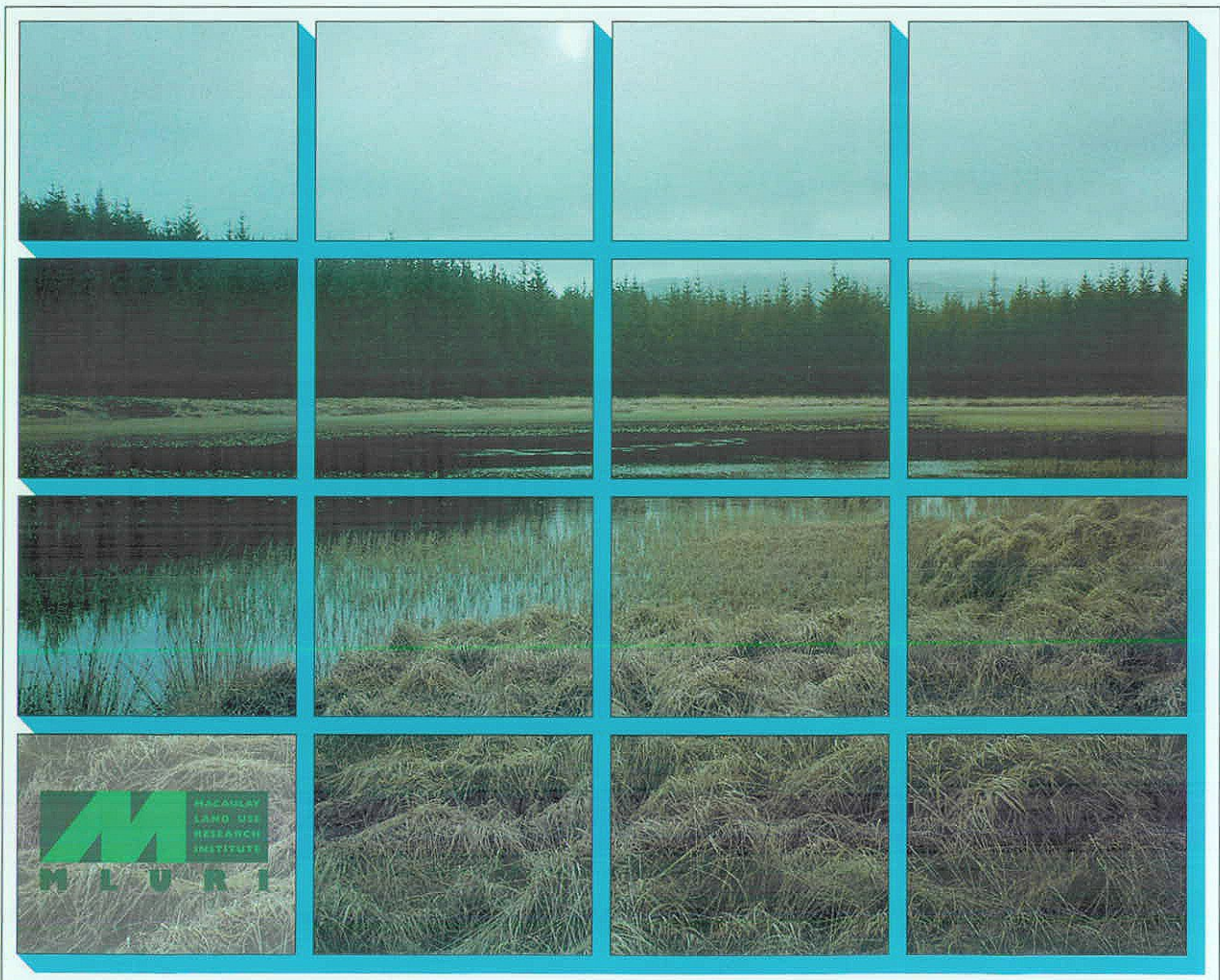Institute of
Hydrology

Report No. 131

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Application of the MAGIC model to the Acid Waters Monitoring Network

