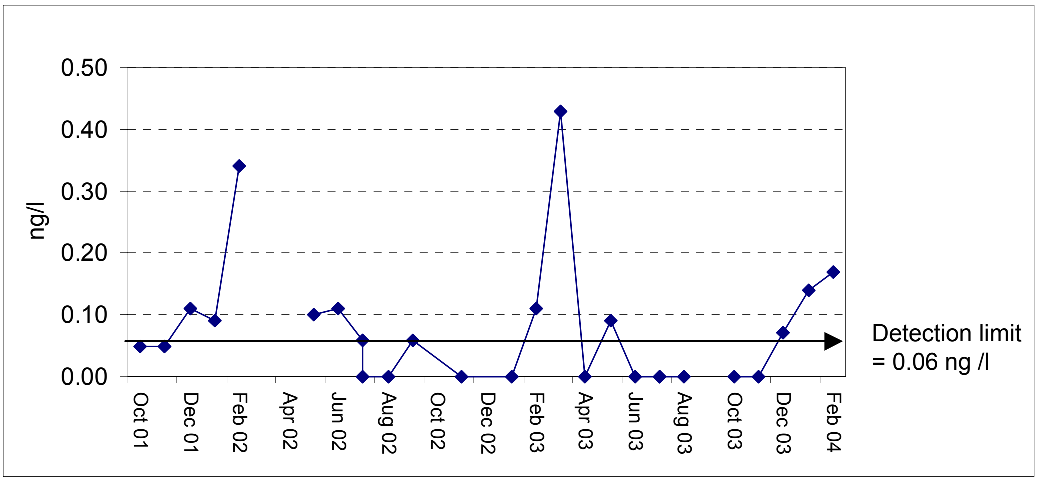


Figure 4.2.5. Methyl mercury concentrations in Lochnagar bulk deposition 2001 – 2003



Job 4.3: Annual sampling and analysis of Hg and other metals in biota and sediment trap material.

Sampling

<u>Sediment trapping</u>

Sediment trapping at Lochnagar began in 1991 as part of the AWMN programme. The sediment traps, deployed c.1m above the sediment-water interface, are a simple tube design with an internal diameter of 5 cm and an aspect ratio (length to diameter) of 7:1. Three traps are deployed together in a triangular array and are emptied annually in late summer. From 1998, an additional array of three traps has been deployed at c. 2m below the water surface in order to obtain information on the relative roles of catchment input and direct deposition. Samples prior to 1997 were preserved for diatom analysis and hence, whilst these archived samples have been analysed for trace metals (see CLAM report), these data are not wholly reliable. In 1997, for the first time, sediment trap samples were preserved specifically for trace metals analysis and this practice has been maintained ever since. Only post-1997 data are considered here. All trap samples were air-dried up to 1999 making them unsuitable for Hg analysis. From 2000, samples were freeze-dried and hence Hg data are available for this and subsequent years.

<u>Terrestrial and aquatic plants</u>

The CLAM report highlighted some plant groups that after consideration were not thought to be suitable for monitoring trace metals at Lochnagar. These included the grasses and rushes *Nardus stricta* and *Juncus sp.* and epilithic (rock-dwelling) diatoms. The latter were considered suitable for more productive systems, but at Lochnagar, the limited growth of diatoms prevented them from being useful as a monitoring tool. As a result of these recommendations from the CLAM report, the sampling programme at Lochnagar was amended for the current 'Freshwaters Umbrella' project.

Samples of the main terrestrial plant species were collected annually in late summer. These included mosses: *Pleurozium schreberi* and *Hylocomium splendens* and ericaceous species: *Calluna vulgaris, Vaccinium myrtillus* and *Vaccinium vitis-idaea.* Leaf and shoot samples for each species were collected at various locations around the catchment and then combined to form a single sample. Plastic gloves were worn during collection and the samples stored in re-sealable plastic bags. The sampled vegetation was rinsed with deionised water and stored cool until being freeze-dried prior to analysis.

Aquatic plants were collected using an Ekman grab operated from an inflatable boat, again during late summer. This grab sampling technique cannot guarantee collection of species especially as many are not growing extensively within the loch. For this reason sampling of all selected species was not always possible in every year. Intensive annual sampling of these species is to be avoided in order that data on macrophyte distribution is not affected in the biennial UK AWMN surveys. The species collected were among the following: liverworts, *Nardia compressa* and *Scapania undulata*; aquatic mosses, *Fontinalis antipyretica* and *Sphagnum auriculatum*, and the aquatic macrophyte, *Isoetes lacustris.* Once sampled by the

Ekman grab, the entire aquatic growth (whole plant excluding root) was collected, washed, freeze-dried and treated as for the terrestrial species.

Zooplankton

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

Macro-invertebrates

For the current project, the sampling and analysis of aquatic macro-invertebrates was introduced in order that further data might be obtained on the pathways of trace metals through the aquatic food-web at Lochnagar. Macro-invertebrate samples were taken using kick-sample techniques in a variety of littoral areas around Lochnagar. Suspended material was collected in a net and emptied into a sorting tray where the macro-invertebrates were picked out using stainless-steel tweezers and transferred to a plastic bag. Samples were then frozen as soon as possible, and freeze-dried prior to analysis.

Analysis

In order to measure trace metals in sediment trap and biological material, samples (c. 0.2 g) were extracted using 8 ml concentrated Aristar HNO_3 at 100°C for 1 hour in rigorously acid leached 50 ml Teflon beakers. For Hg measurements, after digestion, the supernates were carefully transferred into polyethylene tubes. The residue in the beakers was then washed with deionized distilled water and the supernates transferred into the same tubes.

Pb, Cd, Zn, Cu and Ni were measured using atomic absorption spectroscopy (AAS) whilst Hg was measured by cold vapour atomic absorption spectrometry (CV-AAS) following reduction of Hg in the digested sample to its elemental state by 2 ml fresh $SnCl_2$ (10% in 20% (v/v) HCl). Major elements, Fe, Mn, Al, Si, Ti and Ca in sediment trap samples were measured using a Metorex Xmet920 X-ray fluorescence (XRF) spectrometer.

