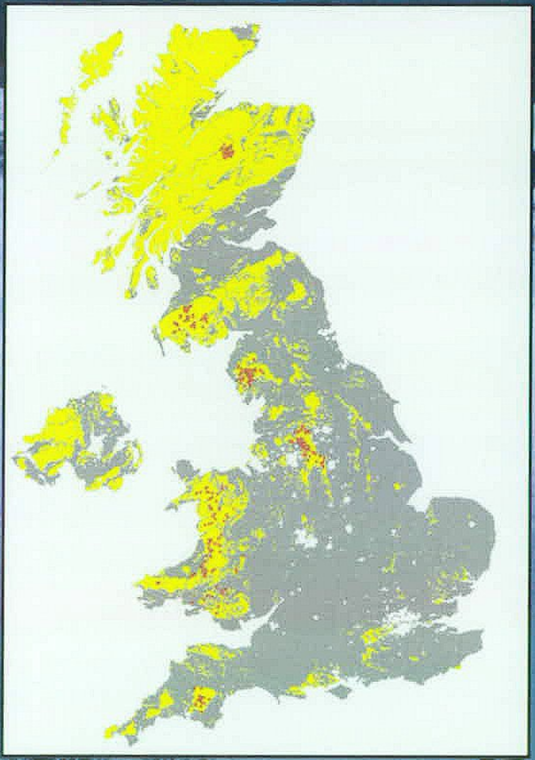
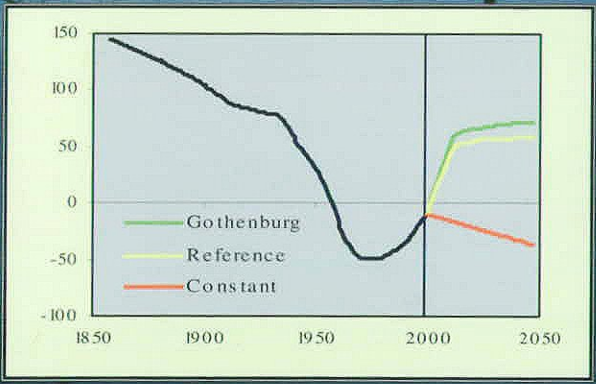
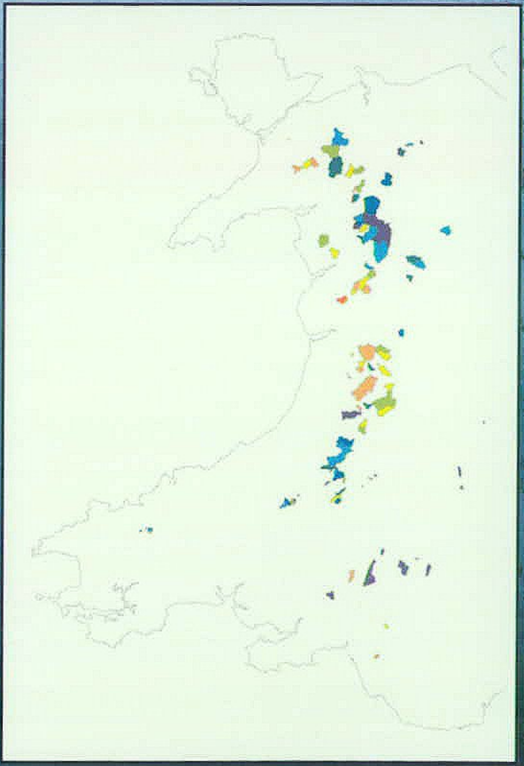
Freshwater Acidification and Recovery in the United Kingdom







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THE MACAULAY INSTITUTE

Freshwater Acidification and Recovery in the United Kingdom

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Executive summary

Acidification of soils and surface waters across Europe and North America results from the emission, transport and deposition of oxides of sulphur and oxidised and reduced forms of nitrogen. Acidification occurs in regions where the geology is acid-sensitive and in regions that have received a large accumulated flux of sulphur and nitrogen deposition. International efforts to decrease acidic emissions and reverse the acidification process have led to agreement and legislation within the UN-ECE Convention on Long-Range Transboundary Air Pollution and the European Union, respectively. The most recent UN-ECE agreement, the Multi-Pollutant Multi-Effect Protocol, was signed in Gothenburg in 1999 and was aimed at limiting emission of sulphur, nitrogen oxides, ammonia and volatile organic compounds by the year 2010.

This study uses the dynamic hydrochemical model, MAGIC (Model of Acidification of Groundwaters In Catchments), calibrated to six acidified and acid-sensitive regions in the UK to;

(i) determine the recovery in surface water chemistry that might be expected under the Gothenburg Protocol by 2050;
(ii) compare the predicted recovery with that predicted to occur under existing agreements (Reference scenario);
(iii) compare these with the regional water chemistry predicted if no further action was taken to limit emissions beyond present day levels.

The model has been calibrated to six acid-sensitive regions of the UK – the Cairngorms, Galloway, the Lake District, the South Pennines, Wales and Dartmoor – using the best available data describing catchment soils, water chemistry, deposition and land-use characteristics. Predictions are made using deposition fields derived from the HARM atmospheric transport and deposition model.

In response to the deposition reductions under the Gothenburg Protocol the model predicts that by 2050 only 2% of sites sampled within the six sensitive areas will have mean Acid Neutralising Capacity (ANC) below zero. This compares with a current figure of 21%. For the Reference scenario, the model predicts 4% of waters below zero ANC. If deposition were to remain at current levels, 25% of sites are predicted to be below zero ANC by 2050. It is clear, therefore, that emission reductions beyond the presently achieved levels will have a significant benefit for surface water chemistry in the UK.

The added 'benefit' of the Gothenburg Protocol over earlier agreements is less clear when the regions are considered together at a UK scale but is evident in some regions. In the most heavily impacted region, the south Pennines, the model predicts 5% of surface waters with ANC below zero in 2050 under the Gothenburg Protocol compared with 12% under the Reference scenario.

The timescale of chemical reversibility and the degree to which pre-acidification chemistry is recovered also varies regionally across the UK as a result of differences in regional weathering rates and soil base cation characteristics. The Lake District, for example, has relatively high weathering rates and relatively low soil base status, promoting a rapid response to change in acid anion input. For Wales and the South Pennines, on the other hand, lower weathering rates and the requirement to replenish larger soil base cation pools slows the surface water recovery. In several regions, notably Galloway, plantation forestry has a significant impact on

predicted recovery in surface water chemistry whereby second rotation planting counteracts deposition reductions, leading to less improvement in water quality at forested catchments.

Significant uncertainties remain in these dynamic model applications relating to extrapolation of soils data, surface water chemistry data and definition of present and future atmospheric inputs, as well as process uncertainty in the model, in particularly the descriptions of sulphur adsorption and controls on nitrate leakage. In addition, there still exists considerable uncertainty in the response of freshwater biota to changes in chemistry.

Nevertheless, dynamic model outputs remain no less certain than steady-state critical loads constructed from similar data, but have the added benefit of providing a timescale for the assessment of existing emission reduction agreements, or for deriving future agreements.

Future research must aim to extend the regional coverage, reduce model uncertainties, incorporate stream systems, interface with Integrated Assessment Models and link with dynamic aquatic and terrestrial biological models.

Chapter 1: Introduction

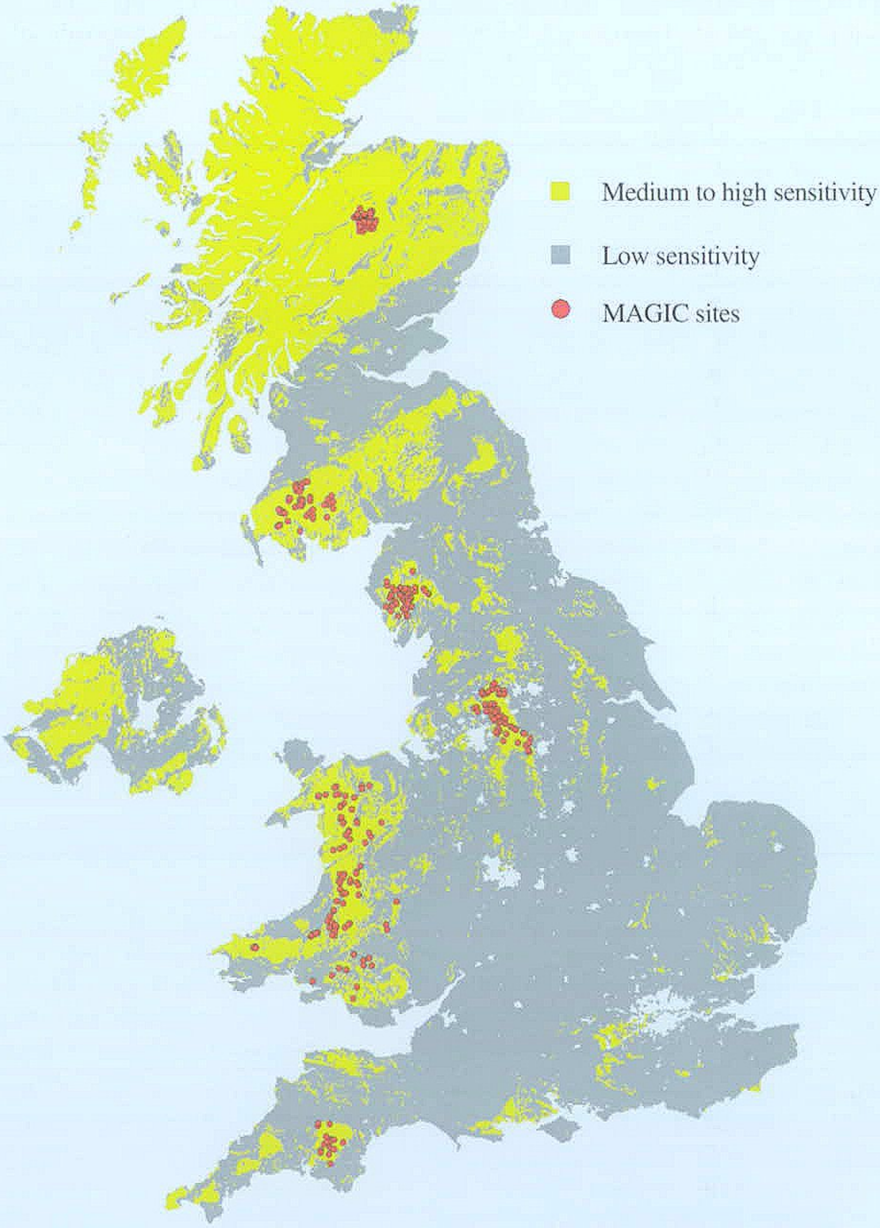
Acidification of soils and surface waters across Europe and North America has been widely documented and results from the emission, transport and deposition of oxides of sulphur (SO_x) and nitrogen (NO_x). Emission of these acidic oxides to the atmosphere increased steadily from the beginning of the "Industrial Revolution" in the mid-19th century to reach a peak in Europe in the mid-1970s as a result of burning fossil fuels. Much of the evidence to support this is derived from the analysis of algae (diatoms) in sediment cores from acidified lakes, which show a progressive change in the fossil assemblage from acid intolerant to acid tolerant species through that time period (Battarbee *et al.* 1988). An additional acidification stress results from the emission, transport and deposition of reduced nitrogen species (NH_y) originating predominantly from agricultural sources.

The process of soil and surface water acidification occurs as a result of the mobility of sulphur (S) and nitrogen (N) ions within the terrestrial environment. For S, little of the deposited flux of ions is retained in the biota and the bulk is transported along hydrological pathways to surface water streams and lakes. In areas where soils are characterised by a large pool of exchangeable base cations or where weathering of base cations is high, the S is buffered by the base cations. This depletion of the base cation store in the soils leads to soil acidification but does not acidify the surface waters. In regions where the bedrock weathering of base cations is slow or where the soils have been depleted of their original store of base cations, the S is transported with H^+ promoting acidification of the surface water. It is clear, therefore, that soil and surface water acidification is not ubiquitous but occurs in regions where the geology is "acid sensitive", for example on granites (slow weathering of base cations) or sandstones (low content of base cations), and in regions which have received a large accumulated flux of S and N (soil store of base cations depleted). In the UK, these regions of acid sensitivity can be demonstrated with respect to underlying geology and soils (Figure 1.1).

A further driver promoting enhanced surface water acidification is plantation forestry (Stoner and Gee 1985). It has been shown from modelling studies (e.g. Jenkins *et al.* 1990) that the trees themselves do not cause surface water acidification in the absence of acidic deposition. In areas of high deposition, however, the trees exacerbate the problem (Harriman and Morrison 1992) through scavenging air pollutants and by uptake of base cations from the soil into the plant biomass. The regional impact of plantation forestry, however, is unlikely to be consistent across the whole of the UK but will depend upon soil characteristics, bedrock geology, planting history and the history of acidic deposition.

The first legislation aimed at reducing S emissions to combat the acidification problem was signed under the auspices of the United Nations Economic Commission for Europe (UN-ECE) Convention on Long Range Transboundary Air Pollution (CLRTAP) in 1985. This was the so-called First Sulphur Protocol whereby the signatory countries committed themselves to a 30% reduction in emissions by 1993 relative to 1980 levels. This was followed in 1994 by the Second Sulphur Protocol (the Oslo Protocol) under which the signatory countries agreed to further reduce emissions by about 80% by the year 2010, again relative to 1980 levels. This latter Protocol was the first attempt to follow an "effects based" strategy utilising the critical loads concept to direct emission reductions at those sources believed to cause the most environmental damage and to afford the best protection to the most acid sensitive ecosystems. Similar

Figure 1.1. UK freshwater sensitivity map and MAGIC site locations



Sensitivity map from Hornung et al. (1995). Location of Northern Ireland relative to Great Britain is approximate.

agreements have been reached with respect to nitrogen emission, the First Nitrogen Protocol being signed in 1988 with an agreement to stabilise N emissions at their 1987 levels by 1994. Outside of the UN-ECE, the EU has passed legislation to limit emissions from Large Combustion Plants.

Finally, in 1999 a new agreement was signed in Gothenburg to limit emissions of sulphur, nitrogen oxides, ammonia and volatile organic compounds. This is the Multi-Pollutant Multi-Effect Protocol aimed at reducing the exceedance of critical loads for S and N and critical levels of ozone in sensitive areas. The Protocol was based on a growing body of evidence that indicates that terrestrial ecosystems are becoming less capable of retaining nitrogen leading to elevated nitrate concentrations in surface waters and recognising that current agreements on S reductions were not sufficient to promote chemical and biological recovery in many regions of Europe. In addition, further legislation is planned within the EU with the aim of setting emission ceilings for S and N.

The result of these agreements and legislation and of changes in the UK industrial sector has been an estimated 75% reduction in UK emissions of SO_2 since 1970. The decline has occurred relatively steadily over that period. For NO_x, emissions have decreased by about 30% since 1970 but this decline has occurred since 1990. Emission of NH_3 is estimated to have remained constant since 1970. The impact of these emission reductions has been observed in measured concentrations of wet and dry deposition although these reductions are not constant across the UK. In terms of the effect on surface water chemistry, very few databases exist to document changes since the early 1970s. Those that do exist, for example some lochs in the Galloway region of Scotland, show a significant decline in sulphate concentration and a concomitant increase in Acid Neutralising Capacity (ANC) and pH (Ferrier *et al.*, 2001). Since 1988, changes in water chemistry and biology have been observed at a network of streams and lakes that comprise the UK Acid Waters Monitoring Network. In the period up to 2000, water chemistry changes reflect observed changes in S deposition with sites located close to significant S sources showing greater reductions in S concentration than those in more remote locations. Similar trends towards less acidic water chemistry have been reported across the whole of northern Europe and North America (Stoddard *et al.* 1999).

As well as data describing the recent time-series of chemical changes at individual sites, an effort has recently been made to initiate regional surveys that describe the spatial extent of surface water acidification in acid-sensitive regions of the UK. These surveys have sampled all "standing" waters within these regions or a sample of streams. In some regions, for example Galloway and Wales, the surveys have been repeated over several years but in all cases, the lakes are sampled only once in any given year. This level of observation presents methodological difficulties as a result of sea-salt inputs which can cause a short-term deviation from the 'mean' chemistry and, particularly at stream sites, chemistry is closely related to flow which varies considerably in time. Nevertheless, regional sampling has enabled quantification of the extent and degree of acidification in the acid-sensitive regions of the UK (e.g. Wright *et al.* 1994, Evans *et al.* 2000, Helliwell *et al.* 2001, Ferrier *et al.* 2001).

The most comprehensive regional survey undertaken in the UK was carried out as part of a programme aimed at quantifying the critical loads of surface waters across the whole UK (CLAG 1995). This survey aimed to sample the most acid-sensitive standing water (or headwater stream if no standing water body) on a $10km^2$ grid across the country. The data collected has formed the basis of UK freshwater critical load maps to date (Curtis *et al.*, 2000).

Critical loads have formed the basis of the recent international agreement on emission reductions. The definition of a critical load is "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt 1988). The methods used to calculate critical loads for freshwaters have to date used steady-state concepts to calculate the required load that will protect the ecosystem at some time in the future. These methods take no account of the time taken for the surface water chemistry to recover to a biologically acceptable level after the deposition has been reduced, nor do they give an indication of the water chemistry that can be expected if the critical load is not achieved.

Dynamic models offer the means to assess the future changes that might be expected in response to future emission reductions. A number of models have been developed in recent years and in the UK, the Model of Acidification of Groundwaters In Catchments (MAGIC, Cosby *et al.* 1985a, 1985b) has been extensively developed and tested (Jenkins *et al.* 1997). The MAGIC model contains mathematical representation of what are considered to be the key chemical processes linking the deposition of acidic pollutants and the acidification of soils and surface waters. In the UK, MAGIC has been applied at a number of sites for which detailed catchment physical and chemical data are available and used to determine the likely recovery of surface waters in response to the Second Sulphur Protocol (Jenkins *et al.* 1997, 1998). MAGIC has also been extensively tested at a number of sites where time-series chemistry data is available and found to closely match the observed patterns in annual mean chemistry. In addition, the model has been shown to predict the observed responses to catchment manipulation experiments conducted in Norway and Sweden (Beier *et al.* 1995). At sites where sediment cores have been collected and palaeoecological reconstructions of pH have been inferred, the MAGIC model has also been shown to closely match the historical build-up of acidification (Jenkins *et al.* 1990). The data from regional surveys, however, provide a unique opportunity to use MAGIC to assess the *regional extent* of recovery from acidification in light of the most recently agreed emission reductions.

At regional scale MAGIC has been applied in two different modes, multiple site application and Monte-Carlo application, each utilising simplifications regarding spatial data describing the catchment areas within the region. Multiple site application involves a unique model calibration to each site within a region using the best available physical and chemical data to describe that site and enables an assessment of which lakes will change over a given time-period (e.g. Collins and Jenkins 1998). Monte-Carlo application simulates 'hypothetical' catchments within a regional range of observed physical and chemical characteristics to address the question of the response all surface waters within a region given that not all sites within a region have been sampled (eg. Sefton and Jenkins 1998). In many of the acid-sensitive regions of the UK, water chemistry samples have been collected from all standing waters and given that high resolution spatial data describing soils and land-use are available; the multiple site application provides the most rigorous and useful analysis.

The data collected as part of the UK CLAG survey has been used for a UK scale dynamic modelling exercise (Evans *et al.* 1998) using a multiple site methodology. Many of the sites included in this analysis were however located in areas not considered acid-sensitive. A more recent approach, and that utilised in the work reported here, is to focus the multiple site MAGIC applications into known acid-sensitive regions. This provides the opportunity to use data of a higher spatial resolution in the calibration process. Consequently, although the regions included in this study cover a relatively small proportion of the UK (Figure 1.1), they do include many of the areas where acidification is a concern. Since the regions also cover a wide gradient of deposition, geology and topography, they provide some indication of future changes in acid-sensitive waters in unsampled regions.

This report documents the most rigorous and detailed regional calibration of MAGIC in the UK to date. The model is applied in six acid-sensitive regions; the Cairngorms, Galloway, the Lake District, the South Pennines, Wales and Dartmoor. Of these, the South Pennines and Galloway represent the most extensively acidified regions in the UK. The model is then used to determine the recovery in surface water chemistry that might be expected under the most recent emission reduction agreement, the Gothenberg Protocol, the Second Sulphur Protocol and constant deposition at present levels. This provides an assessment of the predicted future chemistry that would have occurred without the most recent agreements, and that which would have occurred if no further action were taken on emission reductions.

Chapter 2: Methods

Development of dynamic models to predict the responses of surface waters to changing land-use and acid deposition requires a detailed knowledge and understanding of the soil processes that lead to loss of soil base status and the acidification of surface waters. Such models require simplification of the complex physico-chemical processes that determine ion concentrations throughout the soil column without affecting the model's ability to predict the catchment scale responses. This 'averaging' or 'lumped parameter approach' allows the models to be easily applied on a catchment and regional basis with limited input data required to calibrate and drive the model. The MAGIC model (Cosby *et al.* 1985a) has been widely applied and tested in Europe and North America, as it is one of the models recommended in the UN-ECE handbook on Mapping Critical Loads (Henriksen *et al.* 1989). A full model description is given in Jenkins *et al.* (1997).

2.1. THE MAGIC MODEL

MAGIC uses a lumped approach in two ways:

(i) a myriad of chemical and biological processes active in catchments are aggregated into a few readily-described processes, and

(ii) the spatial heterogeneity of soil properties within the catchment is lumped to one set of soil parameters.

MAGIC consists of a set of equations that quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel, a set of mass balance equations which quantitatively describe the catchment input-output relationships for base cations and strong acid anions in precipitation and streamwater, and a set of definitions that relate the variables in the equilibrium equations to the variables in the mass-balance equations.

The soil-soil solution equilibria equations describe cation exchange using a Gaines-Thomas expression for monovalent and divalent cations. Dissolution and precipitation of inorganic Al is represented as an equilibrium with a solid phase of aluminium hydroxide. Dissolution of carbon dioxide (CO_2) followed by dissociation to bicarbonate (HCO_3) and carbonate (CO_2) is also included. Dynamic mass balance equations are derived for the base cations and strong acid anions because these ions have discrete and measurable sources in the catchment. These are used to calculate the Acid Neutralising Capacity (ANC) as the sum of base cations minus the sum of the strong acid anions ($Ca+Mg+Na+K-SO_4-NO_3-Cl$). ANC in the model is conserved as the soil water moves into the stream and is used as an objective, uncalibrated parameter for comparison with observed data. Ions such as H, Al and HCO_3 have diffuse sources and sinks and so concentrations of these are determined at any time by the model inputs, the total amounts of the strong acid anions and base cations and the equilibrium equations.

The streamwater pH in MAGIC is governed by three processes: (i) the deposition of strong acid anions: SO_4 and NO_3, (ii) the degassing of CO_2 as soil water enters the streamwater compartment of the model; and (iii) organic anion dissociation. Today at the most acidic sites, strong acid anion concentrations provide the main control on pH, with alkalinity generation by CO_2 degassing of minor importance. During the pre-acidification period, when the deposition of strong acid anions is assumed to be low, the generation of alkalinity as HCO_3 has the strongest control over streamwater pH. This degassing of CO_2 is controlled in the model by means of a CO_2 partial pressure. The CO_2 partial pressure (pCO_2) is assumed to be twenty times atmospheric in the soil compartment and twice atmospheric in the streamwater compartment.

Organic anions in MAGIC are simulated by specifying the total amount of monoprotic, diprotic and triprotic anions present in soil and surface water. Theoretical pK values (pH at which maximum dissociation occurs) are chosen for each organic species. The total organic charge is assumed to be a product of the degree of dissociation and the concentration of organic acids present in the soil or streamwater. The ratio of total organic charge to the total organic carbon concentration (TOC, on a weight per volume basis) is the effective charge density of the organic acid. Organic charge is assumed to be the same in both the soil and streamwater compartment of the model.

The strong acid anions Cl, NO_3 and fluoride (F) have no adsorbed phase in the model. The relationship of dissolved and adsorbed SO_4 is assumed to follow a Langmuir isotherm and is concentration dependent. SO_4 is not strongly adsorbed on to the exchange complex in most upland UK soils, which are relatively young and not deeply weathered. Consequently, the values that define the Langmuir isotherm have been set such that SO_4 effectively acts in steady state (maximum soil adsorption capacity E_{max} = 0.01 meq/kg and half saturation constant C = 1000 meq/m^3). MAGIC comprises an extremely simplified representation of N involving a net catchment retention at each time step (zero order uptake) to calibrate the simulated against observed NO_3 concentrations in streamwater. NH_4 was observed at significant concentrations only at some sites in the South Pennines, where it was modelled using a similar procedure.

Standard precipitation and throughfall gauges provide adequate estimates of inputs to catchments and the outputs in runoff are integrated at the catchment outflow, however corresponding estimates of soil parameters characteristic for an entire catchment are more difficult to obtain. Key soil parameters required by the model include depth, bulk density (BD), porosity, CEC (measured at soil pH), and the fraction of exchange sites occupied by calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K). Values need to be aggregated both spatially and with depth at each catchment to obtain single values for each parameter. The input requirements to run the model are the atmospheric deposition and net uptake – release fluxes for the base cations and strong acid anions and temperature. Input fluxes are assumed to be uniform over the catchment and are calculated from concentrations of ions in precipitation and the rainfall volume into the catchment. The atmospheric flux of SO_4 and N species must be corrected for dry deposition of gas, particulates and aerosols. The volume of streamflow of the catchment must also be provided for the model.

In the regional applications documented in this report, MAGIC is implemented in its simplest form: a two-compartment representation of each catchment; the soil and the surface water. Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the surface water compartment and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry.

2.2 CALIBRATION PROCEDURE

Calibration and application of MAGIC at the six regions documented here represents the most rigorous and detailed regional application of the model in the UK to date. The modelling exercise has three main objectives:

(i) to assess whether, and to what degree, the regions recover under current international protocols (the Gothenburg Protocol) for S and N emission reductions;

(ii) to assess the added benefit of implementing the Gothenburg protocol over the Second Sulphur Protocol;

(iii) To assess the likely outcome of not implementing further emission reductions beyond the present levels.

Regional application of MAGIC requires data describing surface water chemistry, soil physical and chemical characteristics and land-use history at sites within each region and regional estimation of rainfall chemistry and volume. Surface water chemistry of the sites in each region are described by the regional sampling surveys. These single samples are assumed to adequately represent the mean annual water chemistry of the sites.

Catchment runoff estimates are calculated from an estimate of evapotranspiration and the gridded rainfall data. This study assumed that the evapotranspiration of high rainfall areas ranges from 10% for a moorland catchment (Jenkins and Cosby 1989; Robson *et al.* 1991) to 20% for a fully forested catchment (Kirby *et al.* 1991). Runoff is then calculated at each catchment by linearly interpolating from 10-20% as a function of the percentage of mature forest cover.

Wet deposition of all major ions is routinely measured at 32 sites across the country as part of the Acid Deposition Monitoring Network (Devenish 1986). The most suitable deposition collectors for each region were determined on the basis of proximity, altitude and sea-salt characteristics. Since MAGIC is based on principals of ion balance, correct simulation of conservative ions (SO_4 and Cl) is important to the accuracy of model predictions of the non-conservative ions. Input fluxes calculated from the nearest ADMN collector are compared with output fluxes at each site and inputs are adjusted as necessary to balance the conservative ions, on the assumption that the difference between outputs and wet deposited inputs is dry and occult deposition. The enhanced input of Cl is assumed to be as neutral sea salt. Base cations and SO_4 are also added in the appropriate sea salt ratios thereby maintaining the observed pH of the rainfall.

Since most UK soils are relatively young they have little capacity to absorb SO_4. This effectively causes SO_4 to be in steady state with respect to the balance between input and output at present day. This pseudo-conservative behaviour enables deposition enhancement for non-marine SO_4 (xSO_4) to be calculated in the same way as for Cl. This extra input of SO_4 is assumed to represent a combination of dry deposited SO_2 and SO_4 aerosols and is added to the input flux as H_2SO_4 in excess of SO_4 required by the sea salt enhancement.

The mass balance method for estimating the dry and occult deposition of Cl and SO_4 component of the rainfall is not applicable to N species due to their strong retention in most terrestrial ecosystems. Interpolated wet and dry deposition for NO_x and NH_x is available on 20 km x 20 km gridded basis for the UK for 1989-92 and this is used directly as a model input.

The historical trend in wet deposited non-marine SO_4 is assumed to follow the sequence described by the Warren Spring Laboratory (1983) and regionally adjusted based on observations since 1980.

MAGIC is not a spatially distributed model and for this application soils were aggregated into one profile that represents both spatial and vertical heterogeneity within each catchment. Catchment boundaries were delineated on soils maps (scales from 1:63,360 to 1:250,000) to define the soil map units and their relative proportions within each catchment. For the Scottish sites, a database held at the Macaulay Institute contains soil profile descriptions surveyed at 5 km^2 scale and soil chemical analyses at 10 km^2. Soil data for the English and Welsh sites were derived from reports and soil memoirs (Lea 1975, Rudeforth 1984).

A typical profile was taken to represent each of the dominant soil types within the catchment and the physical and chemical characteristics were weighted vertically within each profile. Where no representative profile matched the soil types within the catchment, the nearest corresponding soil type was used, providing the soil shared the same parent material and topographic characteristics. The weighted value for each soil parameter was then spatially averaged according to the relative proportions of each soil type within the catchment (Helliwell *et al.*, 1998).

Uptake and enhanced deposition are included as extra fluxes that are specified at each time step linked to forest age and cover. The age and percent mature forest cover at each site is derived from local Forest Enterprise stock maps. These data illustrate tree species, planting year, spatial coverage, clearfelling and rotation. This detailed history, combined with assumptions simplifying the processes involved, allows construction of historical sequences and future forecasts of the key driving variables at each site. In this study, it is assumed that each stand is felled at 50 years of age and immediately replanted such that the same forest growth assumptions are repeated.

At forested sites, runoff yield is assumed to decrease in response to increased ET from a pre-planting level of 10% to 20% at canopy closure. Canopy closure is assumed to be at 20 years age for all stands. Net plant uptake of ions is assumed to peak at 20 years age and decrease thereafter and forest filter deposition is assumed to increase linearly to 20 years age and remain constant until felling (Jenkins *et al.* 1997).

The calibration for each site is carried out sequentially. First, the concentrations of the stream Cl and SO_4 are calibrated by adjusting filter and dry deposition of sea salts and gaseous/particulate sulphur compounds, under the assumption that these ions are in approximate steady-state with respect to atmospheric inputs. Next the NO_3 and NH_4 concentrations are calibrated by adjusting first-order uptake functions to match observed surface water concentrations. Finally, the base cation concentrations are calibrated using an optimisation procedure.

The base cation calibration involves fitting the results of long-term model simulations to currently observed water and soil base cation data (target variables). The target variables consist of surface water concentrations of Ca, Mg, Na, K and soil exchangeable fractions of Ca, Mg, Na, K (based on the catchment weighted average). The target variables thus comprise a vector of measured values all of which must be reproduced by the model at each individual site if a calibration is to be successful. The use of multiple, simultaneous targets in an optimisation procedure provides robust constraints on model calibration (Cosby *et al.* 1985b).

Those physico-chemical soil and surface water characteristics measured in the field are considered 'fixed' parameters in the model and the measurements are directly used in the model during the calibration procedure. Base cation weathering rates and base cation selectivity coefficients for the soils are not directly measurable and are considered as 'adjustable' model parameters to be optimised in the calibration procedure.

The calibrations are performed on simulations run for 140 years to present day. After each historical simulation, the model variables are compared to the observed data, the adjustable parameters are modified as necessary to improve the fit and the historical simulation is re-run. The procedure is repeated until no further improvement in the fit is achieved.

Chapter 3: Model Applications

Region 1: Cairngorms

3.1.1 REGIONAL DESCRIPTION

The Cairngorm mountain region in north-east Scotland is one of the most important nature conservation areas in Europe, with the central mountain area containing some of the best examples of arctic-alpine habitats in Europe and the most extensive remnants of native Caledonian pine forest in Britain (Johnson, 1997). Since the mid-20th century the main land use change in this region has been afforestation. In 1946 the total area of forestry in the Cairngorms was 30.8 km^2, by 1988 the area under cultivation increased to 92 km^2 (Hester *et al.*, 1996). The role of acid deposition in the Cairngorms is minor relative to other areas of the UK further south that receive significantly higher loadings. Although deposition inputs are low (c. 12 kg/ha/yr S and c. 8 kg/ha/yr N) (Monteith and Evans, 2000), the amount of pollution appears sufficient to cause environmental damage in this acid sensitive region.

