The present is the key to the past, but what does the future hold for the recovery of surface waters from acidification?

R.C. Helliwell[a], and G.L. Simpson[b]

[a]Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK
[b]Environmental Change Research Centre, University College London, Department of Geography, Pearson Building, Gower Street, London, WC1E 6BT, UK

Corresponding author. r.helliwell@macaulay.ac.uk, tel: 0044 (0)1224 395152, fax: 0044 (0)1224 395010

Abstract

Analogue matching was used to identify close modern water quality analogues for a set of 59 acid-sensitive lakes in the Galloway region of south west Scotland. Modern analogues were identified that closely matched the pre-disturbance conditions of these lakes using simulated water quality parameters from the MAGIC (Model of Acidification of Groundwater in Catchments) model for key years from 1860-2100. The lakes were matched with hydrochemical samples from a large spatial data set in the UK. For the majority of the 59 lakes, several close modern analogues were identified from the training set for specified years. The close modern analogues for the reference year (1860) were predominantly located in north-west Scotland, an area of low acid deposition and high-status water quality. A clear recovery in the regional surface water acid neutralising capacity (ANC) was simulated by MAGIC in 2015 compared to the situation in 1970 at the height of acid emissions. Predicted trends in surface water chemistry from present day to 2015 indicate some improvement in water quality with c. 23±0.97 % recovery towards pre-acidification (1860) ANC for the region.

Output from the MAGIC model was used with the analogue technique to investigate the combined influence of future changes in deposition and climate on biogeochemical processes and water quality at the Round Loch of Glenhead (RLGH). Our results demonstrate that pre-acidification restoration targets will not be achieved by simply reducing acid deposition, and climate change will further confound the beneficial effects of deposition reductions. Results for 2015 and beyond show that modern analogues for these periods were predominantly concentrated in North Wales, with some in north-west Scotland, Galloway and the Lake District. Evidence from model simulations and modern analogues indicate that more stringent measures to further reduce acid deposition and combat climate change in the future are necessary if the majority of lakes in the Galloway region are to be restored to their pre-acidification target chemistry. The identified analogues for selected periods may be used to study wider ecological conditions to better define reference conditions and future recovery trajectories. That modern analogues were identified for the simulated chemistry in 2100 at RLGH suggests that unprecedented chemical conditions are unlikely to be observed as a result of future climate change.

Keywords

Acidification, chemical recovery, analogue matching, climate change, Galloway region

1. Introduction

Surface water acidification was recognised as a major environmental problem in many parts of Europe and North America during the 1970s and 80s. This recognition has resulted in national and international action to reduce the emissions of acidifying pollutants, which have resulted in a decline in acid deposition. In response, acidified surface waters have begun to show signs of chemical recovery, with declining concentrations of sulphate (SO_4) and increasing pH and acid neutralising capacity (ANC) (Skjelkvåle et al., 2005). Surface water recovery is defined as being a set of conditions whereby the hydrochemistry has returned to its pre-acidified status or to some status that no longer poses a risk to biotic integrity.

This definition is in line with the EU Water Framework Directive (WFD) (European Commission, 2000) that commits Member States to achieve good surface water status by the year 2015. In support of future re-negotiation of emissions agreements to meet these targets, the Model of Acidification of Groundwater in Catchments (MAGIC, Cosby et al., 2001) is one of the key models used to assess time scales of recovery into the future at a European scale (UNECE 2008). The large scale application of dynamic biogeochemical models such as MAGIC have been instrumental in gauging the potential compliance of water bodies to chemical and biological targets in 2015 according to the WFD relative to pre-acidification conditions (Helliwell et al., 2003).

While MAGIC is effective in predicting recovery of soil and surface waters in response to given scenarios of acid deposition (Wright et al., 2005), there are few studies that have investigated the effects of climate change on chemical recovery (Wright et al., 2006). Most dynamic model applications operate on the basis that, apart from changes in acid deposition levels, other factors remain constant. Recently, concerns have been raised regarding the exposure of aquatic ecosystems to a wide variety of impacts and confounding factors such as global climate change (Skjelkvale and Wright, 1998), land-use change, physical manipulation, and other pollutants such as toxic metals (Rose and Rippey, 2002). Confounding factors may be defined as environmental factors that alter the relationship between acid deposition and runoff acidity over time (Evans, 2005). There is a high probability that over the next few decades climate will change and have a confounding effect on chemical recovery, but the rate and extent of change will be dependent on the pollutant and the sensitivity of the ecosystem in question (Posch, 2002). Numerous climate-related effects on surface water chemistry have been identified but few dynamic model applications account for simultaneous changes in climate and deposition. These climate driven processes can affect surface water chemistry, directly as well as indirectly through changes in vegetation and soils of the terrestrial catchments (Wright et al 2006; Evans, 2005). While the mechanisms behind these changes are not specifically incorporated in current versions of acidification models due to a number of complex interactions, Wright et al (2006) conducted a series of sensitivity trials to explore the relative importance of various climate-induced changes on runoff acidity using the MAGIC model. The approach adopted by Wright et al (2006) forms the basis for the climate change assessment discussed here.

Palaeoecological information has been effectively used in the validation of MAGIC simulated water quality from pre-acidification times (Battarbee et al 2005) thereby increasing the confidence in the predictive capability of the model. The main challenge of many techniques that aim to reconstruct past chemical and biological conditions is the lack of information regarding what the appropriate reference state of surface waters should be as there are invariably few, if any, reliable records that predate the onset of change. However, significant progress in using palaeoecological data to define pre-acidification conditions has been made through identifying modern analogues, which are studied to investigate pre-impact conditions in surface waters (Flower et al., 1997; Simpson et al., 2005). MAGIC-simulated hydrochemical parameters can be compared with hydrochemical data from a modern spatial data set with that same set of parameters using the analogue matching technique to identify so-called modern analogues for past or future conditions. These modern analogue lakes may then be studied to gain understanding of components of the ecosystem that are difficult to model or for which data are currently unavailable. Modern analogues are a rich source of ecological information upon which to base future restoration or recovery targets (e.g. Simpson et al 2005). Furthermore, if no modern analogues exist for future simulated conditions, this suggests environmental conditions may in the future move beyond natural environmental ranges, with unknown consequences (e.g. Stralberg et al 2009). One advantage of a dynamic model such as MAGIC over palaeoecological approaches is that the models can be used to provide forecasts or simulations of future conditions as well as historical simulations (hindcasts).

By combining output from the MAGIC model with the analogue matching approach there is potential to identify reference lakes from the modern water chemistry dataset to guide the decision making process of environmental managers based on water quality standards of reference lakes. As few, if any, long-term monitoring data are available for the pre-acidification status of acidified lakes, modern analogues and palaeoecological data are generally the only source of information on the environmental and ecological conditions expected prior to acidification. Whilst this principle can be applied to future conditions, confounding factors may perturb surface waters into states not previously encountered and as a result we may lose modern analogues that represent pre-acidification conditions in presently acid lakes as represented in the modern water chemistry database (Skelkvale and Wright, 1998; Simpson et al 2005). However, as long as the effects of these confounding factors are adequately simulated within dynamic models, the modern analogues for future hydrochemical conditions provide a means to study the entire ecosystems of the analogues and thus gain insights into future ecological status.

In this paper we apply analogue matching for key periods (described in section 3.3) of long term modelled data from 1860 to 2100 for a suite of lakes in the Galloway region of south-west Scotland. We compare MAGIC simulated hydrochemistry with a large modern hydrochemistry dataset covering the whole of the UK to identify appropriate modern analogues. The Round Loch of Glenhead (RLGH) was selected from the regional assessment to demonstrate how this approach can be used to assess the efficacy of the Gothenburg protocol on surface water recovery from acidification; and the integrated effect of deposition and climate change perturbations on water quality in the future.

The objectives of this study were to a) identify analogue lakes from a modern training set of water quality based on MAGIC simulated data from 1860 to gain a better understanding of achievable restoration targets for 59 lakes in the Galloway region and b) to identify analogues based on future projections of water chemistry based on acid deposition reductions and the effects of climate change. Combined, these results will facilitate the setting of realistic water quality guidelines. Such information is potentially highly informative to the assessment of the current and future status of chemical recovery in south-west Scotland, and to evaluate the success or otherwise of emission abatement strategies.