Certified standard reference materials (Buffalo River sediment SRM2704, Stream sediment GBW07305) were digested and analysed during sample analysis. For AAS, reference materials and sample blanks were analysed every 20 samples. The standard solution was measured every five samples in order to monitor measurement stability. Our measured mean concentrations of Hg were 93 ng g^{-1} in Buffalo River sediment (n = 12; relative standard deviation (RSD) = 8.6 ng g^{-1}; certified value = 100 ng g^{-1}). The coefficient of variation and precision was < 5% for Pb, Cd and <15% for Zn, Cu, Ni. For XRF, reference materials were measured every 5 samples. Analytical detection limits for the trap and biota samples are as follows:

Hg (ng/g)	Zn (µg/g)	Ni (µg/g)	Cu (µg/g)	Cr (µg/g)	Cd (µg/g)	Pb (µg/g)
2.8	0.71	0.9	0.83	0.67	0.1	0.83

Results

Mercury (Hg)

Hg data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 4.3.1 along with lake water annual means and Hg annual deposition fluxes, for the years 1997 – 2003. In this Figure, depositional fluxes have been re-calculated (cf. Figure 4.2.4) to run from August to August in order provide a better comparison with the late-summer sampling of the biota and annual traps. The high Hg deposition flux in 2000 is due to high concentrations in the latter half of the year (Figure 4.2.1) and hence in Figure 4.3.1 the high Hg flux appears to shift to 2001 (in fact August 2000 – August 2001).

Of the terrestrial plant species, the mosses *Pleurozium schreberi* and *Hylocomium splendens* continued to show very stable levels year to year and throughout the whole monitoring period and also show comparable concentrations between the two species. Of the other terrestrial plants, *Vaccinium vitis-idaea* and *Calluna vulgaris* appear to show decreasing trends across the monitoring period with the possible exception of a high year in 2002. *Vaccinium myrtilus* also shows high Hg in 2002 although 2003 also appears to be elevated in comparison with the rest of the monitoring period.

In the aquatic species, *Isoetes lacustris* and *Sphagnum auriculatum* continue to show evidence for a decline in concentration (see CLAM report) whilst *Scapania undulata* shows little trend after a high concentration in 1997. Zooplankton continue to show concentrations elevated above those in other biota, possibly as a result of their trophic level, and also show a declining trend. Conversely, macro-invertebrates do not show elevated concentrations and appear to show an increasing concentration trend. However, the increase is only small (55 – 75 ng g^{-1}) and the monitoring period short. There is currently insufficient sediment trap Hg data to determine any trend.

Lead (Pb)

Pb data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 4.3.2 along with lake water annual means and Pb annual deposition fluxes, for the years 1997 – 2003. In this Figure, depositional fluxes have been re-calculated (cf. Figure 4.1.4a) to run from August to August in order provide a better comparison with the late-summer sampling of the biota and annual traps. The last few years appear to show an increase in both depositional flux and lake water concentrations, although for the latter this is really driven by a very high value for 2003. Figure 4.1.1 shows that a series of high concentrations over the second half of the year are the reason for this. These concentrations are the highest yet seen in the dataset.

By contrast, a lot of the biota show declining trends in Pb concentration over the period of monitoring and this is more in agreement with general trends in emission and deposition across the UK (e.g. Playford & Baker, 2000). All terrestrial plant species show declines with *Vaccinium myrtilus, Vaccinium vitis-idaea* and *Calluna vulgaris* all falling below the limit of detection in the last few years. Declining trends are also observed throughout the monitoring period for all aquatic plants although concentrations in *Isoetes lacustris* are elevated again in 2003. The aquatic fauna shows little trend although the concentrations in zooplankton do fall below detection limit in 2003. Apart from this value, as with Hg, the zooplankton show significantly higher concentrations than the macro-invertebrates. The sediment traps also show little trend and the exceptionally high 2000 value for the upper traps remains an anomaly.

Cadmium (Cd)
Cd data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 4.3.3 along with lake water annual means and Cd annual deposition fluxes, for the years 1997 – 2003. In this Figure, depositional fluxes have been re-calculated (cf. Figure 4.1.4a) to run from August to August in order provide a better comparison with the late-summer sampling of the biota and annual traps. Trends in the Cd deposition data are more ambiguous than Hg and Pb as two years of below detection limit values (2001 – 2002) are followed by the highest Cd deposition by far in the dataset. This is due to a small number of high concentration samples at the end 2002 – early 2003 (Figure 4.1.2) and therefore it is possible that this period is anomalously high set against a declining trend (1999 – 2002). 2002/2003 is also the period of highest Cd in lake water in the dataset so far, although in contrast to deposition, these data might suggest a trend of increasing Cd.

Trends in terrestrial plants are ambiguous as a number of years below the limit of detection are interspersed with higher values, including in three out of the five species, a peak concentration in 2003. However, in *Hylocomium splendens* and *Calluna vulgaris* trends are in good agreement with the three highest years in the dataset occurring since 2000 and concentrations for both species falling below the limit of detection in 2002. In general, Cd concentrations are low and therefore, slight inter-annual changes may take concentrations above or below the limit of detection in these species. This being the case, it may be that the terrestrial plants are showing evidence for an increase in concentration, but only continued monitoring will determine this.

Trends in aquatic plants appear to be more certain with all species showing clear increasing trends across the whole of the dataset, in agreement with the possible trend in lake water concentration. This is also seen to occur in the macro-invertebrate data whilst trends are uncertain for the zooplankton. 2000 remains the highest Cd concentration year in this group although 2003 also appears elevated with respect to the rest of the data. As with Hg and Pb, zooplankton concentrations are significantly higher than in the aquatic plants with the exception of *Isoetes lacustris*, which shows similar levels. However, unlike Hg and Pb, the same is true of the macro-invertebrate data. The sediment trap data also show little trend although below detection limit values have been recorded for both sets of traps during the last two years.

Zinc (Zn)
Zn data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 4.3.4 along with lake water annual means and Zn annual deposition fluxes, for the years 1997 – 2003. In this Figure, depositional fluxes have been re-calculated (cf. Figure 4.1.4a) to run from August to August in order provide a better comparison with the late-summer sampling of the biota and annual traps. As with Cd, annual mean Zn concentrations in lake water and annual Zn depositional fluxes are significantly higher in 2003 than in any other year of the dataset. Excluding this year there is little trend in either over the monitoring period.

Figure 4.3.1. Annual depositional Hg flux, mean annual lake water Hg concentration & concentrations of Hg in terrestrial and aquatic biota and sediment traps at Lochnagar. Annual depositional flux runs from August to August in order to provide a comparison with late-summer biotic & trap sampling.