Regional geology is comprised predominantly of acidic Precambrian granites at higher altitude and relatively base rich metamorphic rocks at lower altitude; Moine schists and granulites occur in the north-west of the region along with outcrops of younger Dalradian schists and gneisses (Harrison, 1988; Bain *et al.*, 1994). The Dalradian also contains the majority of calcic rocks, including limestones, dolomites and calc-silicates (Smart *et al.*, 1998). At lower altitudes, freely draining podzolic soils are common along with extensive areas of shallow peat; these soils contrast with those at higher altitudes, which are a combination of poorly developed alpine soils and lithosols. On the higher ground where the gradient is low, patchy areas of blanket peat have formed. As the majority of soils in the upland region are derived from base poor parent material of the Countesswells Association, these soils are generally acid with low base saturation.

3.1.2 SURVEY SITES

The 38 sites included in this study (Figure 3.1.1) cover a 400 km^2 area of the Cairngorms, and an altitudinal gradient of 213 to 1310m. Catchment sizes range from ~2 to 4466 ha. With the exception of the March Burn, all surveyed sites were lochs; at higher elevations, these were typically deep corrie and glacial valley lochs, whereas at lower elevations they were mainly shallower, with lower-relief catchments. Loch areas were generally small relative to their catchments, with loch:catchment ratios <0.1 for 84 % of the sites: this is typical of mountain environments (Helliwell *et al.*, in press).

As described above, the spatial distributions of soils and geology are related to the altitudinal gradient, and a similar pattern is observed in land-use. The ten catchments containing over 10% coniferous forest are all located in the lower, northern part of the study area, as are the only sites with any improved farmland. Loch Pityoulish and Lochan Mor, both of which are at <250m altitude.

Most sampling was undertaken in early April 1999, at which time 26 sites were sampled. The remaining 12 sites were sampled during late June and July 1999. Long-term data for the Allt a'Mharcaidh AWMN site in this region (Figure 3.1.2, Table 3.1.1) suggest that samples collected in spring sampling were rather dilute, probably due to melting snow. This may explain low xSO_4 concentrations relative to the 12-year mean, although some downward trend may also be present in recent years. The July sample for the Allt a'Mharcaidh suggests that conditions during the later surveys were very close to the long-term average.

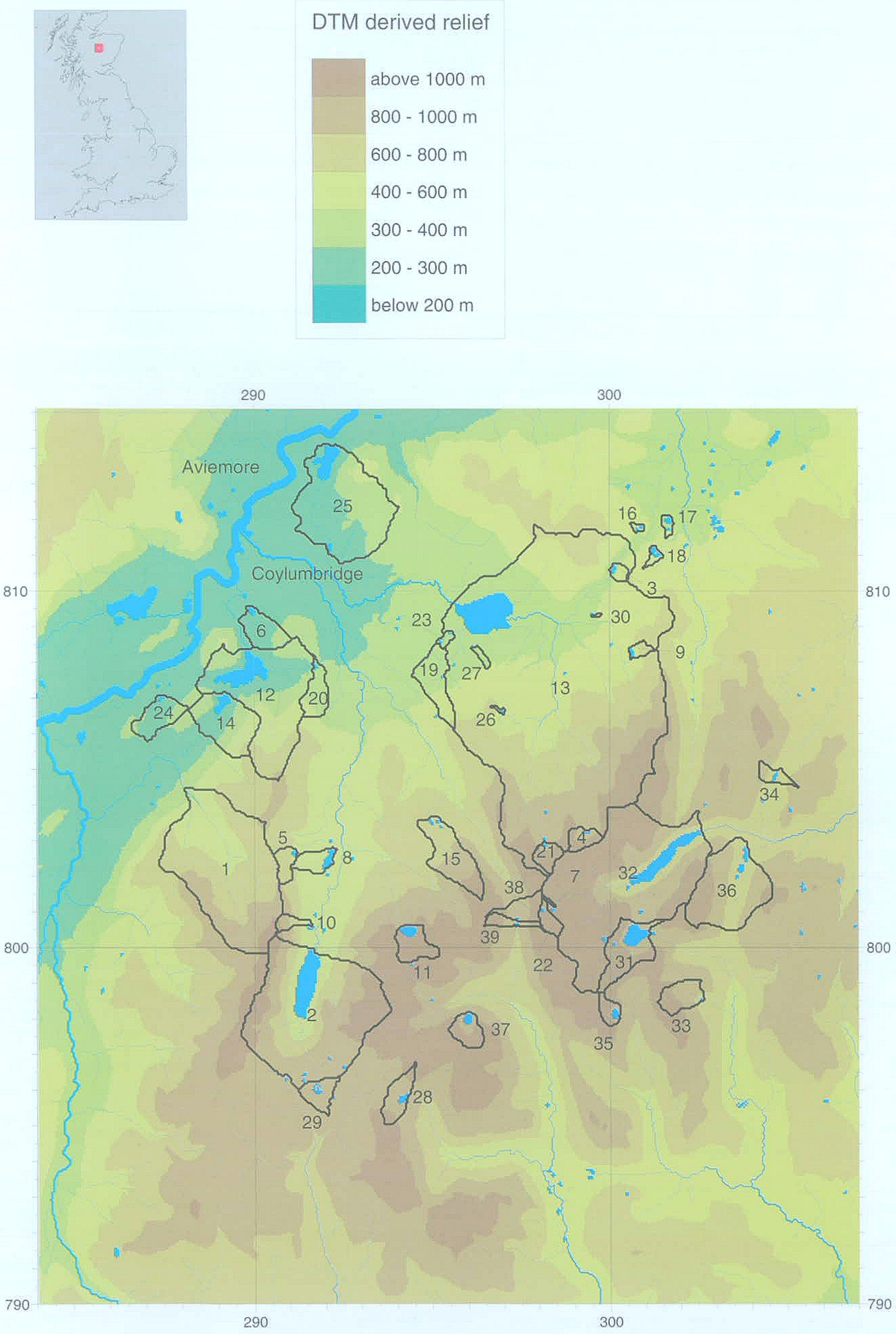


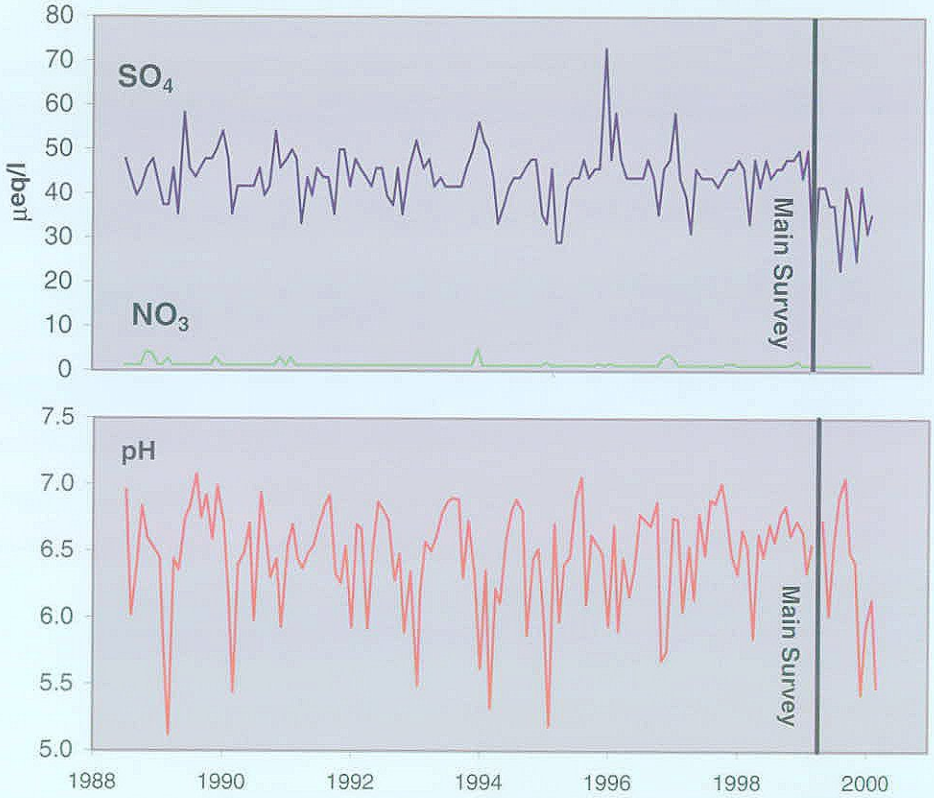
Figure 3.1.1. Location of Cairngorm survey sites (sites listed in Appendix 1)

TABLE 3.1.1. Allt a'Mharcaidh AWMN site solute concentrations

	ANC	pH	SO_4	NO_3	Cl	Na	Ca	Mg
April 1999	33	No data	21	1.3	104	96	29	25
July 1999	57	6.55	38	1.3	104	130	40	25
12-year mean	56	6.45	44	1.5	111	135	41	29

All concentrations in μeq/l except for pH (pH units)

Figure 3.1.2. AWMN data for the Allt a'Mharcaidh



3.1.3 REGIONAL CHEMISTRY

Within this relatively small region a wide range in surface water ANC was observed (-3 μeq/l to 535 μeq/l). Generally the surface water chemistry of the lochs is dilute, with low concentrations of base cations (Ca, Mg, Na, K) and acid anions (Cl, NO_3 and SO_4) (Table 3.1.2). Low SO_4 concentrations reflect low levels of S deposition, and NO_3 concentrations below 10 μeq/l at most sites suggest that soils in the region retain the majority of incoming N. Surface waters are generally more acidic in high altitude areas, due to predominantly poorly buffered thin alpine soils developed on granitic parent material (mean ANC for 23 lochs = 30 μeq/l). At lower altitudes where the geology is comparatively base rich, the surface water ANC is considerably higher (mean ANC for 15 lochs = 157 μeq/l). Helliwell *et al.* (in press) have conducted a comprehensive review of these data.

3.1.4 MAGIC APPLICATION

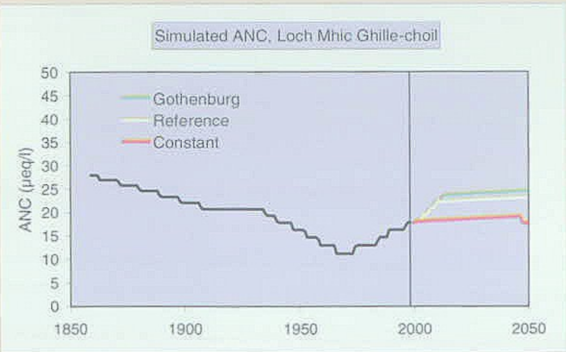
The MAGIC model was applied according to the standard methodologies described in Chapter 2, with a historic simulation from 1850, and three future deposition scenarios based on the 1999 Gothenburg Protocol, 1994 Second Sulphur Protocol ('Reference' Scenario) and a 'Constant' scenario (continued deposition at present-day levels). For the ten afforested catchments in the region, forest cover and stand age were derived from the 1988 Land Cover of Scotland database (MLURI, 1993). Forest cover ranged from 12 % at Loch Gamhna to 100% at Lochan nan Geadas, Inshriach, Lochan nan Nathrach and Lochan na Frithe. At these catchments the impact of future forest management schemes on water quality, given the proposed reduction in S and N emission reductions, are considered. For modelling purposes it was assumed that replanting occurs immediately upon removal of the mature crop (planted mainly in the 1970s). Forest uptake, dry deposition enhancement and changes in discharge linked to forest age were incorporated in the model according to the methods described in Chapter 2.

TABLE 3.1.2. Summary chemistry for the Cairngorm Region

	10th Percentile	Median	90th Percentile
ANC	8	42	180
pH	5.28	6.20	7.03
SO_4	19	31	70
NO_3	1.5	2.5	8.8
Cl	59	117	283
SBC	101	179	506
NH_4	0.8	2.1	4.5
DOC	0.5	2.	8.42

All concentrations μeq/l except for pH (pH units) and DOC (mg/l).

Example 1: Loch Mhic Ghille-choil



Loch Mhic Ghille-choil (NH 921 025) is typical of many moorland catchments included in this region. The catchment is situated at an altitude of 549 m and has an area of 57 ha. The loch is surrounded by shallow peat, whilst large exposures of rock dominate the steeper terrain towards the watershed. The granite geology provides little buffering capacity, and MAGIC simulation indicates that the site has a naturally low ANC. Historically, ANC gradually declined in response to increased sulphur deposition until the late 1970s, but has since recovered slightly, to 18 μeq/l. The concentration of NO_3 is low, and makes only a minor contribution to loch acidification. Model forecasts show a further recovery in ANC to 23 μeq/l in response to reductions in S deposition under the Reference scenario, and 25 μeq/l under the Gothenburg scenario, approaching the pre-industrial value of 28 μeq/l. Predictions for the Constant scenario indicate that ANC will remain largely unchanged in future, suggesting that current deposition is already below the steady-state critical load for this site.

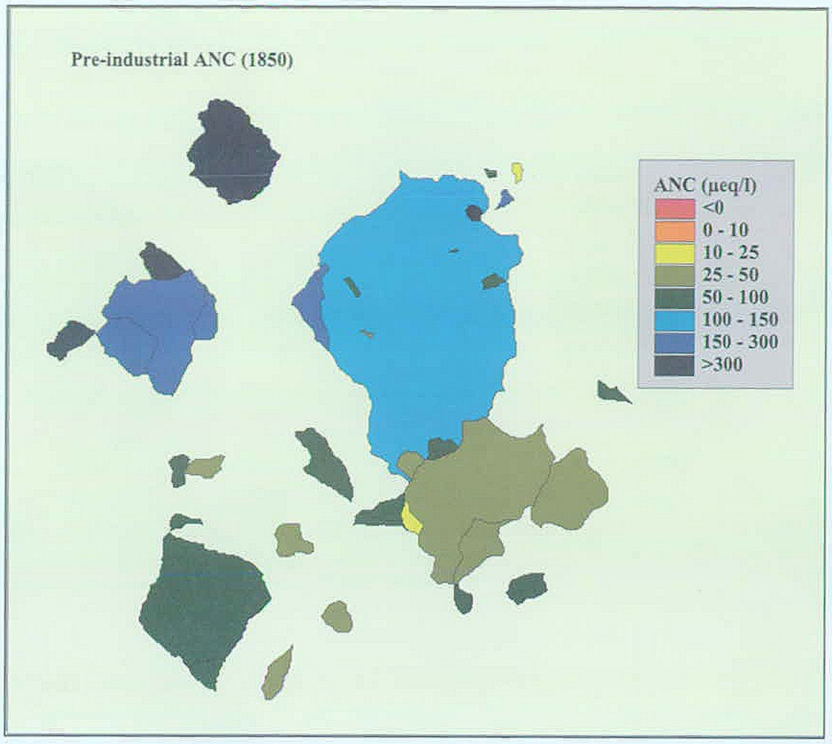


FIGURE 3.1.3. MAGIC simulated pre-industrial ANC (μeq/l), Cairngorms

3.1.5 RESULTS

MAGIC was successfully calibrated to all 38 catchments in this regional study, with a close relationship between observed loch chemistry sampled in 1999 and simulated chemistry. Unlike some of the other regions considered in this report, such as the South Pennines (Section 3.4) pre-industrial ANC appears to have been low at many of the Cairngorm lochs; 14 sites have a MAGIC simulated ANC for 1850 of 50 μeq/l or below (Figure 3.1.3). The naturally low ANC of these sites is due to the low buffering capacity of the upland soils and slow weathering bedrock. A comparison with present day values (Figure 3.1.4a, Figure 3.1.6) indicates that surface water ANC deteriorated across the region from 1850 to 1999 as a consequence of anthropogenic S and N deposition. The most acidic present day conditions are observed in the sensitive southern part of the study area, underlain by granite. Lower altitude catchments, due to the relatively base-rich parent material (schists, gneisses, and calcic rocks), have a generally higher ANC.

Future responses of surface water chemistry are investigated for the three deposition scenarios described in Chapter 2, based on HARM forecasts. The predicted response of surface water ANC under the Constant scenario (Figure 3.1.4b) is varied; at 19 lochs a slight improvement is predicted, whilst 8 lochs remain unchanged (change in ANC < 1 μeq/l), and 11 are expected to become more acidic. For the 38 sites as a whole, simulated ANC declines on average by 11 μeq/l between 1999 and 2050. However, this masks a large discrepancy between moorland and forested sites; at moorlands, the average ANC change in this time is a small increase (2 μeq/l), but forested sites show a large average ANC decline of 43 μeq/l. This major predicted deterioration in the ANC of forested sites is a consequence primarily of base cation uptake by growing forests causing depletion of soil base saturation, intensified by enhanced dry and occult deposition of acidifying pollutants to the forest canopy.

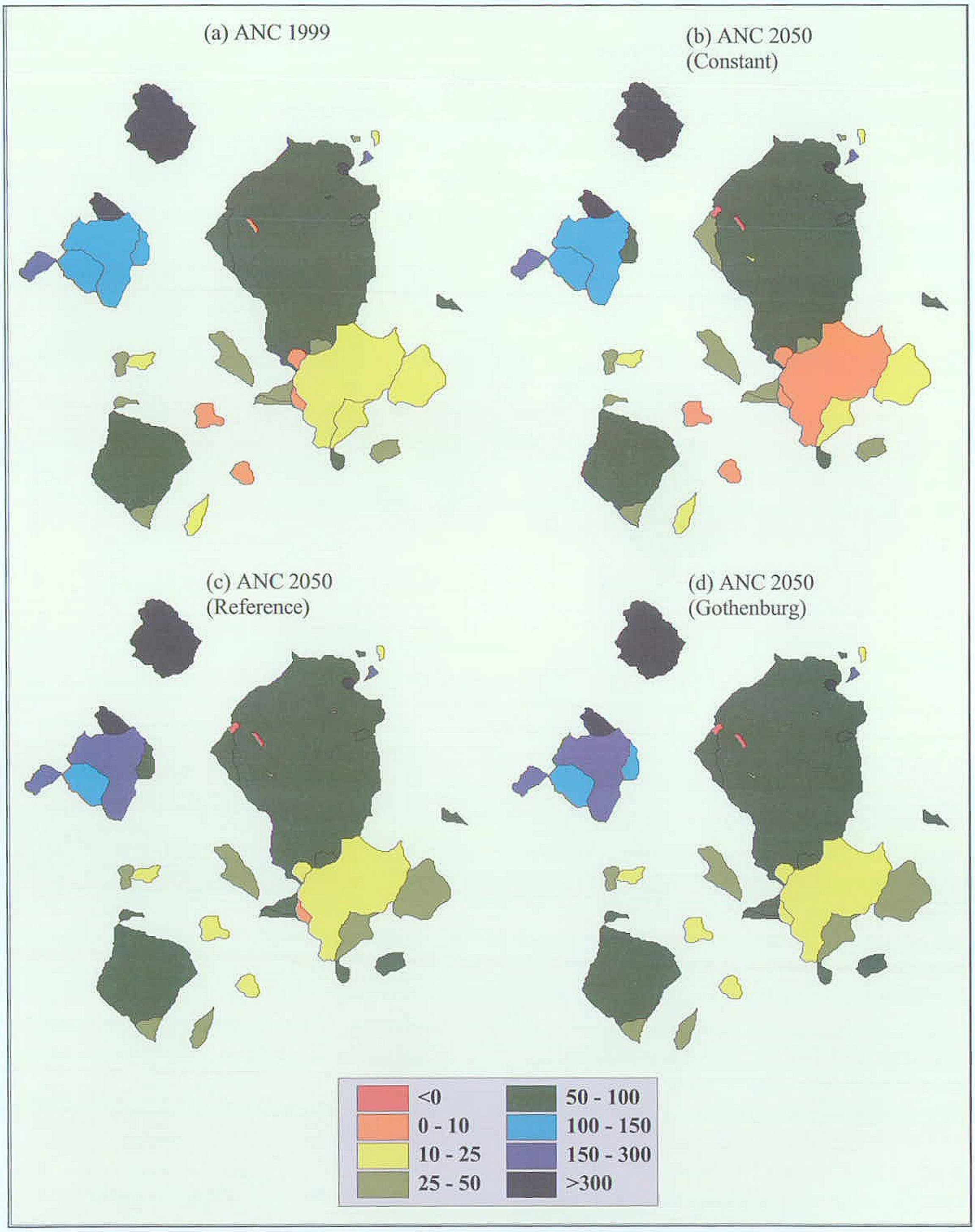
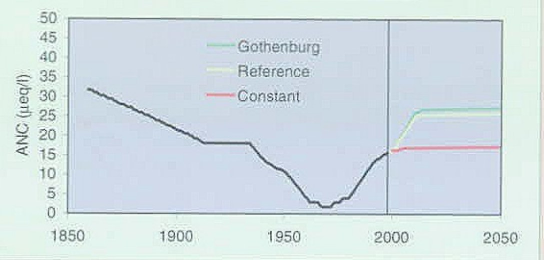


FIGURE 3.1.4. MAGIC simulated present-day and forecast ANC (μeq/l), Cairngorms

Under the more stringent emission reductions associated with the Reference and Gothenburg scenarios, surface water quality improves at a greater number of lochs; ANC is predicted to increase at 31 sites under both scenarios. The impact of these scenarios on loch ANC is very similar (Figure 3.1.4c,d; Figure 3.1.5, Figure 3.1.6)

Example 2: Lochan nan Stuirteag

Simulated ANC, Loch nan Stuirteag



The undulating topography of the Stuirteag catchment (NN 941 957) is representative of much of the Cairngorm plateau. The mean altitude of the catchment is 962 m and at this height, thin alpine soils developed from granite predominate, with clusters of rocks at higher elevation. Vegetation is patchy and composed of a wind-clipped mosaic of fescue and alpine azalea–lichen heath. The background ANC of this loch is low (32 µeq/l), and during the peak period of anthropogenic deposition in the 1970s, simulated ANC declined to a minimum of 2 µeq/l. This substantial acidification can be attributed to the limited capacity of the thin mineral soils in this catchment to neutralise acid deposition. Since the 1970s, loch ANC has risen in response to falling S deposition, and is currently 16 µeq/l. This increase is predicted continue under the Reference scenario, to 26 µeq/l in 2050, with marginally greater recovery predicted for the Gothenburg scenario, to 27 µeq/l. For the Constant deposition scenario, however, ANC is predicted to level off at 17 µeq/l.

with a median recovery under the Reference scenario of 10 µeq/l and under the Gothenburg scenario of 11 µeq/l. For moorland sites alone, the median predicted increases are 12 µeq/l and 13 µeq/l. Given the low degree of acidification in this region, the 2050 ANC levels predicted for many of these lochs are close to those simulated for the pre-industrial period (e.g. Examples 1 and 2).

For both scenarios, ANC is expected to decline at seven forested lochs between 1999 to 2050, despite reductions in acid deposition. It is worth noting, however, that all of these sites are at low-elevation (<400 m) and have a relatively base-rich geology. Thus, even with these ANC reductions, most forested sites remain non-acidic (ANC >0). Two exceptions to this are Lochan nan Geadas and Lochan nan Nathrach, both of which are forecast to have an ANC below –20 µeq/l in 2050 under both scenarios. At these sites, therefore, it appears that even significant reductions in deposition may not be enough to offset the effects of second rotation forest planting in causing depletion of soil base saturation, and acidification of surface waters.

It is clear from these results that both the Reference and Gothenburg Protocols will deliver significant improvements in surface water quality in the Cairngorms, at least for moorland areas. Given the similarities between the two scenarios in this region, however, it is doubtful whether substantial additional environmental benefits to surface waters will be obtained by imposing the more stringent but costly Gothenburg protocol.

Figure 3.1.5. Forecast 2050 vs present day ANC

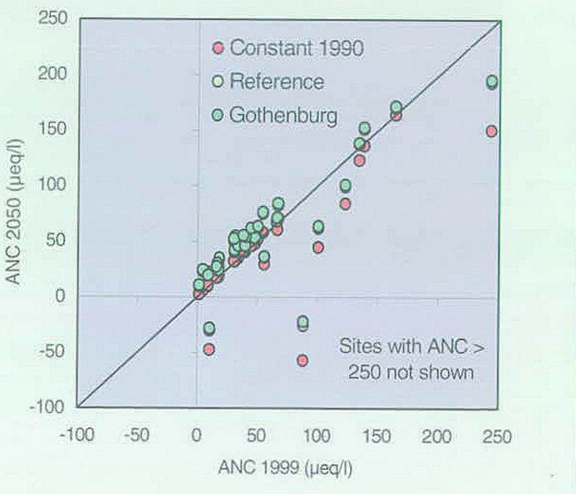
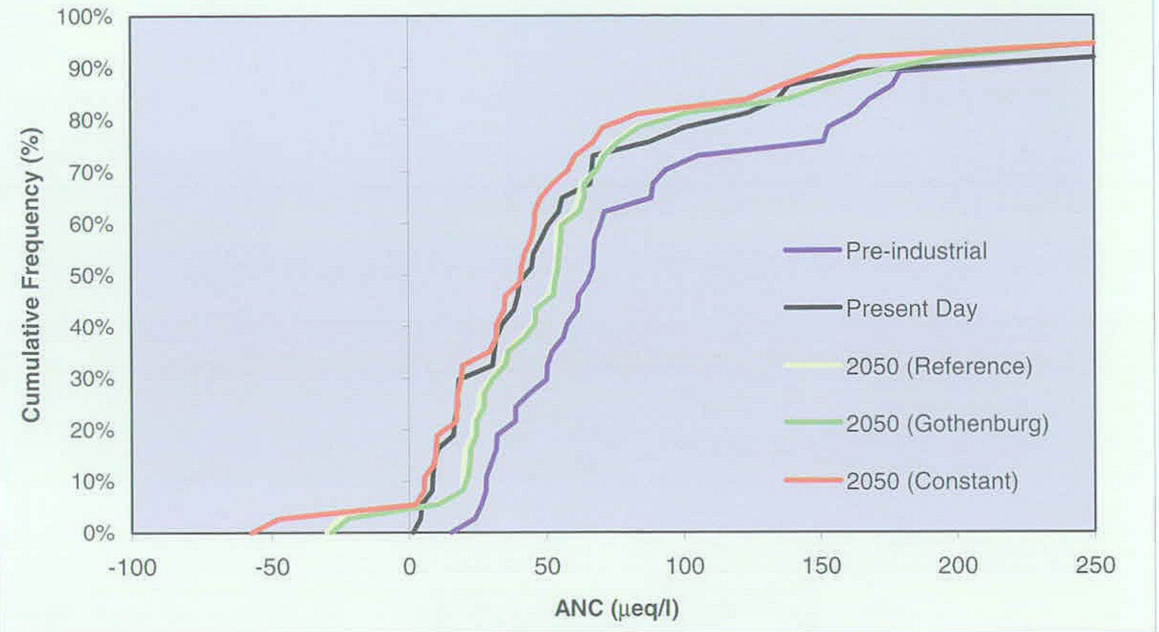
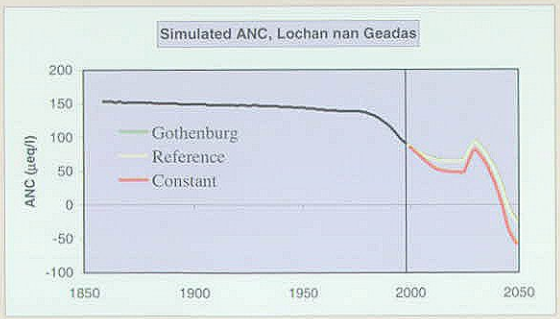


Figure 3.1.6. Cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios)




Simulated ANC, Lochan nan Geadas

Example 3: Lochan nan Geadas

The relatively low-lying Lochan nan Geadas catchment (NH 955 089) is situated at 343 m asl and is entirely forested. Humus iron podzols (Corby soil association) are found throughout the catchment. High concentrations of base cations in the loch result from weathering of Dalradian schists, gneisses and calcitic rocks, and simulated pre-industrial ANC is relatively high (153 µeq/l). Although the supply of base cations was sufficient to sustain good water quality even during the period of high deposition, this delicate chemical balance appears to have been disrupted with the advent of intensive commercial forestry in the catchment in 1975. The model indicates that loch ANC has fallen since this time, and that this decrease will continue even with large reductions in S and N deposition under the Gothenburg protocol. Under all three scenarios, ANC is predicted to become negative after 2040 following second rotation forest planting, decreasing to between −22 µeq/l (Gothenburg) and −57 µeq/l (Constant) by 2050.

Region 2: Galloway

3.2.1 REGIONAL DESCRIPTION

The Galloway region of south-western Scotland (Figure 3.2.1) is a classic acid-sensitive environment. The region is dominated by soils developed from three main geological units: (i) granitic intrusions of Tertiary age, (ii) shales, mudstones and greywacke of Ordovician age and (iii) shales, mudstones and greywacke of Silurian age. These geological types have a low capacity to buffer external acid inputs (Kinniburgh and Edmunds, 1986). Soils developed from these parent materials form the Ettrick and Dalbeattie Associations, which are spatially extensive throughout Galloway. In freely drained areas, soils are generally thin and consist primarily of podzols and peaty podzols, whilst a large proportion of the upland area is covered by blanket peat. Dominant land uses are heather moorland, molinia grassland and extensive commercial forestry plantations. Afforestation began in the 1940s and reached a peak in the 1960s and 1970s. Afforestation has been almost exclusively with non-native conifers, predominantly sitka spruce, (*Picea sitchensis*) and lodgepole pine (*Pinus contorta*).

Acid deposition in Galloway is relatively high (c. 32 kg/ha/yr S and c. 33 kg/ha/yr N) (Monteith and Evans, 2000). Inputs are highest when dominant air masses derive from a south-easterly direction, having passed the heavily industrialised areas of Britain and other parts of Europe. Northern Ireland, to the southwest, provides another pollution source. Consequently within this region, acidification of sensitive upland surface waters is widespread.

3.2.2 SURVEY SITES

Surface water sampling began in 1979 and included 49 lochs in the vicinity of the three largest granitic plutons in the Galloway region. These lochs were resampled in April of 1988, 1993, 1994, 1996, 1997, and 1998. From 1993, eight additional lochs were included in the survey in other geological areas. Lochs range in altitude from 40 to 520 m a.s.l., and vary in character from small mountain pools (minimum loch area 0.6 ha) to large reservoirs (maximum area 820 ha). The catchments of 40 lochs (68% of the total number) are more than 10% forested. Agricultural influences are minor.

For this model application, 'present day' chemistry was estimated as the average of data for April 1996 and 1997. AWMN data for the Round Loch of Glenhead and Loch Grannoch, both of which were included in the regional survey, set the survey data in the context of long-term means (Table 3.2.1, Figure 3.2.2).

TABLE 3.2.1. Galloway AWMN site solute chemistry

(a) Round Loch of Glenhead	ANC	pH	SO_4	NO_3	Cl	Na	Ca	Mg
Mean of Apr 1996 and Apr 1997 surveys	-2	4.79	73	22	168	168	34	46
12-year mean	-30	4.91	64	7	194	172	32	22

(b) Loch Grannoch	ANC	pH	SO_4	NO_3	Cl	Na	Ca	Mg
Mean of Apr 1996 and Apr 1997 surveys	-16	5.34	96	31	214	209	51	58
12-year mean	-68	4.60	93	19	257	222	46	27

All concentrations in μeq/l except for pH (pH units). Survey data not part of AWMN dataset.