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Executive summary

Acidic emissions resulting from fossil fuel burning are known to acidify soils and surface waters in remote areas. Geological characteristics generally determine the regional acidification response, although land-use change has been identified as a key factor in accounting for variations within regions. In June 1994 international agreement to limit sulphur (S) emissions across Europe was achieved under the Convention on Long Range Transboundary Air Pollution. This was the so-called Second Sulphur Protocol or Oslo Protocol. The agreement was negotiated on the basis of an 'effects oriented' approach, founded on the critical loads concept, and established national emission targets to be reached by 2010. The philosophy behind this approach was to target the emission reductions that would produce the most effective deposition reduction at the most acidified areas.

The UK Acid Waters Monitoring Network was established in 1988 to provide a high quality chemical and biological database with which to assess surface water response to reductions in acidic emissions. It provides a unique collection of headwater catchments which span a range of S and N deposition, geological sensitivity to acidic deposition and degree of afforestation.

In this study the MAGIC model has been applied to 21 sites of the UK Acid Waters Monitoring Network to determine:
i)   the likely response of soil and surface water acidification to the Second S Protocol;
ii)   the level of deposition reduction required to produce recovery at sites where the Second S Protocol is inadequate; and
iii)   the role of afforestation in future acidification status.

The model has been calibrated using a consistent methodology for all sites. Best available soils, water chemistry, land-use and deposition data have been used for the calibration procedure. Predictions into the future are driven by estimated deposition at each site from a source-receptor model (HARM) based on agreed national emissions under the Second S Protocol.

The MAGIC model provides a close match with observed soil and mean annual surface water chemistry at the 21 sites. Uncertainty in model simulations, introduced into the calibration procedure, largely reflects the variation in mean annual surface water chemistry over eight years of observations at these sites. The close match to observed data demonstrates the portability of the model across a wide range of catchment physico-chemical conditions. Historical pH reconstructions using

diatoms, from pre-industrial time to present day, are available at 11 lake sites in the network. These provide an independent validation of the model and MAGIC simulated pH reconstructions generally match diatom reconstructions with respect to the magnitude and timing of the pH change.

In general, predicted response to the Second S Protocol is for a small increase in pH at all sites in the next 30 – 50 years but this will not be sustained beyond that period as acidic inputs are predicted to still be in excess of base cation supply from weathering. In the longer term this will promote further acidification at the acid sensitive, and currently acidified sites, unless further reductions in Sulphur and Nitrogen can be achieved. The benefit of targeting either Sulphur or Nitrogen reductions is site specific and depends on the relative deposition loads and, most importantly, on the current and future Nitrogen leakage from the terrestrial system.

Future afforestation policy is expected to have a significant effect on acidification status. Two forestry scenarios have been implemented at the currently afforested sites; (i) remove all forest as it reaches 50 years age and allow the land to revert to moorland vegetation; and (ii) remove forest as it matures but immediately re-plant a second rotation forest. These two scenarios represent a best and worse case, respectively. Under the re-planting scenario, surface water pH is predicted to further decline. The magnitude of this decline is related to current acid status rather than degree of forest cover. This further strengthens the conclusion of earlier work that forests promote acidification in areas of high acidic deposition but have little detrimental effect on surface water chemistry in areas of low deposition.

MAGIC provides the only technique to allow calculation of critical loads with the purpose of achieving a biologically relevant surface water chemical criteria in a given time-scale. The relevance of choice of chemical criteria and time-scale of recovery are assessed with respect to critical loads estimated using empirical approaches. In general, critical loads calculated using MAGIC are lower at the acidified sites as a result of the requirement to recover within a given time-frame. The calculated critical loads at these sites would require substantial reductions in emissions of sulphur and/or nitrogen over and above those already negotiated.

Further work must attempt to incorporate better process representation of N dynamics into the model to enable assessment of any future N protocol and must include the development of a regionalisation methodology to allow economic assessment of the impacts of emission control policies.