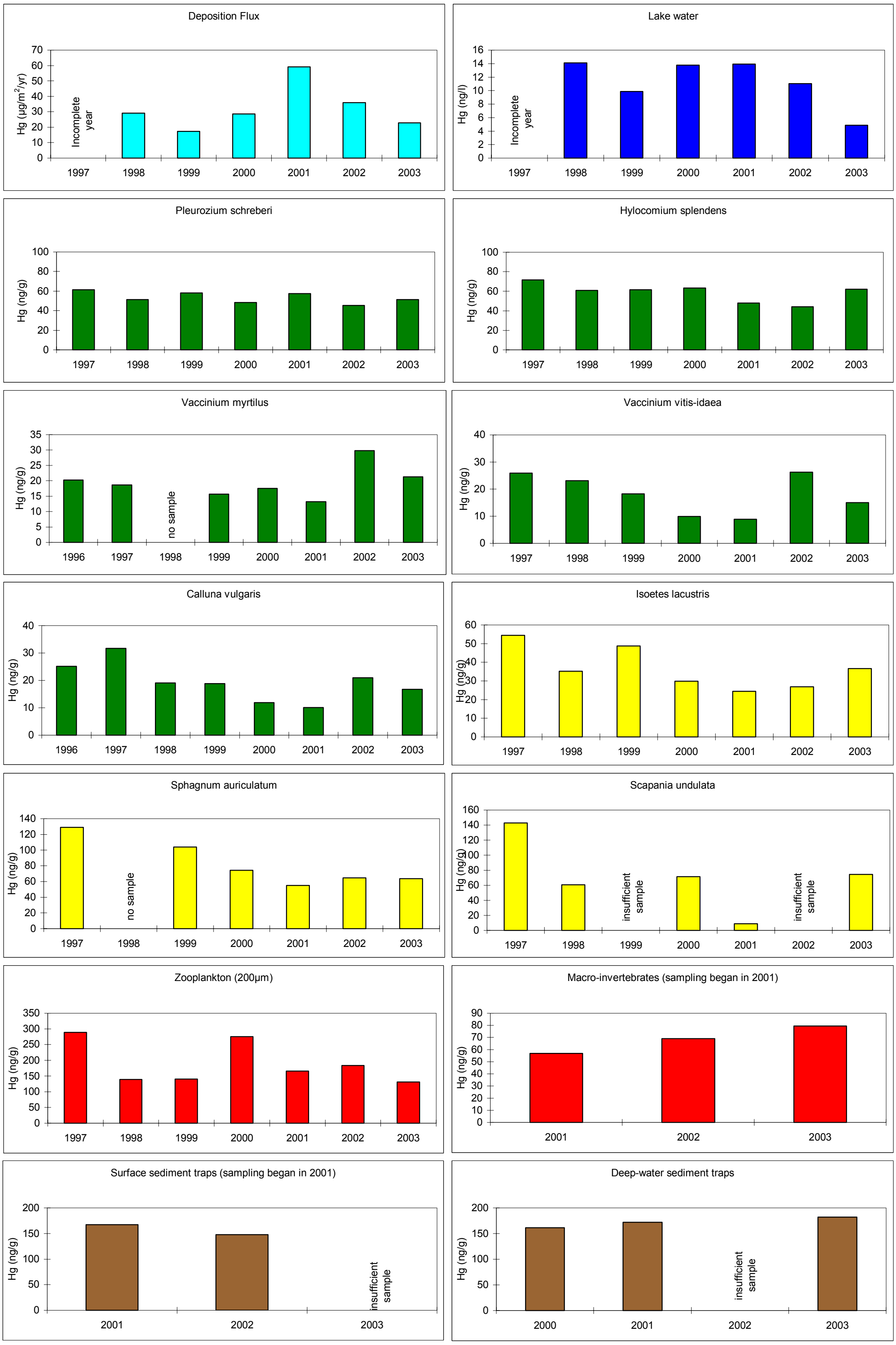


Figure 4.3.2. Annual depositional Pb flux, mean annual lake water Pb concentration and concentrations of Pb in terrestrial and aquatic biota & sediment traps at Lochnagar. Annual depositional flux runs from August to August in order to provide a comparison with late-summer biotic & trap sampling.