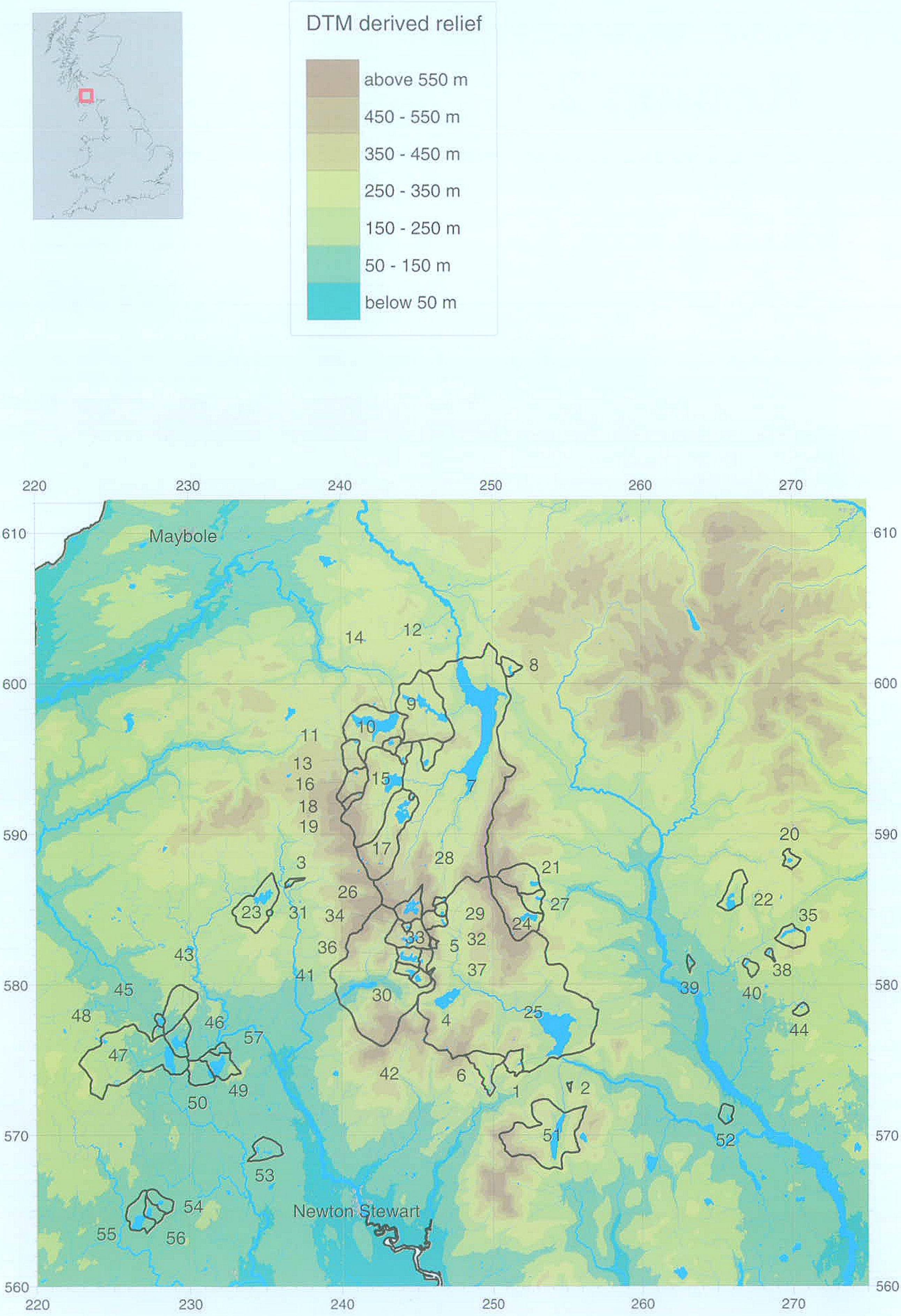
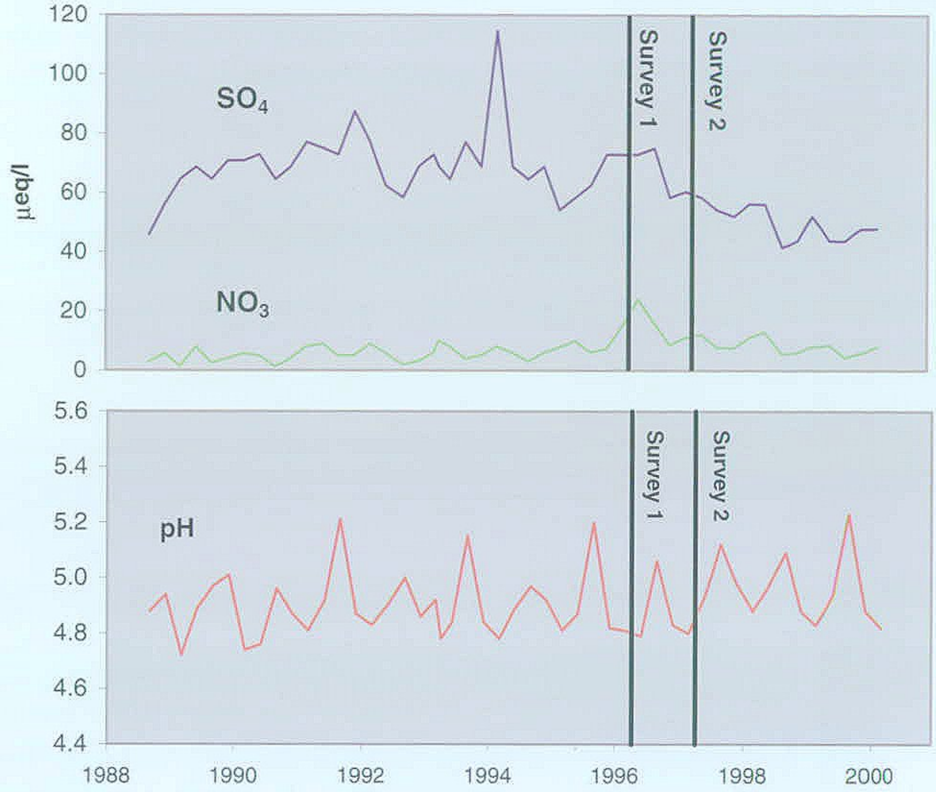


Figure 3.2.1. Location of Galloway survey sites (sites listed in Appendix 1)

Figure 3.2.2. AWMN data for Round Loch of Glenhead



In general, while some differences can be identified between survey and long-term means, concentrations of most solutes are similar. The largest discrepancies are for NO_3, which is much higher in the regional surveys relative to long-term means at both lochs. NO_3 concentrations exhibit relatively high seasonality in this region, and samples taken in spring, when concentrations are generally highest, may therefore provide an over-estimate of long-term means at other lochs in this dataset. SO_4 concentrations during the regional surveys are closer to long-term means, although in recent years levels have declined significantly at AWMN sites in the region (e.g. Figure 3.2.2).

3.2.3 REGIONAL CHEMISTRY

The extent of acidification in Galloway is evident from a regional assessment of loch chemistry (Table 3.2.2). SO_4 concentrations are high relative to most of the other regions included in this study, and a substantial number of sites are acidified (ANC <0 in 11 lochs, pH <5.0 in 17 lochs). Lochs with low ANC are found in moorland areas with granitic geology and

TABLE 3.2.2. Summary chemistry for the Galloway Lochs

	10th Percentile	Median	90th Percentile
ANC	-11	52	191
pH	4.6	5.56	6.53
SO_4	69	93	153
NO_3	7	22	35
Cl	157	214	436
SBC	271	377	798
NH_4	1.1	1.9	4.5
DOC	2.6	5.5	11.2

All concentrations μeq/l except for pH (pH units) and DOC (mg/l).

organic soils, e.g. the Merrick Mountains and Cairnsmore of Fleet. A number of lower-elevation forested sites on sensitive geology are also severely acidified, including large water bodies such as Clatteringshaws Loch (397 ha) and Loch Grannoch (112 ha). In areas with more weatherable bedrock, acidification is less apparent, with ANC exceeding 100 µeq/l at 20 sites, mainly in outlying eastern and western areas of the study region. NO_3 concentrations appear high at many sites, indicating substantial catchment nitrogen leaching, although as noted above, levels observed in the spring surveys may represent seasonal peaks, rather than annual average conditions.

3.2.4 MAGIC APPLICATION

MAGIC was applied to 57 lochs in Galloway, according to the standard methods described in Chapter 2. For the large number of forested sites in the region, detailed information on forest cover and stand age was obtained from forestry stock maps. For forecast simulations, it was assumed that all forest stands are felled after 50 years and immediately replanted.

A close correspondence between observed (mean 1996-1997) and simulated (1997) surface water ANC suggests an acceptable model calibration to the Galloway region. Only one out of 57 catchments failed to calibrate. This catchment contains a major A-road, and appears to be heavily contaminated by road-salt. For the 56 catchments that were successfully calibrated, the response of surface waters to three emissions scenarios, in combination with assumed forest replanting, was assessed.

3.2.5 RESULTS

Historical reconstructions of ANC in 1850 indicate that 69% of surface waters in Galloway had a pre-industrial ANC of more than 100 µeq/l (Figure 3.2.3). Lochs with a pre-industrial ANC < 100 µeq/l are located predominantly in the high rainfall area of the Merrick Mountains, where weathering of the granitic bedrock is low, and soil base cation stores are small. Two of the most naturally acid lochs in this high altitude area are Loch Enoch and Loch Dow by

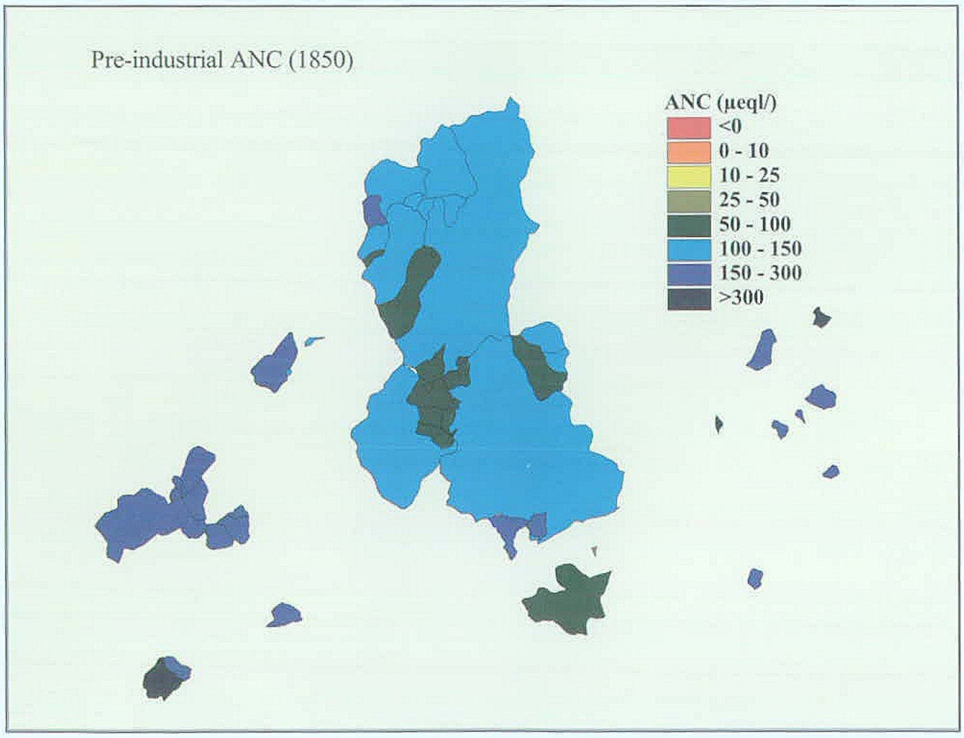


Figure 3.2.3. MAGIC simulated pre-industrial ANC, Galloway

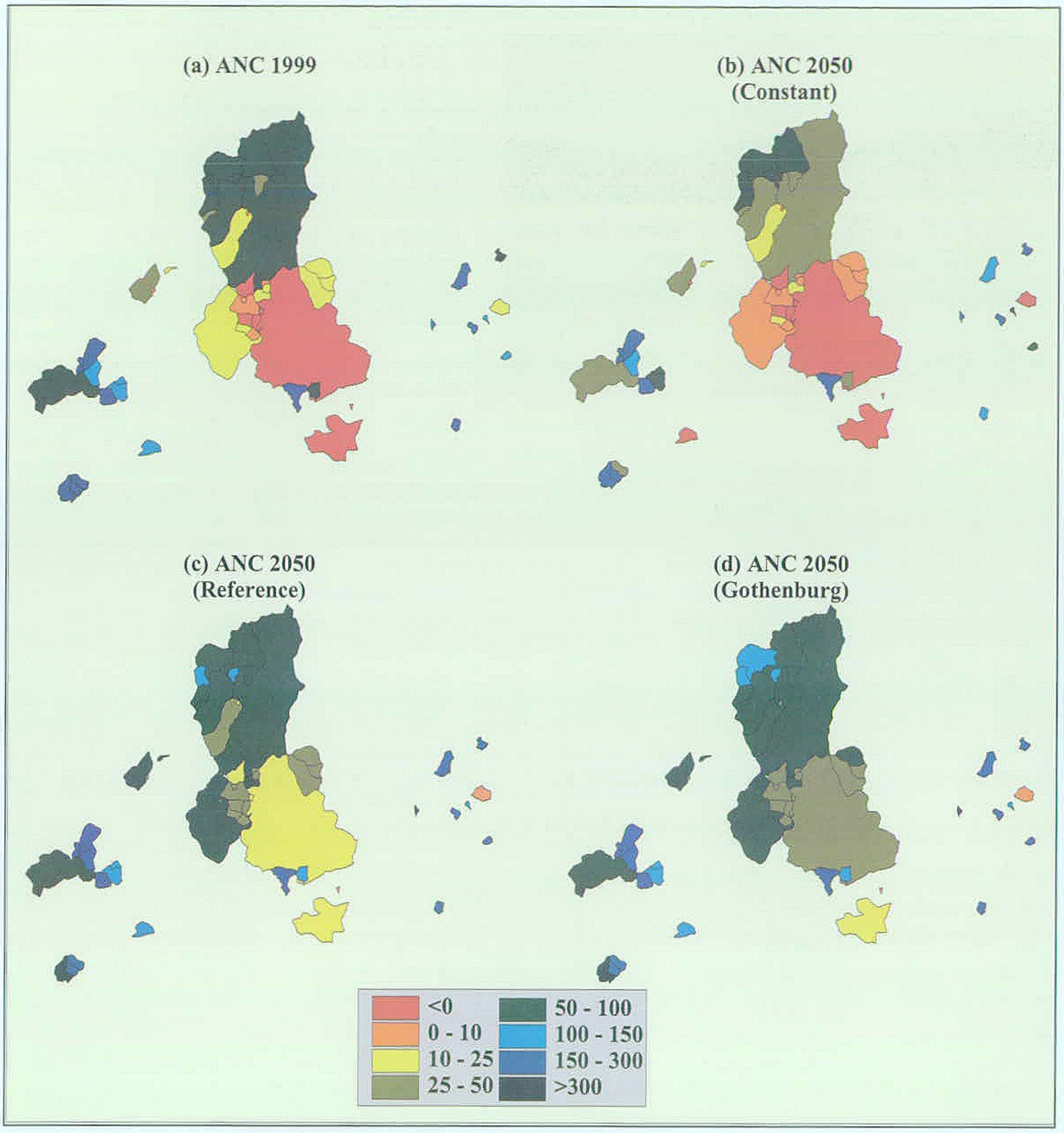
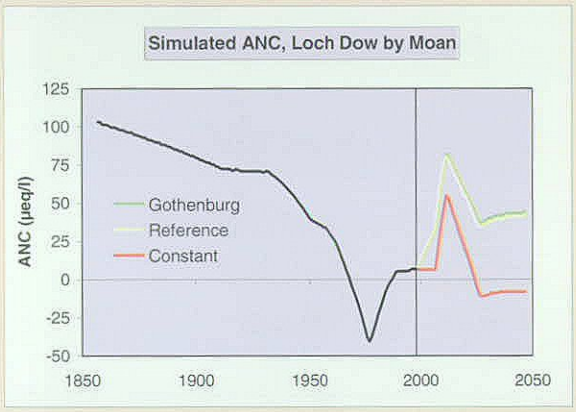


Figure 3.2.4. MAGIC simulated present-day and forecast ANC (μeq/l), Galloway

Round, with simulated 1850 ANC of 50 and 64 μeq/l respectively. From 1850 to 1970s all sites acidified, many to strongly negative ANC levels, but some recovery appears to have occurred since this time. Nevertheless, sites remain acidified, with 1999 loch ANC levels on average 81 μeq/l lower than simulated 1850 values, and nine lochs still have a negative ANC, including large water bodies such as Clatteringshaws Loch and Loch Grannoch. In the central southern part of the region, acidification is particularly severe due to a) extensive afforestation in lower-lying catchments, and b) the low buffering capacity of the high mountain lochs (Figure 3.2.4a).

Example 1: Loch Dow by Moan

Loch Dow is one of the smallest lochs included in this regional survey (surface area 1 ha) and lies at an altitude of 230 m. The loch drains a 12 ha catchment with a maximum altitude of 280 m. Catchment soils are primarily peats (71 % cover) and peaty podzols. The catchment was entirely afforested with exotic species such as Sitka spruce in one phase between 1960 and 1964. The loch is currently acidic, with an ANC close to zero and a pH of 4.3. The historical simulation shows that surface water ANC declined in response to increasing sulphur deposition during 1940-70. This acidification was intensified by forest planting and growth during the same period. Some recovery has since taken place due to reductions in S and N deposition, and further recovery is forecast in future under the Reference and Gothenburg scenarios. Initially this recovery is reinforced by the felling of mature forest, but subsequent replanting causes re-acidification due to (i) enhanced inputs of S and N due to canopy filtering, and (ii) greater base cation uptake by the forest. ANC in 2050 is forecast to be 42 µeq/l and 45 µeq/l under the Reference and Gothenburg scenarios respectively. Under the Constant scenario, although transient recovery is again observed due to forest harvesting, subsequent re-acidification is far more severe, leading to a 2050 ANC of –8 µeq/l.

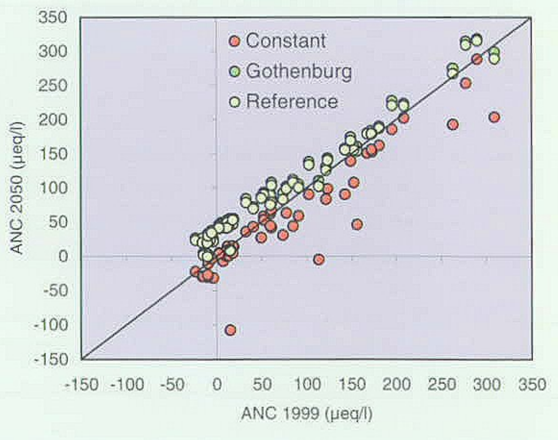


Simulated ANC, Loch Dow by Moan

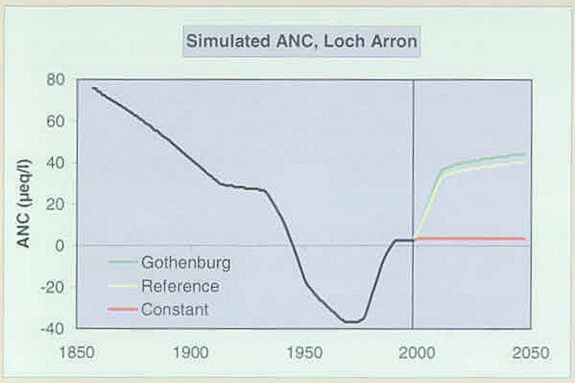
There are clear spatial patterns in the response of regional loch chemistry to the deposition scenarios. Under the Constant scenario, acidification in the poorly-buffered southern part of the region increases, with almost all lochs in this area having a very low or negative ANC by 2050 (Figure 3.2.4b). Overall, the average predicted ANC decline for the region is 21 µeq/l, increasing the number of lochs with a negative ANC to 12 (21% of modelled sites) by 2050 (Figures 3.2.5, 3.2.6). There are large differences in the behaviour of moorland and forested catchments, with moorlands on average predicted to show only a marginal ANC decrease of 1 µeq/l, and forests a much larger decrease of 35 µeq/l. This indicates that second rotation forest planting, and the resulting depletion of soil base saturation due to uptake and enhanced acid deposition, would contribute significantly to further acidification in this region under a constant deposition scenario.

MAGIC predictions for the Reference scenario show substantial ANC increases at the majority of lochs in response to reductions in acid deposition. Increases are greatest at some of the most acidified sites (Figure 3.2.5), and as a result, all 56 lochs are predicted to have a

Figure 3.2.5. Forecast 2050 vs present day ANC



Example 2: Loch Arron



Loch Arron is one of the highest lochs in the Galloway region, lying at 450m altitude. The loch (3 ha) drains a catchment of 26 ha, which gently undulates to an altitude of 531 m. The catchment lies on the Loch Doon granite intrusion and the rocks include tonalite and those of a tonalite/granite transition. Catchment soils are dominated by peaty podzols, and vegetation by Molinia, Erica, and Trichophorum. Present day ANC is 3 µeq/l, and pH is 4.65. The loch has a relatively low simulated pre-industrial ANC (75 µeq/l), indicating that the catchment has little capacity to buffer acid inputs. Consequently, MAGIC simulation suggests that Loch Arron began to acidify during the 19th century, with ANC declining progressively to a minimum of -37 µeq/l in 1971. The acid status is forecast to improve under the Reference and Gothenburg scenarios, with simulated ANC increasing to 42 µeq/l under the Reference scenario and 45 µeq/l under the Gothenburg scenario). Under a constant deposition scenario, ANC is predicted to remain virtually unchanged at 4 µeq/l in 2050.

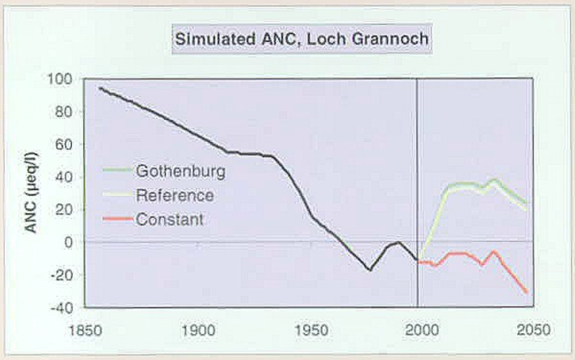
positive ANC by 2050. The average predicted ANC increase for the whole dataset under this scenario is 24 µeq/l, but again recovery is expected to be greater at lochs with moorland catchments (33 µeq/l) than those draining coniferous forestry (17 µeq/l). Furthermore, considerable heterogeneity of response is observed among the 33 forested sites, depending on catchment sensitivity and forested area; four lochs with over 45% forested area are predicted to continue acidifying under this scenario, despite reductions in acid deposition.

Additional reductions in S and N deposition under the Gothenburg scenario generate relatively small additional increases in ANC for this region (Figures 3.2.5, 3.2.6). The average ANC increase for all sites is 28 µeq/l, whilst average increases for forest and moorland sites are 37 µeq/l and 21 µeq/l respectively. This small additional improvement is, however, sufficient to reduce the number of lochs with ANC in the 0-25 µeq/l range from seven under the Reference scenario, to three (Figure 3.2.4c,d).

In summary, survey data show that the Galloway region is currently severely acidified over much of its area. Model simulations indicate that maintaining deposition at current levels, along with replanting of the coniferous forests in this region, will lead to a significant further deterioration in water quality, with ANC falling by over 20 µeq/l on average, and the percentage of surveyed lochs with ANC < 0 rising from 16% to 21%. Emissions reductions under the Reference scenario will, however, be sufficient to cause a substantial increase the ANC of most lochs, with all predicted to have a positive ANC by 2050. Recovery is expected to be particularly strong at the currently acidic high moorland sites. At forested sites, however, second rotation forest planting is likely to slow, or in some cases reverse, this recovery due to falling deposition levels.

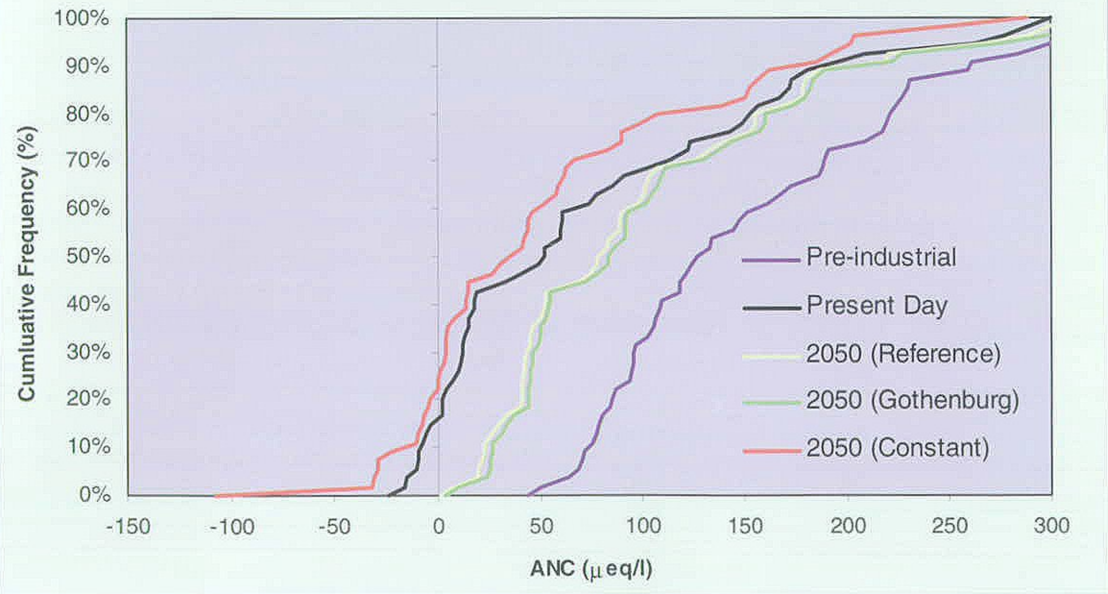
Example 3: Loch Grannoch

Loch Grannoch has a large surface area (114 ha), and lies at an altitude of 210 m. The loch drains a catchment of 1287 ha with a maximum altitude of 601 m. Geologically it forms part of the Cairnsmore of Fleet granite pluton. Catchment soils comprise blanket peat, peaty podzols and peaty gleys, with rankers and exposed rock at higher altitude. The catchment is extensively afforested (66%) with Douglas fir and Sitka spruce. Planting occurred in two phases: in 1962 and 1977-78. The moorland area is characterised by acid Molinia heath species with Calluna and Myrica gale locally abundant. The loch is very acidic with present day ANC -16 µeq/l, and pH 4.6. The catchment has very limited buffering capacity, and historic ANC simulation shows severe acidification in response to rising acid deposition and afforestation. Despite falling deposition since the 1970s, MAGIC suggests that Loch Grannoch is continuing to acidify at the present time. With the introduction of either the Reference or Gothenburg scenarios, coinciding with felling of first-rotation forest, significant recovery is initially forecast, but second rotation forest planting results in re-acidification from 2030 onwards, to an ANC of around 20 µeq/l by 2050. Under the constant deposition scenario, continued loch acidification is forecast, with ANC falling below –30 µeq/l by 2050.



Further emissions reductions agreed under the Gothenburg protocol appear to generate small additional benefits in Galloway, increasing 2050 ANC by around 4 µeq/l compared to the Reference scenario. This reduction will, however, have the effect of reducing the number of lochs in the most sensitive ANC classes.

Figure 3.2.6. Cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios)



Region 3: The Lake District

3.3.1 REGIONAL DESCRIPTION

The Lake District, in Cumbria, north-west England, is a deeply glaciated mountainous area, with maximum elevations above 950m. The region is of high conservation and recreational value, and is protected by National Park status.

Away from the major valleys, land-use is limited to low-density sheep grazing, with relatively little commercial forestry. Much of the upland area comprises steep bare rock and scree, and soils are predominantly thin peaty rankers, with peats present on some lower-relief areas, and brown podzols and peaty gleys on lower slopes. Geology is highly heterogeneous, consisting of Skiddaw Slates in the northwest, metamorphosed igneous rocks of the Borrowdale Volcanics Series in the central area, and Silurian slates, shales and greywackes of the Windermere group in the southeast. Several granite intrusions are also present in the west of the region. As a result of this geologic variability, acid-sensitivity also varies widely; surface waters located on the Windermere sediments are relatively well-buffered, whilst those on the weathering-resistant Borrowdale Volcanics and granites are most susceptible to acidification. Local features such as basic igneous intrusions within the Borrowdale Volcanics also appear to have a significant impact on the acidity of individual surface waters.

Rainfall in the Lake District is high, and spatially variable (1.4 to 4.0 m per year in the catchments studied). Deposition is also high, with 1996 inputs for the two AWMN sites in the region estimated as 21-26 kg/ha/yr non-marine S, and 20-25 kg/ha/yr N (Monteith and Evans, 2000). Previous studies in the region provide evidence of acidification at a number of upland tarns (e.g. Sutcliffe *et al.*, 1982; Whitehead *et al.*, 1997; Tipping *et al.*, 1998). A recent survey of 55 Lake District streams by Thomton (1999), however, found that most were not strongly acidified. Analysis of long-term data for five tarns by Tipping *et al.* (1998) suggests that significant chemical recovery has taken place since the 1970s.

3.3.2 SURVEY SITES

A total of 53 standing waters were sampled for this study (Figure 3.3.1). Given the established insensitivity of surface waters on Windermere group sediments, confirmed by previous pH measurements of a number of tarns in this area (E. Tipping, unpublished data), this area was excluded from the survey. Elsewhere, all natural lakes with areas exceeding 0.5ha and no improved farmland were sampled (37 lakes in total), along with three reservoirs and 13 smaller tarns. Overall, lake areas ranged from 0.05 to 34 ha, and catchment areas from 0.5 to 466 ha. The majority of sites were small, deep corrie lakes with steep rocky catchments, whilst the smallest tarns were typically shallower, and located on peaty plateau areas. Lake altitudes ranged from 65 to 720m, and only two catchments contained forestry. The highest density of lakes occurs in the southwest of the region, with fewer lakes present on the Skiddaw slates in the north.

Sampling was carried out in May 16th-20th 2000, during a period of moderately wet weather, with slightly above-average streamflows. A comparison of survey data with long-term means for the Scoat Tarn AWMN site (Table 3.3.1, Figure 3.3.2) suggests that conditions were fairly close to average at this time. Slightly below-average SO_4 concentrations reflect a downward trend in the long-term data, whilst Cl concentrations are slightly high, possibly because of elevated sea-salt concentrations in recent rain.

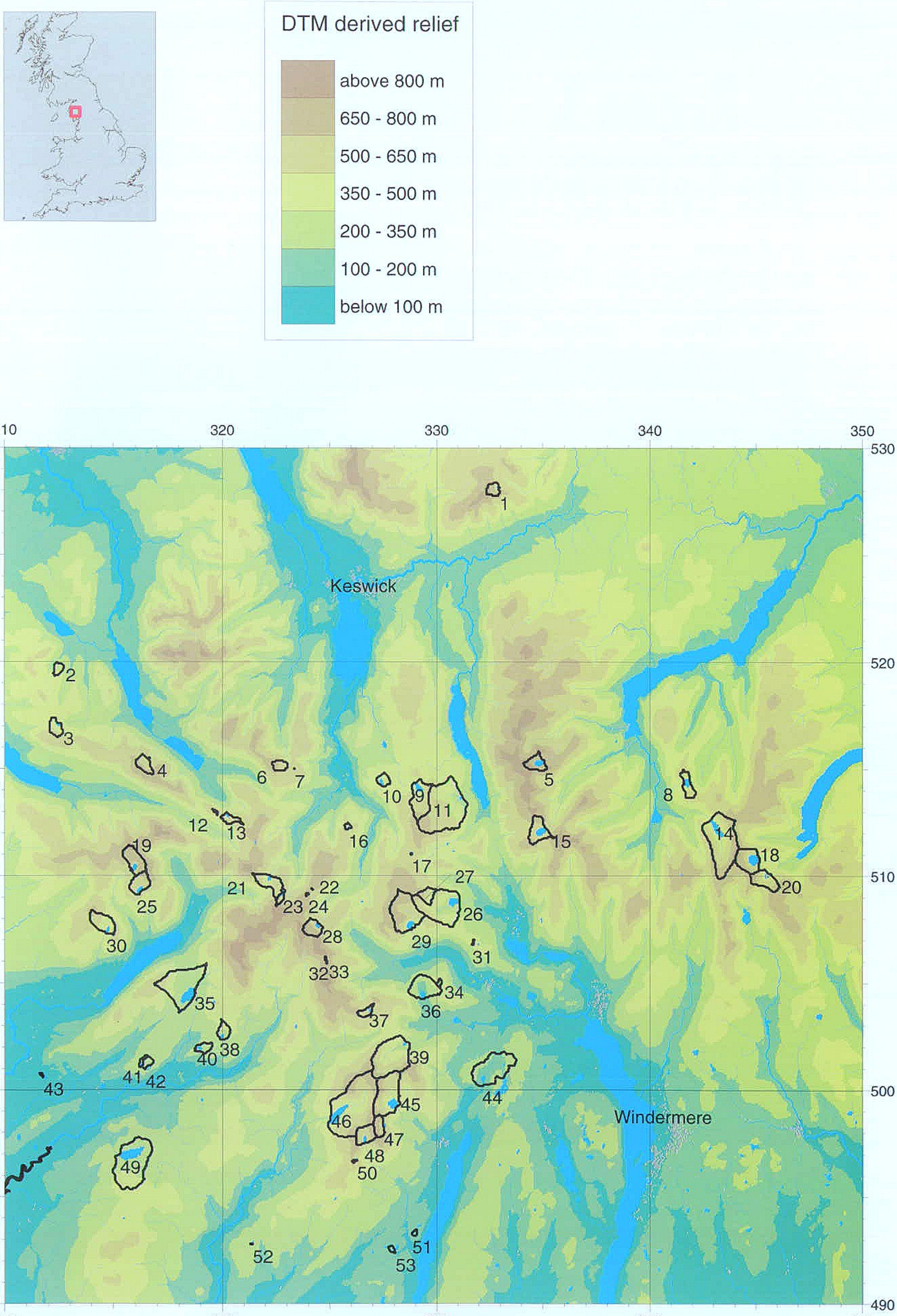


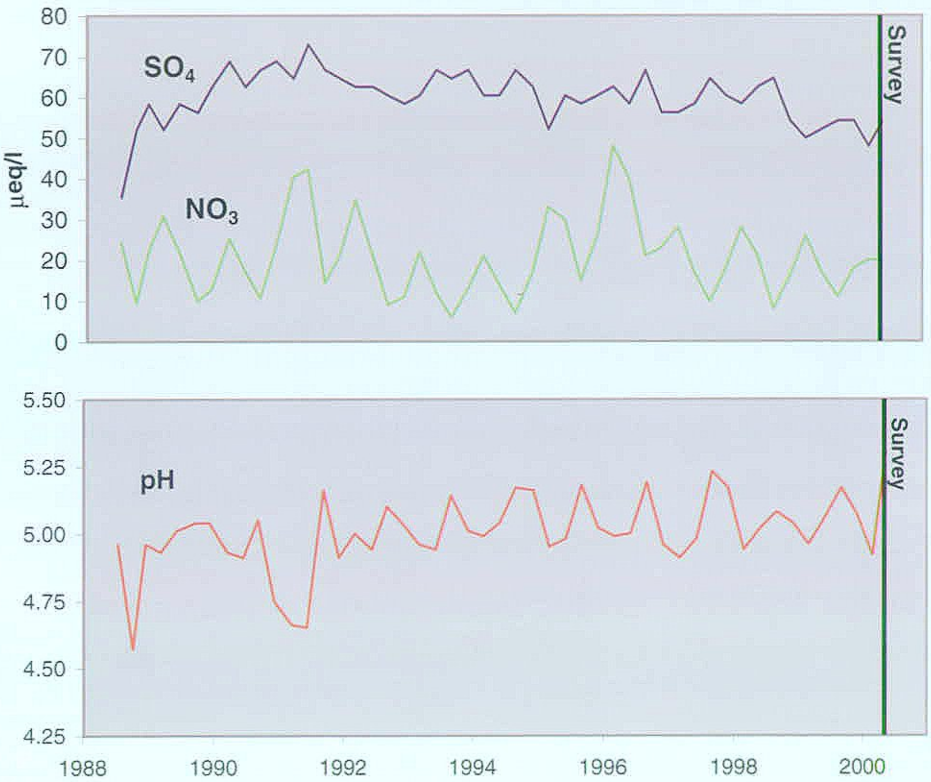
Figure 3.3.1. Location of Lake District survey sites (sites listed in Appendix 1)

TABLE 3.3.1. Scoat Tarn AWMN site solute concentrations

	ANC	pH	SO_4	NO_3	Cl	Na	Ca	Mg
May 2000 Survey	-61	5.3	54	20	223	157	25	48
12-year mean	-39	5.0	60	21	182	161	32	47

All concentrations in µeq/l except for pH (pH units)

Figure 3.3.2. AWMN data for Scoat Tarn



3.3.3 REGIONAL CHEMISTRY

Lake chemistry varies considerably among the sites (Table 3.3.2), with ANC ranging from –61 to 524 µeq/l (17 lakes with ANC <0), and pH from 4.9 to 7.3. There is no simple geographical pattern to lake acidity, with the larger acid tarns including Seathwaite Tarn, Levers Water, Angle Tarn and Scoat Tarn on the Borrowdale Volcanics, Eel Tarn and Stony Tarn on granite, and Scales Tarn and High Nook Tarn on Skiddaw slates. A high proportion of the smaller hilltop tarns are also acidic. Spatial variation in acidity is particularly strong within the Borrowdale volcanics group, reflecting the importance of local geologic variability; at sites associated with basic dolerite intrusions, in particular, ANC can exceed 100 µeq/l even in lakes with small, steep catchments and thin soils.