2. The study area

The location of 59 sites on two major geological types in the Galloway region is shown in Figure 1 and a summary of the catchment characteristics is shown in Table 1. The catchments were selected to represent a regional distribution of acidified lakes in relation to acid deposition, forest cover, soil type and geology. The region is acid sensitive, with highly siliceous granitic bedrock covered by either organo-mineral soil or organic rich acidic soils, which offers only limited ability to neutralise acid inputs from the atmosphere (Wright *et al*., 1994). Granitic bedrock, found at high elevations, is resistant to weathering, and provides a relatively low supply of base cations to neutralise acidic deposition, compared to the greywackes at lower altitude that are relatively base rich.

Decades of acid deposition and large-scale afforestation in the mid 20th century have exacerbated the problem of soil and water acidification in the region (Puhr et al., 2000). To the south and west of the region, moorland communities predominate. Fifty nine sites in the region of Galloway are used in the analogue matching procedure to identify suitable analogues for a lake region known to have been significantly affected by acid deposition. In addition modern analogues were identified on the basis of their match to model predictions of hydrochemistry based on deposition and climate change impacts on biogeochemical processes at a small intensively studied catchment located in the Merrick mountains namely the Round Loch of Glenhead (RLGH). This site was selected principally because it is a key site in the UK Acid Water Monitoring Network ((UKAWMN) which was established to assess the effect of emission reductions on selected acid sensitive freshwaters), and because over the past 21 years there has been significant developments in terms of techniques for palaeolimnological reconstructions that have been used to validate hindcast MAGIC simulations for surface water pH (Battarbee et al., 2005, 2008).

3. Methods

3.1 The MAGIC model

MAGIC is a process-orientated model, developed to predict the long-term effects of acidic deposition on soil and surface water chemistry (Cosby et al., 2001). The model consists of; (i) soil-soil solution equilibrium equations in which the chemical composition of the soil solution is assumed to be governed by simultaneous reactions involving cation exchange, dissolution and speciation of inorganic and organic carbon; and (ii) mass balance equations in which fluxes of major ions to and from the soil and surface water are assumed to be governed by atmospheric inputs, mineral weathering, net uptake by biomass and loss in runoff. Recent work on UK upland lakes (Cooper and Jenkins, 2003) has demonstrated a direct link between S input and output fluxes, confirming that in-catchment processes have a minor impact. Therefore, SO_4 was treated as 'pseudo-conservative', with current surface water outputs equal to deposition inputs. MAGIC produces long-term reconstructions and predictions of soil and surface water chemistry in response to scenarios of acid deposition, land use and climate change (with regard to the Round Loch of Glenhead). Nitrogen dynamics within the model embrace the N saturation concept (Stoddard, 1994) with the inclusion of dynamic equations for N cycling. The introduction of a soil organic 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 being nitrification (biological conversion of NH_4^+ to NO_3^-) and immobilisation (Gundersen *et al*., 1998; Jenkins *et al*., 2001). For this study, MAGIC was applied on an annual time-step. Soil physico-chemical parameters were represented as a single soil box (by weighting soil data vertically and spatially within the catchment), with a number of simplifying assumptions. Note that, in the model and throughout this paper, ANC is calculated using the charge balance definition, as the sum of base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+) minus the sum of acid anions (Cl^-, SO_4^{2-} and NO_3^-).

3.2 Model Calibration

The MAGIC calibration procedure followed is that documented by 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).

3.3 Acid deposition and land use sequences

Historic sequences of anthropogenic S, NOx and NHy deposition were obtained by scaling current deposition to reconstructed emission sequences (Bettelheim and Littler 1979; Warren Spring Laboratory 1987; Simpson et al. 1997). For the period 1980 to 2000, deposition records from Eskdalemuir, south-west Scotland were used to refine deposition sequences. The calibration year was 2000. Sulphur and nitrogen deposition forecasts were based on projections from the FRAME model and represent the current legislation scenario (CLE). CLE is based on the Gothenburg protocol (Multi-Pollutant Multi Effects Protocol aimed at reducing the exceedance of critical loads for S, N and Ozone in sensitive areas) to the UN-ECE Convention on Long-range Transboundary Air Pollution and other national and EU legislation. Modelled data represent important periods in the transition of ecosystems from pristine to acidified to the recovery stage, these include the pre-acidification condition (1860); period of maximum acid emissions (1970); ‘present day’ (2000), the year to achieve good ecological status of surface water under the WFD (2015), full implementation of CLE (2030) and long term forecast (2100).

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 in acid sensitive areas of the UK 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 were constructed for the key driving variables based on a 50 year crop rotation (Helliwell et al., 2003). Calibration of the MAGIC model with these deposition and land use sequences provides the basic model setup behind the ‘Base Case’ scenario.

3.4 Climate perturbations

Details of climate perturbations were published as part of a pan-European study by Wright et al., 2006. In the current study the same principles were adopted at the Round Loch of Glenhead. The general purpose of the sensitivity trials was to investigate the relative importance of future changes in climate on various biogeochemical processes using the MAGIC model. Thus the biogeochemical processes were tested sequentially, and the magnitude of perturbation was chosen to be sufficiently large and rapid to encompass a major climate change, but yet not completely unrealistic with respect to possible scenarios of climate change for the next 100 years. The extent of change for the perturbations investigated here was largely informed from experimental manipulations and other relevant research (Wright et al 2006). The justification for testing the sensitivity of a selection of climate driven biogeochemical processes is covered in detail by Wright et al (2006). Details of the climate induced biogeochemical perturbations used at the Round Loch of Glenhead are summarised in Table 2. The direction and magnitude of future biogeochemical projections were based on evidence from a number experimental and manipulation studies throughout the UK and Europe (Wright et al 2006). To assess the overall impact of climate perturbations on biogeochemical processes and future surface water chemistry, all sequences from the trials reported by Wright et al (2006) were modelled simultaneously. These data were used to identify analogues of future water quality that are driven by reductions in acid deposition and climate change, namely ‘All perturbations’ in Table 2.

3.5 Modern analogue approach

Analogue matching (Overpeck et al., 1985; Flower et al., 1997) is a palaeoecological technique used to identify the *k*-closest sites from a modern set of lakes that are most similar, in terms of a suite of variables or parameters, to the impacted lake prior to the onset of change. The *k*-closest sites are selected on the basis of their similarity to organisms in the target sample that are preserved in lake sediments, and are known as modern analogues. The pre-impact or reference condition flora and fauna for the target lake can then be inferred on the basis of the species found living in the modern analogues today (Simpson et al., 2005). Here we replace matching on biological variables with matching on hydrochemical variables. The identification of modern analogue sites involves the use of similarity or distance coefficients to determine how similar any two sites are in terms of a set of descriptor variables, and the process is known as analogue matching. Numerous similarity or distance coefficients have been developed to deal with different types of descriptors. Euclidean or Manhattan metric distance coefficients are appropriate for the analysis of hydrochemical data in cases where the descriptors are all quantitative, though may be unsuitable for variables that differ markedly in scale unless suitably transformed. Gower (1971) proposed a general coefficient of similarity, in which each descriptor is processed separately according to its type (Eq 1).

$$S(x_1, x_2) = \frac{1}{P}\sum_{j=1}^{p} S_{12j} \qquad \text{Eq (1)}$$

where $S(x_1,x_2)$, the similarity between objects x_1 and x_2, is the average over the p descriptors of the individual similarity computed for the j^{th} descriptor (S_{12j}). The data used here consist only of quantitative descriptors. As such the similarity between x_1 and x_2 for the j^{th} descriptor is

$$S_{12j} = 1 - \left[\frac{\left|x_{1j} - x_{2j}\right|}{R_j}\right] \qquad \text{Eq (2)}$$

where R_j is the range taken by the j^{th} descriptor (Eq 2). This is the Manhattan metric of data standardised by the range, expressed as a similarity.