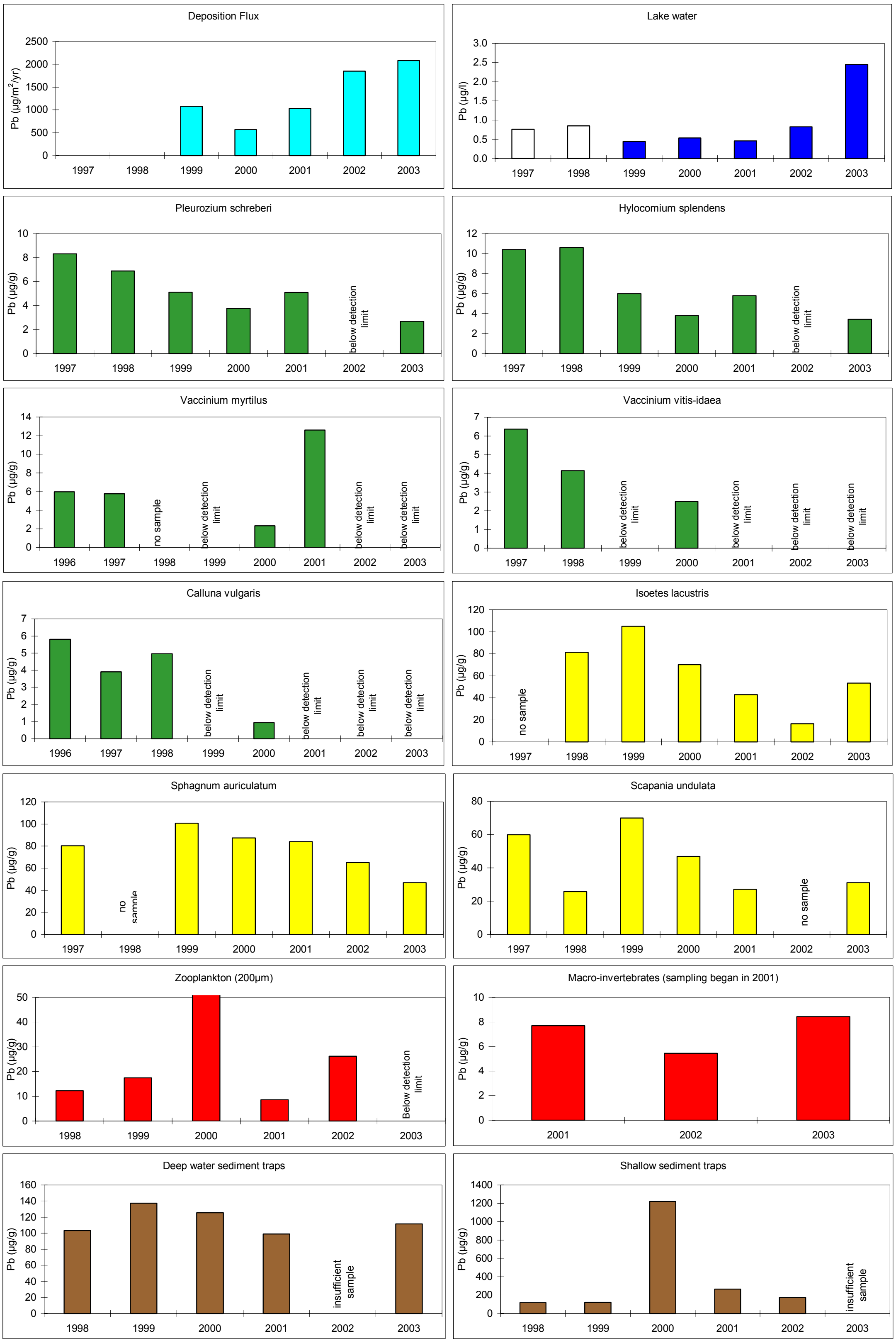


Figure 4.3.3. Annual depositional Cd flux, mean annual lake water Cd concentration and concentrations of Cd in terrestrial & aquatic biota and sediment traps at Lochnagar. Annual depositional flux runs from August to August in order to provide a comparison with late-summer biotic & trap sampling.

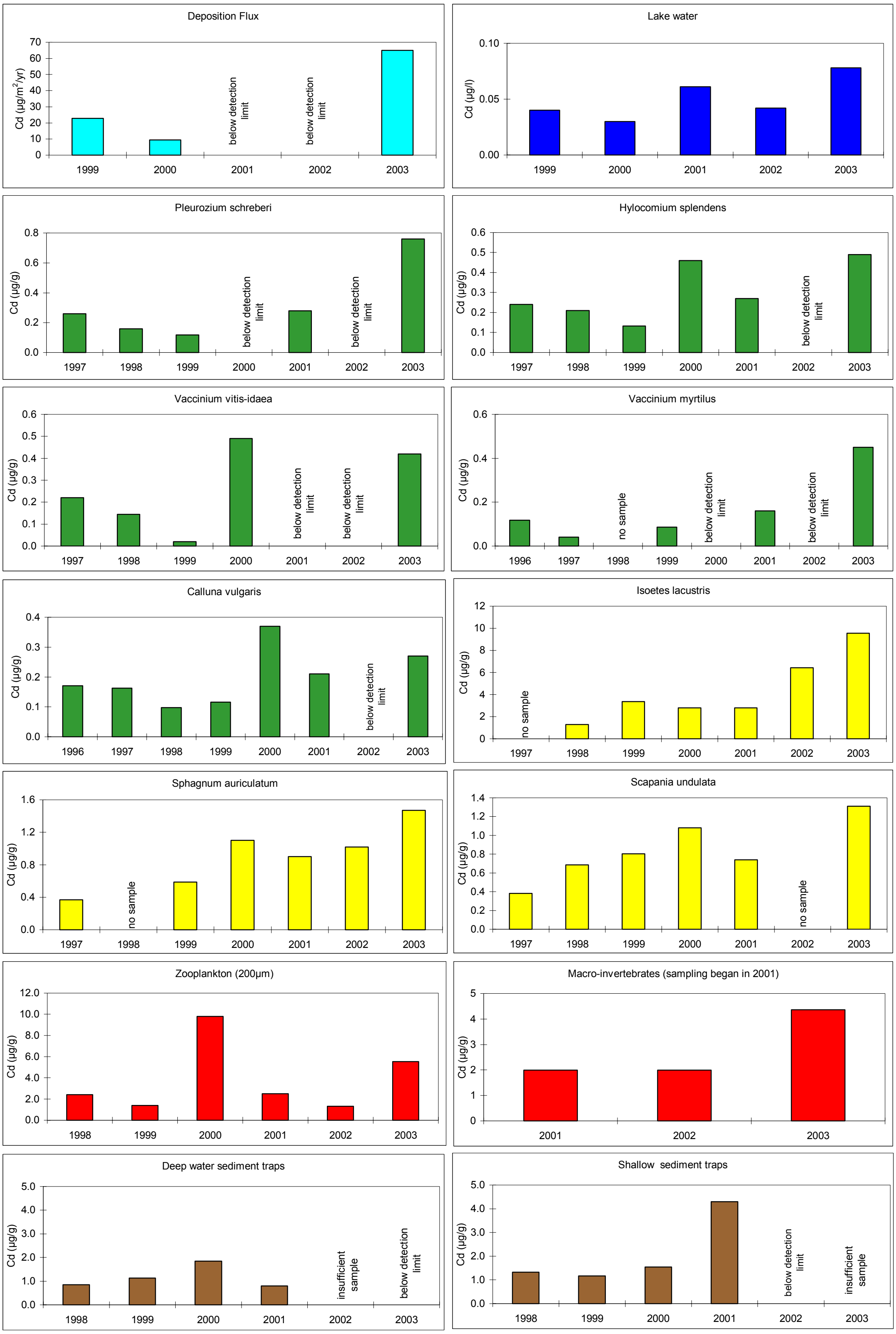
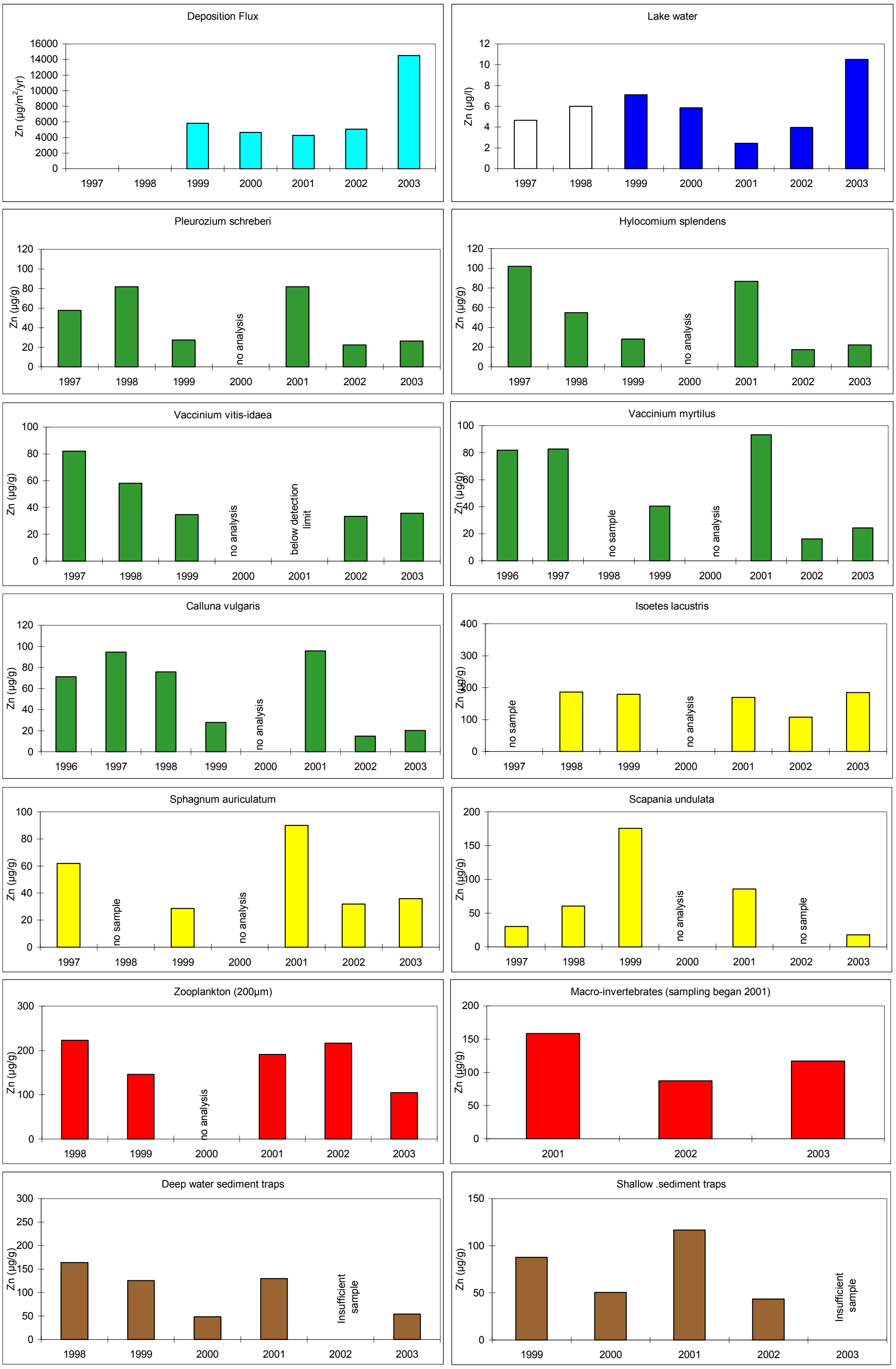