Variations in SO_4 are more subdued, consistent with a primarily atmospheric source, whilst NO_3 varies substantially, from below detection limits to 47 µeq/l. This variation is closely related to catchment characteristics, with minimum concentrations associated with lower-relief

TABLE 3.3.2. Summary chemistry for the Lake District Region

	10th Percentile	Median	90th Percentile
ANC	-30	31	257
pH	5.07	6.18	6.75
SO_4	44	62	89
NO_3	1.6	7.3	31
Cl	130	175	316
SBC	200	297	611
DOC	0.8	2.5	5.1

All concentrations µeq/l except for pH (pH units) and DOC (mg/l).

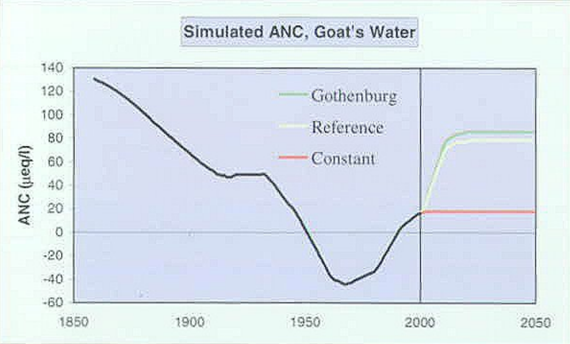
catchments with deeper soils, and maximum concentrations with steep, rocky catchments that have little soil or vegetation in which to store deposited nitrogen. At these sites, NO_3 represents a major contributor to lake acidity, with concentrations approaching those of non-marine SO_4. Chloride concentrations are generally high, with the maximum concentrations observed in the west of the region, closer to the coast. Additionally, Sutcliffe and Carrick (1983) have suggested previously that anomalously high Cl concentrations in some tarns on the Borrowdale Volcanics, particularly those close to the Old Man of Coniston, may indicate an internal source, possibly from small inputs of highly saline (connate) groundwater. Data from the current survey appear to support this for a number of sites, and the implications for modelling are discussed below.

3.3.4 MAGIC APPLICATION

MAGIC was applied according to the methods given in Chapter 2. Only two catchments were partly afforested (Harrop Tarn and Parkgate Tarn) and stand ages for these sites were estimated from field observations.

As noted above, an internal saline groundwater source has been hypothesised for some Lake District tarns. Due to the replacement of Na by Ca within the bedrock, tarns with water from this source should be characterised both by high Cl concentrations, and by negative non-marine

Example 1: Goat's Water



Goat's Water, adjacent to the Old Man of Coniston in the Southern Lake District, is a typical corrie tarn. The 0.7 km^2 catchment has an altitudinal range of 502 to 803m, and is one of the steepest included in the survey. Much of the catchment is either bare rock or scree, and thin peaty rankers underlie the remaining area. With little soil or vegetation to immobilise deposited N, NO_3 concentrations were the highest observed in the region (47 µeq/l). Although weathering rates are moderately high, reflected in a high modelled pre-industrial ANC, the cation exchange pool associated with the thin soils is small, and lake chemistry is thus highly responsive to changes in acid deposition. Although ANC is currently positive (16 µeq/l), therefore, MAGIC suggests values were negative between 1951 and 1990, falling to –44 µeq/l in 1968. Recent recovery at Goat's Water is predicted to continue strongly under the Reference scenario, with ANC reaching 78 µeq/l by 2050. Under the Gothenburg scenario, 2050 ANC is forecast to be 85 µeq/l. In both simulations, catchment soils equilibriate very rapidly with the reduced deposition levels, so there is little further change in ANC after 2010. Similarly, with constant deposition, ANC is predicted to remain virtually unaltered at 18 µeq/l in 2050.

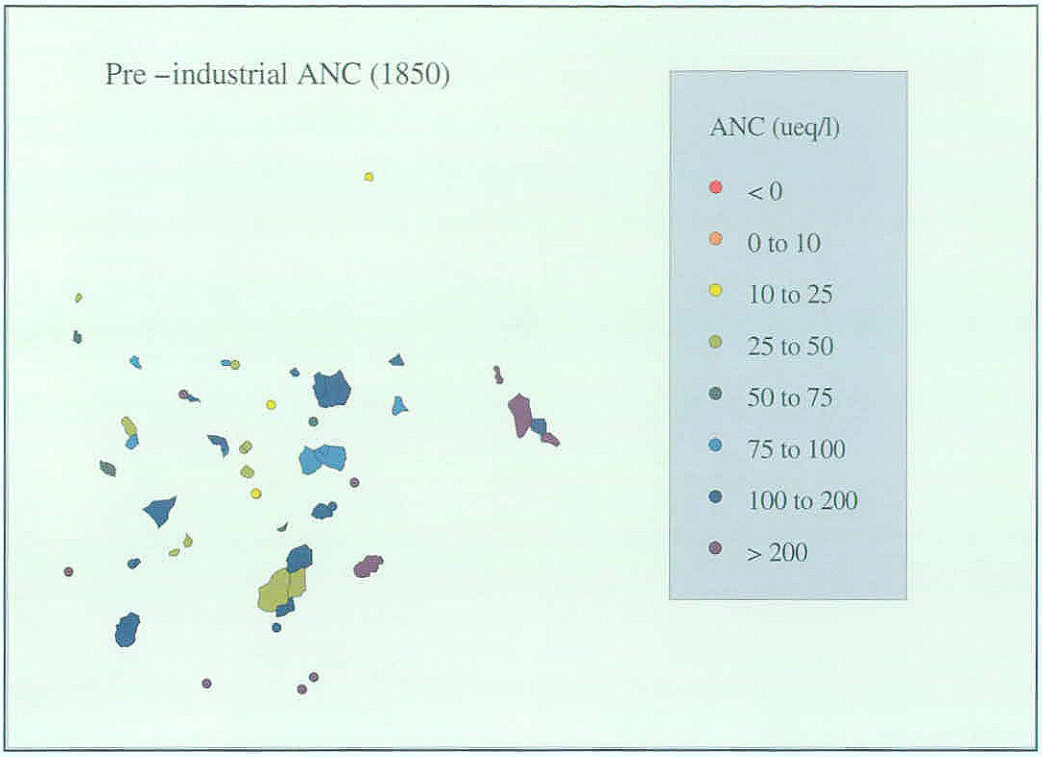


FIGURE 3.3.3. MAGIC simulated pre-industrial ANC, Lake District

Na. This situation was observed for a cluster of sites in the Coniston area, with strongly negative xNa at Goat's Water and Blind Tarn, and smaller negative values at Seathwaite Tarn, Low Water and Levers Water. At these sites, therefore, Cl concentrations above a threshold of 200 μeq/l (based on nearby sites) were considered to reflect an internal source, and a Cl input flux calculated and entered in the MAGIC calibration. Cl and sea-salt base cation deposition fluxes were adjusted accordingly, in order to maintain an overall Cl balance. Base cation weathering rates were optimised within the calibration, as normal, but tended to be higher at these sites due to the internal saline source.

3.3.5 RESULTS

MAGIC was calibrated to 51 out of 53 Lake District sites. Park Gate Tarn and Innominate Tarn could not be calibrated due to strongly negative non-marine sodium concentrations, probably indicative of unrepresentative sampled chemistry.

MAGIC simulated pre-industrial ANC (Figure 3.3.3), although positive at all sites, ranges widely within the region. This variability largely mirrors the current spatial pattern, and the highly variable weathering rates associated with differences in underlying geology. As noted earlier, sites with a low present day ANC (Figure 3.3.4a) are scattered throughout much of the Lake District, although most are in central or western areas. Although ANC has declined at both sensitive and non-sensitive sites (Figure 3.3.5, 3.3.6), MAGIC suggests that the majority of sites currently with negative ANC had a pre-industrial ANC between 15 and 50 μeq/l.

MAGIC simulations indicate that, with future deposition maintained at current levels, lake chemistry will remain almost unchanged (Figures 3.3.4a,b) The majority of sites, especially those that are more acidic, undergo a marginal improvement in ANC, whilst a small number of sites acidify slightly (Figure 3.3.5). As a result, the mean ANC of the 51 sites is unchanged by 2050, and the overall distribution of ANC within the region remains virtually

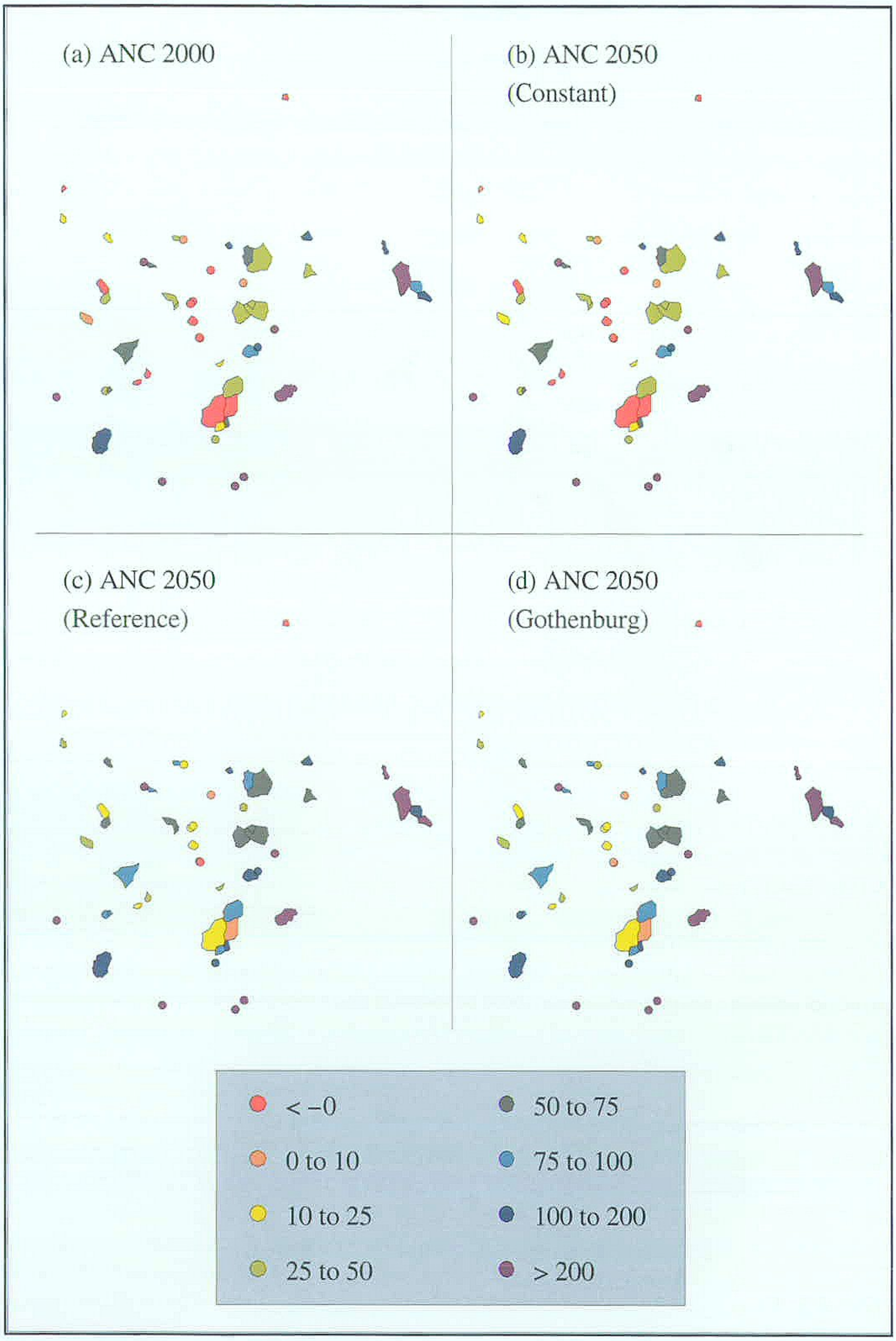


Figure 3.3.4. MAGIC simulated present-day and forecast ANC, Lake District

unaltered (Figure 3.3.6). The implication of this result is that the weathering and leaching of base cations in most catchments are approximately in balance, so that soil base saturation, and hence lake acidity, remain constant (increased future leaching of nitrogen, which was not modelled during this study, could however alter this

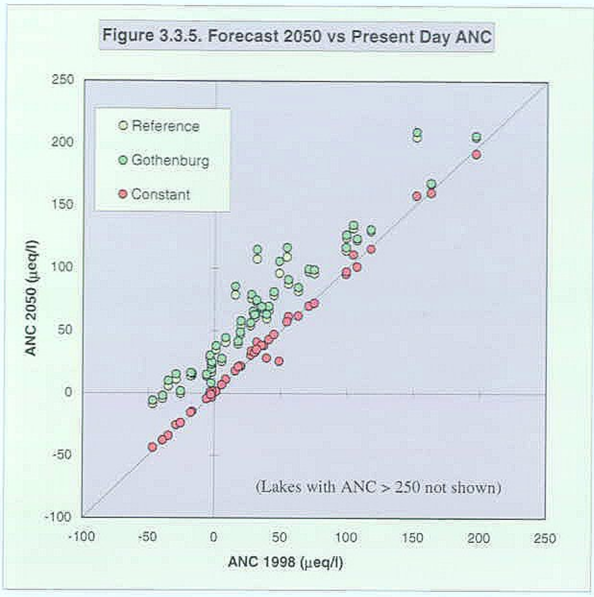


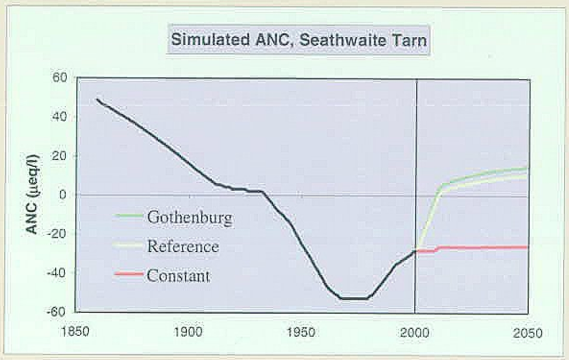
Figure 3.3.5. Forecast 2050 vs Present Day ANC

balance). The absence of widespread ANC decline under this scenario may also partly reflect the minor impact of forestry in this region.

In response to the Reference Scenario, all sites show recovery, with MAGIC predicting a mean lake ANC increase of 30 μeq/l by 2050. Large improvements are predicted at the more acidic sites (Figures 3.3.4 – 3.3.6), reducing the number with a negative ANC from 14 (27%) to 3 (6%). However a number of relatively large tarns such as Levers Water, Seathwaite, Scoat and Angle Tarns are predicted still to have a very low positive ANC (<20 μeq/l), and these sites will therefore remain susceptible to transient acidic episodes.

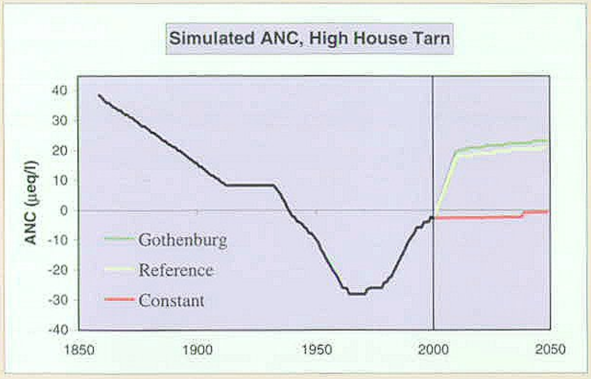
Under the Gothenburg protocol, additional reductions in S and N deposition translate into further ANC recovery at all sites. As a result, the number of sites with a negative ANC is reduced to two. Overall, however, the mean increase in ANC by 2050 (33 μeq/l) is only slightly greater than that expected for the Reference scenario.

Example 2: Seathwaite Tarn


Simulated ANC, Seathwaite Tarn

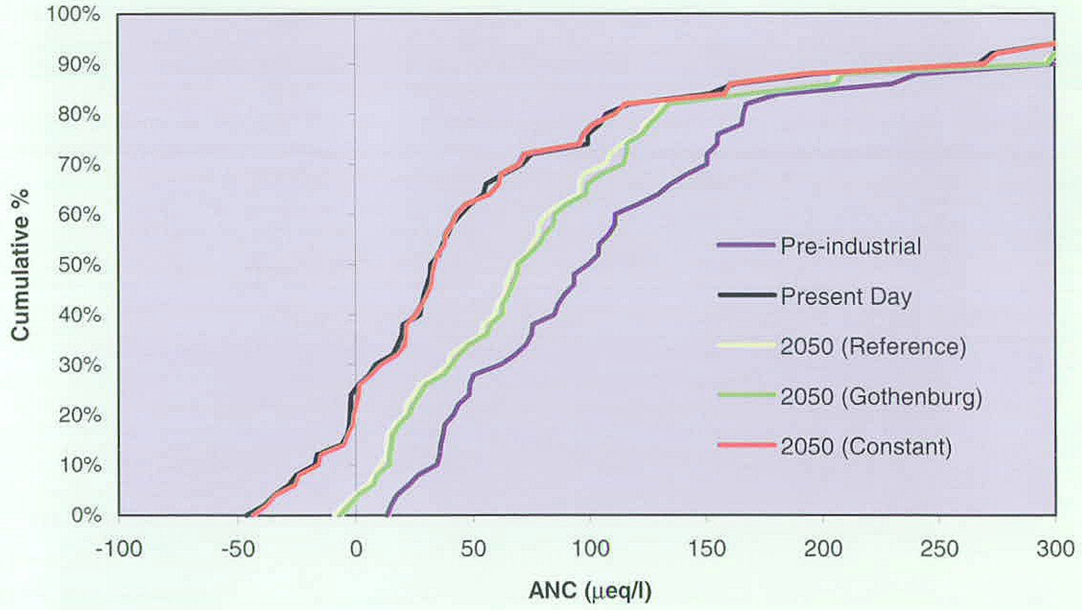
Seathwaite Tarn is adjacent to Goat's Water (see preceding box) in the southern Lake District. The catchment is similarly steep and rocky to that of Goat's Water, but is substantially larger (4.7 km^2), and contains an area of valley peat around the lake inflow. The tarn itself is dammed for water supply, and has an area of 0.3 km^2. Despite its closeness to Goats Water, Seathwaite Tarn has only around half the Ca concentration, and as a result is markedly more acidic (present day ANC –28 μeq/l). The much lower weathering rate within this catchment is evidenced by a MAGIC pre-industrial ANC of just 48 μeq/l. The tarn has already recovered slightly from a minimum ANC of –52 μeq/l, and under the Reference scenario ANC is predicted to become positive in 2010, continuing to rise thereafter to 11 μeq/l in 2050. For the Gothenburg scenario, simulated ANC reaches 15 μeq/l by this time. With constant deposition at current levels, although ANC is predicted to rise slightly, it will remain severely negative in the long-term at around –26 μeq/l.

Example 3: High House Tarn



High House Tarn, located at an altitude of 670m on a plateau area between Langdale and Wasdale, is typical of the small hilltop tarns in this study. The catchment is small and relatively flat, with outcrops of bare rock and ranker soils interspersed with deeper, peaty soils in basin areas. The tarn is shallow (<1m) and drains through the peat. Present day ANC is –3 μeq/l, and low base cation concentrations indicate limited weathering within the underlying bedrock. However, NO_3 levels are also low (5 μeq/l), suggesting that the deeper soils are able to immobilise most incoming N. MAGIC simulation indicates that pre-industrial ANC for this tarn was relatively low at 38 μeq/l, and became negative in 1939, falling below –25 μeq/l during the 1960s and 1970s. Recent recovery is predicted to continue under the Reference scenario, with ANC becoming positive in 2002 and reaching 21 μeq/l by 2050. Slightly greater recovery (to 24 μeq/l) is predicted for the Gothenburg scenario, but under continued deposition at current levels the tarn is expected to maintain a negative ANC in future.

Figure 3.3.6. Cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios)



Region 4: South Pennines

3.4.1 REGIONAL DESCRIPTION

The South Pennines are located in Northern England, at the centre of the largest industrial area in the UK. Surrounding cities including Manchester, Sheffield, Bradford and Leeds were at the forefront of the Industrial Revolution during the 19th Century, and the acute atmospheric pollution that resulted is evident throughout the region in soot contamination of blanket bogs (Lee, 1981), and has also been identified as the cause of major vegetation change, including the widespread loss of *Sphagnum* mosses (Ferguson and Lee, 1983). Although emissions have fallen in recent years, deposition remains high relative to other acid-sensitive areas of the UK: 1992-94 total non-marine sulphur deposition exceeded 30 kg S/ha/yr throughout the region, with total N deposition in the range 18-30 kg N/ha/yr (RGAR, 1997). These values are among the highest values recorded for either pollutant anywhere in the UK. Freshwater and terrestrial critical loads are severely exceeded throughout the region.

The South Pennines consist of a narrow, relatively low-elevation (<600m) corridor of moorland oriented approximately north-south, with extensive urban areas on either side (Figure 3.4.1). The upland area is almost entirely underlain by acid-sensitive Carboniferous millstone grits, with less sensitive coal measures to the west and east. Deep blanket peats cover much of the upland plateau, grading to ironpan stagnopodzols, stagnohumic gleys and brown earths at lower elevations. Land-use is primarily unimproved rough grazing at higher elevations, with some improved grazing on lower slopes. Afforestation is less widespread than in most of the other regions under consideration, limited mainly to small plantations on the southeastern moorland fringe.

3.4.2 SURVEY SITES

The 60 sites sampled for this study are all headwater reservoirs. Most are small (100 – 10000 Ml) earth embankments, which were constructed in large numbers in this region during the mid to late 19th century (White *et al.*, 1996). Catchments were selected to contain less than 25% improved farmland, and samples were collected close to outflows wherever possible. All reservoirs were sampled during the week of 20-25 April 1998, following a period of high rainfall and some snow. Most were at or close to capacity, so it is unlikely that water supply abstraction had a significant impact on water chemistry at this time.

Although it was not sampled as part this survey, the River Etherow AWMN site provides an indication of conditions at this time relative to the long-term record. The twelve-year time series (Figure 3.4.2) shows that SO_4 concentrations were relatively low in 1998, and this is also illustrated by a comparison of long-term mean concentrations with those at the time of sampling (Table 3.4.1); however this reflects a general downward trend at this site rather than an unrepresentative sampling period. NO_3 concentrations show very little seasonality, and concentrations in April 1998 were close to the long-term mean. The Etherow is an extremely flashy stream site, and dilution of base-rich groundwater during high flows causes major short-term variability in base cation concentrations, ANC and pH. This variability is much less evident in available long-term pH records for surveyed reservoirs (Evans and Jenkins, 2000), and therefore the problems of temporal representation are less severe than the Etherow data would indicate. However, these data do suggest that base cation concentrations, pH and ANC may have been slightly below average at the time the survey was undertaken.

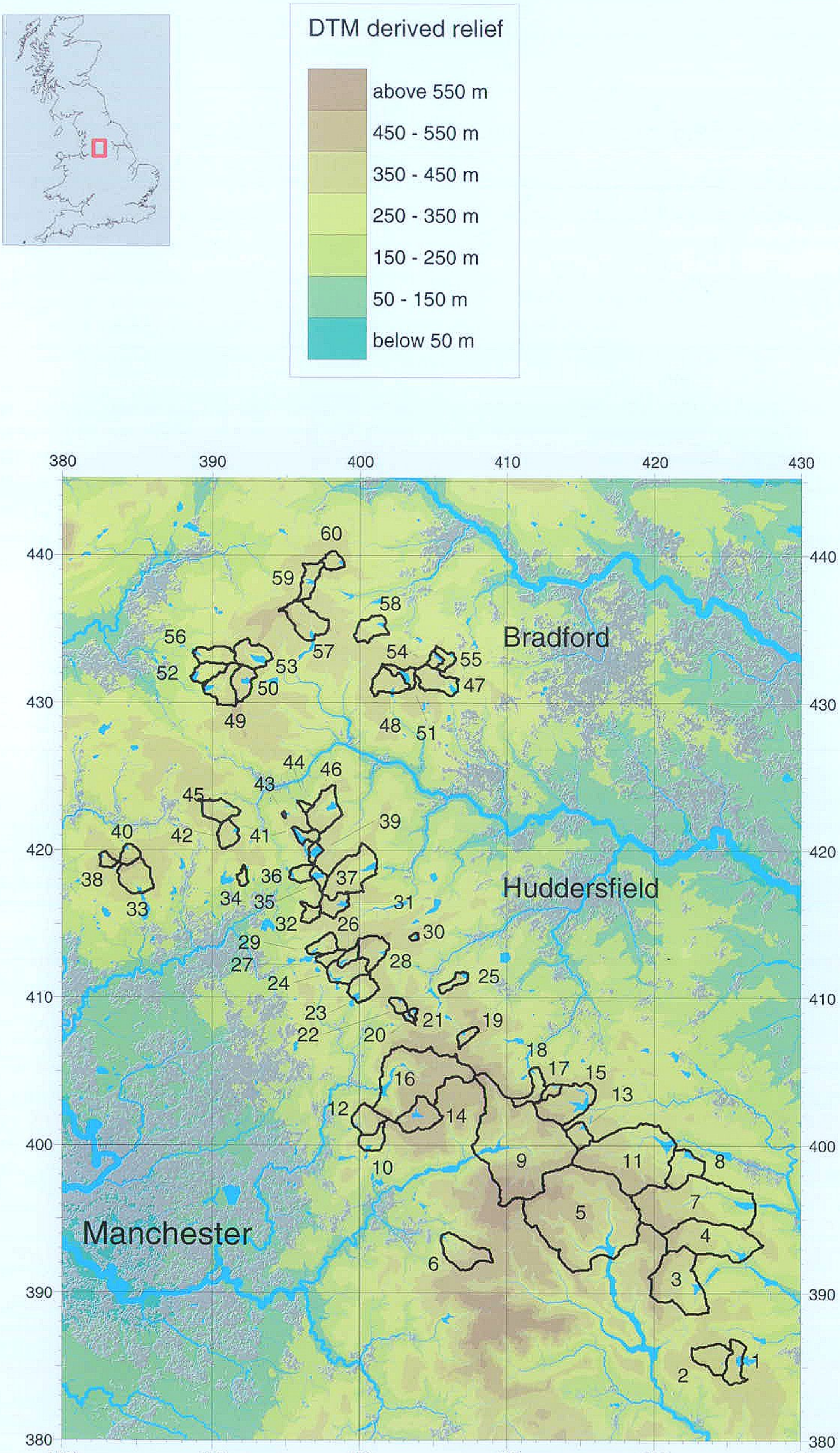


Figure 3.4.1. Location of South Pennine survey sites (sites listed in Appendix 1)

Figure 3.4.2. AWMN data for the River Etherow

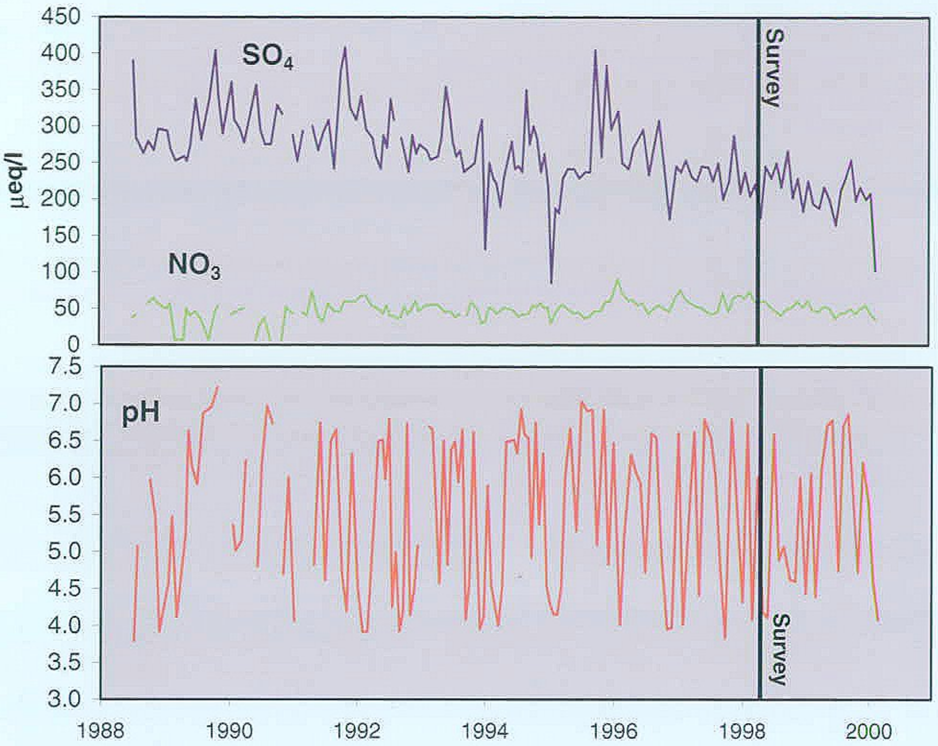


TABLE 3.4.1. River Etherow solute concentrations at the time of the reservoir survey.

	ANC	pH	SO_4	NO_3	Cl	Na	Ca	Mg
April 1998*	11	5.10	198	60	192	191	98	92
12-year mean	31	5.47	262	49	306	299	168	162

All concentrations in µeq/l except for pH (pH units)
* Average of samples collected on April 1st and May 6th 1998.