Gower's coefficient was implemented in the R computer language (R Development Core Team, 2009) using the analogue package (Version 0.6-6; Simpson 2007, Simpson and Oksanen, 2009). The analogue package was also used to perform the analogue matching. Eight hydrochemical parameters were used in the matching routine; Ca, Mg, Na, K, SO_4, Cl, NO_3, and pH. Whilst the most recent version of MAGIC (as applied here) has a simplistic representation of C dynamics (including the production of DOC and organic acids), its inclusion in the analogue matching procedure would reduce the number of possible analogues selected because DOC data were not available for a subset of the modern data set samples. It was therefore agreed that DOC should be omitted from the matching routine.

There is no statistical theory upon which a cut-off or threshold on the dissimilarity scale can be chosen to best discriminate between analogue and non-analogue sites. As such, the distribution of pair-wise dissimilarities computed on the training data (the modern water chemistry data set) is used as a guide to select an appropriate cut-off. Usually, a low percentile of this distribution is selected (Simpson, 2007), such as the 5^{th} or 2.5^{th}. Here, owing to the strong skew to small values observed in the distribution of pair-wise dissimilarities, we selected the 2^{nd} percentile of this distribution yielding a dissimilarity cut-off of 0.0169. Monte Carlo simulation (10000 simulations) from the observed pair-wise dissimilarities confirmed this choice of similarity, suggesting a Monte Carlo p-value of 0.02 for the significance of this threshold (Simpson 2007).

3.6 Modern water chemistry data set

The modern water chemistry data set used to analogue match with the MAGIC hindcasts/forecasts comprises 5000+ water samples from lakes, rivers/streams and artificial water bodies across the UK. For the purposes of this study only the lake sites were selected for the training set, resulting in 1391 lake sites being represented. Due to inherent variability in water chemistry from a single site, we chose to include all available samples for each of the 1391 sites in the training set, where available. However, the vast majority of the data holdings are single spot samples. This resulted in a final training set of 2455 water samples against which to match the MAGIC hindcasts/forecasts. The modern chemistry training set consists of spot samples, mainly sampled in the early to mid 1990s supplemented by more recent, target regional surveys in early to mid 2000s. As a result, the hydrochemistry of any identified modern analogues may have changed since the spot samples were collected.

4 Results

4.1 Regional variations in observed surface water chemistry

Differences in observed surface water chemistry result from a range of catchment specific factors including acidic and sea salt deposition, geological characteristics and land use. Bedrock geology has a strong influence on surface water ANC and pH, with 24 of the most acid lakes being situated on the granitic plutons in the region (median 6.85 µeq l^{-1} and pH 5.03 respectively, Figure 1). The chemistry is considerably more acid than the 35 sites that are underlain by greywackes (median 100.1 µeq l^{-1} and pH 6.43 respectively). The granitic bedrock is resistant to weathering and the median sum base cations (Ca + Mg+Na+K) for the region is 217.4 µeq l^{-1} compared to 1033.1 µeq l^{-1} for the catchment underlain predominantly by the more base rich greywackes. Enhanced inputs of dry and occult deposition, increased evapotranspiration and lower runoff at the forested sites result in the greatest concentration of xSO_4 (anthropogenic SO_4 calculated as the total SO_4 minus marine SO_4, determined as chloride concentration (in µeq l^{-1}) multiplied by 0.104, the ratio of SO_4 to chloride in sea salt) and Cl (47.01 µeq l^{-1} and 207.9 µeq l^{-1} respectively) in contrast to the moorland sites (38.13 µeq l^{-1} and 131.21 µeq l^{-1} respectively).

4.2 Simulated surface water chemistry (1860 to 2100)

MAGIC was successfully calibrated to 59 sites in the Galloway region and the simulated present day surface water ANC closely matches the observations ($r^2 = 0.96$). This implies that the difference between the sum of strong base cations and strong acid anions corresponds to observed chemistry.

MAGIC simulated ANC for 1860 are skewed to the higher, non acid classes indicating the target hydrochemical reference conditions prior to the Industrial Revolution for the region (Figure 2a). While 24 sites have an ANC >100 μeq l^{-1} a further 33 sites have an ANC between the ranges 40-100 μeq l^{-1} which is above the critical threshold for acid sensitive aquatic organisms. The model indicates that surface water acidification occurred from the mid nineteenth century to the 1970s, a time representing peak acid deposition across the UK (Figure 2). A clear shift in this distribution to more acidified surface water was simulated in response to high S deposition, and to a lesser extent N deposition inputs, in 1970 (Figure 2b). From 1860-1970 the magnitude of the ANC decline is predicted to be greater for sites situated on acid sensitive granite bedrock. In 1970 modelled ANC at 23 lakes declined to <20 μeq l^{-1}; below this threshold the critical load is exceeded and ecosystem damage can occur (Curtis and Simpson, 2004). In general, the largest decrease in ANC was predicted to occur at those sites with the lowest initial ANC, and hence the biggest sensitivity to acidic inputs. With the implementation of international protocols in the mid 1980s and the more recent Gothenburg Protocol, reductions in acidic emissions are predicted to reverse acidification processes for surface waters at most sites to 2015 and beyond (Figure 2d,e,f). The number of sites falling into the ecologically damaging ANC classes <20 μeq l^{-1} declined from 23 in 1970 to 12 in

2015, and 6 by 2100. All sites in 1860 had a simulated ANC greater than 20 μeq l^{-1} (Figure2a).

The frequency distribution of surface water pH followed a similar pattern to ANC with the highest pH values being simulated prior to the onset of industrialisation in 1860 (Figure 2g). In 1970, approximately half (51%) of the sites acidified to below a pH of 5.5 (a critical threshold for salmonids, below which they experience physiological problems) compared to 7% in 1860 (these sites are inherently acid). Projected trends in surface water pH reveal a significant recovery in the critical pH classes of <5.5 (46% in 2000, 27% in 2015, 24% in 2030 and 17% in 2100, Figure 2i, j, k, l).

Regional simulated background (1860) concentrations of NO_3 were ≤6.31 μeq l^{-1}. By 1970 many of the sites show clear signs of elevated surface water NO_3^- (Figure 2n). The percentage of predicted NO_3^- to the total anthropogenic acid anion concentration (NO_3^-+xSO_4) increases from a median of 5.77±0.79%, 6.58±0.82%, 21.22±1.68, 35.37±2.04, 37.04±2.00, 43.92±1.91 for the years 1860, 1970, 2000, 2015, 2030, 2100 respectively. These results indicate that xSO_4 remains the dominant anion in the lakes and there are still significant benefits from reducing S inputs in terms of restoration targets for acidification.

4.3 Analogue matching

A number of analogues were identified for key years (1860, 1970, 2000, 2015, 2030, and 2100) for each of the Galloway MAGIC sites (Figure 3). There was a high degree of variability in the number of analogues between sites and years, and it was not possible to identify analogues for all sites within the selected cutoff (Figure 3). Analogues were selected if the MAGIC modelled chemical composition of the lakes matched with the suite of chemistry in the modern training set. The modelled composition of the lakes changed through time in response to deposition and this largely determined the number of analogues identified in Figure 3. Of the 59 MAGIC sites, only one, Loch Heron, has no analogues within the training set for any of the time periods. A further six (Knockstring, Howie, Garwuachie, Loch of the Lowes, Ronald and Black Loch) sites have analogues for only a few of the selected time periods. Many of the MAGIC sites have no, or very few, analogues for the time period of greatest acidification pressure (1970). The lack of analogues for 1970 reflects the general improvements in water quality across the UK. This is clearly a significant result from a policy perspective as it demonstrates the efficacy of current and previous EU emission reduction protocols in the chemical recovery of some of the most acid sensitive areas of the UK from 1970 to 2000 (Figure 3). Figure 4 shows surface water pH of the selected close modern analogues for each of the time periods under study. In all cases the pH of the close modern analogues for a single time period are well constrained and vary very little in terms of absolute pH values. This figure demonstrates that there is a wide gradient of acid sensitivity between sites; and the magnitude of acidification (from 1860 to 1970) and recovery is highly variable through time. A key feature of the close modern analogues for the reference conditions of many of the Galloway lakes is that they are predominantly located in the north-west of Scotland, the area of the UK that has received the lowest levels of acid deposition.