Figure 4.3.4. Annual depositional Zn flux, mean annual lake water Zn concentration and concentrations of Zn in terrestrial and aquatic biota & sediment traps at Lochnagar. Annual depositional flux runs from August to August in order to provide a comparison with late-summer biotic & trap sampling.



The terrestrial plants show similar trends with each other. With the exception of *Vaccinium vitis-idaea*, which shows a concentration below the limit of detection, all other terrestrial species show high values in 2001. However, 2001 appears to be a high anomaly set against a trend of declining concentrations in all species. Neither aquatic flora nor fauna shows any trend and unlike the other metals discussed above, the zooplankton and macro-invertebrate concentrations show similar levels to those of the aquatic macrophytes. The sediment traps may show a declining trend, though as with the terrestrial plants 2001 appears to be a high year, especially in the surface sediment traps.

Copper (Cu)
Cu data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 4.3.5 along with lake water annual means and Cu annual deposition fluxes, for the years 1997 – 2003. In this Figure, depositional fluxes have been re-calculated (cf. Figure 4.1.4a) to run from August to August in order provide a better comparison with the late-summer sampling of the biota and annual traps. As with Pb, Cd and Zn, 2003 appears to have been high for both annual depositional Cu flux and mean annual lake water Cu concentrations. Both parameters fell below the limit of detection for much of 2001 and concentrations and fluxes have increased in the two years since then. It is therefore uncertain whether there is an increasing trend in Cu or not. Certainly the 2003 values are the highest in the dataset.

Terrestrial plant Cu concentrations show little trend although *Vaccinium vitis-idaea* may show declining concentrations since 1999. Interestingly, in the CLAM report, covering the early monitoring period, there was also little trend observed in the terrestrial plants, apart from a possible Cu increase in *Vaccinium vitis-idaea.* Once again, this shows the value of long-term monitoring data. The same is true of the sediment trap data. In the CLAM report it was suggested that there was an increasing concentration trend in both surface and deep traps. However, as Figure 4.3.5 shows, over the longer dataset, there are no clear trends in the trap data. Aquatic flora and fauna also show no clear trends. *Isoetes lacustris* and *Scapania undulata* may show declining trends in Cu concentration since 1999, whilst Cu concentrations in *Sphagnum auriculatum* show little trend except an exceptionally high Cu concentration in 2000. This high value also occurs in the zooplankton, set against a background of little obvious trend, whilst the shorter macro-invertebrate dataset increases over the three year period since monitoring began.