1 Introduction

Over the past four decades the phenomenon of acid rain has evolved from a scientific curiosity to a global issue of public concern and controversy. Its adverse effects give rise to local, regional, national and even international concern. A variety of environmental effects have been attributed to acidic deposition and its gaseous precursors. These include the acidification of soils and surface waters, harmful effects on human health, decreased fish stocks, forest dieback, reduced crop yields, corrosion of building materials and reduced atmospheric visibility.

The assertion that increased industrialisation and the burning of fossil fuels was at the heart of the problem was fiercely debated in the UK during the 1970s and 1980s. Continuing research has filed a large body of evidence linking fossil fuel burning to acidic emissions and deposition. The problem faced today is how to reduce acid deposition and allow natural ecosystems to recover such that pre-acidification biological populations can be restored. At the heart of this issue is the hypothesis that reduced acidic emissions will promote reduced acidic deposition and lead to recovery of acidified areas. The key question now is "to what degree in time and space should acidic oxide emissions be reduced to allow this recovery to take place?"

The role of conifer afforestation in the acidification of surface waters has been a prominent issue which has further complicated the acidification and reversibility process (Nisbet et al., 1995). Following a Forestry Commission and Department of the Environment (DoE) workshop in 1990, it was agreed that forestry had a minimal impact on acidification in areas of low acid deposition. However, in areas of high acid deposition forests contribute to enhanced acidification, largely through their ability to filter atmospheric pollutants and thereby enhance inputs of acidic oxides (DoE & Forestry Commission, 1991). This effect is particularly marked in "even-aged" conifer plantations in upland areas (Stoner & Gee, 1985).

As scientific understanding of the processes controlling acidification has developed so has the perceived need to protect the environment for the future. The implementation of long term monitoring programmes and international agreements to curtail acid deposition have focused attention and scientific effort on the development of dynamic modelling approaches to not only understand the processes involved in the spatial and temporal extent of acidification but more importantly, to predict the future consequences of the policy decisions undertaken today. Here we present the results of a detailed study involving the application of a catchment based soil and surface water acidification model, the Model of Acidification of Groundwaters

In Catchments (MAGIC, Cosby et al., 1985 a,b) to the sites comprising the UK Acid Waters Monitoring Network (AWMN, Patrick et al., 1991).

The objectives of this research programme are: to quantify the spatial extent and degree of recovery of surface water acidification in response to the most recent international agreement relating to the reduction of sulphur (S) emissions; to determine the deposition reduction required to achieve recovery within a given time scale; and to assess the impact of land management policy at afforested sites in conjunction with emission reduction scenarios.

1.1 Sulphur and nitrogen in surface water acidification

Surface waters in geologically sensitive parts of North America and Europe have become increasingly acidified by the deposition of strong acid anions from the atmosphere, namely non-marine sulphur (S) and nitrogen (N), since the industrial revolution in the mid-nineteenth century (Likens et al., 1979; Haines, 1986). Severely affected areas have experienced many symptoms of acid deposition including forest dieback and the impoverishment or loss of freshwater biota (Muniz, 1991). The most emphatic evidence for surface water acidification comes from diatom based reconstructions of lake pH (Battarbee et al., 1988; Flower et al., 1987) which have shown a steady decline in the pH of surface waters in geologically sensitive areas of high acid deposition.

The process by which deposition of S and N causes acidification of soils and surface waters is commonly termed the "mobile anion" theory whereby the deposition of non-marine anions: sulphate (SO_4), nitrate (NO_3) and, to a lesser extent, chloride (Cl) have been implicated as the cause of the loss of alkalinity (ANC) and increasing hydrogen ion (H) concentrations in surface waters. In simple terms, anions which are not retained within the catchment system are transported via hydrological pathways to surface waters and the nature of their associated cation determines the acidification response. If base cations are available on soil exchange sites, the anion enters the surface water system as a neutral salt with no acidification effect, although if the S deposition flux is greater than the base cation weathering, soil acidification will result. In time, as the soil base cations are depleted, the buffering capacity is exhausted and the anion is transported in association with H ions causing an increase in surface water acidity. Clearly, the acidification effect of a given anion deposition flux at a catchment, and the

timing of that effect, is a function of the size of the soil base cation store and this is closely related to the weathering supply of base cations.