It was not feasible to present maps showing the location of analogues for all 59 sites in the region for the 6 keys years. For this reason the RLGH was selected from the region to demonstrate how the spatial distribution of analogues changed through time in response to a reduction in S and N deposition. For example, Figure 5a shows the locations of close modern analogues for 1860 (hindcast) at the Round Loch of Glenhead. Whilst the majority of sites are located in the north west of Scotland, a small selection was identified in areas of less acid geology in north Wales, which cannot be considered minimally impacted as they receive elevated level of acid deposition. Why these sites are similar to the reference condition chemistry of RLGH is yet to be determined, yet this observation tallies with the results of Simpson et al (2005), who found modern analogues in the same region for the reference conditions of several UKAWMN lakes when matching was performed using diatom and Cladocera abundance data. Nonetheless, the north-west of Scotland contains many of the biological analogues for acidified sites in the UKAWMN determined by analogue matching of diatom and Cladocera sub-fossil assemblages from sediment core samples (Simpson et al., 2005). This finding supports the results from the current study, whereby suitable modern reference sites for acidification were identified in the north-west of Scotland.. In contrast, analogues for the RLGH from MAGIC simulations in 1970 show a shift in the location of the analogue sites from semi-pristine areas of the UK to acid impacted areas (Figure 5b). In 2015, close modern analogues sites for the RLGH under ‘base case’ conditions are distributed primarily in the north and north-west of Scotland, and north and central Wales (Figure 5c). Model projections to 2100 show a shift in the distribution of the analogues to the English Lake District and north Wales however only 4 analogues could be identified for this time period (Figure 5d). In line with the objectives of this study, the sparse number of spatial analogues with chemical information that match these longer term MAGIC projections (2100), indicate that given projected deposition reductions, total restoration of water quality to pre-industrial levels is not achievable.

4.4 Assessment of climate change impacts on simulated surface water chemistry

4.4.1 Base case

The sensitivity of MAGIC to various climate induced changes that influence biogeochemical processes were tested at the RLGH. Figure 6 illustrates the relative magnitude of the response to these various changes applied singly and in combination (all perturbations). The base case (no climate effects) comparison of year 2030 relative to year 2000 shows a continued recovery of surface water ANC in response to the expected continued decrease in S and N deposition (Figure 6a). NO_3^- concentrations (Figure 6b), however, first decrease slightly in response to decreased N deposition and then increase around 2020 due to the beginnings of N saturation as the soil C/N ratio declined with N enrichment. This increase in NO_3^- will impede the recovery of ANC. Lake pH shows significant recovery from 4.98 in 2000 to a pH of 5.82 in 2100. The percentage recovery of pH by 2015 (base case scenario) relative to the reference condition (1860) is 24%. The longer term recovery (2100) is predicted to be 61%.

4.4.2 Climate perturbations

Sensitivity trials of possible climate induced responses indicate that the generation of DOC accelerates the recovery rate of ANC relative to the base case (Figure 6a). Of all the climate induced perturbations, DOC invoked the greatest recovery in ANC relative to 1860 and into the future (38% by 2015 and 59% by 2100). The RLGH is 10km from the coast and increased inputs of seasalts are predicted to have a greater effect on ANC in the future by impeding the rate of recovery compared to the base case (Figure 6a). The percentage recovery of ANC by 2015 (seasalt perturbation) relative to the reference condition (1860) is 12%. The predicted longer term recovery by 2100 is 41%. Discharge has a similar effect on ANC in the longer term (post 2040). When all climate perturbations were included in the forecast simultaneously (All perturbations, Figure 6), the ANC increased dramatically until 2030, thereafter, the lake shows signs of declining ANC. In contrast to the study by Wright et al (2006), increased decomposition of soil organic matter and the size of the organic matter pool at the RLGH had no effect on lake NO_3^- concentrations, however increased discharge was found to cause a greater decrease in NO_3^- concentrations relative to the base case until the point of NO_3^- saturation thereafter NO_3^- steadily increased (Figure 6b). Whilst the response of lake pH is similar to ANC from 2000-2100, all perturbations result in a depression of the pH below the base case and again enhanced seasalt inputs have the greatest confounding effect on chemical recovery (Figure 6c). With the seasalt influence, the percentage recovery of pH by 2015, relative to the reference condition (1860), is 13 %. The predicted longer term recovery at the RLGH is 55% by 2100.

4.5 The use of modern analogues to define surface water chemistry in response to reductions in acid deposition and climate change at the Round Loch of Glenhead

The spatial distribution of analogue sites for water quality in 2015 and 2100 were identified in response to the Gothenburg Protocol in Section 4.3 (Figure 5). Here we show how climate can modify terrestrial and aquatic biogeochemical processes and surface water quality and hence the distribution of analogues sites. Figure 7 shows the distribution of close analogue sites using the simulated suite of parameters generated by MAGIC with the climate perturbations. There is only a small difference between the general location of analogues sites between the base case (Figure 5) and climate change perturbations in 2015 (Figure 7). By 2100 the distribution of analogue sites changed significantly between the base case and all climate perturbations, with 5 analogue sites in the low pollution region of the north west of Scotland and the majority of analogues in north Wales. This change can be attributed to the predicted increase in the ionic strength of the lake in response to the climate perturbation in 2100 ((sum of base cations (SBC) and sum of acid anions (SAA)) increased by 7% and 5.4% respectively). A larger number of analogues were identified with the climate perturbations (18) in 2100 compared to the base case (4 analogue sites). This suggests that hydrochemical conditions under future climate change currently exist within the modern population of lakes in the UK. As such, the effects of climate change on hydrochemistry of RLGH are unlikely to vary wildly outside the modern range, a result which suggests a limit on the impact of altered temperature and precipitation regimes.

Discussion

The EU Water Framework Directive requires lakes to be classified according to the assemblage of chemical and biological elements they currently support. The system specified for this classification is a state-changed system, comparing any lake's current condition with its condition at a reference state. This requirement is key to the first objective of this study and was achieved through the identification of a suite of reference lakes that represent pre-acidification conditions from MAGIC simulated hydrochemical data, and the novel analogue matching approach. In combination these methods provide a robust platform to predict the timing and extent of future recovery in line with the WFD.. We can now ask what chemical characteristics we should expect for a fully restored lake and whether current emission reduction plans are adequate to allow such restoration targets to be achieved in line with the second objective of this study.

The implementation of the Gothenburg Protocol is predicted to result in a substantial improvement in surface water ANC throughout the Galloway region. Predicted trends in surface water chemistry from present day to 2015 (the year to achieve good ecological status of surface water under the WFD) indicate a moderate improvement in water quality with c. 23±0.97 % recovery towards pre-acidification ANC for the region (‘Recovery’ is defined as the forecast ANC recovery to 2030 as a percent of the net ANC decline from pre-industrial conditions to present day i.e. $[ANC_{2015}-ANC_{present\ day}]/[ANC_{present\ day}-ANC_{1860}]$ x 100. The general distributions of modern analogue sites in 1860 and 2015 are comparable with the exception of one analogue site in the English Lake District. The recovery in Galloway is relatively slow as a result of the low base-status of soils at high altitude sites and extensive afforestation in lower-lying catchments. At afforested sites, second rotation forest planting is likely to slow, or in some cases prevent further recovery despite large reductions in S and N deposition. A combination of base cation uptake by the forest, enhanced deposition to the forest canopy and decreased water yield concentrating pollutants in surface waters may further contribute to the delayed recovery of ANC towards reconstructed pre-industrial reference conditions in the region. Projected trends in surface water quality beyond 2015 indicate that recovery continues at the moorland sites at a much slower rate, and at the forested catchments the surface waters begin to re-acidify. This regional study illustrates the importance of catchment characteristics in determining the wide range of surface water responses to changes in deposition for key years over the 240 year period. In the longer term, beyond 2030 (full implementation of CLE), the model indicates that increased N leakage to surface waters may cause deterioration in the chemical status. Longer term forecasts to 2100 indicate a loss of analogues from the north west of Scotland and a couple identified in both the Lake District and north Wales.