Nickel (Ni)
Ni data for the terrestrial and catchment plant species, macro-invertebrates and zooplankton are shown in Figure 4.3.6 along with lake water annual means and Ni annual deposition fluxes, for the years 1997 – 2003. In this Figure, depositional fluxes have been re-calculated (cf. Figure 4.1.4a) to run from August to August in order provide a better comparison with the late-summer sampling of the biota and annual traps. As with Pb, Cd, Zn and Cu, 2003 appears to have been high for both annual depositional Ni flux and mean annual lake water Ni concentrations. Both parameters fell below the limit of detection for much of 2002 and concentrations and fluxes increased again in the following year. It is therefore uncertain whether there is any trend in Ni although the 2003 values were the highest in the dataset.

Figure 4.3.5. Annual depositional Cu flux, mean annual lake water Cu concentration and concentrations of Cu in terrestrial and aquatic biota & sediment traps at Lochnagar. Annual depositional flux runs from August to August in order to provide a comparison with late-summer biotic and trap sampling.

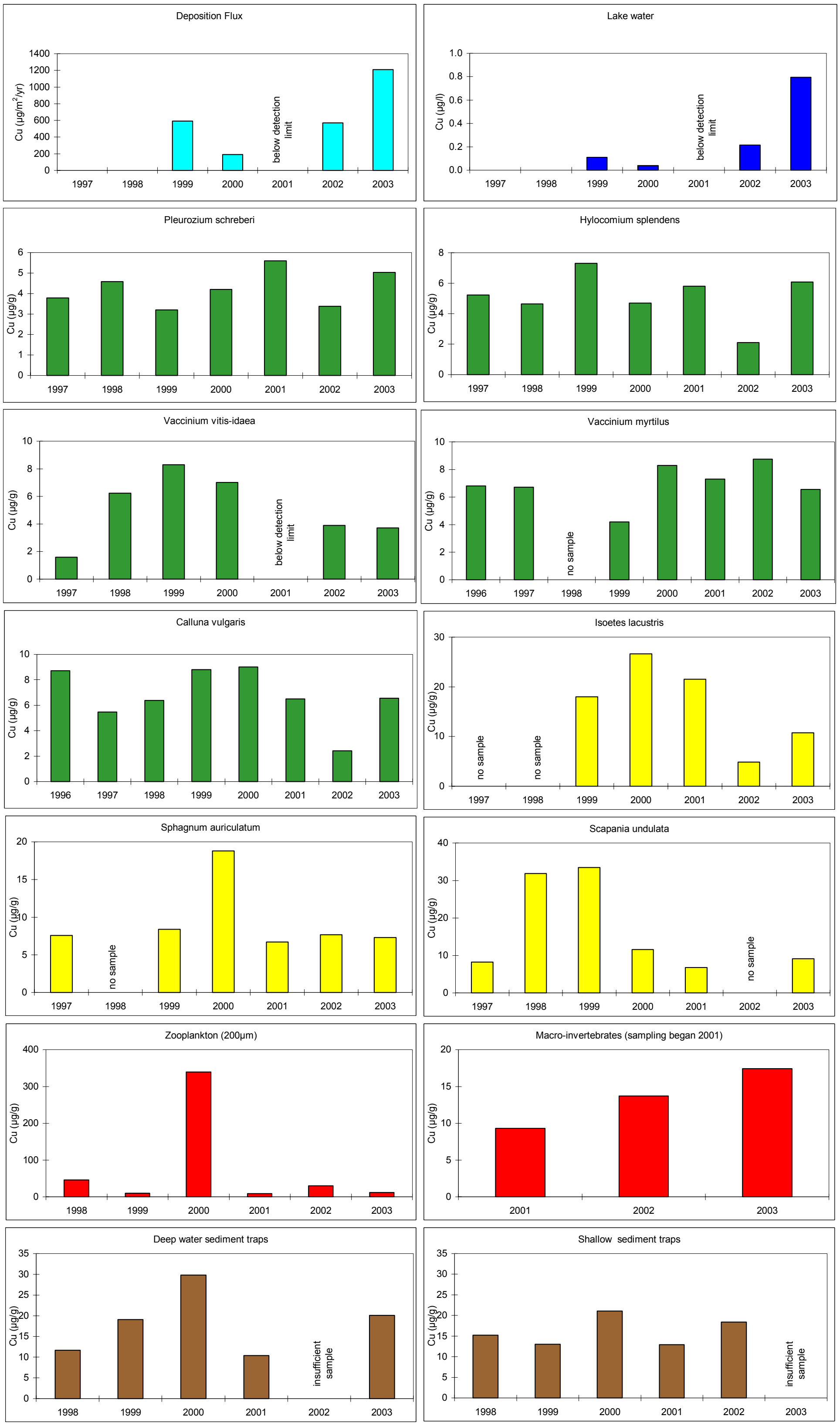
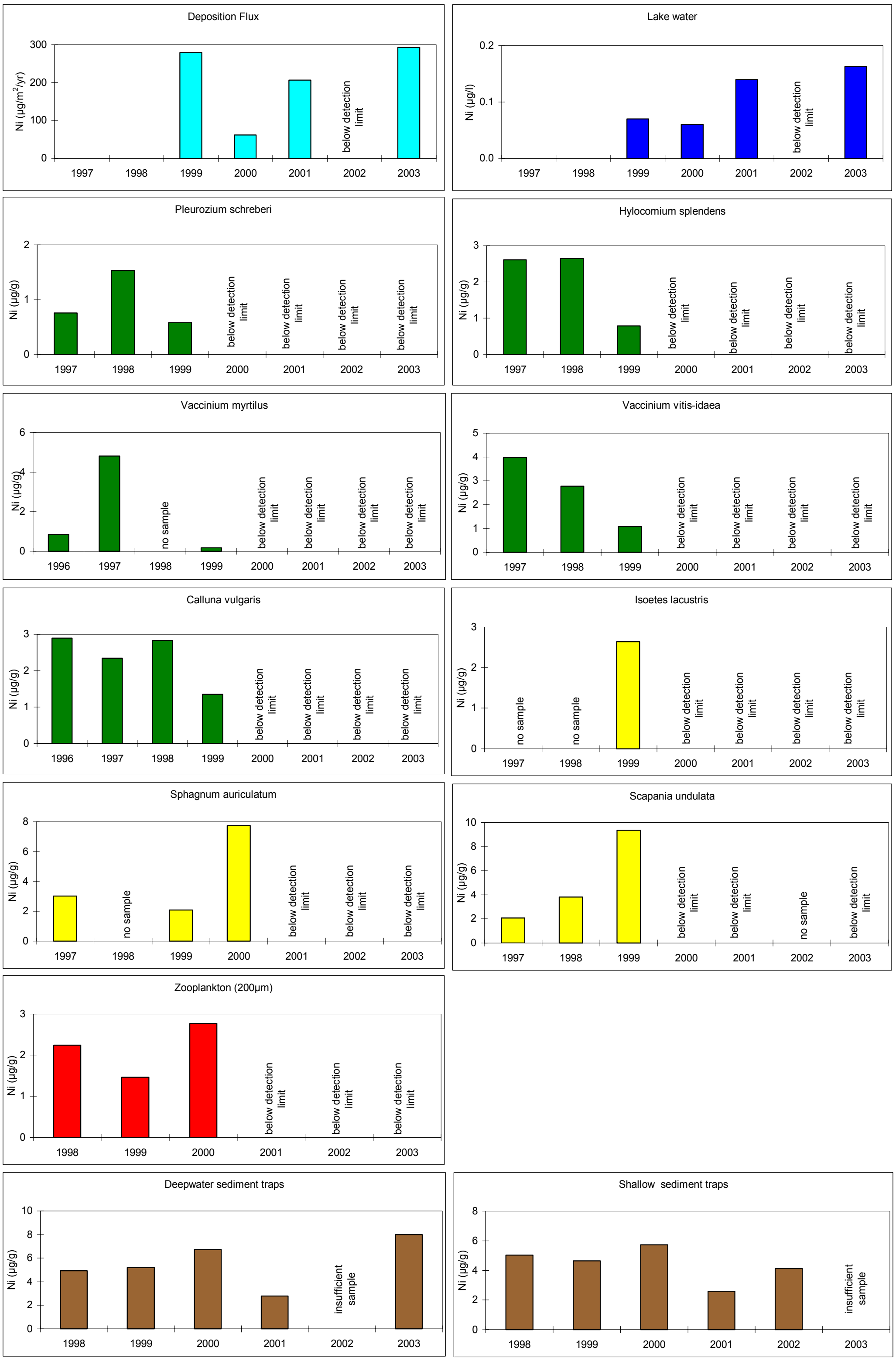