Evidence for the "mobile anion" theory is complicated by the chemical and biological utilisation of different ions within the ecosystem. N is tightly cycled within the terrestrial ecosystem and in most cases only a small degree of loss to streamwater is observed (Bormann et al., 1977). SO_4 is, however, only retained to a small degree and is usually in excess of the biological requirements of the terrestrial ecosystem (Turner et al., 1980). Soil retention of SO_4 is controlled by the presence of sesquioxides of iron (Fe) and aluminium (Al) which are not present in appreciable amounts in the thin weathering profiles of glaciated soils (Singh, 1984) such as those commonly found in the UK. Ion budget studies have been used to support the hypothesis that deposition of non-marine SO_4 has resulted in increased SO_4 concentrations in runoff water (Galloway et al., 1984).

It is also clear that acidic deposition alone does not control soil and surface acidification status. Areas worst affected by acidic deposition are located in regions dominated by base poor geology (Hendry et al., 1980). Soil development on such lithologies results in thin base poor soils with a small base cation pool and slow release of base cation weathering products from the bedrock. Base cation stores in such soils are rapidly depleted in response to incoming acidic deposition resulting in the acidification of soils and surface waters.

1.2 International agreements and the critical loads assessment

During the 1950s initiatives were taken to reduce ground level concentrations of air pollutants in Europe and North America, primarily in response to human health considerations but also in response to discolouration of building materials. The implementation of the "tall stacks" policy in the UK in 1952 meant that pollution, and in particular sulphur dioxide (SO_2), was transported further afield. Observations of acidified lakes and loss of fish stocks in Scandinavia raised the question of whether transboundary air pollution might be responsible. This led to the realisation that acidic deposition was a Europe-wide problem requiring international solutions and so to the establishment of an SO_4/SO_2 monitoring network (European Monitoring and Evaluation Programme, EMEP) to identify those areas worst affected. This would also provide the necessary information on which to develop control strategies.

In 1979, the United Nations Economic Commission for Europe (UN – ECE) established the convention on "Long Range Transboundary Air Pollution"

(LRTAP) to promote reduction in the emission of S and N across Europe. The first attempt at a European emission control policy was put in place in 1985 with the adoption by the convention of a 30% reduction in emission of SO_2 by 1993 based on a datum of 1980. The UK however failed to sign the protocol basing their decision mainly on the arbitrary nature of the chosen base line year of 1980 given that UK emissions in this year were well below those in 1979 (Murlis, 1995). Nevertheless, the UK accepted the importance of SO_2 reductions and began a programme of emission reductions at a few of the larger UK power stations including Drax B in Yorkshire (Battarbee, 1995). Subsequently, in 1986 the UK accepted an EC directive for large combustion plants (LCPD) which required a 60% reduction in S emissions by 2003 based on a datum of 1980. The implementation of international agreements in the late 1970s and early 1980s to curtail S emissions from non-marine sources has prompted the reversal of acidification at the more severely impacted sites (Wright & Hauhs, 1991).

It was generally recognised that this approach was not targeting emission reductions to areas where they were most needed. A more scientifically robust approach to emission reductions strategies was developed commonly referred to as the "critical loads" approach.

The critical loads approach was first embraced by Canada in the 1970s as a means of identifying areas affected by acid deposition. The concept of the critical loads approach is based on a "dose-response" relationship and has been widely applied to addressing pollution problems (Vollenwieder, 1968). A critical load for an ecosystem is defined as 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 & Grennfelt, 1988).