Analogues were identified for the majority of sites in the Galloway region and for most time periods, however no analogues were selected from the hydrochemical dataset for Loch Heron, and a further six sites (Knockstring, Howie, Garwuachie, Loch of the Lowes, Ronald and Black Loch) have analogues for only a few of the selected time periods (Figure 3). This reflects the sampling bias in the Freshwater Umbrella data set, which predominately contains water chemistry samples from the most sensitive freshwater in each 10 km grid square for use in national critical loads assessments. In addition, the modern chemistry dataset consists of spot samples, mainly sampled in the early to mid 1990s supplemented by more recent, target regional surveys in early to mid 2000s. Overall, based on these two considerations, the analogues reported here may represent a bias towards the more acid, lower pH and ANC sites in the UK.

The inclusion of climate change impacts at the RLGH demonstrates that overall, potential biogeochemical processes driven by changes in temperatures and rainfall in the future may delay recovery. In these circumstances less stringent restoration targets to those specified in 1860 should be considered. The sensitivity trials (Figure 6) give a first indication of possible consequences of climate change on biogeochemical processes that operate at a catchment scale. Actual climate change could affect these factors simultaneously and the combined effect could be larger or smaller than either alone (Wright et al 2006). Where all climate perturbations were combined to determine modern analogue sites for the RLGH it is important to recognise that the hydrochemical output reflects the gross effect of a number of complex and interactive processes within the soil and lake.

The MAGIC model (Cosby et al., 2001) has been applied, tested and validated at numerous catchments throughout Europe and North America. The RLGH is one of several catchments throughout the UK with detailed palaeoecological information that provides a record of the timing, rate and magnitude of biological and chemical change. Battarbee et al. (2005) compared different diatom–pH transfer functions against MAGIC simulated pH from pre-industrial times and found diatom inferred pH to be ~0.6 pH unit more acid than the MAGIC simulated pH. Assuming that MAGIC over predicts pH in pre-industrial times (reference condition) this may have implications on the selection of analogue sites in this study as pH was used as a parameter in the matching. Recent MAGIC applications (Wright et al., 2006 and Evans, 2005) have tested climate induced responses with the existing model structure. Uncertainties exist into the mechanisms and rates by which climate changes affect key biogeochemical processes and at present the state-of-science appears insufficient to provide the insight required to allow these processes to be programmed directly into process models such as MAGIC. Sensitivity trials with the MAGIC model at the RLGH demonstrate that the role of climate change on the concentration of organics acids (DOC) in soils and surface waters emerges as an important factor, however DOC is not currently included as a parameter in the analogue approach.

Despite these uncertainties, many studies reported in the literature predict past and future changes in water chemistry with little or no evaluation of the viability of such predictions. The long term simulated data presented here are constrained to realistic ranges based on the occurrence of lakes with a similar chemical signature within the modern hydrochemical dataset, therefore giving more credibility to the assessment of surface water compliance with regard to achieving restoration targets.

Conclusion

It has been suggested that future global environmental change could lead to environmental conditions unlike those that presently exist in acid, upland aquatic ecosystems (Skjelkvale and Wright, 1998). If environmental conditions were to change markedly, recovery targets for acidified lakes and streams would have to be adjusted beyond the range of current hydrochemical conditions, and suitable candidate reference lakes would be unlikely to exist, under such climatic conditions.

Palaeoecological reconstructions of the reference state, and palaeo-based analogue matching for this state in particular, would be of very limited use in such circumstances. This paper represents the first application of the analogue matching technique to long term MAGIC predictions for the Galloway region of south-west Scotland. Identification of modern reference lakes plays an essential role in fulfilling the aims of the EU WFD and in defining suitable restoration targets against which emission reductions policy can be evaluated. Here we show that modern analogues for the reference states of 59 Galloway lakes can be identified from a population of modern lake data by comparing them with MAGIC hindcasts. The majority of the modern analogues identified are located in the north-west of Scotland, an area of relatively low acid deposition and in areas of North Wales that are geologically complex with areas of intermediate igneous rocks and the Ordovician shales that are less sensitive to the effects of deposition (Helliwell et al .2007).

The results clearly demonstrate that given a suitable modern training set against which to match MAGIC predictions, close modern analogues for the predicted hydrochemistry of the Round Loch of Glenhead under climate change can be identified. Results for the Round Loch of Glenhead suggest that modern analogues that are similar to the future hydrochemical conditions predicted by MAGIC under perturbed climatic conditions currently exist in the UK lake population. This suggests that the analogue approach may remain relevant for the identification of suitable recovery targets and candidate reference lakes in the face of unprecedented climate change. It is also clear from model predictions that surface water quality will deteriorate beyond 2030 at the RLGH in response to climate change and, in light of these finding, more realistic hydrochemical goals should be considered in future assessments of upland water quality. However, further work is required to confirm these results with MAGIC forecasts including climate change at other sites, and to relate the climatic perturbations used here to actual GCM forecasts of climate change in the UK.

Acknowledgements

This study was supported by the Euro-limpacs project (the Commission of European Communities GOCE-CT-2003-505540), the Rural and Environment Research and Analysis Directorate of the Scottish Government, and by the UK Government's Department for the Environment, Food and Rural Affairs (DEFRA). The modern water chemistry data set and part of the MAGIC model development was funded by the UK DEFRA Freshwater Umbrella and Critical Loads and Dynamic Modelling research programmes. The authors are particularly grateful to Sheila Gibbs for sample preparation, managing the regional hydrochemistry database, and to the analytical group at the Macaulay Institute for sample analysis. We also acknowledge Jack Cosby and Dick Wright for their expertise in the initial phase of MAGIC sensitivity trials, Malcolm Coull for producing Figure 1 and two anonymous reviewers for comments.

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Figure 3: Level plot showing the number of analogues per time period for each of the 59 Galloway lakes. Empty (white) blocks indicate that no analogues for that time period could be identified.

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Figure 7: Location of close modern analogues lakes for the Round Loch of Glenhead based on changes in biogeochemical processes that are sensitive to deposition and climate. The size of the circle is proportional to the similarity (1/dissimilarity).

Table 1
Click here to download Table: Table 1.doc

Table 1. Names, locations and catchment statistics for the sites included in the Galloway region

Site name	ID	Easting m	Northing m	Lake area ha	Total area ha	Forestry %
Loch Arron	GAL001	244326	583818	2.7	20.5	0
Balloching	GAL002	245564	594738	9.2	234.3	16
Barscobe	GAL003	266890	581405	4.6	91.5	33
Black Loch	GAL004	249630	572890	2.8	35.5	43
Black	GAL005	227970	565529	6.0	53.3	45
Black by Ochiltree	GAL006	231907	575651	2.6	49.3	57
Brack	GAL007	268381	582147	3.7	17.5	27
Bradan	GAL008	242399	597360	215.5	1495.0	28
Brechbowie	GAL009	243239	596084	7.9	87.5	14
Clatteringshaws	GAL010	254237	577007	387.5	9811.8	35
Cornish	GAL011	240892	594097	5.4	345.0	10
Loch Doon	GAL012	249779	597677	818.9	12981.5	23
Dornal	GAL013	229229	576159	43.8	632.8	41
Dow by Moan	GAL014	235337	584808	1.3	9.0	78
Dow by Narroch	GAL015	246169	582559	0.5	13.9	0
Dow by Round	GAL016	245755	580784	0.5	8.4	0
Drumlanford	GAL017	228004	577508	9.5	44.0	22
Dry	GAL018	246691	585648	2.4	21.0	31
Loch Dungeon	GAL019	252500	584400	35.4	641.5	9
Loch Enoch	GAL020	244600	585300	50.2	222.0	0
Fannie	GAL021	244670	592421	1.2	6.3	81
Finlas	GAL022	245915	598296	76.9	1096.0	6
Fyntalloch	GAL023	231704	574517	72.5	307.6	37
Garwuachie	GAL024	234319	569039	3.7	240.5	71
Girvan Eye	GAL025	241174	592665	1.9	26.8	23
Goosie	GAL026	244038	594886	5.2	94.8	8
Gower	GAL027	228882	577210	6.2	355.0	49
Loch Grannoch	GAL028	254100	569800	111.4	1432.0	40
Harrow	GAL029	252783	586686	13.7	385.3	28
Heron	GAL030	227208	564873	12.7	173.5	33
Loch Howie	GAL031	269700	583400	17.7	193.5	52
Lochinvar	GAL032	265850	585392	39.3	309.8	22
Kirriereoch Loch	GAL033	236400	586600	6.9	20.8	67
Knockstring	GAL034	269761	588225	6.1	59.5	33
Loch Gower	GAL035	254952	573512	0.6	6.9	92
Long Loch of Dungeon	GAL036	246679	584128	3.9	240.3	7
Long Loch of Glenhead	GAL037	244523	580830	10.2	95.3	0
Lilies Loch	GAL038	251727	574704	1.9	133.5	20
Loch of the Lowes	GAL039	246876	570464	2.5	59.3	82
Loch Macaterick	GAL040	244000	591200	74.4	961.8	13
Mayberry	GAL041	228618	575073	67.9	1777.8	53
Minnoch	GAL042	253049	585721	6.6	820.5	21
Moan	GAL043	234771	585787	51.8	544.5	71
Mossdale	GAL044	265614	571078	5.4	89.5	8
Moss Ruddock	GAL045	263178	581572	3.0	22.8	0
Loch Muck	GAL046	251300	600800	9.6	233.0	31
Nahinie	GAL047	227858	577126	1.5	54.5	18
Loch Narroch	GAL048	245234	581552	3.3	42.3	0