3.4.3 REGIONAL CHEMISTRY

Of the 60 sampled sites, almost half had a negative ANC and a pH below 5.0 (Table 3.4.2). At the most acidic sites, ANC was lower than –100 µeq/l and pH below 4.0. Sulphate concentrations were extremely high (median 220 µeq/l) and a median nitrate concentration in excess of 40 µeq/l indicates that freshwaters throughout the region are at an advanced stage of nitrogen saturation. These data have been analysed in detail by Evans *et al.* (2000). Available long-term data from this region suggest that some degree of pH recovery has occurred since 1980, driven by large reductions in sulphate concentrations, but this appears to have been slowed by increased leaching of nitrate (Evans and Jenkins, 2000; Monteith and Evans, 2000).

TABLE 3.4.2. Summary chemistry for Pennine Reservoirs

	10^{th} Percentile	Median	90^{th} Percentile
ANC	-85	13	108
pH	4.08	5.27	6.60
SO_4	165	248	353
NO_3	26	41	77
Cl	175	243	544
SBC	285	601	964
NH_4	1.5	4.0	8.9
DOC	2.5	4.9	7.8

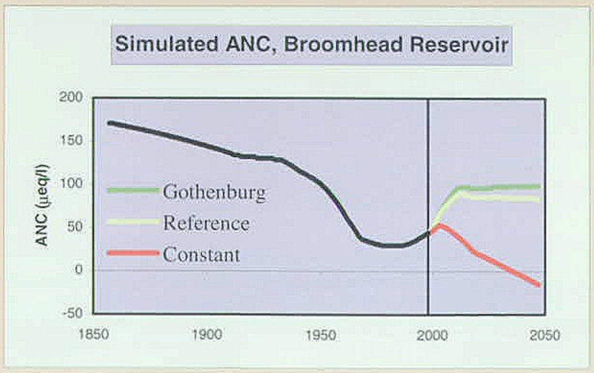
All concentrations µeq/l except for pH (pH units) and DOC (mg/l).

3.4.4. MAGIC APPLICATION

MAGIC was applied to the South Pennines based on the procedures described in Chapter 2, but some adjustments were required to take account of apparent internal sources of sulphur in the region. These are believed to include both fertiliser inputs and geological sources (Evans *et al.*, 2000), and were found to be most significant for catchments containing improved land, and those underlain by coal measures. Based on an assessment of maximum xSO_4 concentrations for unimproved gritstone catchments, and on estimates of S deposition for the region, threshold concentrations were defined as 200 µeq/l xSO_4 for moorland and 250 µeq/l for forest catchments. Any additional xSO_4 was assumed to be derived from internal sources, and added as a constant weathering input rather than as deposition.

Other local anthropogenic sources were not incorporated in the model, although both nitrogen fertilisers and road-salt may influence some sites. Fertiliser inputs are significant, however, at only a small number of non-acidic sites, and so the error resulting from omitting local sources was considered minor. Road-salt inputs were assumed to be equivalent to deposited sea-salt, and were therefore incorporated where necessary in the deposition flux.

Example 1: Broomhead Reservoir



Broomhead is a large (5000 Ml) water supply reservoir draining a 20 km^2 catchment on the east side of the South Pennines. Soils and land-use are varied; the upper part of the catchment is peat moorland, the lower part a mixture of moorland, forestry (13% of total area) and some improved grazing on mineral soils. Although hindcast model simulation indicates that the reservoir has acidified, ANC remains relatively high at 49 µeq/l. Under the Reference scenario ANC is expected to increase to 2010, but then to decline slightly due to base cation uptake during second rotation forest growth. This effect is less marked under the Gothenburg scenario, which predicts greater ANC recovery after 2010. Under a constant deposition scenario, however, major acidification of this site is predicted, with ANC falling to -14 µeq/l by 2050. This suggests that combined effects of continued acid deposition at current levels, and second rotation forest uptake, will cause further depletion of soil base saturation at this site.

Finally, it is worth noting that many of the reservoirs in this study had not been constructed at the beginning of the MAGIC simulation in 1850. For completeness, these sites are still included in plots of 1850 chemistry, which can be considered approximately that of the stream draining the same catchment area at that time.

3.4.5. RESULTS

Of 60 sites to which MAGIC was applied, 58 were successfully calibrated. MAGIC simulated ANC for 1850 for these sites (Figure 3.4.3) illustrates that, prior to industrialisation, surface waters in the South Pennines were not acidic. Around ten higher-elevation sites with peat-dominated catchments have a simulated pre-industrial ANC between 30 and 100 μeq/l, indicating sensitivity to acidification, but for over half of all sites, pre-industrial ANC is predicted to have exceeded 150 μeq/l. These surface waters can therefore be considered relatively well buffered, and would probably have supported a relatively diverse acid-sensitive ecosystem at this time.

Despite this buffering, the present day map (Figure 3.4.4a) shows that acidification is now widespread and severe; over 40% of survey sites were found to have a negative ANC. As expected, the most acidic conditions are observed in poorly buffered reservoirs located on the peat plateau, mainly in the central and northern parts of the study area. However, many larger, lower elevation sites were also found to have a low or negative ANC.

MAGIC forecasts for different scenarios give widely differing predictions of future surface water chemistry in this region. Under the 'Constant' scenario of stable future S and N deposition (Figure 3.4.4b) conditions are forecast to worsen dramatically, with ANC falling below zero at many currently non-acidic sites, including the larger Peak District catchments in the south of the study region.

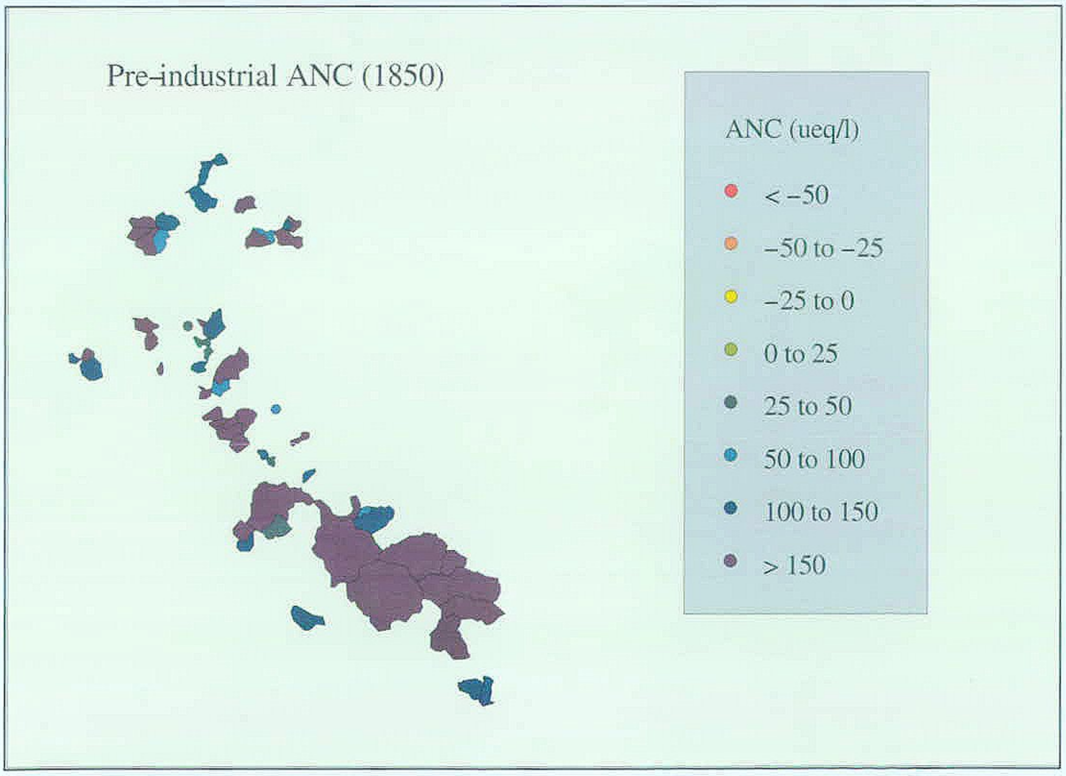


FIGURE 3.4.3. MAGIC simulated pre-industrial ANC, South Pennines

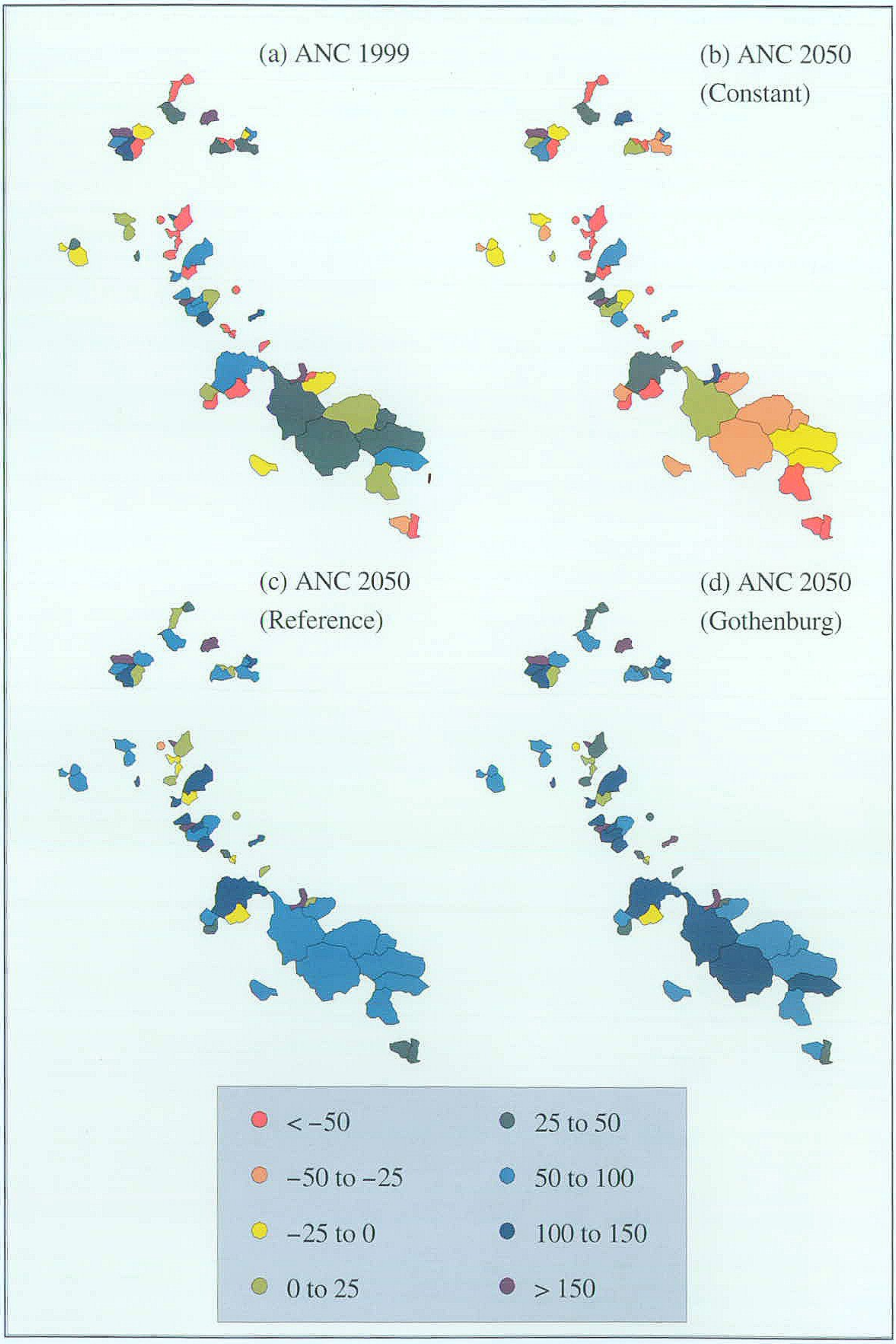
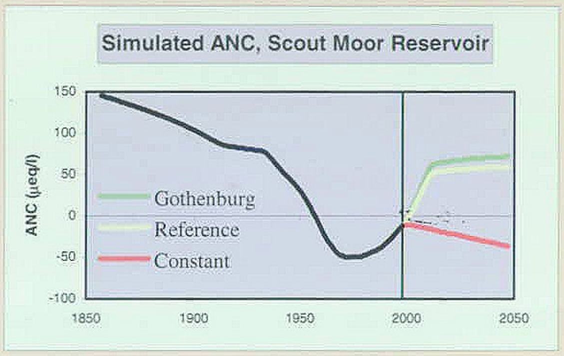


FIGURE 3.4.4. MAGIC simulated present-day and forecast ANC (μeq/l), South Pennines

Example 2: Scout Moor Reservoir

This small reservoir is typical of many in the region, located in a steep-sided valley draining open moorland. Soils include peats on the moorland plateau and stagnopodzols on valley slopes, and agricultural impacts are minimal. Scout Moor is currently acidic, with an ANC of -13 µeq/l and a pH of 5.1. Model simulations indicate that ANC fell to a minimum of -43 µeq/l during the 1970s, but has since recovered. Like many other sites, however, further recovery can only be expected with continued deposition reductions; maintaining deposition at present day levels will cause the site to re-acidify as soil base saturation continues to decline. Deposition reductions under the reference scenario appear sufficient to generate substantial and sustained further recovery, to an ANC of 59 µeq/l by 2050. The Gothenburg scenario is forecast to produce additional improvement in water quality, to a 2050 ANC of 72 µeq/l. This represents a return to conditions last simulated for the 1930s.



Simulated ANC, Scout Moor Reservoir

This acidification of relatively well-buffered catchments is also evident in a comparison of forecast and present-day ANC (Figure 3.4.5) and in cumulative frequency distributions (Figure 3.4.6). Both plots indicate that, whilst conditions are expected to remain largely unchanged at the most acidic sites under constant deposition, ANC is predicted to undergo severe decreases at sites currently with an ANC between 0 and 100 µeq/l. As a result, the number of sites with a negative ANC is forecast to increase from 26 at present day to 38 in 2050 under this scenario, with a median predicted ANC change of -26 µeq/l for the survey set as a whole. These results suggest that current levels of acid deposition, although lower than peak levels observed during the 1970s, continue to exceed the buffering available from weathering at most sites. As a result, soil base saturation will continue to fall, and surface waters to acidify, without further reductions in acid deposition in future.

Predictions for the Reference and Gothenburg scenarios both demonstrate substantial improvements in ANC relative to present day (Figures 3.4.4c,d). Many previously acidic sites are expected to return to positive ANC values, and the extreme negative values occurring at the present time are no longer observed. The magnitude of predicted recovery is greatest at the lowest ANC sites, and least for sites currently with an ANC of over 100 µeq/l

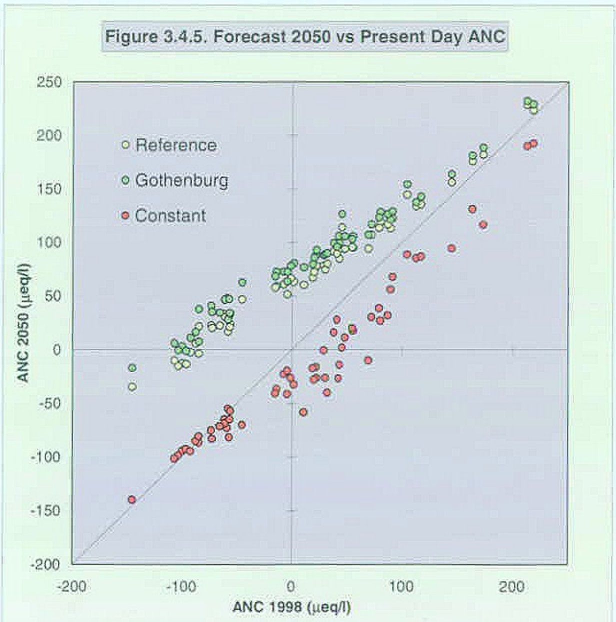
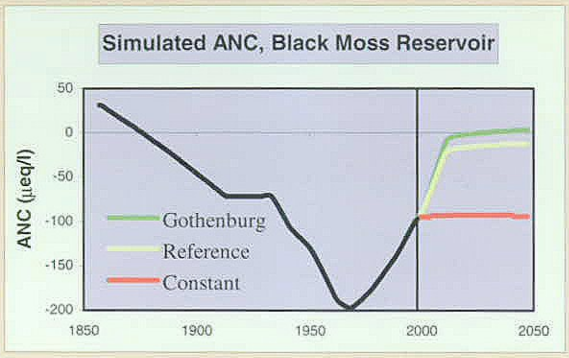


Figure 3.4.5. Forecast 2050 vs Present Day ANC

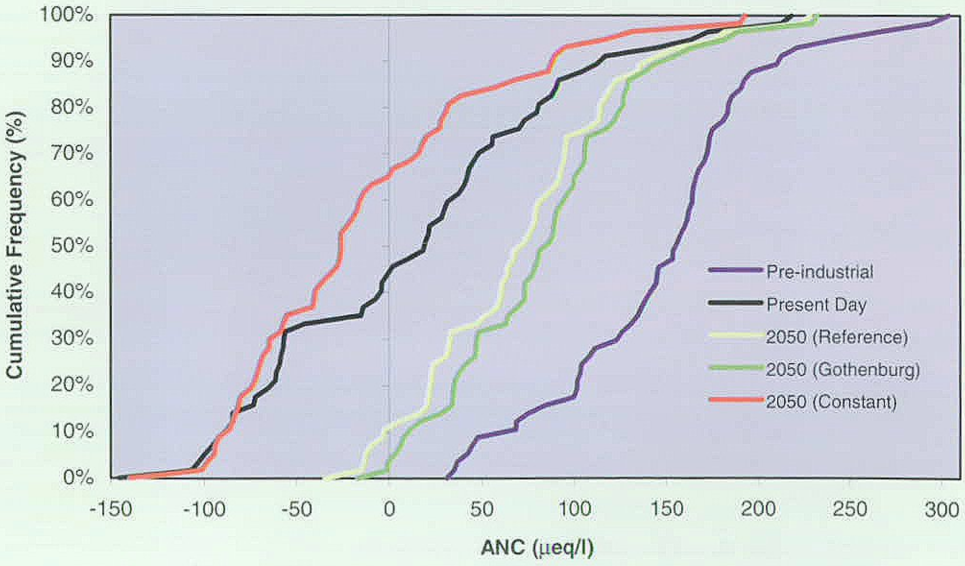
Example 3: Black Moss Reservoir



Black Moss is one of a number of reservoirs located on the blanket peat. Catchment relief is extremely low, with water supplied from beyond the natural drainage basin by catchwater drains. The reservoir is highly acidic, with an ANC of –103 µeq/l, pH of 4.06, and very low base cations reflecting an absence of weatherable material. NO_3 concentrations are moderate, and this site also has unusually high levels of NH_4.The lack of catchment buffering is evident in very rapid historic acidification, with MAGIC simulating a pre-industrial ANC of 31 µeq/l, and a negative ANC from 1872, falling to –198 µeq/l in 1967. Although conditions are less severe today, the site remains acidic, and ANC is predicted to remain almost unchanged at present-day levels under the Constant scenario. Whilst the reference scenario is forecast to lead to recovery, ANC remains negative in 2050. However, additional deposition reductions under the Gothenburg protocol appear sufficient to raise ANC levels to positive values by this time.

(Figure 3.4.6). On average, ANC predicted for 2050 under the Gothenburg scenario is 12 µeq/l higher than for the Reference scenario. Although this difference is relatively small, the differences between scenarios are greatest at the more acidic sites (Figure 3.4.5, 3.4.6), and are sufficient to reduce the number of surface waters predicted to have a negative ANC in 2050 from 7 to 3 (Figure 3.4.3 c, d). The more stringent emission controls agreed under the Gothenburg Protocol may therefore deliver significant improvements in freshwater status for this impacted region.

Figure 3.4.6. Cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios)



Region 5: Wales

3.5.1 REGIONAL DESCRIPTION

The study region encompasses streams draining 102 catchments across Wales, but is focused on the upland areas in the west (Figure 3.5.1). Most sites are distant from major emission sources, although deposition is moderately high (non-marine sulphur deposition for 1992-94 was 15-30 kg S/ha/yr, total N deposition was 16-24 kg N/ha/yr over the same period), in part due to high rainfall. The Cambrian Mountains occupy much of the study area, extending from south-central Wales to the north coast, and are characterised by moderate relief (elevations mostly less than 600m) and acid-sensitive Lower Palaeozoic sedimentary geology. In the northwest (Snowdonia) maximum elevations exceed 1000m, and a mixture of acid-igneous and meta-sedimentary bedrock underlies the area, much of which is also vulnerable to acidification. Soils are relatively uniform throughout the region, with peats widespread on hilltops, grading to ferric stagnopodzols, stagnohumic gleys and brown podzols at lower altitudes. Rankers are also present in the more mountainous areas of Snowdonia. Land-use is predominantly either rough moorland or coniferous forestry plantation at higher elevations, with improved pasture in lower valleys.

Rainfall, runoff, stream and soil chemistry, land use and atmospheric deposition data for each catchment were derived from a variety of sources and at different spatial and temporal scales. Sixty-four of the sites were forested and detailed histories were obtained from Forestry Enterprise describing the number and age of stands within each catchment. The soils data was obtained from the Soil Survey and Land Resource Centre.

3.5.2 REGIONAL CHEMISTRY

Stream chemistry for each site was derived from the Welsh Acid Waters survey undertaken in 1995 (Stevens *et al.*, 1997). Samples were collected monthly and analysed for all major ions; annual geometric means were then used for the model calibration procedure.

TABLE 3.5.1 Stream Chemistry for the Wales region

	10th Percentile	Median	90th Percentile
ANC	-6.8	69	317
pH	5.6	6.3	6.9
SO_4	70	107	196
NO_3	3.3	12	46
Cl	169	225	337
SBC	286	410	792

All concentrations µeq/l except for pH (pH units)

At only two sites does observed mean annual pH fall below 5.0. This, in part, reflects the fact that stream sampling was predominantly undertaken during periods of relatively low flow. At 15 sites, 12 forested and 3 moorland, however, mean annual ANC was <0 µeq/l indicating that many streams are likely to suffer adverse biological impacts in response to present day chemistry. In general, the most acidic conditions occur in the central Cambrian Mountain area, particularly in the forested areas around Plynlimon and Devils Bridge, and north of Machynlleth. Acid sites are also present in parts of western Snowdonia, and at some streams in South Wales, close to industrial areas. Sulphate is the dominant acidic anion at all sites, but while NO_3 concentrations are relatively low for the region as a whole, some sites are known to exhibit marked seasonal N dynamics. This can contribute significantly to seasonality in ANC, so that ANC minima may be markedly lower than the annual geometric mean value used in this regional application.

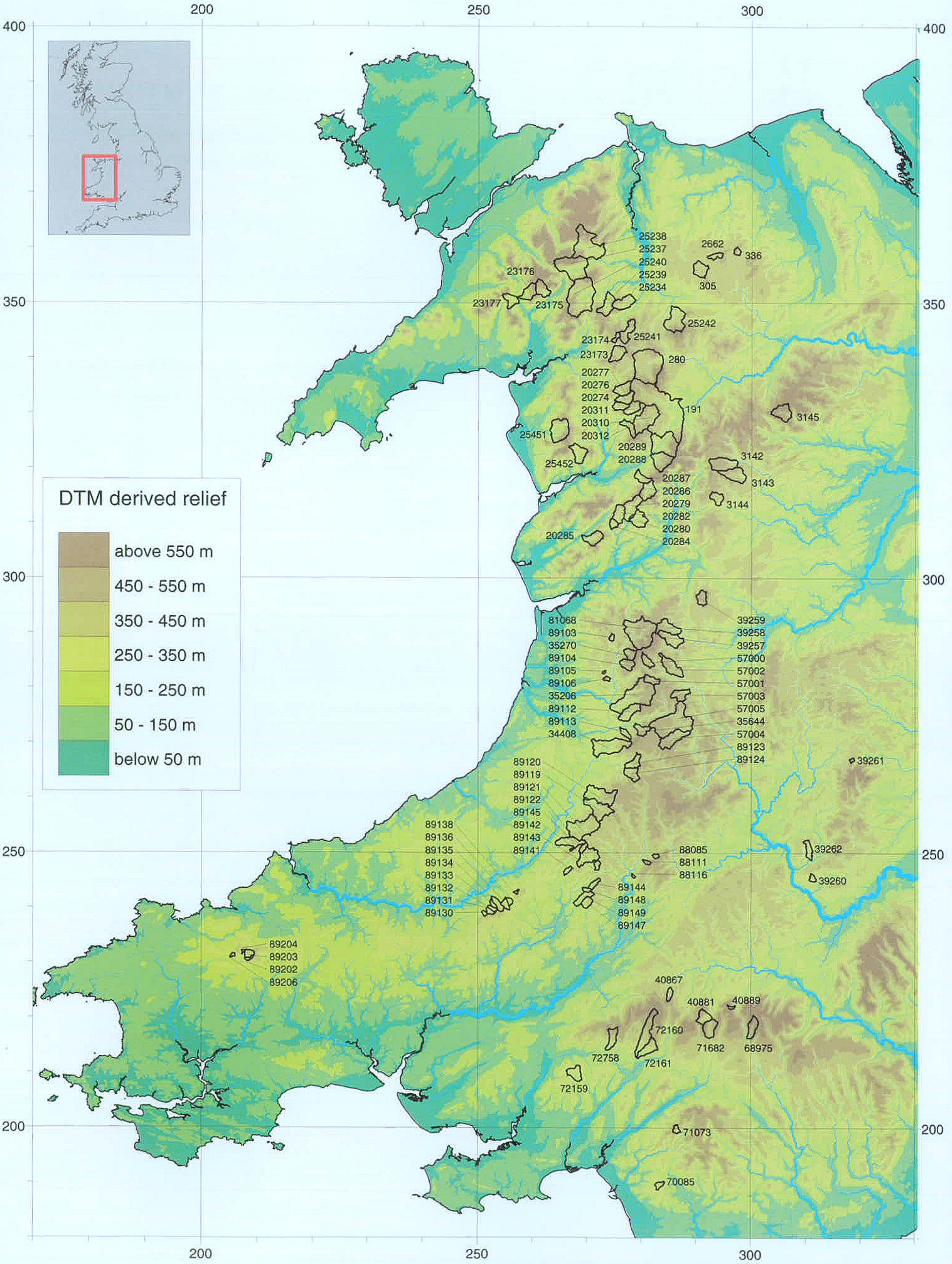
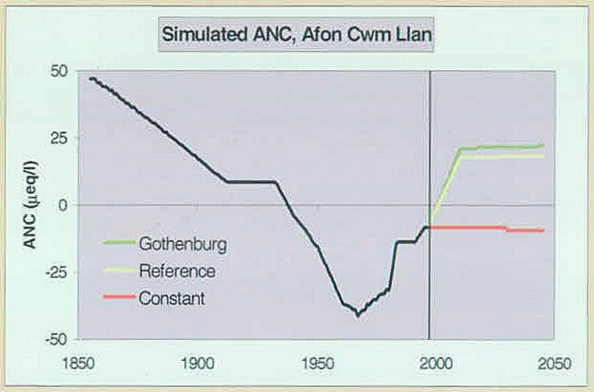


Figure 3.5.1. Location of Welsh survey sites (sites listed in Appendix 1)

Example 1: Afon Cwm Llan



Afon Cwm Llan is a small (7.4km^2) steep moorland catchment draining part of the Snowdon massif. Soils are thin, acidic and dominated by rankers, brown podzols and gleys. Weathering rates are low, as indicated by a simulated pre-industrial ANC of just 47 µeq/l. The limited buffering capacity of catchment soils has contributed to significant acidification since the onset of industrialisation, with ANC falling to a minimum of -41 µeq/l in 1967. Although some recovery has occurred since in response to emissions reductions, present day ANC remains negative, at -8 µeq/l. Simulations for the Reference scenario show a marked increase in ANC, to 18 µeq/l in 2050, while the Gothenburg scenario provides additional improvement, to 22 µeq/l. Under constant deposition, however, ANC is predicted to remain negative, decreasing marginally to –9 µeq/l.

3.5.3 RESULTS

101 of 102 sites within the region were successfully calibrated. Forested sites were subject to a future forest management scenario whereby each stand is felled at 50 years age and replanted immediately. No changes in land use were assumed at moorland sites. Figures 3.5.2 and 3.5.3a illustrate that significant acidification has occurred since industrialisation. Model predictions indicate that there were no sites with an ANC <0 µeq/l and only 3% of sites with an ANC <50 µeq/l in 1850. In comparison, 42% of sites currently have an ANC of <50 µeq/l, and 14% of sites now have a negative ANC. All sites are predicted to have undergone a decline in ANC, with a median decrease of 75 µeq/l.

The 101 streams show varying responses to the constant deposition scenario (Figure 3.5.3b); 70 sites show decreases in ANC, 8 sites show less than a 1 µeq/l change, and 23 sites show increases. The overall effect of these changes is to increase the percentage of sites with a low positive ANC (49% <50 µeq/l) but there is no change in the number of sites with negative ANC (Figure 3.5.5). As in other regions, the greatest ANC decreases are predicted at forested sites; the average ANC change between 1999 and 2050 is –13 µeq/l for catchments with ≥10% forestry, compared to –3 µeq/l for unforested sites. At some forested sites under the Constant scenario, ANC is simulated to be lower in future than during the deposition peak of the 1970s. This simulated worsening of acidification is due to the continuing predicted decline in soil base cation content due to forest uptake under conditions of high deposition.

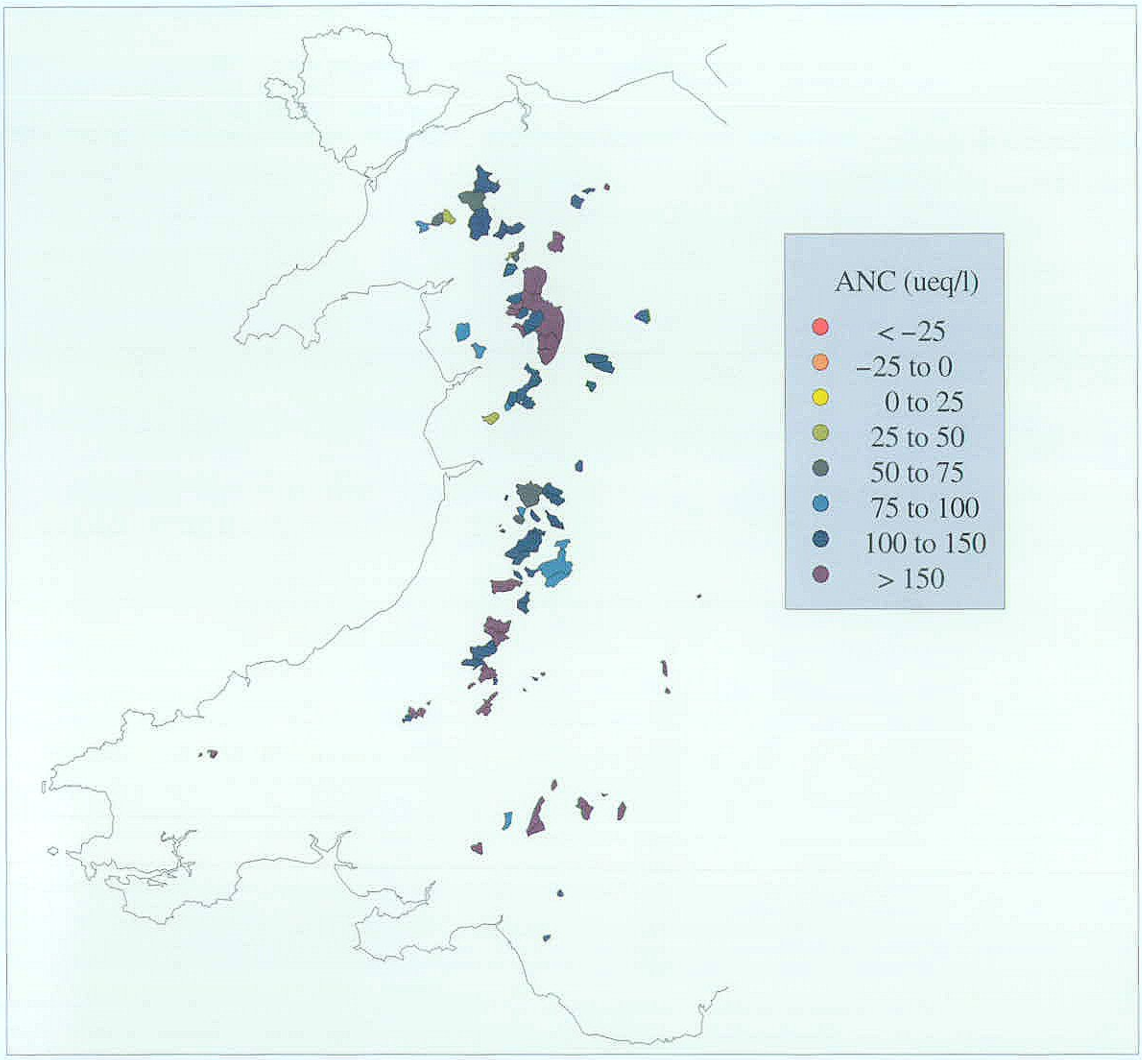


Figure 3.5.2 MAGIC simulated pre-industrial ANC, Wales

Results for the Reference scenario (Figure 3.5.4a) contrast markedly with those for the Constant scenario. Substantial increases in ANC are observed at sites throughout the study region (Figure 3.5.4a), and although three streams are predicted to acidify slightly, all 101 are predicted to have a positive ANC in 2050. The median increase in ANC for all sites is 27 µeq/l by 2050. Figures 3.5.5. and 3.5.6 suggest that recovery will generally be greatest at those sites that are currently most acidified. Under the more stringent emission reductions of the Gothenburg scenario (Figure 3.5.4b), a slight increase in chemical recovery is predicted, with a median ANC increase of 31 µeq/l. Again, the benefits of the Gothenburg protocol relative to the Reference scenario appear greatest at lower-ANC sites (Figure 3.5.6.).