Critical loads can be estimated for different parts of an ecosystem and are based upon damage to, or loss of, a receptor. In the case of soils and freshwaters, for example, sensitive receptors have been defined as trees and brown trout, respectively. Chemical criteria for the soil and water can be defined as a level beyond which biological damage will occur, e.g. base cation : Al molar ratio of 1.0 in soil water and ANC – 0 are commonly used thresholds for soils and freshwaters, respectively. The critical load for the whole ecosystem then becomes the lowest critical load calculated for each component of that ecosystem, such that the most sensitive component organism is protected. In real terms, the definition can lead to problems since the true critical load is probably zero and so even the critical loads approach to emission reduction inevitably involves compromise on the degree of damage to be accepted.

The methods used to calculate critical loads vary depending on the chosen biological receptor (i.e. the organism suffering damage) and the availability of

data required for model application. Sverdrup et al. (1990) proposed a three tier system for critical load calculation depending on available data; Level 0 (empirical) including the Skokloster approach for soil critical loads (Nilsson & Grennfelt, 1988): Level 1 approach (equilibrium models), including the Steady State Water Chemistry model (SSWC, Henriksen, 1980) for surface waters and the Steady State Mass Balance method (SSMB, Nilsson & Grennfelt, 1988) and the PROFILE model (Sverdrup & Warfvinge 1988) for soils; Level 2 approach (dynamic models), including MAGIC (Cosby et al., 1985 a; b), SAFE (Sverdrup et al., 1995) and SMART (Posch et al., 1993).

In June 1994 the Oslo Protocol on Further Reductions of S Emissions (Second S Protocol) was signed by 28 EU countries. The agreed emissions reduction for the UK involves a 70% reduction by 2005 and 80% by 2010 (based on 1980 levels). This new protocol embraces the critical loads approach. The overall emission reduction represents a compromise based on promoting optimum compliance with calculated critical loads across all the member states with the intention of protecting 95% of the ecosystem within each designated mapping unit.

1.3 The role of dynamic models

For the UK, the negotiation of the Second S Protocol was underpinned by critical load calculations based on steady state models: the SSWC and the diatom model (Battarbee et al., 1993) for surface waters and the SSMB for soils. These methods, based upon the empirical link between present day soil and water chemistry and deposition flux, give no indication of the time over which chemical recovery will be achieved in response to reduced acidic oxide emissions. The models also neglect the time component of acidification namely SO$_4$ adsorption and short term soil buffering processes (Reuss & Johnson, 1985) that delay both the onset of acidification and its concomitant recovery under deposition reduction scenarios (Cosby et al., 1985 a,b; Cosby et al., 1986).

Dynamic models offer the only opportunity to determine the level of deposition reduction required to achieve a given water chemistry target (for example ANC = 0) within a given time scale.

Furthermore, equilibrium models only include land-use implicitly because land-use impact influences current water chemistry and this is used in the calculation of critical loads. The impact of future land-use changes on water chemistry, such as deforestation and re-planting, in combination with changes in acid deposition, can only be determined using dynamic modelling approaches.

Maps to illustrate the exceedance of critical loads under the new S protocol in 2010, assuming the agreed reductions are met (DOE, 1995) have been produced. However, in terms of ecosystem recovery, these are irrelevant as they simply identify those areas where atmospheric deposition is predicted to be below the calculated critical load at a given time. Clearly, surface water acidity may not decrease for many years following the decrease of deposition flux below the steady-state critical load. Dynamic models offer the only possibility for assessing both this time lag and the degree of impact in areas where the critical load continues to be exceeded.

2 The MAGIC model

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. The main thrust of hydrochemical modelling has focused on the development of physically based conceptual models to make quantitative predictions of the effects of acid deposition on soil and surface water quality. Such models, however, also 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 a regional basis with limited input data required to calibrate and drive the model.