Neldricken	GAL049	244519	582977	31.4	458.0	0
Ochiltree	GAL050	231704	574517	72.5	505.3	32
Round Loch of Dungeon	GAL051	246602	584700	4.1	83.8	19
Round Loch of Glenhead	GAL052	245000	580400	12.7	102.5	0
Riecawr	GAL053	243351	593465	85.4	1509.0	40
Ronald	GAL054	226529	564242	47.7	351.3	33
Skelloch	GAL055	240987	596169	5.8	563.0	28
Trool	GAL056	241583	579982	55.6	3271.8	11
Valley	GAL057	244366	581772	33.8	698.0	0
Aldinna	GAL058	236500	593800	4.2	146.5	3
Derclach	GAL059	244403	598991	15.9	131.0	4

Table 2
Click here to download Table: Table 2.doc

Table 2 Response of surface water to change in climate induced responses based on Wright *et al*., 2006(Perturbations are ramped from 2000-2030).

Factor	Perturbation
Base case	Current Legislation (CLE) with N dynamics
Seasalts	Increase deposition of Cl, Mg, Na by 50%
Runoff	Increase discharge by 20%
Weathering	Increase Ca, Mg, Na, K, SO_4 by 20%
Decomposition	Derived from [a]CLIMEX, increase decomposition of soil C (1000 mmol $m^{-2}yr^{-1}$)
Organic acids	Increase DOC by 50% in soil and lake
pCO_2	Increase pCO_2 by 30% in soil and lake
All perturbations	All of the above

[a]CLIMEX* van Breemen et al., 1998

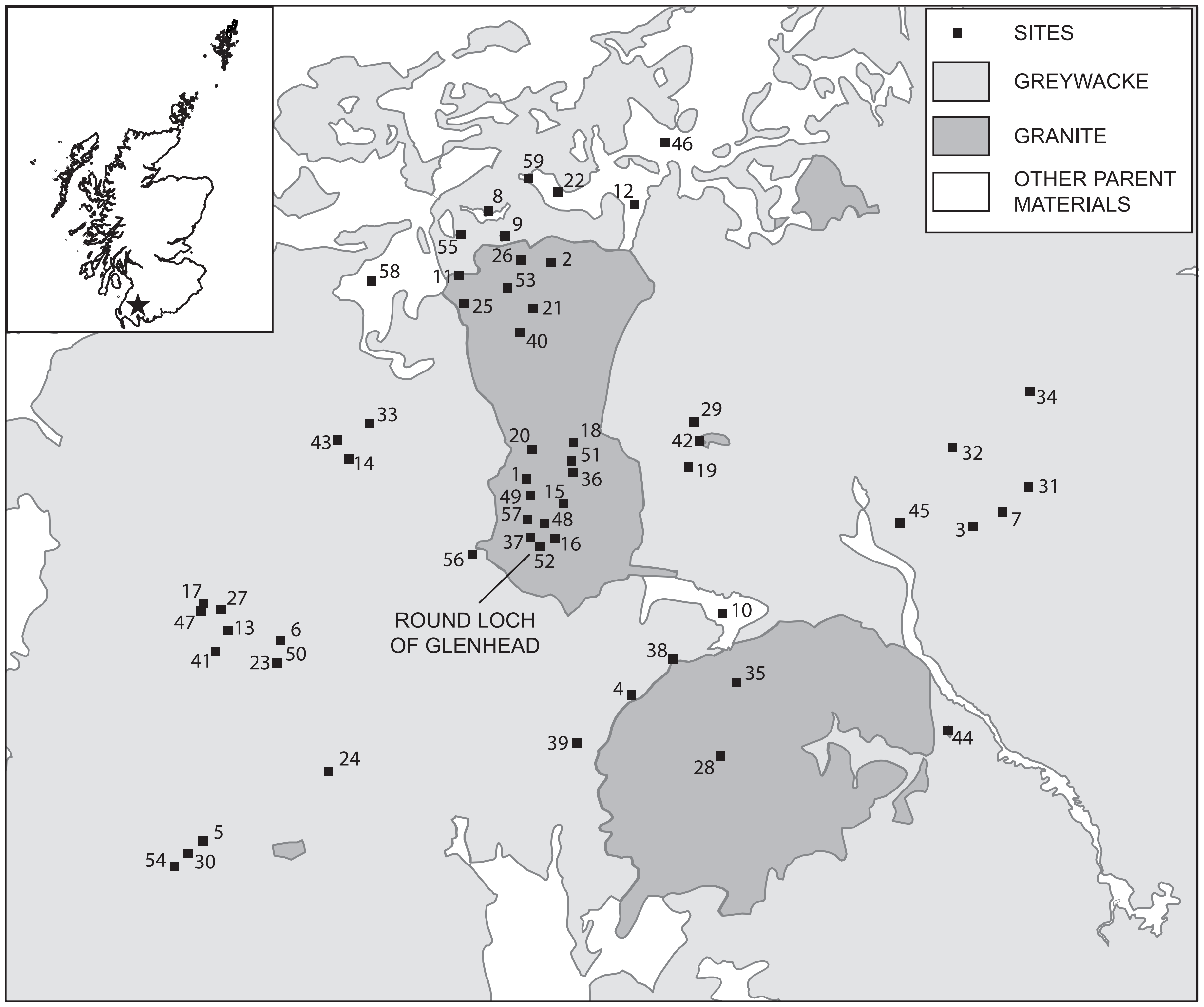
SITES
GREYWACKE
GRANITE
OTHER PARENT MATERIALS
ROUND LOCH OF GLENHEAD
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
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Figure 2