Regarding the effects of forestry, the Welsh region contrasts markedly with other areas modelled; results suggest that it may have a far smaller negative impact on recovery under reduced deposition scenarios than is predicted elsewhere. In fact, the median predicted ANC increase for sites with more than 10% forestry under the Gothenburg scenario (36 µeq/l) exceeds the median predicted increase for 100% moorland sites (26 µeq/l). These results appear inconsistent with those for other regions, where some forested sites are predicted to re-acidify under the same

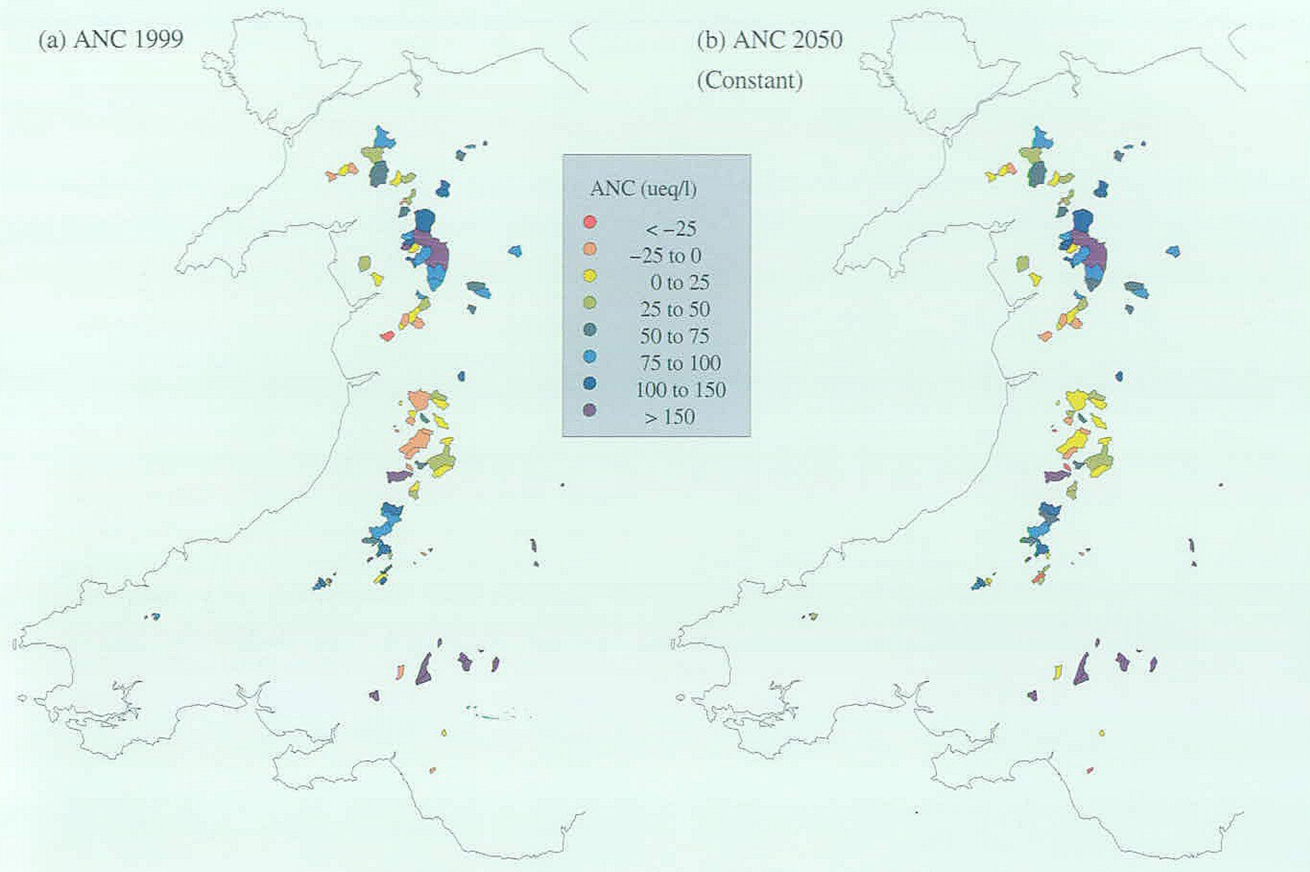


Figure 3.5.3 MAGIC simulated present day and 2050 ANC (Constant Deposition Scenario), Wales

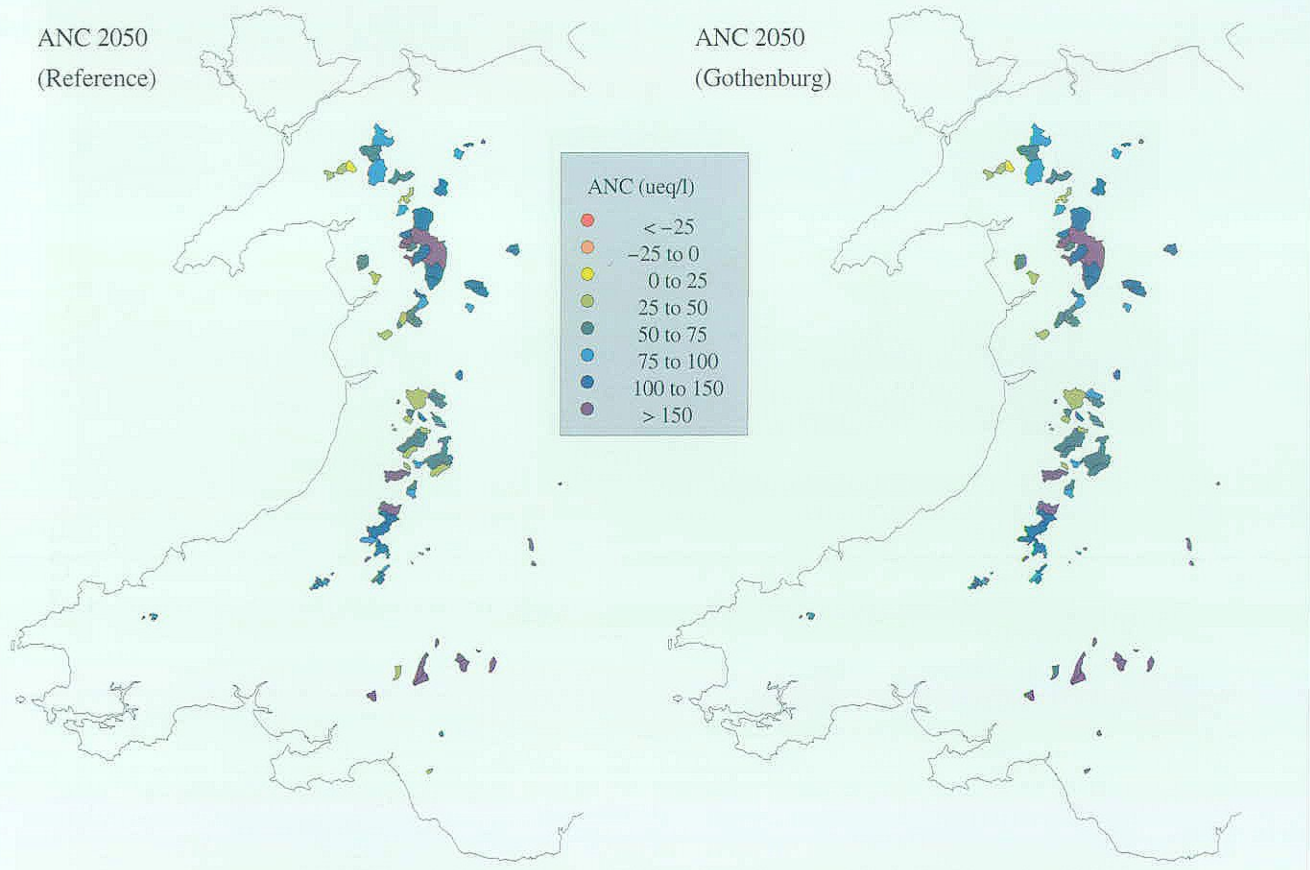


Figure 3.5.4 MAGIC simulated 2050 ANC –Reference and Gothenburg Scenarios, Wales

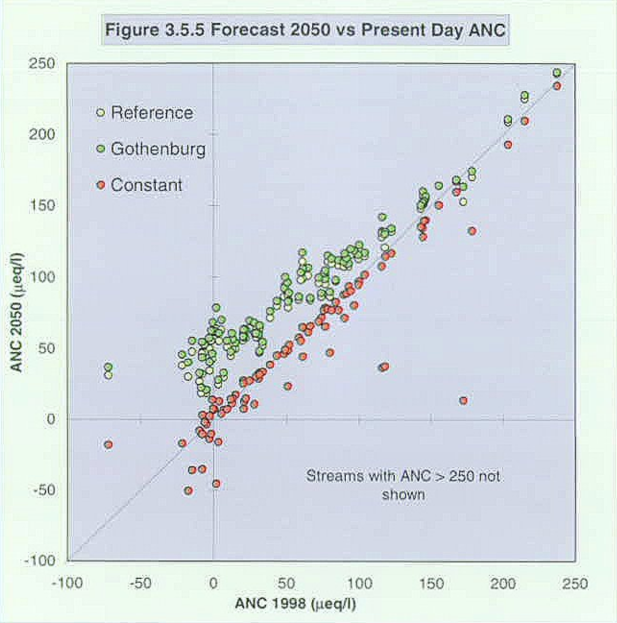
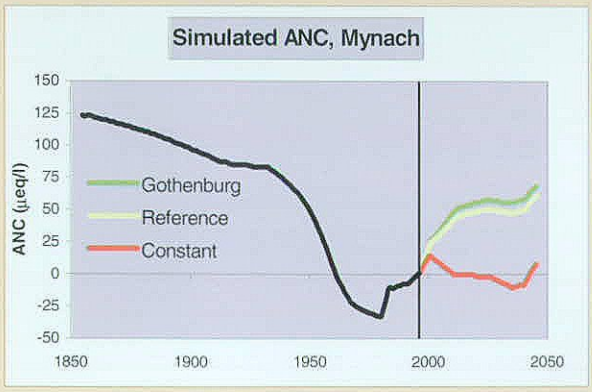


Figure 3.5.5 Forecast 2050 vs Present Day ANC

scenarios. However, this apparent discrepancy can be linked to the characteristics of the Welsh catchments, and specifically to calibrated weathering rates. For the two groups of sites defined above, the moorland sites have a median calibrated weathering rate of 200 meq/m^2/yr, whilst forested catchments appear generally to be sited in areas of greater geological buffering, with a median weathering rate of 258 meq/m^2/yr. Furthermore, 80% of forested sites have weathering rates exceeding 200 meq/m^2/yr, whereas at almost all forested sites in the other regions calibrated, weathering rates are below this value. Thus, in regions such as Galloway and the Cairngorms, forest uptake requirements are high relative to the supply from weathering, and additional leaching due to acid deposition, even at reduced levels, is sufficient to significantly deplete soil base saturation. In Wales, uptake is proportionally smaller, and reduced future levels of acid deposition exert less stress on soil base cation stores, thereby permitting streamwater ANC to increase.



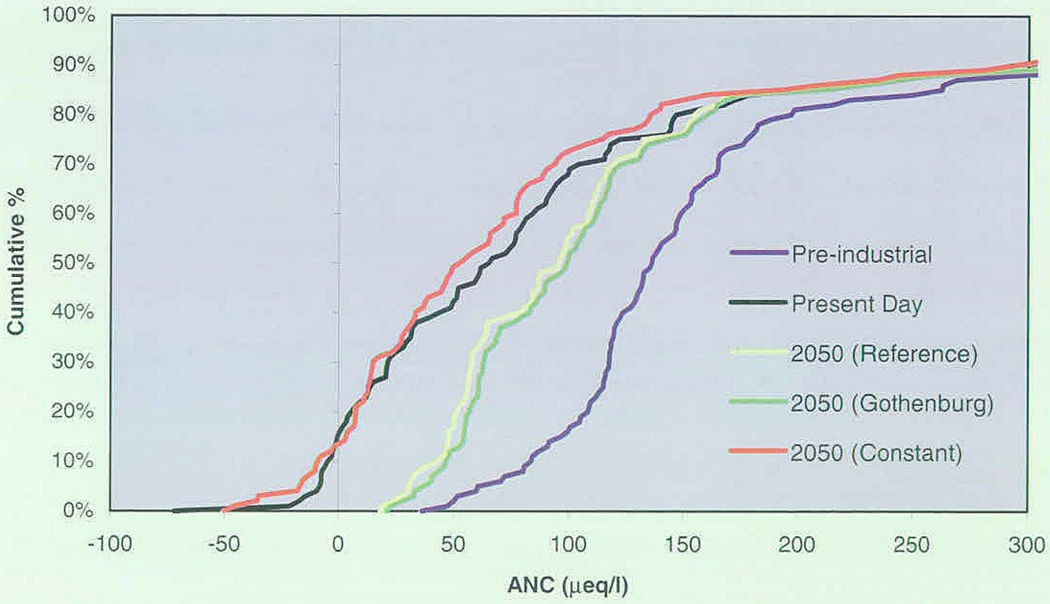
Simulated ANC, Mynach

Example 2: Mynach

Mynach is a relatively large (24.5 km^2) forested catchment in mid-west Wales. Approximately 54% of the catchment is currently forested with half this area having been planted prior to 1955. A number of other smaller stands have also been planted over the intervening years. Stagnopodzols, and to a lesser extent, peat and brown podzols are the dominant soil types within the catchment. Stream ANC has declined from c. 125 µeq/l in pre-industrial times to a present day value of –1 µeq/l. This decline has been driven not only by acidic deposition, but also by the acidifying processes associated with afforestation. Significant recovery is predicted under the Gothenburg and Reference scenarios, to over 60 µeq/l. In contrast, the Constant scenario shows ANC continuing to fluctuate around zero. Forest management contributes to ANC variability; felling of stands after 50 years, for example, causes a simulated transient increase in ANC at present day and around 2045.

Although these results suggest that most forested sites will recover in future in response to reduced acid deposition, it should be emphasised that this does not imply that forestry has had no detrimental impact on water quality in Wales; forested sites currently have a lower median ANC (44 μeq/l) than moorlands (74 μeq/l) despite having higher calibrated weathering rates, and as noted earlier, model forecasts indicate that forested sites would acidify further if deposition were maintained at current levels. For any individual forested site, present day ANC would be higher than is currently observed, and a higher ANC would be attained in future, had that site not been afforested. Equally, a currently forested site would recover to a greater extent if trees were felled at maturity and the sites allowed to return to moorland, than if trees are replanted. Finally, it is worth noting that cycles of forest growth, felling and replanting introduce large fluctuations in the acidity of runoff, and that at many sites in the Welsh dataset, minimum levels of ANC simulated within this cycle during the next 50 years are lower than ANC predicted for 2050; this is illustrated in Example 2.

Figure 3.5.6. Cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios)



Region 6: Dartmoor

3.6.1 REGIONAL DESCRIPTION

The 365 km^2 Dartmoor National Park (Figure 3.6.1) in Southwest England consists mainly of open moorland. The region has not been glaciated and the topography consists of an undulating plateau, rising to a peak elevation of 600m, incised by a number of steep river valleys. There are no natural lakes. The moorland area consists mainly of unimproved rough grassland and heather, with a relatively small proportion given over to coniferous forestry plantation. Soils are predominantly peat on the high moorland, ironpan stagnopodzols and stagnohumic gleys at intermediate locations, and brown podzols at lower altitudes, with virtually the entire region underlain by a large granite intrusion. Like much of the Wales study area, Dartmoor is located to the west of major emission sources but, with high rainfall, receives moderate levels of acid deposition. Given the region's proximity to both north and south coasts, marine ion deposition is high. Terrestrial and freshwater critical loads are both substantially exceeded throughout the upland area (RGAR, 1997; CLAG, 1995).

3.6.2 SURVEY SITES

Since Dartmoor surface waters were not surveyed specifically for this study, surface water data for modelling were compiled from three sources. The best record available is for the Narrator Brook AWMN site, where monthly samples have been collected since 1991. The second dataset used comprises 9 streams draining upland tributaries of the River Dart, which were sampled monthly from September 1998 to February 1999 as part of a project undertaken by CEH Wallingford for National Power plc. (Cooper *et al.*, 2000). The final dataset includes ten sites (four streams, four pools and two reservoirs) sampled once between November 1991 and December 1993 as part of the national survey of the Critical Loads Advisory Group (CLAG, 1995).

Chemical conditions during the regional surveys are compared to long-term data for Narrator Brook in Figure 3.6.2 and Table 3.6.1. These show little evidence of systematic change over the decade, with both SO_4 and NO_3 having remained fairly constant; concentrations of both anions were similar at all sampling times (unusually high NO_3 concentrations at Narrator Brook during the National Power survey may have been specific to this catchment). Temporal variations in pH at Narrator Brook are more pronounced, and there is some upward trend over the monitoring period, but conditions appear to have been fairly uniform at the times surveys were undertaken (Table 3.6.1).

TABLE 3.6.1. Narrator Brook solute concentrations during regional surveys

	ANC	pH	SO_4	NO_3	Cl	Na	Ca	Mg
CLAG 1 (Nov 1991)	-1	5.77	77	5	310	270	35	67
CLAG 2 (Apr 1992)	-16	5.74	73	4	304	248	33	67
CLAG 3 (Dec 1993)	12	5.49	77	9	265	248	28	67
National Power Survey (Sep 1998 – Mar 1999)	2	5.73	75	18	269	245	32	67
12-year mean	18	5.80	74	7	271	251	34	65

All concentrations in µeq/l except for pH (pH units). CLAG 1: Blackabrook, Crazywell Pool, Spurrels Cross Pool; CLAG 2: Meldon Reservoir, Redlake, Venford Reservoir, Shilley Pool, Haytor Quarry Pool; CLAG 3: West Okement River, East Dart.

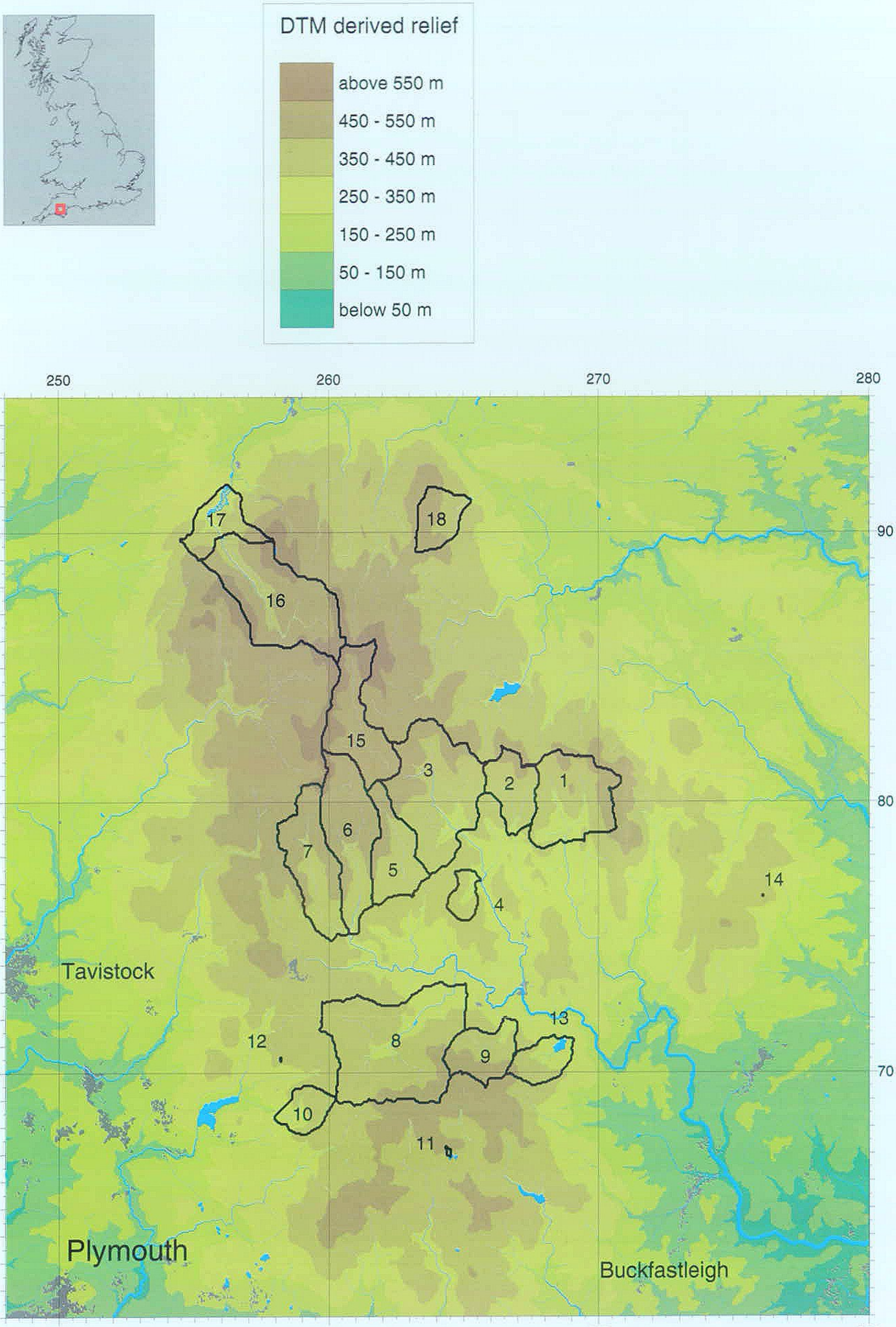
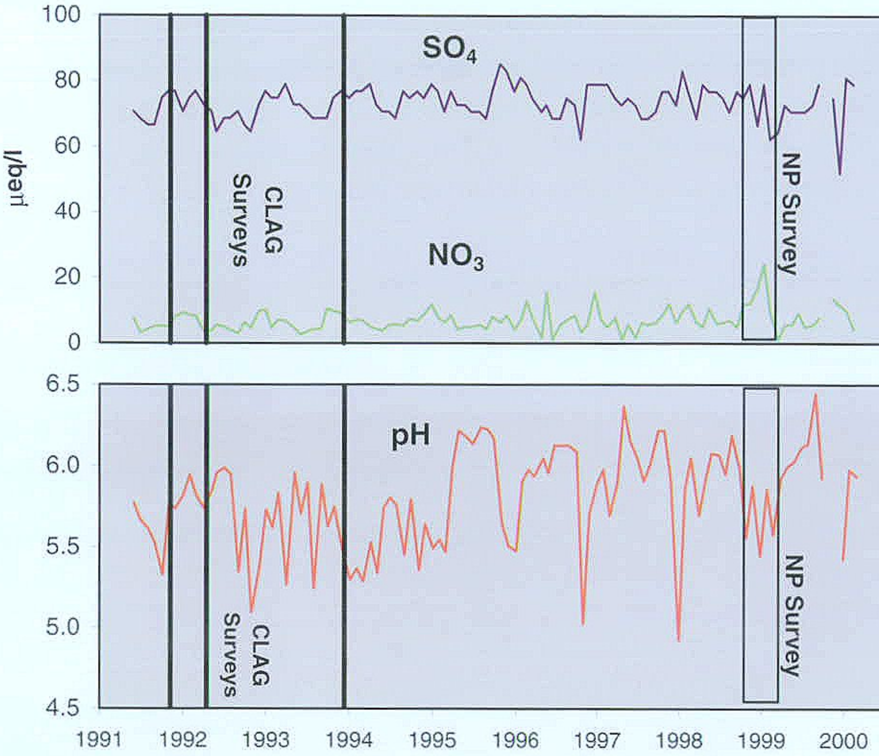


Figure 3.6.1. Location of Dartmoor survey sites (sites listed in Appendix 1)

Figure 3.6.2. AWMN data for Narrator Brook



3.6.3 REGIONAL CHEMISTRY

Despite differences in data sources and site characteristics, chemical variations among Dartmoor sites are small (Table 3.6.2), perhaps reflecting the homogenous geology of the study region. Most sites have a low but positive ANC, and a pH between 5.0 and 6.0. Sulphate concentrations are moderate (median 68 µeq/l), with a median non-marine SO_4 concentration of 41 µeq/l.

TABLE 3.6.2. Summary chemistry for Dartmoor survey sites.

	10th Percentile	Median	90th Percentile
ANC	-4	17	51
pH	4.98	5.60	6.08
SO_4	50	68	91
NO_3	1	11	22
Cl	210	335	448
SBC	285	336	448
NH_4	N/A	N/A	N/A
DOC	1.4	2.7	3.8

Nitrate concentrations are low at most sites, suggesting that catchments are not nitrogen saturated. Higher levels of both SO_4 (99 µeq/l) and NO_3 (39 µeq/l) at Bellever Stream are likely to be due to the effects of afforestation, as this is the only fully forested site. Sea-salt concentrations are high at all sites, reflecting the influence of marine ion deposition noted above.

3.6.4. MAGIC APPLICATION

MAGIC was applied to the Dartmoor region according to the methods described in Chapter 2, using national datasets for soils, deposition and rainfall. Forest areas (two catchments) were estimated from Ordnance Survey 1:25,000 maps, and in each case enhancement of dry deposition by the forest canopy was estimated by comparison of stream chemistry to that of an adjacent moorland catchment. Forest histories for these catchments were not obtained, so as an approximation based on observations of stand age, trees were assumed to have been planted in four equal five-year blocks between 1952 and 1972.

3.6.5 RESULTS

Of the 19 sites, 17 were successfully calibrated. The two sites that failed, Spurrels Cross Pool and Blackabrook, were both sampled in November 1991. Both had very high Cl concentrations, and negative concentrations of non-marine Na and Mg, consistent with the impact of a sea-salt episode. Although monthly sampling at Narrator Brook did not capture this event, an episode in January 1998 caused a near doubling of Cl concentrations and a 1-unit reduction in pH, suggesting that such large events can occur in the region. Negative non-marine cation concentrations are clearly not representative of long-term mean conditions.

For the 17 calibrated sites, simulated pre-industrial ANC (Figure 3.6.3) indicates that most surface waters in the region are inherently acid-sensitive, with a pre-industrial ANC of less than 100 μeq/l. Even the relatively low pollutant deposition in this region, therefore, has been sufficient to cause a number of sites, particularly small moorland pools, to acidify to ANC<0. A number of the larger stream and reservoir catchments also have a present day ANC below 10 μeq/l (Figure 3.6.4a), and as at Narrator Brook, are likely to experience acidic episodes, with potential damage to the biota.

Under a scenario of continued deposition at present day levels (Figure 3.6.4b), little change is observed; 14 sites show slight (< 4 μeq/l) ANC increases, two show no change, and three show continued acidification. The number of sites with negative ANC increases from three to four. These results suggest that, at most sites, catchment soils are approximately at a steady state under current levels of acid deposition, with little overall increase, or decrease, in base saturation (or subsequently ANC) predicted if these deposition levels are maintained in future.

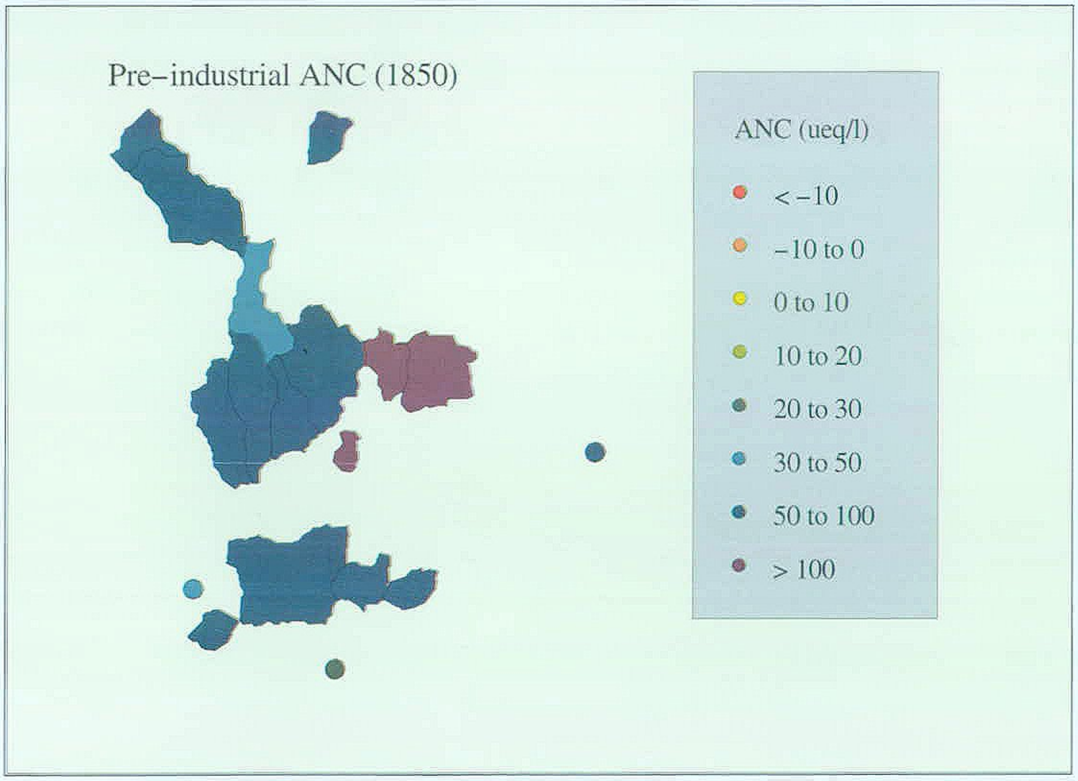


FIGURE 3.6.3. MAGIC simulated pre-industrial ANC, Dartmoor

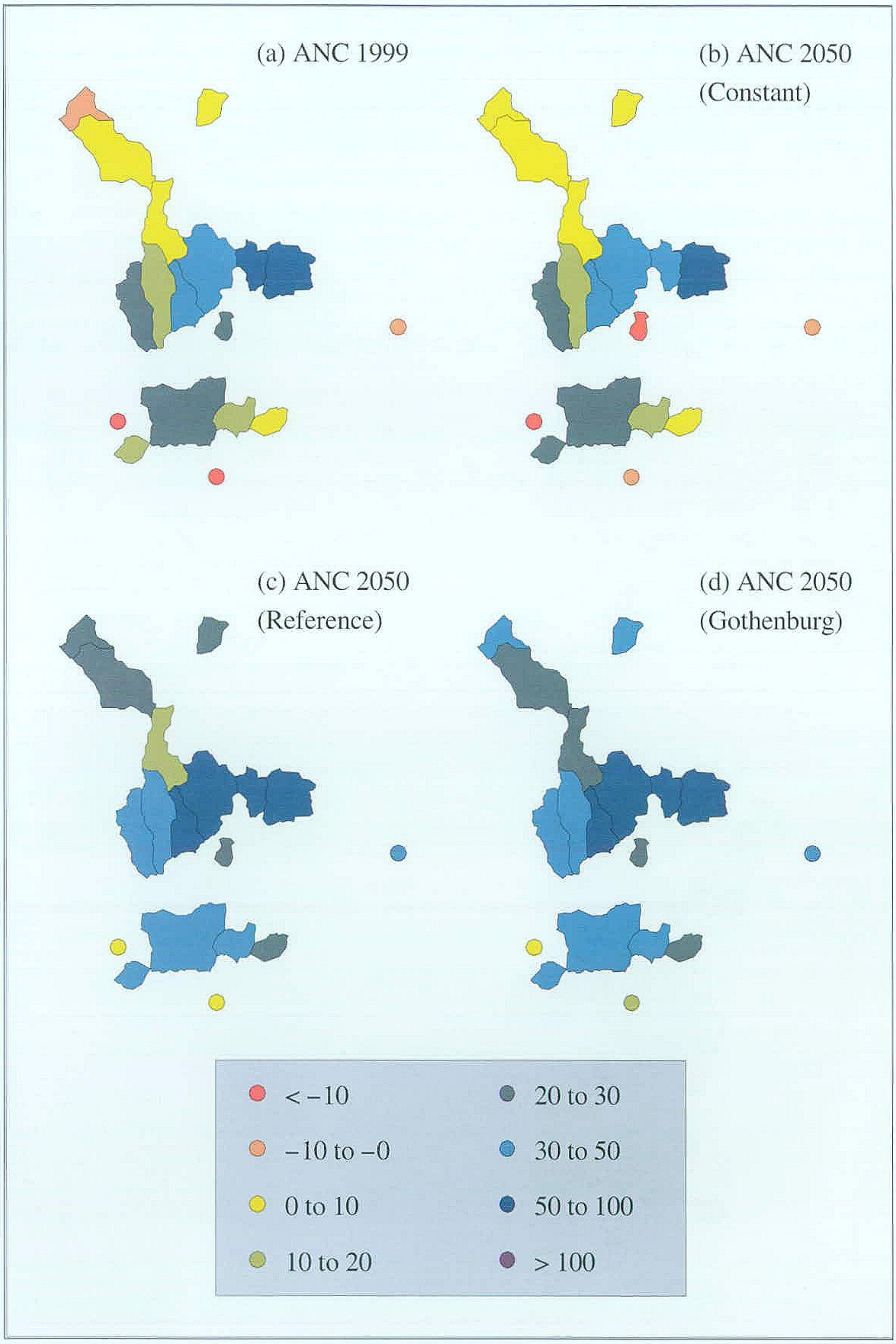
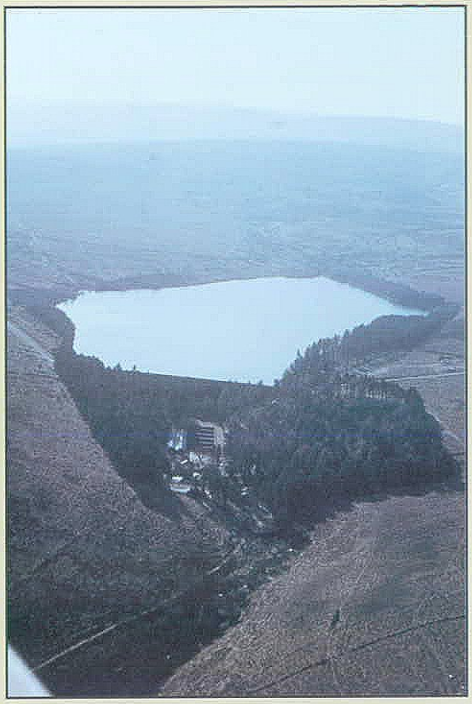
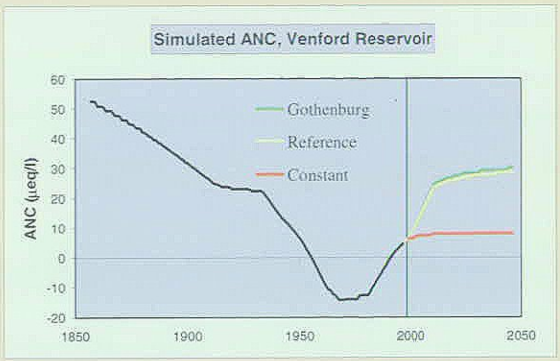