Figure 4.3.6. Annual depositional Ni flux, mean annual lake water Ni concentration and concentrations of Ni in terrestrial and aquatic biota & sediment traps at Lochnagar. Annual depositional flux runs from August to August in order to provide a comparison with late-summer biotic & trap sampling. Macro-invertebrate data (sampled since 2000) are all below detection limit).



For all terrestrial and aquatic biota, Ni concentrations were below the limit of detection for the whole of the project period. The only levels above detection limit therefore occur during the CLAM project and this suggests a decline in concentration over the full monitoring period. Macro-invertebrate monitoring, introduced to the programme following CLAM, has failed to show any concentrations above the limit of detection and hence results are not included on Figure 4.3.6. By contrast, Ni continues to be measurable in sediment traps where there is little indication of a trend. As with the lake water and deposition flux, 2003 was the peak year for the deepwater traps whilst insufficient sample weight prevented the full suite of analyses in 2002. The recent introduction of a large diameter trapping array should prevent this from happening in the future.

Discussion

The 'Freshwaters Umbrella' project has allowed an additional three years of data to be added to the trace metals monitoring completed by CLAM at Lochnagar. Although some aquatic macrophyte samples were not collected for the reasons outlined above, and bad weather prevented the occasional collection of lake water and bulk deposition samples during winter, in general this has been an additional three complete years of data. Furthermore, there have been no analytical problems and all data are thus reliable and accurate. These new data are invaluable in confirming trends and resolving issues identified in the CLAM report. For example where Hg in bulk deposition was thought to be increasing it can now be seen that this was driven by some elevated values in the latter half of 2000. The longer dataset can now reveal that the trend is for a decrease in deposited Hg. Similarly, Cu concentrations in some terrestrial and aquatic plant species showed increases across the CLAM dataset which with the benefit of three further years can now be seen to be in decline. These two examples show the benefits that only longer term monitoring can bring and our confidence in trends observed within the current dataset can only become greater the longer monitoring is permitted to continue. The move of this trace metal monitoring to the UK AWMN and the longevity this will bring can therefore only be a good thing.

In the meantime, whilst the current dataset remains unique within the UK and probably Europe, it still remains too short to attempt any statistical work on the temporal trends. However, over the next AWMN contract this dataset will hopefully reach ten years and then this can be attempted. In the meantime, obvious trends are simply, but cautiously, identified by eye. With this in mind, Table 4.1 summarises those trends observable from Figures 4.3.1 – 4.3.6. Macro-invertebrate trends should be treated with still more caution as, having been introduced in the current project, they only cover three years data and are thus at the same stage that the rest of the dataset was at the end of CLAM.

It is apparent that the trends are more complex than was first assumed at the end of CLAM. In this earlier project a number of terrestrial and aquatic macrophytes were shown to be in "good agreement" with trends in metal depositional fluxes and lake waters. Table 4.3.1 shows that this is now more usually not the case, although where there are clear trends, for example in the decrease in Hg, a number of biological tools continue to show "good agreement". However, the examples of Pb, and to a lesser extent Ni, are intriguing, as where many biota are showing clear declines, those drivers to which they are presumably responding (depositional fluxes and / or lake water concentrations) show either no trend or the opposite trend. The next phase of monitoring is therefore crucial. Not only will this permit further years of data to be added to help resolve these issues, but the implementation of statistical tests will permit, not only the more rigorous identification of any trends, but also the significance of any decrease or increase. Thus, where we may identify a "clear" trend the change may not be statistically significant and this may explain why similar trends are not observed in other compartments.

These ambiguous trends are not confined to our dataset. For example, data for trace metals in atmospheric deposition at Banchory (c. 30km from Lochnagar) (Playford & Baker, 2000) show that following a period of major decline since the 1970s, during which time trends were very clear, recent annual data show low concentrations, but little continuing trend. Selecting any 3 – 5 year period within the last ten years could provide evidence for trace metal deposition increases, decreases or no change depending on which section was selected. It is only by viewing the data over a long period that these changes can be put into their correct context. It is therefore important not to try and "over-interpret" every increase and decrease in our current dataset, as these may well turn out to be short-term phenomena. More important is to try and maintain this monitoring so that real trends become apparent over the longer-term.