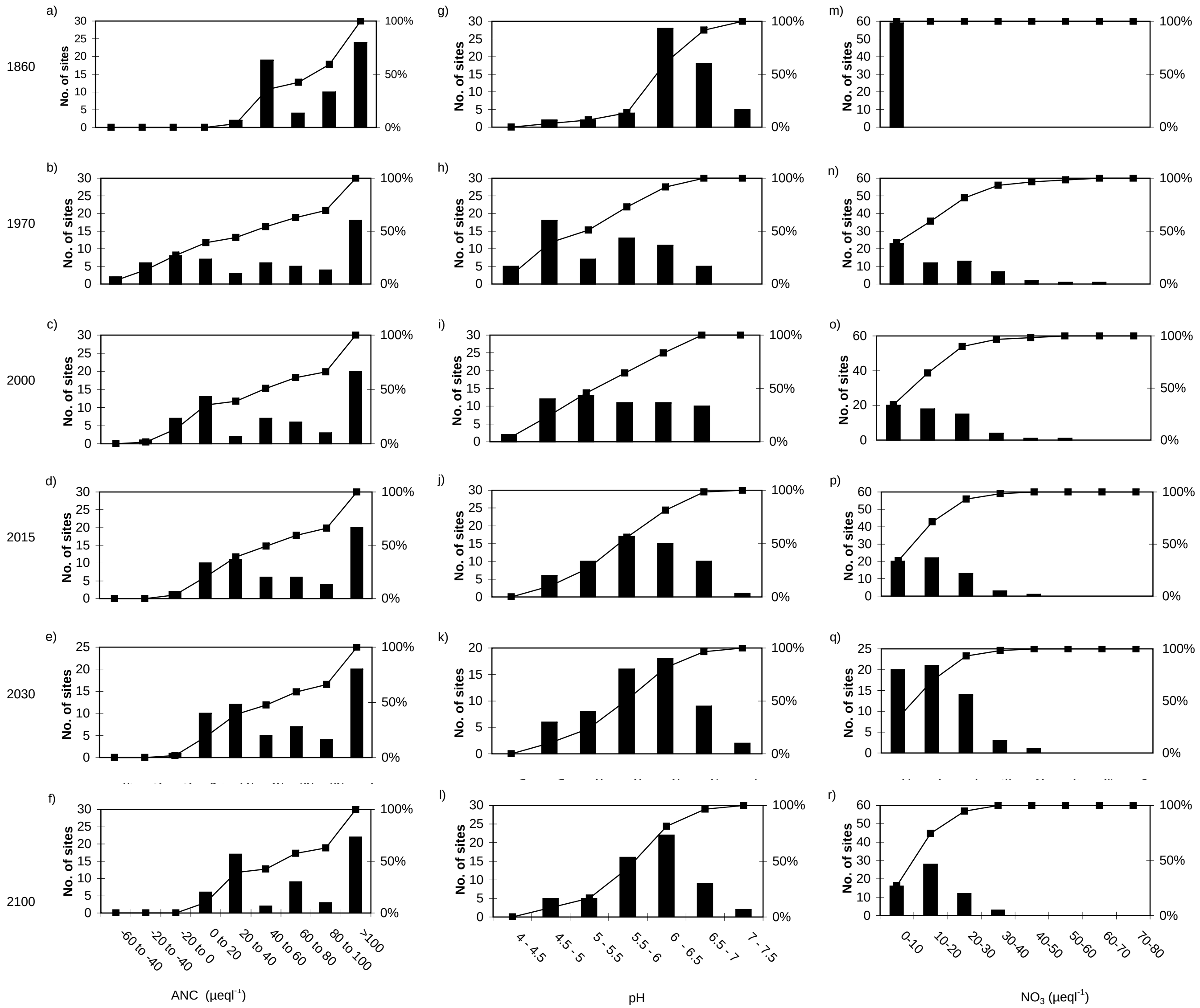
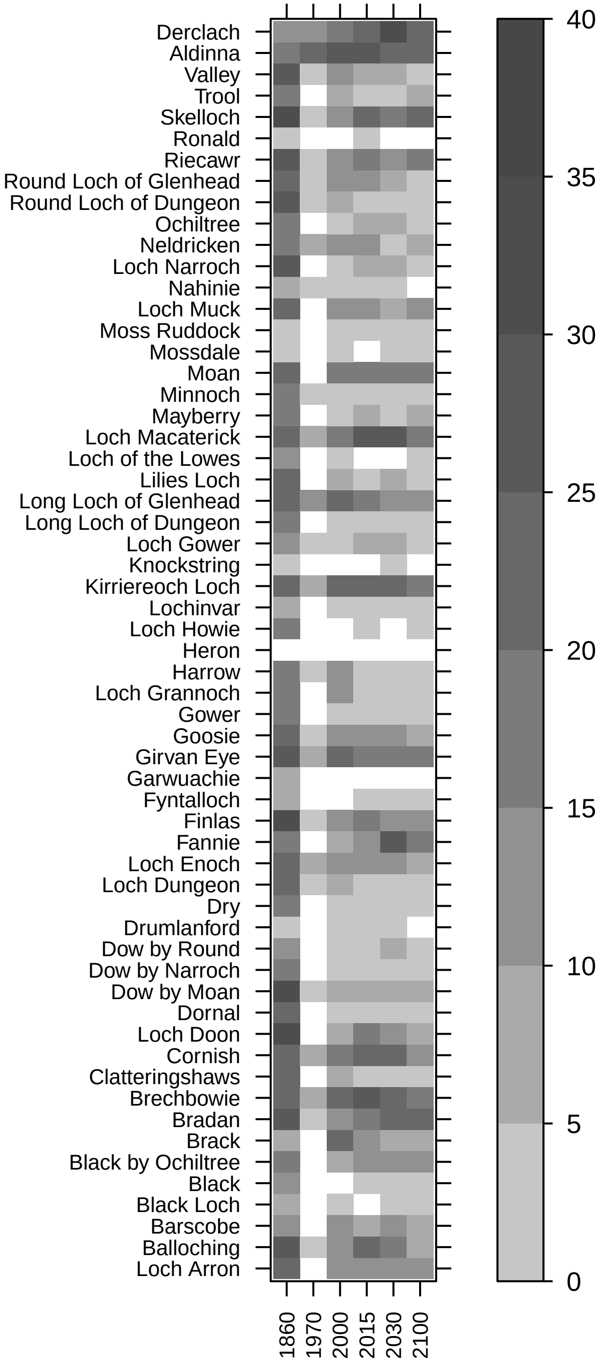
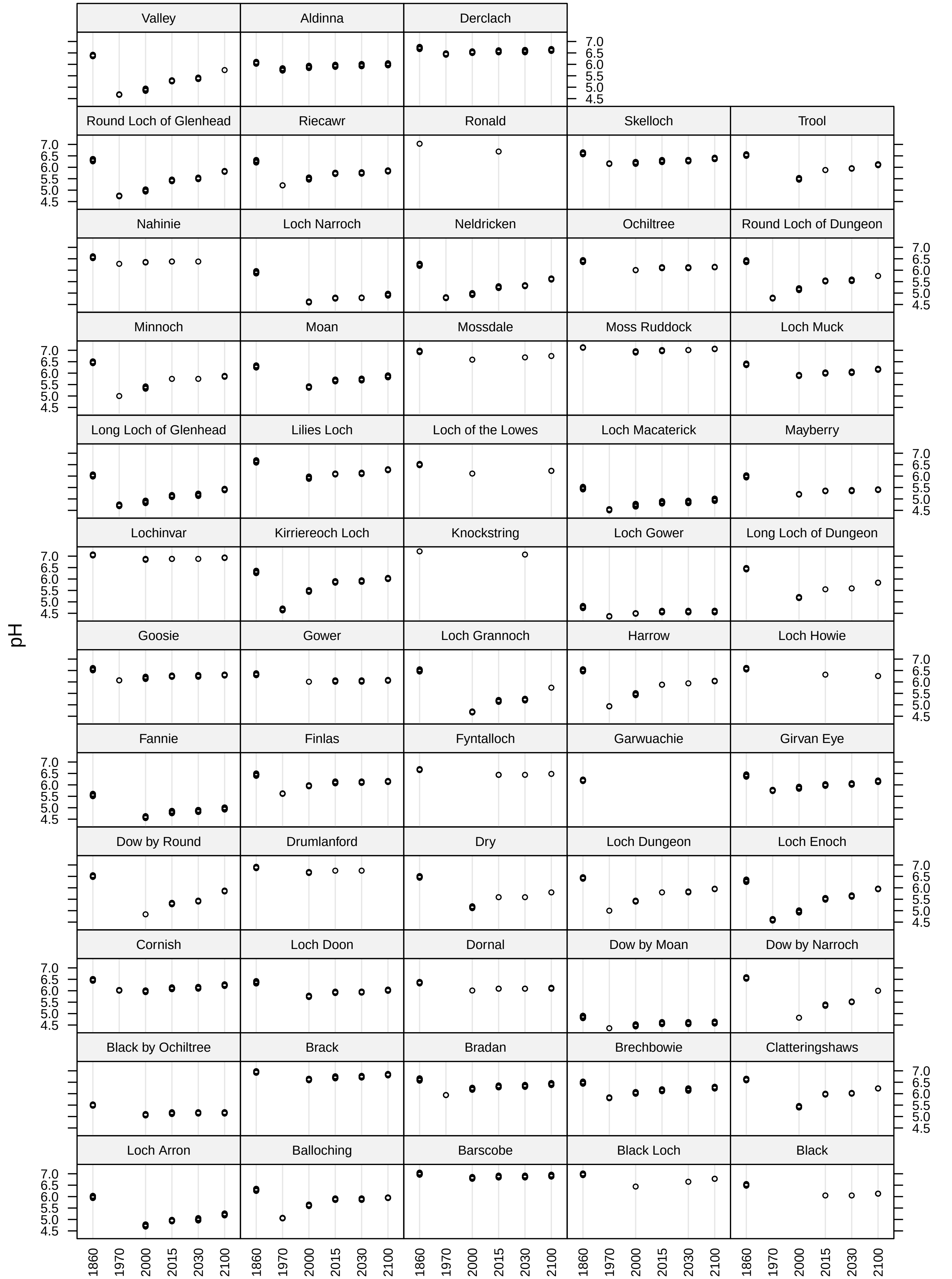