FIGURE 3.6.4. MAGIC simulated present-day and forecast ANC (μeq/l), Dartmoor

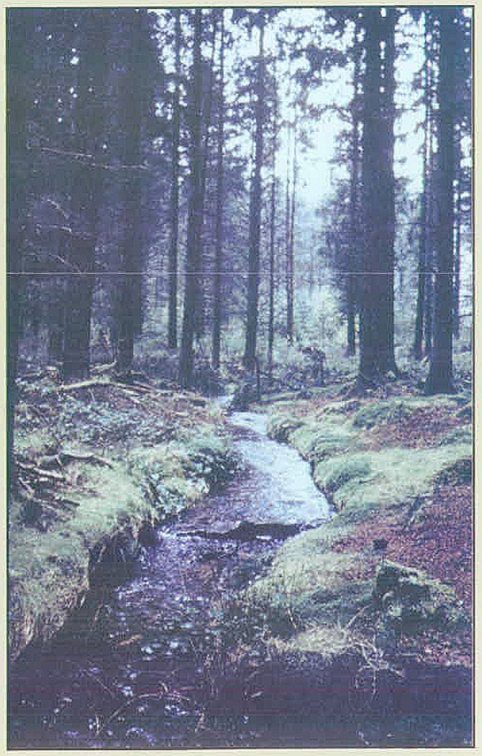
Example 1: Venford Reservoir

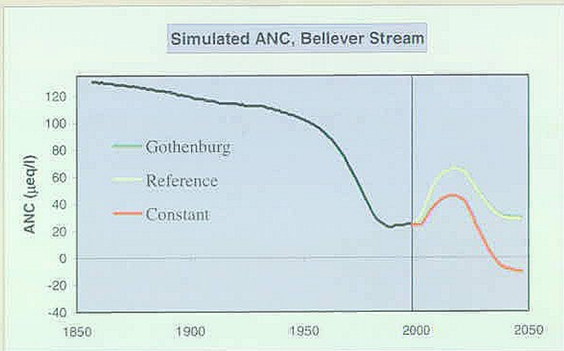




Venford reservoir is one of only two reservoirs included in the Dartmoor dataset, but its peaty moorland catchment and chemical characteristics are typical of many of the other sites in the region. MAGIC simulation suggests that this site has always had a fairly low ANC, with limited capacity to buffer acid inputs. Relatively low levels of historic acid deposition appear to have been sufficient to reduce ANC to negative values during the 1970s. Recovery to positive ANC over the last two decades is forecast to continue under the Reference and Gothenburg scenarios, increasing ANC from 6 μeq/l at present to over 28 μeq/l in 2050. Differences between the two scenarios are small, however. Under a constant deposition scenario, MAGIC simulation indicates that recovery will be minimal, levelling off at around 8 μeq/l.

Example 2: Bellever Stream





Bellever stream is the only completely forested site sampled on Dartmoor. Nitrate and sulphate concentrations (39 μeq/l and 99 μeq/l) are both very high for the region, reflecting the influence of forest dry deposition enhancement. Present-day ANC (28 μeq/l) is relatively high, however, suggesting that this brown podzol-dominated catchment is not particularly acid-sensitive. Simulated pre-industrial ANC is also high (130 μeq/l). Despite this, forecasts suggest more reductions in acid deposition will generate only short-term recovery at this stream, with runoff re-acidifying to present day values by 2050, following second rotation forest planting. Under the Constant scenario, initial recovery during forest harvesting is outweighed by subsequent acidification, and ANC is predicted to become negative under by 2050. Under all three deposition scenarios, simulated base cation supply from weathering is unable to meet the demands of forest uptake, leading to the continued loss of soil base saturation

An exception to this general pattern is Bellever Stream, the only forested catchment in the survey set. This is predicted to undergo major acidification under this scenario, from 25 µeq/l at present day to –10 µeq/l in 2050 (See example 2). This severe predicted acidification results from second-rotation conifer planting, as forest uptake apparently strips base cations from the exchange complex far more rapidly than acid deposition. However, acid deposition provides the strong acid anion flux required to transport acidity from the soil to the stream, leading to the negative ANC values forecast.

Under the Reference Scenario, considerable improvements in water quality are predicted. ANC is predicted to rise at all sites, with a median increase of 20 µeq/l. All modelled surface waters are forecast to have a positive ANC by 2050. Very similar results are attained for the Gothenburg scenario, with a median simulated ANC increase of 21 µeq/l. Unlike the Constant scenario, neither the Reference or Gothenburg scenarios predict re-acidification of the forested Bellever stream during the next 50 years, but simulated recovery at this site (4 µeq/l for both scenarios) remains the smallest of any modelled site in the region.

Figure 3.6.5. Forecast 2050 vs Present Day ANC

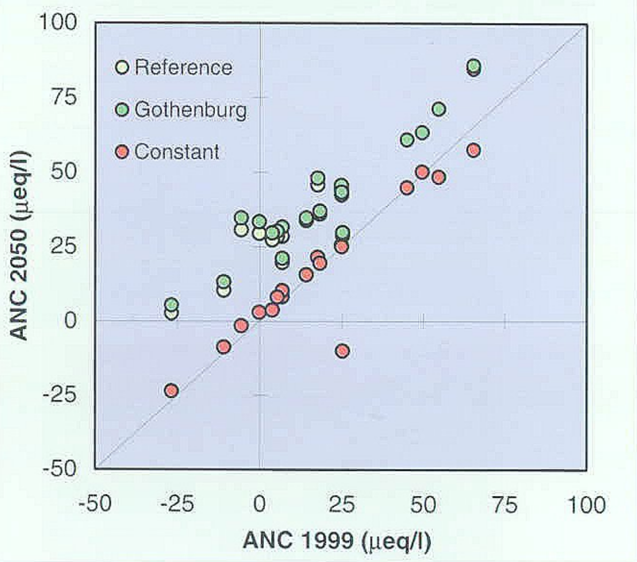
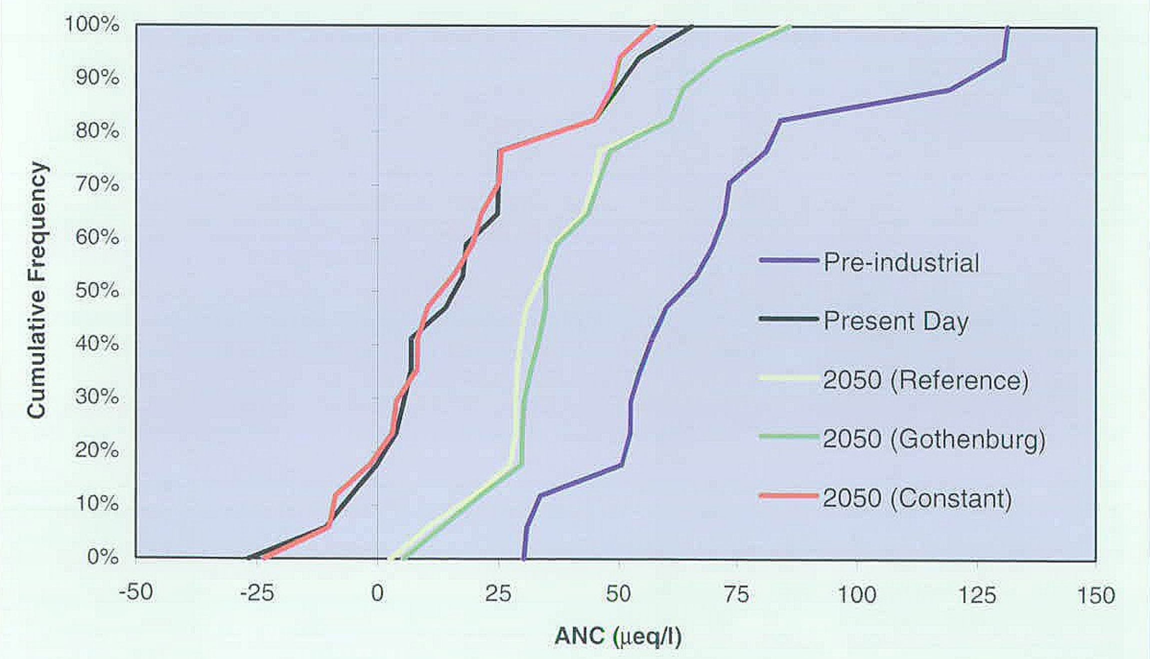


Figure 3.6.6. Cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios)



Chapter 4: Discussion

4.1. MODEL RESULTS

4.1.1. Effects of deposition scenarios

In total, 322 surface waters, from six major acid-sensitive areas of the UK, have been modelled using MAGIC during this study. These sites, most of which are either currently acidified or are sensitive to acidification, represent a consistent dataset with which to assess the likely impacts of different deposition scenarios on surface waters across the UK. For the 322 sites as a whole, the Reference scenario (Second Sulphur Protocol) is predicted to generate a substantial improvement in surface water ANC relative to present day conditions (Figure 4.1). The median forecast ANC increase under this scenario is 27 μeq/l (Table 4.1). This is estimated to represent approximately 42% of the total ANC increase that would be required to return these surface waters to the pre-industrial conditions reconstructed using MAGIC. Improvements are particularly evident in the most acidified systems, with the number of sites with ANC below zero falling from 68 (21%) at present to 12 (4%) in 2050 (Figure 4.1, Table 4.2). It should be noted, however, that these general patterns mask considerable inter- and intra-regional heterogeneity. Median predicted increase in ANC varies by more than a factor of five, from 10 μeq/l in the Cairngorms to 56 μeq/l in the South Pennines (Table 4.1). The percentage recovery towards pre-acidification ANC also varies regionally, from a median of 32% in Galloway to 57% in the Cairngorms, as does the number of sites at which ANC is predicted to remain negative. Reasons for these variations are discussed later.

Figure 4.1. Combined cumulative frequency distribution of ANC for pre-industrial, present day and 2050 (Reference, Gothenburg and Constant scenarios) for calibrated sites in all six regions

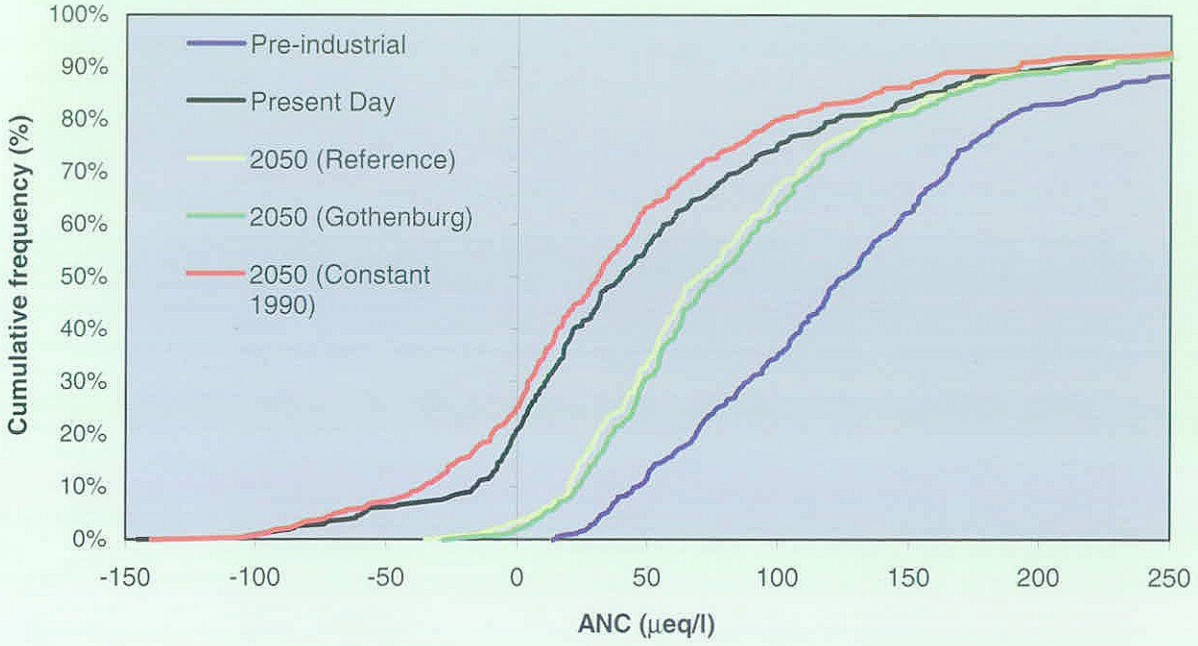


Table 4.1. Regional median forecast changes in ANC, and percentage recovery towards reconstructed pre-industrial conditions, for Reference, Gothenburg and Constant deposition scenarios, to 2050.

Region	Sites	ΔRef (μeq/l)	*Recovery* %	ΔGoth (μeq/l)	*Recovery* %	ΔConstant (μeq/l)	*Recovery* %
Cairngorms	38	9.6	57%	10.8	62%	1.0	5%
Galloway	56	28.9	32%	32.4	36%	-13.0	-13%
Lake District	51	27.8	54%	30.3	59%	2.0	4%
S. Pennines	58	55.6	40%	67.2	49%	-25.5	-23%
Wales	101	26.8	39%	30.7	45%	-3.7	-6%
Dartmoor	18	19.7	47%	20.7	51%	1.3	3%
All sites	322	27.1	42%	30.4	48%	-3.0	-4%

'Recovery' is defined as the forecast ANC recovery to 2050 as a percentage of the net ANC decline from pre-industrial conditions to present day, i.e. $[ANC_{2050} - ANC_{present\ day}]/[ANC_{present\ day} - ANC_{1850}] \times 100\%$

Compared to the Reference scenario, additional emissions reductions associated with the Gothenburg protocol are predicted to generate a small additional recovery in all regions, with a median ANC increase across all sites of 30 μeq/l by 2050, and the number of sites with a negative ANC in 2050 reduced to 7. Again, large regional differences are evident, with by far the largest difference between the two scenarios (12 μeq/l) predicted for the South Pennines, close to emissions sources. In the remaining regions, median ANC increases resulting from the Gothenburg protocol exceed those under the Reference scenario by less than 4 μeq/l. This seems a surprisingly small gain in freshwater ANC, given the large additional emission reductions required by the Gothenburg protocol, and is a reflection of the relatively small differences in acid deposition between the two scenarios forecast by HARM for more remote areas of the UK.

Loch Arron, a moorland catchment in Galloway (see Section 3.2), provides a representative example. HARM modelled S deposition under the Reference scenario at this site is 36% of the 1990 value, whilst under the Gothenburg Scenario this is reduced to 29% (N deposition is similar for the two scenarios). Since sulphur adsorption was considered negligible for this study, changes in loch xSO_4 concentrations occur in proportion to those

Table 4.2. Sites in each region with negative ANC at present day, and in 2050 under the Reference, Gothenburg and Constant Deposition scenarios.

Region	Sites	ANC < 0 (present day)	ANC < 0 (Reference)	ANC < 0 (Gothenburg)	ANC < 0 (Constant)
Cairngorms	37	0	2	2	2
Galloway	56	9	0	0	12
Lake District	51	13	3	2	11
S. Pennines	58	26	7	3	38
Wales	101	16	0	0	14
Dartmoor	18	4	0	0	4
All sites	322	68	12	7	81

in S deposition, falling at Loch Arron from 53 μeq/l at present day to 19 μeq/l (Reference) and 15 μeq/l (Gothenburg) in 2050. The additional xSO_4 reduction resulting from the Gothenburg protocol is thus only 4 μeq/l at this site, and the resulting increase in ANC is therefore also small. This situation appears, from the results obtained in this study, to be typical of many of the sites modelled in more remote regions.

Although predicted differences in recovery between the Reference and Gothenburg scenarios appear minor for some regions, it should be emphasised that both scenarios are predicted to generate significant recovery at most sites, and a major reduction in the number of sites with a negative ANC. By contrast, model forecasts suggest that maintaining deposition at current levels would lead to a further deterioration in water quality, with median ANC for the full dataset decreasing by 3 μeq/l to 2050 (Table 4.1). Some inter-regional variation is evident, with marginal increases in median ANC predicted for the Cairngorms, Lake District and Dartmoor, a small decrease for Wales, and larger decreases for Galloway and the South Pennines. Overall, 58% of modelled sites are predicted to undergo a decrease in ANC under this scenario, implying that base cation supplies from weathering at these sites are unable to balance the leaching demands of current acid anion deposition (and, at forested sites, vegetation uptake). This leads to the continued depletion of soil base saturation, and to increased levels of acidity and aluminium in surface waters. The number of sites with negative ANC is predicted to increase from 68 to 81 under this scenario (Table 4.2), demonstrating that critical loads are currently exceeded at a significant number of sites where ANC has not yet fallen below zero. At 9% of sites, ANC is not predicted to change, implying that these sites are currently in balance with regard to acid deposition and weathering, whilst at the remaining 33% of sites, small ANC increases suggest that higher weathering rates are already allowing soil base saturation to regenerate at current deposition levels.

4.1.2. Regional Variations

As noted above, the extent of forecast recovery varies considerably between the six regions modelled, and can be linked to a range of regional and catchment-specific factors. One of the most important is the impact of forestry, which model simulations suggest can greatly alter the response of otherwise similar catchments in the same regions. This is considered separately in the following section and therefore, in order to assess the other factors influencing freshwater recovery on a consistent basis, the analysis in this section has been restricted to moorland catchments.

For moorland sites in each region, the median percentage change in sulphur deposition was calculated from the HARM prediction for each scenario (Table 4.3). These show some regional variability, with a maximum 80% reduction in the South Pennines, and a minimum 66% reduction in Wales. In terms of the predicted change in SO_4 concentrations in surface waters, however, differences are considerably greater. The largest absolute SO_4 decreases are observed in the Pennines, where deposition and hence surface water concentrations are currently extremely high, and where the absolute reduction in sulphur deposition is predicted to be very large. At the other extreme, regions such as the Cairngorms and Dartmoor are more remote from emission sources, current deposition is lower, and the absolute changes in both input and output S concentrations are therefore expected to be small. Percentage reductions in N deposition are fairly constant between regions, but again the predicted absolute reduction in surface water NO_3 concentrations varies significantly as a function of current levels of N leaching. Changes in ANC follow a similar spatial pattern to those in SO_4, with the greatest magnitude of recovery expected in regions that are currently most impacted; this is intuitively logical, since areas that

Table 4.3. Median changes in deposition and surface water chemistry in moorland sites for each region under the Gothenburg Scenario.

Region	Deposition		Surface Waters				Weathering	Soil base
	ΔS	ΔN	ΔSO_4	ΔNO_3	ΔANC	$\Delta ANC/$	Rate	cations
	%	%	µeq/l	µeq/l	µeq/l	$(\Delta SO_4+\Delta NO_3)$	meq/m^2/yr	eq/m^2
Cairngorms	-70%	-33%	-12	-1	12	91%	72	1.8
Galloway	-73%	-32%	-38	-9	40	85%	182	7.7
Lake District	-76%	-34%	-31	-3	30	90%	241	9.3
South Pennines	-80%	-35%	-162	-19	77	43%	173	22.2
Wales	-66%	-36%	-52	-2	26	47%	200	19.3
Dartmoor	-71%	-35%	-26	-3	22	76%	88	18.8

Base cation weathering rates are the median of MAGIC-optimised values for all calibrated moorland sites in each region. Soil base cation pools are based on soil depth, bulk density, cation exchange capacity and present day base saturation.

have experienced the most severe acidification damage would be expected to show the greatest recovery.

It is interesting to note, however, that recovery in ANC as a proportion of the reduction in SO_4 and NO_3 concentrations ($\Delta ANC/[\Delta SO_4+\Delta NO_3]$, calculated from the present day to 2050). Regional median ratios of ANC increase to acid anion decrease vary from 0.43 to 0.91 (Table 4.3). Thus, in regions such as the Cairngorms and Lake District, the ANC response to a unit reduction in acid deposition is predicted to be around double the response in Wales or the South Pennines. Differences between regions can be attributed to a number of factors, but key influences include weathering rates, and the size of the soil base cation pool. The latter is important because, although the neutralisation of acidity through exchange with soil base cations acts to reduce acidification, the reverse process in which this stored acidity is released will also act to restrict recovery. Two opposing situations can therefore be envisaged, both leading to waters with a low present-day ANC (Figure 4.2). In example A, the high weathering rate gives a high pre-industrial ANC, but with little soil buffering the response to acid deposition is a severe acidification. However, a reduction in sulphur deposition leads to substantial recovery. In example B, weathering is low and soil buffering high, so that although pre-industrial ANC was low, the response to deposition changes is strongly damped, and predicted recovery smaller.

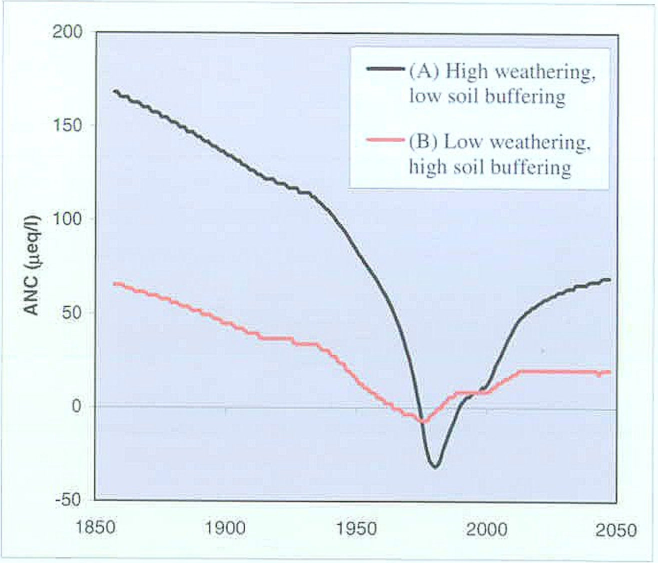


Figure 4.2. Two MAGIC simulations for a single site with altered weathering rates and soil buffering capacity.

Of the regions included in this report, the situation in example A is most closely approximated by the Lake District. Here, weathering rates are relatively high (Table 4.3) but soils generally thin, so both the predicted ANC increase, and the ANC increase as a proportion of acid anion decrease, are high. The Galloway moorland lochs also appear to be relatively responsive to changes in acid deposition; predominantly located in high mountain areas within the region, these catchments have low soil base cation pools and moderate weathering rates.

In the Cairngorm region, calibrated weathering rates are much lower, but the thin mountain soils of the granite massif provide minimal base cation buffering (Table 4.3). Consequently, surface waters here are highly sensitive to changes in acid deposition, and these data suggest that, had the Cairngorms been subjected to the levels of acid deposition seen elsewhere in the UK, severe acidification would have resulted.

The other three regions included in this study all have markedly higher soil base cation pools, and therefore appear much less responsive to changes in acid deposition. In Wales and the South Pennines in particular, over half of the forecast reduction in acid anion concentrations is predicted to be offset by decreases in base cation concentrations, rather than increases in ANC. Both of these regions, then, although strongly impacted by acid deposition, would be significantly more acidic at present-day if these large soil buffering stores were not present.

In general, the model predictions for future recovery of acidified waters appear reasonably consistent with an analysis of long-term trends in European surface waters by Evans *et al.* (2001b). This study suggested that, on average, around 50% of the reduction in surface water SO_4 and NO_3 concentrations during the last two decades has translated into an increase in ANC, but that substantial heterogeneity around this value occurs depending on catchment buffering characteristics.

4.1.3. Effects of Forestry

MAGIC model simulations show a divergence between future chemistry simulations for moorland and forested sites. In all regions other than Wales, the average recovery in ANC to 2050 under the Gothenburg scenario is greater for moorland catchments than for those containing significant (>10%) coniferous forestry (Table 4.4). In four of the regions, the difference in average ANC change between moorland and forest sites is over 10 µeq/l. In three regions (the Cairngorms, Galloway, and Wales) a number of forested sites are forecast to acidify over the next 50 years despite large reductions in S and N deposition.

Model predictions for soil base saturation (Table 4.5) provide a clearer indication of the impacts of forestry on upland soils. The results suggest that, whereas soil base saturation can be expected to increase slightly in most moorland soils under the Gothenburg scenario, soils in over 75% of forested catchments in all six regions will undergo a continued decline in base saturation. Even with the forecast reductions in acid loading under the Gothenburg Protocol, then, the combination of base cation uptake by

Table 4.4. Forecast ANC changes at forested sites under the Gothenburg scenario

Region	Number of forested sites	Average ANC change, moorland sites (µeq/l)	Average ANC change, forested sites (µeq/l)	Percentage of forested sites with ANC decrease
Cairngorms	10	+12	-19	70%
Galloway	33	+37	+21	9%
Lake District	1	+30	+24	0%
South Pennines	10	+77	+62	0%
Wales	54	+26	+36	4%
Dartmoor	2	+22	+11	0%

Table 4.5. Forecast base saturation changes at forested sites under the Gothenburg scenario

Region	Number of forested sites	Average Base Saturation change, moorland sites	Average Base Saturation change, forested sites	Percentage of forested sites with BS decrease
Cairngorms	10	+0.2%	-3.8%	89%
Galloway	33	+0.9%	-0.8%	79%
Lake District	1	+1.1%	-1.2%	100%
South Pennines	10	-0.1%	-1.0%	100%
Wales	54	+0.2%	-0.6%	85%
Dartmoor	2	+0.1%	-0.5%	100%

growing forests, and elevated leaching by enhanced dry deposition to the forest canopy, may exceed the supply of base cations from weathering at many catchments. It is worth noting that since the values given are lumped for whole catchments, and most of the study catchments are not fully afforested, the degree of base saturation decline in forest soils may be more severe than these whole-catchment values would suggest.

Inter-regional differences in model forecasts reflect a number of factors, including levels of acid deposition, weathering rates, and the nature of afforestation in the region. In the South Pennines, for example, acid deposition is forecast to decline substantially from currently high levels, and forest plantations do not occupy more than 25% of any catchment. Consequently, the impact of forestry is small relative to the impact of reductions in acid anion inputs. In Galloway and Dartmoor, with smaller deposition reductions and, in the sampled catchments, generally greater forested areas, the proportional impact of forestry on ANC change is larger. The most extreme effects of forestry are observed in the Cairngorms, where absolute changes in acid deposition are small, and weathering rates low; large predicted decreases in both ANC and base saturation for some forested sites in this region suggest that the supply of base cations from weathering may be unable to meet the demands of forest growth in the long-term.

The differing situation in Wales, as discussed in Section 3.5, appears to result from a general tendency for conifer plantations in the region to be located on areas of more weatherable geology, where surface waters respond more rapidly to reductions in acid deposition despite the impact of forestry. The predictions of continued acidification at a minority of forested Welsh sites confirm that, where planting occurs in more acid-sensitive areas, forests will cause similar detrimental effects as in other regions. In addition, the continued decline of base saturation simulated by MAGIC at almost all forested sites (Table 4.5) suggests that the widespread recovery predicted over the next 50 years may not be sustainable in the longer-term, as depletion of soil base cation pools may cause surface waters to re-acidify.

In general, then, it appears that the second rotation forest planting simulated within this model application will have a significant detrimental effect on surface waters at most of the forested sites considered. ANC recovery at these sites is generally less than that at comparable moorlands, and in most cases soil base saturation is predicted to fall further in the future due to a combination of leaching and uptake. At a number of sites, this depletion of soil buffering appears sufficient to cause runoff to acidify further over the next fifty years, despite the major emission reductions agreed under the Gothenburg protocol. It is interesting to note that these predictions appear to be consistent with long-term monitoring data from the UKAWMN; the application of MAGIC to 21 AWMN sites (Jenkins *et al.*, 1997), based on the same methodology for modelling forest impacts, predicted increases in ANC at most moorland sites in response to reduced acid deposition, but a continued decline in ANC at all five forested sites. A trend analysis of monitored data from 1988 to 2000 (Evans and Monteith, 2001) suggests that in Galloway, the moorland Round Loch of Glenhead is now recovering, whereas the forested Loch Grannoch has acidified further during this period. In Wales, the moorland Llyn Llagi and Afon Gwy both have rising pH trends, whilst there has been no recovery to date at the forested Llyn Cwm Mynach and Afon Hafren. However, it should be noted that the simulation of forestry within MAGIC is highly simplified, and subject to a number of uncertainties. These are discussed below.

4.2 UNCERTAINTIES IN MODEL APPLICATIONS

The results obtained from this study should be interpreted with respect to existing uncertainties in both the model structure, and in the available data. The model calibrations utilise the best available data for inputs and parameterisation based on observation (water chemistry), extrapolation (e.g. rainfall, deposition chemistry, soil chemistry) and modelling (future deposition estimates). The low resolution of deposition inputs, in particular, may have led to overestimates of pollutant inputs at some sites, and underestimates at others. Similar errors are likely to have arisen from the generalisation and interpolation inherent in the soils maps used to derive lumped catchment soil characteristics, and in the assignment of uniform physical and chemical characteristics to soil associations. By applying the model at a multiple site basis, however, individual site errors should to some extent balance out, providing a more robust assessment at the regional scale than would be obtained for individual sites viewed in isolation.

The use of HARM to model future deposition represents a further source of uncertainty in the model application. Estimates of future S and N deposition reductions were made by scaling HARM forecasts for each scenario to HARM 1990 baseline deposition. It is possible that this use of a 1990 baseline may have led to some overestimation of the magnitude of deposition reductions for surface waters between the time of sampling (1995 to 2000) and 2010. As a result, it is possible that model forecasts may to some extent overestimate the degree of recovery that may be expected by this time.

With regard to the structure of the MAGIC model, the main uncertainty lies in the representation of N dynamics and in particular, the controls on future N leakage. The results presented here provide essentially a pragmatic assessment based on the assumption that catchments will continue to retain N as a fixed proportion of the deposited N. In this respect, this could be interpreted as a "best" case scenario; any increased leaching of N in future would reduce surface water ANC relative to the predictions given in this study. Further uncertainty lies in the representation of S dynamics and in particular, the assumption that soil SO_4 adsorption is rather low in the UK uplands. The ability of soils to retain and slowly release SO_4 as deposition decreases will affect the predicted time to recovery although it may have little influence on the degree of recovery over a 50-year period.