The introduction of the macro-invertebrates into the monitoring at the start of this current project was intended to provide more information on the movement of metals through the food-web. CLAM data had shown that zooplankton data were considerably elevated above those of aquatic macrophytes and epilithic diatoms and it was thought that this might possibly be due to the different trophic levels of these groups. The introduction of macro-invertebrates was thus expected to provide further supporting data for this but this has not been seen to be the case. In most cases it can be seen that macro-invertebrate data show similar concentrations to those of the aquatic macrophytes and considerably lower than those of the zooplankton. The exception is for Cd where macro-invertebrates showed similar levels to those of zooplankton.

Further investigation is therefore required to determine why this should be the case. Over the next period of monitoring we will attempt to do this by attempting to analyse the macro-invertebrates at a more species specific level, whilst there is a possibility that $\delta^{15}N$ measurements could be undertaken in order to ascertain the true trophic level of each of these groups. The final and highest level of the food-web at Lochnagar is the impoverished fish population. Sampling of fish at Lochnagar was undertaken as part of the EMERGE project, but the population is so small that they could not be included in a monitoring programme. However, the metals data from this study should soon be available for us to compare with the rest of the food-web and although these data are, of necessity, one-off samples, they will provide interesting comparative data for the rest of our dataset.

One further issue of interest is exemplified by the case of Ni in our dataset whereby, with the exception of the sediment trap samples, concentrations were below detection limit for all compartments for the whole three years. The usefulness of continuing monitoring in these situations is thus open to question. For how long are below detection limit values useful? For sure, it is good to know that levels of deposited pollutants are very low and it maybe that once such a situation has been attained for a period of years then the monitoring frequency for that pollutant could be reduced. We will continue to monitor Ni over the next few years as it is still measurable in sediment traps and concentrations in deposition and lake water appear to have increased to above detection limit again over the last year. This situation will be kept under review.

Finally, whilst the value of the Lochnagar dataset is beginning to be realised and temporal trends are starting to emerge (e.g. MeHg) or become more resolved, currently, it is unknown how the levels in the various compartments at Lochnagar compare with other upland and acid sensitive sites across the UK. Further, it is unknown whether these trends are typical of UK upland waters or an isolated example. Therefore, apart from the enormous value of a metals dataset from a second site, expanding this monitoring to an additional location would increase the value of the ongoing long-term Lochnagar dataset and also allow us to have more confidence in our interpretations of those observed trends. It is to be hoped that the move of the Lochnagar monitoring to the UK AWMN might allow that at least one additional site might be included in this metals monitoring programme and, with the wealth of background data already available, AWMN sites are the obvious candidates for this extended work. Not only are they comparable to Lochnagar in terms of altitude, lack of direct impact etc., but they also provide a good spatial distribution across the UK and as a consequence a broad depositional gradient from high deposition sites in the Lake District to the more ‘pristine’ north-west of Scotland. Resources permitting, sites which would be of great value in a metals monitoring “proto-Network” would be Scoat Tarn (Lake District, high deposition) Llyn Llagi (Wales, high altitude, providing deposition gradient mid-way between Lochnagar and Scoat Tarn), Loch Coire Fionnaraich (NW Scotland, low deposition ‘reference’ site) and Blue Lough (AWMN site in Northern Ireland).

Conclusions

- Up to the end of 2003, we have up to 7 years of high quality data for trace metals in a rage of ecological compartments at Lochnagar including: bulk deposition, lake waters, terrestrial and aquatic plants, aquatic invertebrate fauna and sediment traps.

- Few of the potential trends identified at the end of the CLAM project have been shown to continue whilst most have been shown to be short-term phenomena emphasising the need for long-term monitoring data prior to any attempt at statistical interpretation.

- With this in mind, recent lake water and deposition data lead to an ambiguity in trends. In particular, 2003 is seen to be unusually high for most metals, except Hg. Although these high fluxes are not due to unusually high rainfall, it is likely that this is an anomaly. The declining trend in Hg is observed over a period of years and is more likely to be “real”.

- Similarly, Pb in both lake water and bulk deposition appears to have been increasing over a number of years, although this is in contrast to most biota Pb data which appear to show declines over the monitoring period.

- The lack of clear trends is probably a result of two factors. First, the short lifetime of the monitoring period and second, current low levels of metal emission and deposition following decades of considerable decline. Long-term monitoring will resolve both these issues.

- Intra-annual methyl Hg data are beginning to show intriguing temporal trends with elevated levels in winter deposition. The reason for this is unclear and this pattern is not known to be observed elsewhere.

- Nickel levels have been below detection limit for a number of parameters over the period of the project, although have been seen to increase slightly over the last year in deposition and lake water. However, Ni levels remain detectable in sediment trap data. This situation will remain under review as long periods of below detection limit values are of limited use.

- Whilst the Lochnagar data are valuable and continuing this monitoring remains a priority, their usefulness and our confidence in observed trends would be increased by the introduction of monitoring at other sites. It is hoped that the move of the trace metal monitoring at Lochnagar to the UK AWMN will allow this expansion to occur.

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Table 4.3.1: Summary of metals monitoring trends 1997 – 2003.
*** Data for macro-invertebrates covers 2001 – 2003 only**
↓ denotes decreasing trend; ↑ denotes increasing trend; ↔ denotes no change; ? denotes uncertainty in trend direction.

	Annual Deposition Flux	Mean annual lake water	*Pleurozium schreberi*	*Hylocomium splendens*	*Vaccinium myrtilus*	*Vaccinium vitis-idaea*	*Calluna vulgaris*	*Isoetes lacustris*	*Sphagnum auriculatum*	*Scapania undulata*	Zooplankton	Macro-invertebrates	Upper sediment traps	Deep sediment traps
Hg	↓?	↓	↔	↔	↔	↓	↓	↓	↓	?	↓?	↑*	?	?
Pb	↑	↑	↓	↓	↓?	↓	↓	↓	↓	↓	?	↔*	↔	↔
Cd	↓?	↑?	?	↑?	?	?	↑?	↑	↑	↑	↔	↑*	?	?
Zn	↔	?	↓	↓	↓?	↓	↓	↔	↔	?	↔	↔*	?	↓
Cu	↑?	↑?	↔	↔	↓?	↔	↔	↓?	↔	↓	↔	↑*	↔	↔
Ni	?	?	↓	↓	↓	↓	↓	↓	↓	↓	↓	?*	↓?	↔