1860
1970
2000
2015
2030
2100
No. of sites
ANC (µeql⁻¹)
pH
NO3 (µeql⁻¹)
-60 to -40
-20 to -40
-20 to 0
0 to 20
20 to 40
40 to 60
60 to 80
80 to 100
>100
4 - 4.5
4.5 - 5
5 - 5.5
5.5 - 6
6 - 6.5
6.5 - 7
7 - 7.5
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
0%
50%
100%

Figure 3



Derclach
Aldinna
Valley
Trool
Skelloch
Ronald
Riecawr
Round Loch of Glenhead
Round Loch of Dungeon
Ochiltree
Neldricken
Loch Narroch
Nahinie
Loch Muck
Moss Ruddock
Mossdale
Moan
Minnoch
Mayberry
Loch Macaterick
Loch of the Lowes
Lilies Loch
Long Loch of Glenhead
Long Loch of Dungeon
Loch Gower
Knockstring
Kirriereoch Loch
Lochinvar
Loch Howie
Heron
Harrow
Loch Grannoch
Gower
Goosie
Girvan Eye
Garwuachie
Fyntalloch
Finlas
Fannie
Loch Enoch
Loch Dungeon
Dry
Drumlanford
Dow by Round
Dow by Narroch
Dow by Moan
Dornal
Loch Doon
Cornish
Clatteringshaws
Brechbowie
Bradan
Brack
Black by Ochiltree
Black
Black Loch
Barscobe
Balloching
Loch Arron
1860
1970
2000
2015
2030
2100
40
35
30
25
20
15
10
5
0

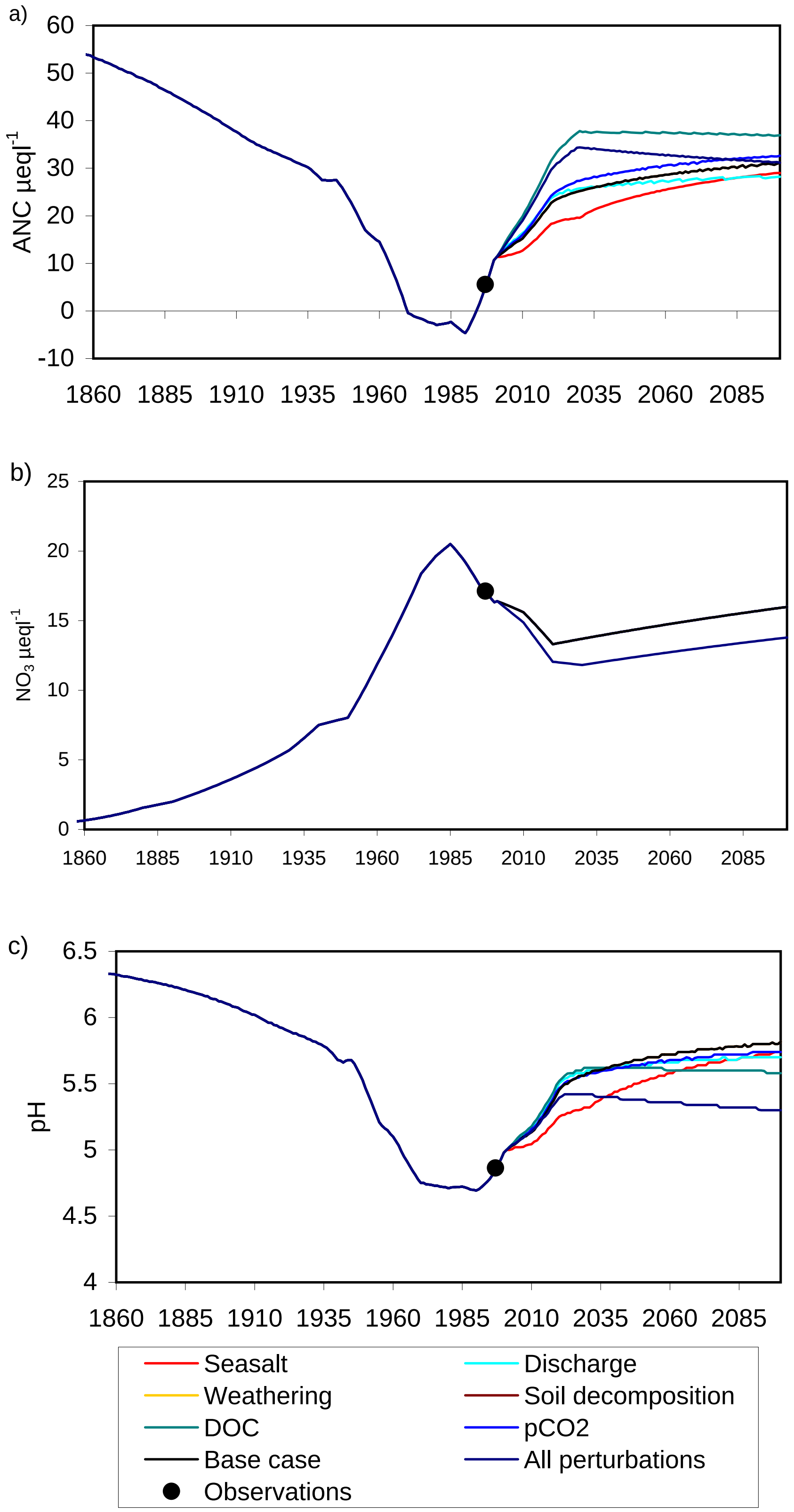
Figure 4



Valley
Aldinna
Derclach
Round Loch of Glenhead
Riecawr
Ronald
Skelloch
Trool
Nahinie
Loch Narroch
Neldricken
Ochiltree
Round Loch of Dungeon
Minnoch
Moan
Mossdale
Moss Ruddock
Loch Muck
Long Loch of Glenhead
Lilies Loch
Loch of the Lowes
Loch Macaterick
Mayberry
Lochinvar
Kirriereoch Loch
Knockstring
Loch Gower
Long Loch of Dungeon
Goosie
Gower
Loch Grannoch
Harrow
Loch Howie
Fannie
Finlas
Fyntalloch
Garwuachie
Girvan Eye
Dow by Round
Drumlanford
Dry
Loch Dungeon
Loch Enoch
Cornish
Loch Doon
Dornal
Dow by Moan
Dow by Narroch
Black by Ochiltree
Brack
Bradan
Brechbowie
Clatteringshaws
Loch Arron
Balloching
Barscobe
Black Loch
Black
pH
7.0
6.5
6.0
5.5
5.0
4.5
1860
1970
2000
2015
2030
2100

Figure 5

Figure 6



a)
ANC µeql-1
60
50
40
30
20
10
0
-10
1860 1885 1910 1935 1960 1985 2010 2035 2060 2085
b)
NO3 µeql-1
25
20
15
10
5
0
1860 1885 1910 1935 1960 1985 2010 2035 2060 2085
c)
pH
6.5
6
5.5
5
4.5
4
1860 1885 1910 1935 1960 1985 2010 2035 2060 2085
Seasalt
Weathering
DOC
Base case
Observations
Discharge
Soil decomposition
pCO2
All perturbations

Figure 7