Finally, the simplified treatment of forest processes within MAGIC creates a number of additional uncertainties for afforested catchments. The uptake rates applied are uniform across all catchments, and a 50-year growth cycle is assumed for all forest stands. Both factors may however vary according to catchment characteristics and climate. It is also possible that uptake may fall in future (with a concurrent slowing of forest growth) if soil base saturation becomes severely depleted. The model further assumes that the full tree biomass is removed on harvesting, but brash, stumps and needles remaining within the catchment may retain a significant proportion of the tree base cation content. Return of these base cations to the soil exchange complex (rather than rapid flushing to the stream) may partially mitigate the effects of forestry on long-term soil and stream acidification. Finally, the model forecast used assumes that forests are replanted without any associated treatments. Fertiliser or lime additions might substantially offset the acidifying impacts of afforestation.

4.2. REPRESENTIVITY OF MODEL APPLICATIONS

In addition to the uncertainties in model structure, and in interpolated and modelled input data, the value of the model output is dependent on the extent to which observations of surface water chemistry are representative of the wider status of surface waters in UK upland areas. In this respect, it is important that observations of water chemistry are (a) temporally representative of average conditions at individual sites; and (b) spatially representative of water quality within the regions studied, and to some extent also of conditions in other, unsampled sensitive regions.

4.2.1. Temporal representivity

In this study, the MAGIC model has been applied using an annual time-step to predict changes in mean annual chemistry of surface waters. Since the model relies on a calibration to observed data, it is important that the present day observations are a true representation of the annual mean. In this respect, streams, due to their high episodic variability, generally require more samples to provide an estimate of mean chemistry than standing waters. In this study, the only regions with significant numbers of streams were Wales and Dartmoor. For Wales, each stream was sampled monthly over a one-year period, and the estimates of mean annual water chemistry used to calibrate MAGIC are consequently believed to be accurate. Streams on Dartmoor were sampled six times, except for four streams sampled as part of the Critical Loads survey. For the majority, therefore, the mean chemistry is considered to be representative, but the single samples collected at these four streams may be less representative of annual conditions.

In the other regions, standing waters were sampled in order to minimise the problem of temporal variation. All samples were collected in spring, in accordance with the procedures used for the Critical Loads survey, as conditions during this period are considered to be close to the annual average. In Galloway, the mean of two spring samples from consecutive years was used to represent mean annual chemistry, whilst in the Cairngorms, Pennines and the Lake District, a single spring sample was collected at each site. Although episodicity is less pronounced for standing waters, there are clearly risks that these samples may have been collected during unrepresentative periods. This potential problem was assessed by comparing conditions at AWMN sites in each region during survey periods to those observed in the long-term record. In the Cairngorms and South Pennines, conditions when some samples were collected are believed to have been slightly more dilute than average due to preceding snowmelt (Cairngorms) and rainfall (South Pennines). In Galloway, relatively high concentrations were observed for NO_3, which has a large seasonal cycle in this region peaking in winter/spring. In the Lake District, high Cl concentrations indicated slightly above-average levels of sea-salt during the survey period. For all these regions, therefore, it is unlikely that the one-off survey approach exactly replicated long-term average chemical conditions, leading to some error in the MAGIC calibration. However for the majority of sites, these errors appear to be minor, and are unlikely to significantly impact model output. Given the prohibitive cost of regular sampling at a large number of sites, these errors may be unavoidable for this type of extensive regional modelling (or critical loads) assessment, and for this reason it is important that more robust, site-specific model applications be maintained in order to validate regional studies.

4.2.2. Spatial representivity within regions

In all the regions studied, a decision was made to focus on acid-sensitive systems, rather than all surface waters within that area. This sampling strategy, while inherently biased, is considered justifiable given that non-sensitive systems (either agricultural or on well-buffered geology) are of little ecological or policy significance in relation to acid deposition. In addition, while the exclusion of these sites will affect the frequency distribution of ANC values in a region, it obviously will not alter the absolute number of acidified sites observed.

Of greater concern, then, is the extent to which the sites sampled represent the wider population of acid-sensitive freshwaters within a region. This can be relatively easily assessed for standing waters, which are present in limited numbers in all the study regions, and which each represent single, identifiable locations. The Cairngorm, Galloway and Lake District surveys incorporated *all* substantial lakes above the limit of improved agricultural land in those regions, whilst the South Pennine survey included *all* headwater reservoir catchments containing little or no farmland. These surveys can therefore be considered representative of the population of acid-sensitive standing waters in these regions. It is less certain, however, whether these standing waters can also be taken to represent the status of streams in the same regions. This is particularly uncertain where the distribution of each freshwater type differs within a region. In the Lake District, for example, most mountain tarns are located on Borrowdale Volcanics geology, but the small number of tarns on the Skiddaw Slates are also acidic. Since streams draining Skiddaw slates are likely to be acidified to a similar extent, this geology is under-represented by a survey of lakes only. Similarly, in Galloway a recent survey of tributaries of the River Cree (Cooper *et al.*, 1999) showed that many were severely acidified, but because there are few lochs within the upper Cree catchment, this area is again under-represented in the loch survey.

For streams, it is more difficult to assess spatial representivity, because water chemistry varies along the stream length and the observed values are thus highly dependent on the site chosen for sampling. There is evidence that the Welsh Acid Waters sites used for MAGIC calibration, although mostly collected in areas of high geologic sensitivity to acid deposition, may under-estimate the true severity of acidification across Wales as a whole. In the Welsh Acid Waters Survey, priority was given to site accessibility, with most samples collected at the highest road access point on the stream. As a result, most catchments are relatively large, and many contain areas of improved farmland. By comparison, Welsh catchments in the Critical Loads survey were mostly smaller, and those in upland areas were generally above the limit of improved farmland (both lakes and streams were included). These differences in sampling strategy are reflected in the number of acidic sites sampled: of 102 sites in the Welsh Acid Waters survey, only two had a pH below 5.0, and 15 had a negative ANC. In contrast, 19 of the 158 Welsh sites in the Critical Loads survey had a pH below 5.0, and 40 had a negative ANC. It is, therefore, likely that the survey sites modelled in this study provide an underestimate of the extent of current and future acidification in Wales.

On Dartmoor, similar issues arise with the selection of stream sampling points, although fewer catchments contain improved farmland. Because the Dartmoor modelling dataset was compiled from several sources, the sampling protocols are not consistent, and a smaller number of sites were modelled than in other regions. However, given the small total area, and since this was the only region where both standing waters and streams were included, it is felt that this dataset should provide a reasonable indication of regional acid status.

4.2.3. Spatial representivity within the UK

This regional modelling study focused on areas known or believed to be susceptible to acidification, based on the freshwater sensitivity map (Figure 1.1). These regions together comprise a significant proportion of the total area of the UK believed to be sensitive to acidification, and also cover a wide gradient of deposition, geology and topography. It is thought, therefore, that results from this study should provide some indication of current conditions, and future changes, in other, unsampled acid-sensitive waters regions. However, future national-scale dynamic model assessments should ideally incorporate a number of additional areas, for many of which there is currently little surface water data:

- *Scottish Highlands*: Almost all of the Scottish Highlands, as well as the Hebrides, Orkney and Shetland, are highly sensitive to acidification. Although data from the Critical Loads survey (Figure 4.3) show a large number of sites in this area with a low pH, many of these sites were strongly affected by sea-salt acidification at the time of sampling (Evans *et al.*, 1998). Data from AWMN streams in northwest Scotland suggest that these often experience transient pH depressions during sea-salt events, but that they are not acidified in the long-term given the very low acid deposition in the region. It may, therefore, only be in areas closer to the population centres of the central lowlands, such as the Trossachs and Southern Grampians, that waters are chronically acidified. Elsewhere, the situation is likely to reflect that observed in the Cairngorms, with moderate levels of acidity and relatively small changes in response to emissions reductions.

- *Southern Uplands*: Much of the Southern Uplands of Scotland are classed as acid-sensitive, and waters have been shown to be severely acidified in Galloway. In the remainder of the region, however, data from the Critical Loads survey provide little evidence of widespread acidification.

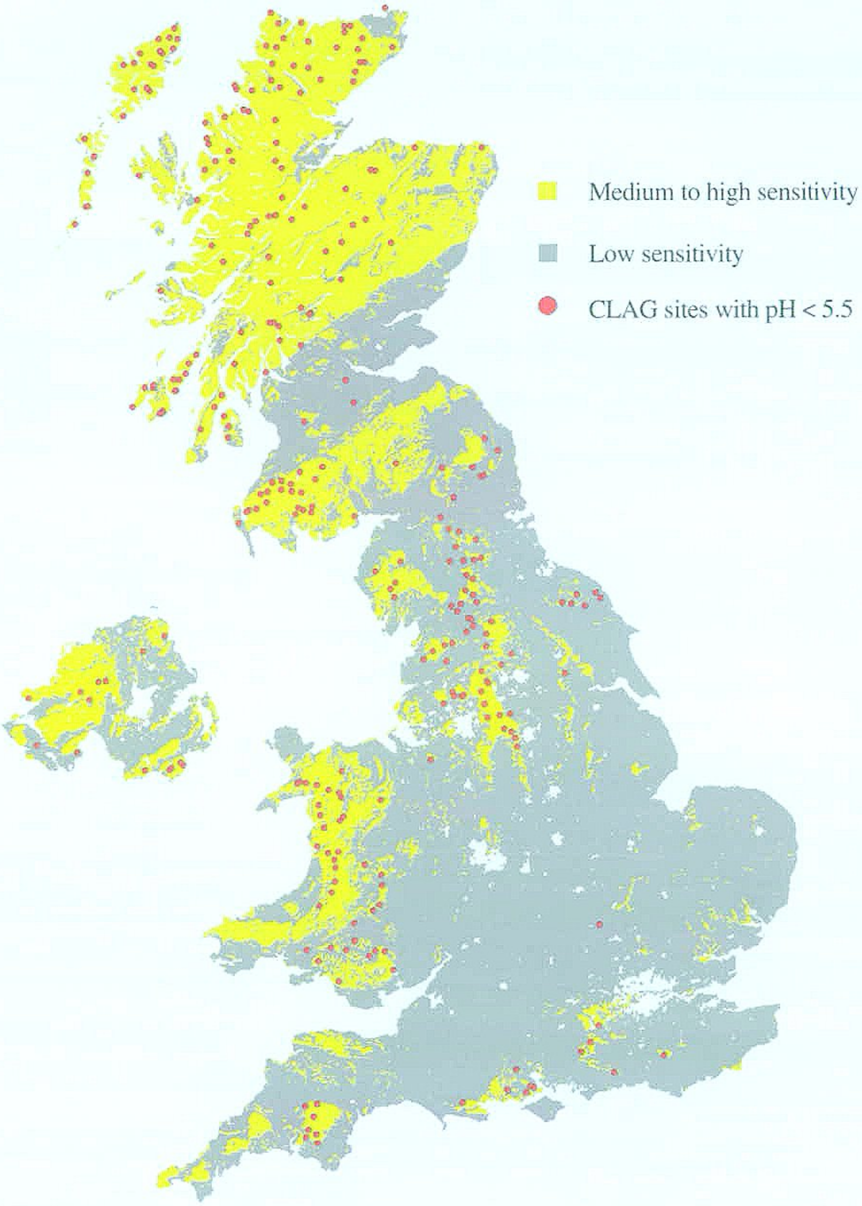
- *Northern England*: Apart from the Lake District and South Pennines, acid-sensitive regions of Northern England are small, and widely separated (Figure 4.2). High levels of acid deposition, however, are likely to have caused significant acidification in these sensitive regions, and this is confirmed by Critical Loads survey data. Acidic surface waters, many with a very low pH, occur in non-calcareous parts of the Northern Pennines, the Forest of Bowland, parts of Northumberland, and the North York Moors. Monitoring of pH at several streams in the North York Moors (Chadwick, 2000) also shows evidence of intense acidification in this region. These areas, in which few sites have previously been sampled, represent a priority for future surveys.

- *Southern England*: Most of this area is insensitive to acidification, but a recent survey of 40 surface waters on heathland and forest areas of Surrey and Hampshire underlain by base-poor sandstones (C. Evans, unpublished data) has provided evidence of severe acidification at some locations. Similarly acidic surface waters have also been observed on heathland in the New Forest and Dorset during the Critical Loads survey, and at the Old Lodge AWMN site in Ashdown Forest, Sussex. Acid-sensitive lowland areas, although small in extent, are of high ecological value, and have in the past largely been omitted from studies of freshwater acidification in the UK.

- *Southwest England*: The moors of Devon and Cornwall, particularly those underlain by granite, are sensitive to acidification, although deposition is moderate to low in this region. It is likely that the Dartmoor data included in this study should provide a reasonable indicator of acid status in other sensitive areas of the Southwest.

- *Northern Ireland*: Northern Ireland represents a significant gap in the current coverage of regional MAGIC applications in the UK. Data from the four AWMN sites in the region, and from the Critical Loads survey, show evidence of acidification in the Mourne Mountains, Sperrin Mountains and Glens of Antrim. The Mourne Mountains appear to be the most severely impacted, with high concentrations of both SO_4 and NO_3 in runoff, and this area will be surveyed during 2001/2002.

Figure 4.3. UK freshwater sensitivity map showing acidic sites from the Critical Load Survey



Sensitivity map from Hornung et al. (1995). Location of Northern Ireland relative to Great Britain is approximate.

Chapter 5: Conclusions

In terms of assessing the likely response of surface water chemistry to the Gothenburg Protocol in the UK, the MAGIC model predicts a substantial decrease in acidity by 2050 in all acid-sensitive regions, such that only 2% of the 322 sites modelled have ANC less than zero compared with 21% at present day. For the Reference scenario, which reflects earlier agreements, 4% of waters are predicted to have ANC less than zero in 2050. If deposition were to remain at current levels into the future, the number of sites with ANC less than zero would increase to 25%. The benefits of the emission reductions to UK surface waters, therefore, are clear, and appear sufficient to return the majority of currently acidified waters to a positive mean ANC by 2050.

While undoubtedly encouraging, it must be emphasised that these improvements in surface water ANC do not represent a return to pre-acidification status. Even under the Gothenburg scenario, model simulations suggest that the predicted ANC increases will, on average, represent just 48% of the ANC change required to return surface waters to 'natural' conditions. Under the Reference scenario, the increase is smaller, at 42%. As a result, many of the sites studied will retain a low positive ANC in 2050 (8% of sites are predicted to have an ANC < 20 μeq/l under the Gothenburg scenario, and 11% under the Reference scenario). At these sites, it is probable that ANC will continue to fall below zero in response to episodic, seasonal and inter-annual variations in water chemistry, and that they may remain biologically impoverished as a result.

At a broad scale, the added 'benefit' of the Gothenburg Protocol over the Reference scenario appears relatively small. At most sites, the additional increase in ANC obtained is only a few micro-equalivalents per litre, reflecting the small differences in HARM model predictions of S and N deposition for the two scenarios. This general pattern masks considerable variability in the predicted response of the individual regions, however. For example, in the most heavily impacted region, the South Pennines, the predictions show 12% of surface waters with ANC below zero in 2050 under the Reference scenario, but only 5% under the Gothenburg Protocol. In other regions the differences between the two scenarios are smaller, and this reflects the present day regional deposition fluxes, and the intention of the Gothenburg Protocol to target reductions to sensitive areas receiving highest deposition.

Plantation forestry is a further driver of water chemistry changes in some of these regions. The model predictions under the Gothenburg Protocol and assuming second rotation forestry show a widespread further reduction in soil base saturation, which significantly slows or prevents recovery of ANC at many forested sites. Perhaps the biggest overall impact is predicted in the heavily forested Galloway region, but second rotation forest was also predicted to lead to future acidification of some waters in relatively unimpacted regions, notably the Cairngorms and Dartmoor. This assessment, however, makes broad assumptions about the chemical impacts of forests and replanting practices and does not include chemical additions to the forest at any stage.

The timescale of chemical reversibility and the degree to which the simulated pre-acidification ANC is achieved also varies regionally as a result of catchment and regional specific factors controlling soil base cation characteristics and weathering rate. For example, in the Lake District calibrated weathering rates are high but soils are generally thin and the base cation exchange pool is small. As a consequence, decreased SO_4 input promotes a rapid and almost equivalent increase in ANC, and so the model predicts that within 50 years and under the Gothenburg Protocol the region will recover 60% of the ANC lost relative to modelled pre-industrial conditions. On the other hand, at many sites in the South Pennines and Wales, thicker soils result in much smaller changes in response to decreased SO_4 input as the soil exchange pool is slowly replenished, and under the same scenario these regions recover only 40% of ANC lost relative to pre-industrial conditions.

Despite this predicted recovery in surface water chemistry, the prospects for biological recovery remain unresolved. It is likely that biological recovery will lag the chemical recovery as a result of the dynamics of recolonisation and because biota are affected by acid episodes which will continue to occur on streams, which provide spawning areas for fish populations, even after the mean chemistry reaches ANC zero. Indeed, the use of ANC zero as a biological threshold is the subject of debate, but this is beyond the scope of this analysis.

This analysis must be interpreted with respect to existing uncertainties in model structure and input data. However, Many of these uncertainties in dynamic models, particularly those regarding measured and extrapolated data and the process uncertainty relating to future N leakage, are also inherent in empirical and steady-state methods for calculating critical loads. In essence, dynamic models require little extra data than that required for steady-state critical load calculations for surface waters and are subject, therefore, to similar uncertainties. Dynamic models, however, offer two key advantages in the assessment of emission reduction strategies; the ability to quantify the timescale of water chemistry response to a given reduction and, conversely, the scope to assess the deposition load required to achieve a water chemistry target within a specified timescale. Regional model applications, such as those reported here, offer the opportunity to add these dynamic aspects of ecosystem recovery to the Integrated Assessment methodology utilised in negotiating emission reductions. The links to Integrated Assessment Models require new research, as does the coupling of aquatic and terrestrial biological models to the dynamic chemical model, to provide a full assessment tool.

Future modelling at regional scale needs to incorporate more acid-sensitive regions, in particular north-west Scotland, central Scotland, Northern Ireland, Snowdonia, sensitive lowland areas in southern England, the North York Moors, and several further areas of northern England Increased confidence in the predictions would also result if further regional surveys of water chemistry supported the results of the existing 'one-off' synoptic surveys given the assumption that the single sample represents the annual mean chemistry of the site. In addition, a new regionalisation technique has been developed for streams (Cooper *et al.* 2000, Evans *et al.* 2001a) and the potential for this to be used within a predictive modelling framework should be assessed and developed.

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Appendix 1: Location of Study Sites

Site numbers for each region correspond to labels on site location maps

Region 1: Cairngorms

Site number	Site name	Easting	Northing
1	Allt a'Mharcaidh*	288100	804500
2	Loch Einich	291500	799000
3	An Lochan Uaine	300100	810600
4	Lochan Coire an t-Sneachda	299400	803200
5	Lochan Beanaidh	291100	802700
6	Lochan Mor	289900	809500
7	Lochan Buidhe	298400	801100
8	Loch Mhic Ghille-chaoile	292100	802500
9	Lochan na Beinne	300600	808300
10	Lochan t-seilich	291500	800600
11	Loch Coire an Lochain	294500	800500
12	Loch An Eilein	289500	807500
13	Loch Morlich	296500	809500
14	Loch Gamhna	289000	806700
15	Lochan Odhar	295000	803500
16	Lochan a'Chait	300700	811700
17	Un-named lochan, Ryvoan Pass	301600	811900
18	Lochan a Gharbh-choire	301300	811000
19	Lochan nan Craobh Loisgte	295200	808600
20	Lochan Deo	291800	807900
21	Lochan Coire an Lochain	298200	802900
22	March Burn	298100	801000
23	Lochan nan Geadas	295500	808900
24	Un-named lochan on Alltan Donn	287500	807000
25	Loch Pityoulish	292000	813500
26	Lochan Dubh a Chadha	297000	806700
27	Lochan nan Nathrach	296100	808400
28	Loch nan Stuirteag	294100	795700
29	Loch nan Cnapan	291700	796000
30	Lochan na Frithe	299400	809400
31	Loch Etchachan	300500	800500
32	Loch Avon 3	301500	802500
33	Lochan Uaine	302600	798600
34	Lochan A'Bhainc	304700	804700
35	Lochan Uaine	300100	798100
36	Dubh Lochan	303800	802500
37	Lochan Uaine	296000	798000
38	Pools of Dee (upper)	297400	800800
39	Pools of Dee (lower)	297400	800600

*Allt a'Mharcaidh AWMN site not used in model application

Region 2: Galloway

Site number	Site name	Easting	Northing
1	Lillie's Loch	251000	574000
2	Loch Gower	254000	573000
3	Kirriereoch Loch	236000	586000
4	Dow Loch	245000	580000
5	Dow Loch	246000	582000
6	Black Loch	249000	572000
7	Loch Doon	248000	599000
8	Loch Muck	250000	599000
9	Loch Finlas	246000	598000
10	Loch Bradan	242000	597000
11	Loch Brechbowie	243000	596000
12	Loch Balloching	245000	594000
13	Loch Skelloch	240000	596000
14	Loch Goosie	244000	594000
15	Loch Riecawr	243000	593000
16	Cornish Loch	241000	594000
17	Loch Macaterick	244000	591000
18	Loch Girvan Eye	241000	592000
19	Loch Fannie	244000	592000
20	Knockstring Loch	269000	588000
21	Loch Harrow	252000	587000
22	Lochinvar	266000	585000
23	Loch Moan	235000	586000
24	Loch Dungeon	252000	584000
25	Clatteringshaw's Loch	254000	577000
26	Loch Enoch	244000	585000
27	Loch Minnoch	252000	586000
28	Dry Loch	246000	585000
29	Round Loch of the Dungeon	246000	584000
30	Loch Trool	240000	579000
31	Loch Dow	235000	584000
32	Long Loch of the Dungeon	246000	584000
33	Loch Neldricken	244000	582000
34	Loch Arron	244000	583000
35	Loch Howie	270000	583000
36	Loch Valley	244000	581000
37	Loch Narroch	245000	581000
38	Loch Brack	268000	582000
39	Moss Ruddock Loch	263000	581000
40	Barscobe Loch	266000	581000
41	Long Loch of Glenhead	244000	580000
42	Round Loch of Glenhead	245000	580000
43	Loch Gower	228000	577000
44	Lowes Loch	270000	578000
45	Drumlamford Loch	228000	577000
46	Loch Dornal	229000	575000
47	Loch Mayberry	228000	575000
48	Loch Nahinie	227000	577000

Site number	Site name	Easting	Northing
49	Loch Ochiltree	232000	574000
50	Loch of Fyntalloch	231000	574000
51	Loch Grannoch	254000	570000
52	Mossdale Loch	265000	571000
53	Garwachie Loch	234000	568000
54	Black Loch	228000	565000
55	Loch Ronald	226000	564000
56	Loch Heron	227000	564000
57	Black Loch	231000	575000

Region 3: Lake District

Site number	Site name	Easting	Northing
1	Scales Tarn	332800	528200
2	High Nook Tarn	312400	519900
3	Floutern Tarn	312400	517100
4	Bleaberry Tarn	316500	515400
5	Red Tarn	334700	515200
6	Dalehead Tarn	322900	515300
7	Launchy Tarn	323300	515000
8	Angle Tarn	341800	514400
9	Blea Tarn	329100	514000
10	Dock Tarn	327400	514400
11	Harrop Tarn	331200	513600
12	Innominate Tarn	319700	512900
13	Blackbeck Tarn	320200	512800
14	Hayeswater	343100	512300
15	Grisedale Tarn	334700	512000
16	Tarn at Leaves	326900	512200
17	Greenup Tarn	328800	511000
18	Blea Tarn	344800	510700
19	Scoat Tarn	315900	510400
20	Small Water	345500	510000
21	Styhead Tarn	322200	509800
22	High House Tarn	324100	509400
23	Sprinkling Tarn	322800	509200
24	Un-named near High House Tarn	324000	509200
25	Low Tarn	316200	509300
26	Easedale Tarn	330700	508700
27	Codale Tarn	329700	508800
28	Angle Tarn	324300	507600
29	Stickle Tarn	328700	507700
30	Greendale Tarn	314600	507400
31	Lang How Tarn	331800	506800
32	Three Tarns 2	324800	506000
33	Three Tarns 1	324800	506000
34	Lingmoor Tarn	330200	505100
35	Burnmoor Tarn	318300	504300
36	Blea Tarn	329300	504400

Site number	Site name	Easting	Northing
37	Red Tarn	326700	503700
38	Stoney Tarn	320000	502500
39	Greenburn Reservoir	323500	502200
40	Eel Tarn	318900	501900
41	Siney Tarn	316300	501200
42	Blea Tarn	316500	501000
43	Parkgate Tarn	311800	500500
44	Yewtree Tarn	332200	500400
45	Levers Water	328000	499300
46	Seathwaite Tarn	325000	498500
47	Low Water	327400	498400
48	Goat's Water	326700	497700
49	Devoke Water	315500	496900
50	Blind Tarn	326300	496700
51	Kelly Hall Tarn	328800	493300
52	Stickle Tarn	321400	492800
53	Torver Reservoir	328000	492600

Region 4: South Pennines

Site number	Site name	Easting	Northing
1	Upper Redmires Reservoir	425800	385500
2	Rivelin Brook Reservoir	424800	386400
3	Strines Reservoir	422900	390400
4	Agden Reservoir	426000	392500
5	Howden Reservoir	417000	393000
6	Hurst Reservoir	405600	393700
7	Broomhead Reservoir	426300	395900
8	Midhope Reservoir	422200	399400
9	Woodhead Reservoir	409000	399700
10	Higher Swineshaw Reservoir	400500	399700
11	Langsett Reservoir	420900	399900
12	Iron Tongue Cloug h Reservoir	399800	401200
13	Upper Windleden Reservoir	415200	401200
14	Chew Reservoir	403700	401800
15	Winscar Reservoir	415200	402500
16	Dovestone Reservoir	401600	403600
17	Snailsden Reservoir	413400	403900
18	Riding Wood Reservoir	411800	405000
19	Wessenden Head Reservoir	407000	407400
20	Black Moss Reservoir	403300	408700
21	Swellands Reservoir	403700	409000
22	Redbrook Reservoir	402600	409700
23	Castleshaw Upper Reservoir	399600	410100
24	Dowry Reservoir	398400	411200
25	Deer Hill Reservoir	407100	411400
26	Readycon Dean Reservoir	398700	412300
27	Cold Greave Clough Reservoir	397000	412600
28	March Haigh Reservoir	401500	413000

Site number	Site name	Easting	Northing
29	Norman Hill Reservoir	396900	413100
30	Cupwith Reservoir	403800	414100
31	Green Withens Reservoir	398600	416300
32	Draught Hill Reservoir	395900	416300
33	Naden Higher Reservoir	385200	417300
34	Hills Clough Reservoir	392100	417700
35	Blackstone Edge Reservoir	397200	418300
36	Higher Chelburn Reservoir	395400	418300
37	Baitings Reservoir	400600	418700
38	Scout Moor Reservoir	382700	419600
39	Whiteholme Reservoir	397000	419800
40	Cowpe Reservoir	384300	420200
41	Warland Reservoir	395900	420900
42	Ramsden Clough Reservoir	391600	421300
43	Gaddings Dam	394800	422400
44	Heeley Dam	395800	423200
45	Gorpley Reservoir	391200	423400
46	Withens Clough Reservoir	398200	423800
47	Ogden Reservoir	406300	430700
48	Upper Dean Head Reservoir	402200	430800
49	Cant Clough Reservoir	389700	430900
50	Upper Gorple Reservoir	392200	431400
51	Warley Moor Reservoir	403100	431600
52	Hurstwood Reservoir	388800	431600
53	Widdop Reservoir	393200	432900
54	Thornton Moor Reservoir	405300	433000
55	Stubden Reservoir	406200	433200
56	Swinden Reservoir	388900	433300
57	Upper Walshaw Dean Reservoir	396700	434600
58	Leeshaw Reservoir	401400	435200
59	Watersheddles Reservoir	396600	438100
60	Keighley Moor	398700	439400

Region 5: Wales

Site number	Site name	Easting	Northing
191	Dyfyrdwy	287900	331100
280	Tryweryn	283800	339800
305	Alwen	292000	356200
336	Fechan	297800	358700
2662	Nant y Foel Ddu	291700	358400
3142	Hirddu	297420	321360
3143	Cownwy	298950	318310
3144	Banwy	294400	313520
3145	Disgynfa	307280	329500
20274	Hir	275100	332000
20276	Ganol	274900	332300
20277	Gain	275500	333500
20279	Ceiswyn	277800	310400

Site number	Site name	Easting	Northing
20280	Dulas North	277900	310500
20282	Llefenni	276500	310400
20284	Cwm Eiddew	274400	308900
20285	Nant Iago	269000	307800
20286	Cerist	282500	316400
20287	Helygog	279100	319600
20288	Harnog	281600	322400
20289	Wnion	281700	322900
20310	Mawddach	278800	329300
20311	Bryn Llin Mawr	277400	329700
20312	Ceirw	276800	328900
23173	Cynfal	274700	341800
23174	Pistyll	275100	342800
23175	Cwm y Llan	263000	351400
23176	Colwyn	257600	350900
23177	Tributary of Colwyn	257300	350000
25234	Glascwm	278800	350600
25237	Nant y Gwryd	270000	357200
25238	Llugwy	271800	358000
25239	Cwmpenamnen	273700	352200
25240	Lledr	271100	351600
25241	Afon Conwy	277900	344600
25242	Calettwr	285700	349400
25451	Cwm Nantcol	263300	326200
25452	Cwm Mynach	268300	320900
34408	Meurig	271800	267500
35206	Mynach	274400	276700
35270	Nant y Moch	276700	286900
35644	Nant Milwyn	278900	273700
39257	Biga	287000	289180
39258	Llwyd	287280	290560
39259	Trannon	290440	295280
39260	Tributary of Glas Brook	319000	267000
39261	Cwm y Gerwyn	314400	252000
39262	Tributary of Edw	310900	248800
40867	Un-named stream	285100	225400
40881	Senni	292500	220700
40889	Un-named stream	297200	222300
57000	Balencyff	282400	284100
57001	Celliogyn	282300	282100
57002	Bidno	287700	282200
57003	Troedyresgair	288800	279900
57004	Hirin	289000	272200
57005	Elan	288900	272300
68975	Nantcrew	299400	216400
70085	Sychbant	284300	190300
71073	Nant Du	287300	199400
71682	Llia	292700	216500
72159	Un-named stream	267600	208900
72160	Giedd	279100	212900

Site number	Site name	Easting	Northing
72161	Nant Cyw	279200	212800
72758	Amman	273500	214300
81068	Hengwm	277800	288900
88085	Llyn Brianne L15	282200	249700
88111	Llyn Brianne L18	280500	248800
88116	Tributary of Tywi	278200	246400
89103	Un-named stream	274200	288600
89104	Peithnant	276000	284900
89105	Un-named stream	273300	283300
89106	Un-named stream	274300	281800
89112	Peiran	277500	274800
89113	Tributary of Ystwyth	276200	272900
89119	Berwyn	269400	259700
89120	Groes	269400	259900
89121	Brefi	268100	254500
89122	Clywedog Upper	264400	251600
89123	Egnant	276900	265600
89124	Mwyro	276900	265500
89130	Iar	251100	239500
89131	Ceiliog	251700	240000
89132	Ceredig	251800	240200
89133	Cynhenfod	252400	241700
89134	Hust	252500	242000
89135	Duar	255100	241900
89136	Llwydcoed	255300	241700
89138	Wernant Upper	256500	242800
89141	Clawdd	265200	246200
89142	Cothi Upper	270700	248300
89143	Tributary of Cothi	271500	246900
89144	Nant Dar	270300	243800
89145	Twrch Upper	268500	250400
89147	Dulais	269900	240000
89148	Tributary of Cothi	269200	243700
89149	Annell	267900	240500
89202	Preseli 3	207800	230500
89203	Preseli 4	207800	230900
89204	Preseli 5	207300	231400
89206	Preseli 10	205600	233800

Region 6: Dartmoor

Site number	Site name	Easting	Northing
1	West Webburn River	268750	78500
2	Walla Brook	266900	78800
3	East Dart River at Postbridge	264800	78900
4	Bellever Stream	265600	77100
5	Cherry Brook	263400	77000
6	West Dart River	260800	75150
7	Cowsic River	260700	75150
8	Swincombe River	264700	73200
9	O Brook	266450	71950
10	Narrator Brook	258100	68500
11	Redlake	264500	66900
12	Crazywell Pool	258200	70450
13	Venford Reservoir	268700	71300
14	Haytor Quarry Pool	276100	76500
15	EastDart River at Sandy Hole	262600	81100
16	West Okement Weir Pool	256050	89850
17	Meldon Reservoir	256350	91650
18	Shilley Pool	265250	91200