In the 1980s Reuss (1980, 1983) proposed a simple mathematical model describing the equilibrium between dissolved and adsorbed ions in the soil – soil water system. This approach was later expanded by Reuss and Johnson (1985) to include the effects of carbonic acid (H_2CO_3) on a simple system involving calcium (Ca) and SO_4. MAGIC has its roots in the work of Reuss and Johnson and incorporates all major base cations in soils and surface waters and also complexation reactions involving Al and the role of SO_4 adsorption in soils (Cosby et al., 1986; Hornberger et al., 1986). The main ion fluxes related to tree growth, particularly in relation to plantation forestry, were incorporated into the model in 1990 (Cosby et al., 1990; Jenkins et al., 1990c) to provide a more complete understanding of the processes controlling surface water acidification and the complex relationships between changing acid deposition and land-use.

2.1 Model structure

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 which 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.
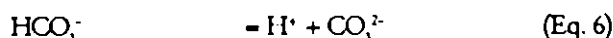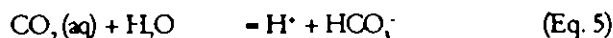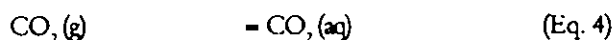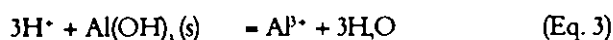
The soil-soil solution equilibria equations describe cation exchange using a Gaines-Thomas expression for monovalent (Eq. 1) and divalent cations (Eq. 2),

dissolution and precipitation of inorganic Al represented as an equilibrium with a solid phase of aluminium hydroxide (Eq. 3), and dissolution of carbon dioxide (CO_2) (Eq. 4) followed by dissociation to bicarbonate (HCO_3) (Eq. 5) and carbonate (CO_3) (Eq. 6):

$$S\,Al\,Ca \quad = \quad \frac{\{Ca^{2+}\}^3\ EAl^2}{\{Al^{3+}\}^2\ ECa^3} \qquad (Eq.\ 1)$$

$$S\,Al\,Na \quad = \quad \frac{\{Na^+\}^3\ EAl}{\{Al^{3+}\}\ ENa^3} \qquad (Eq.\ 2)$$

where the brackets represent ion activities in soil water, E signifies the fraction of the cation adsorbed on the soil (in relation to the Cation Exchange Capacity (CEC)) and S_{xy} is the calculated selectivity coefficient. These coefficients are not true thermodynamic equilibrium constants but vary from soil to soil and may vary over time for a single soil. They must also represent an average or lumped set of soil cation exchange reactions for the whole catchment.

$$3H^+ + Al(OH)_3\ (s) \quad = Al^{3+} + 3H_2O \qquad (Eq.\ 3)$$

$$CO_2\ (g) \quad = CO_2\ (aq) \qquad (Eq.\ 4)$$

$$CO_2\ (aq) + H_2O \quad = H^+ + HCO_3^- \qquad (Eq.\ 5)$$

$$HCO_3^- \quad = H^+ + CO_3^{2-} \qquad (Eq.\ 6)$$

For each of the base cations and strong acid anions in the model a dynamic mass balance equation (Eq. 7) can be written.

$$\frac{dXT}{dt} \quad = Fx + Wx - Q \cdot (X) \cdot n \qquad (Eq.\ 7)$$

Where, XT is the total amount of ion X in the soil (eq m^{-2}); Fx is the atmospheric flux of that ion into the watershed (eq m^{-2} $time^{-1}$); Wx is the net uptake-release flux of the ion (eq m^{-2} $time^{-1}$); (X) is the total molar concentration (free plus complexed) of the ion in streamwater; n is the charge of the ion; and Q is the volume flow of the stream. Streamwater concentrations are calculated from the model equations for any time in the model run based on the total amounts of each ion in the catchment at that time.

The mass balance equations are written for the base cations and strong acid anions because these ions have discrete and measurable sources in the catchment. 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 considered to be twenty times atmospheric in the soil compartment and twice atmospheric in the streamwater compartment, thereby generating HCO_3 alkalinity through de-gassing as soil water enters the streamwater.

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 referred to as 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 and pK values are set at pH 4.5 for monoprotic, 10.25 for diprotic and 20.5 for triprotic organic acids. This effectively produces a monoprotic acid as the dominant organic acid in both soil and streamwater for these systems in the pH range 4 to 7.

The additional equations needed to relate the variables in the mass-balance equations to the variables in the equilibrium equations are definitions of alkalinity, total ion amounts in the catchment, the lumped physical characteristics of the soil and the SO_4 adsorption process. The total amount of each base cation in the catchment is the product of the exchangeable fraction, the total CEC of the catchment soils (eq kg^{-1}), the bulk density of the soil per unit area (kg m^{-2}) plus the aqueous concentration and the pore water volume of the soil per unit area (m).

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 (Eq. 8).

Total adsorbed sulphate $= \dfrac{E_{max} \cdot 2 \cdot (SO_4^{2-})}{(C + 2 \cdot (SO_4^{2-}))}$ (Eq. 8)

where, E_{max} is the maximum soil adsorption capacity (meq kg^{-1}) and C is the half saturation constant (meq m^{-2}). A complete summary of model equations, parameters and inputs is given in Appendix 1.

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, $E_{max} = 0.01$ meq kg^{-1} and $C = 1000$ meq m^{-3}.

Most catchments have no internal source of S, although there is evidence from the Loch Dee Project (Giusti, 1992) that the Caledonian graywackes and slates that underlie the Dargall Lane (site 9) catchment contain a weathering source of S. This occurs primarily in the form of iron pyrites (FeS) which, upon surface oxidation, releases sulphuric acid (H_2SO_4) contributing to natural acidification and SO_4 concentrations in streamwater. No detailed geochemical evidence is available on a regional basis to make any site specific assumptions regarding S weathering and this source has been disregarded for the purposes of this, and all other applications of the MAGIC model.

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. Ammonium (NH_4) is not measured routinely at the AWMN but surface water concentrations are assumed to be low at all sites and so 100% uptake is assumed. The percentage NO_3 uptake in the soil compartment of the model required to balance observed NO_3 concentrations in the runoff water are given in Appendix 3.3.

Standard precipitation and throughfall gauges provide adequate estimates of integrated 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 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, soil and streamwater temperature and pCO_2. 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. For the

applications described in this report, the model is calibrated using average hydrological conditions i.e. mean annual precipitation and streamflow volume.

Implemented in its simplest form, the model is a two-compartment representation of a catchment (Figure 2.1). Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry. The chemistry model is essentially a discrete module however, and can be applied as often as necessary to describe a particular catchment — if a catchment has extensively developed A and B horizons in the soil (e.g. a podsol) and the soil processes are different in the two horizons, the model can be configured using three compartments and this is more applicable to consideration of soil acidification *per se*. For this study, a two compartment model is employed as surface water responses are the primary foci.

2.2 UK applications of MAGIC

The MAGIC model has previously been applied to several catchments in the UK. Initially, it was applied at Loch Dee in south west Scotland to determine its validity in areas receiving high sea-salt deposition (Cosby *et al.*, 1986). Application of the model to multiple catchments in Wales at Plynlimon (Whitehead *et al.*, 1988a) and Llyn Brianne (Whitehead *et al.*, 1988b) and in a regional, Monte Carlo based framework for 120 sites in Wales (Jenkins *et al.*, 1990b) has since established MAGIC as a powerful tool for assessing the consequences of changing acid deposition and land-use for soil and surface water acidification.

The model has been applied at a number of sites to assess its sensitivity. A single soil layer structure has been tested against a two soil layer structure for the same sites, Round Loch of Glenhead in south west Scotland and the Allt a' Mharcaidh in the Cairngorms, and the results indicate that both structures provide similar long term predictions of water chemistry (Jenkins & Cosby, 1989). The sensitivity of the model to soil physical and chemical fixed parameters (CEC, BD, depth) has been assessed at the Allt a' Mharcaidh and stresses the importance of an appropriate soil weighting procedure (Jenkins *et al.*, 1988). In addition, the cation exchange representations in MAGIC have been tested experimentally in the laboratory and found to be appropriate (Grieve, 1989). Validation against long-term diatom-based pH reconstructions have also proved successful and reinforce the confidence in future model predictions (Jenkins *et al.*, 1990a).

The model has been further enhanced to incorporate the main driving variables and fluxes associated with land-use change in catchments, particularly afforestation (Cosby *et al.*, 1990). The modified model has been tested through site applications in the Loch Ard forest, central Scotland, and scenario analysis indicates that forests grown in areas not receiving acidic deposition do not promote surface water acidification (Jenkins *et al.*, 1990c). This conclusion has been corroborated through a model application to a recently planted site at Llyn Brianne in mid-Wales where the predicted pH decline closely matches observed changes in annual pH over a period of eight years (Waters & Jenkins, 1991) and through a regional application to 40 lakes in south west Scotland (Wright *et al.*, 1994).

MAGIC is one of several dynamic models included in the UN - ECE Handbook on Mapping Critical Loads (Henriksen *et al.*, 1989) and has been used extensively within the UK Freshwaters Critical load programme (Jenkins and Shaw, 1993; DOE, 1994).
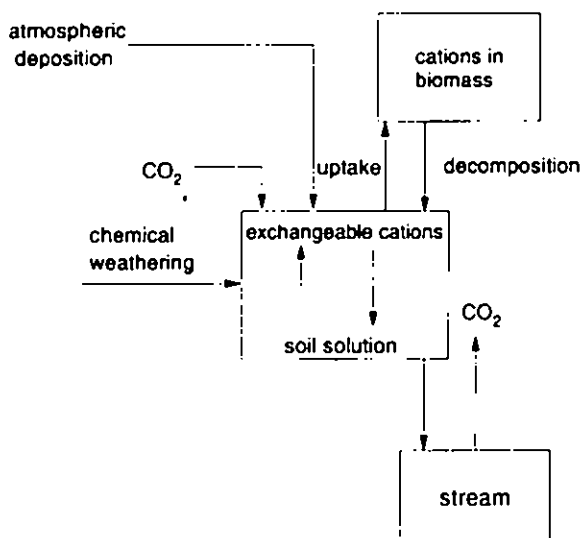

Figure 2.1 Schematic representation of the flows and stores in MAGIC

3 Calibration procedure

Calibration and application of MAGIC at the 21 AWMN sites represents the most rigorous and detailed site specific application of the model in the UK to date. The modelling exercise has three main objectives:

i) to calibrate and apply the model to forecasts of reduced acid deposition to assess whether, and to what degree, the sites recover under current international protocols for S emission reduction;

ii) to calculate critical loads (and exceedances) and compare these to current steady state (Level 1) approaches; and

iii) to assess the interaction between acid deposition and afforestation at currently afforested sites.

3.1 Data sources and model parameterisation

The application of MAGIC to the AWMN sites requires data describing surface water chemistry, rainfall chemistry and volume, soil physical and chemical characteristics and land-use history. Of the 22 sites in the network, 21 are used since adequate soils data are not available for the River Etherow in Yorkshire. AWMN catchments

have been monitored for streamwater chemistry since 1988. At the 11 lake sites, sediment cores have been collected for diatom based reconstructions of historical lake water pH. All sites have nearby deposition chemistry collectors that form the core of the UK Acid Deposition Monitoring Network (ADMN) and the five forested sites have documented land-use history relating to forest planting.

3.1.1 Stream water chemistry (AWMN)

The AWMN was set up in 1988 to monitor surface water acidity at a range of geologically sensitive upland areas of the UK (Figure 3.1). The network spans a gradient of acid deposition, geological sensitivity and land-use with control sites in remote areas of low acid deposition. Twenty sites were originally chosen for the network, with two further sites added in 1990 (Blue Lough and Coneyglen Burn). The AWMN represents the only regional network monitoring long term chemical and biological trends relating to acid deposition in the UK. Site selection within the AWMN was also aimed at assessing the impacts of afforestation in combination with acid sensitivity and acid deposition. Five of the

Site	Name	Grid ref.	Area (ha)	Forestry %
1	Loch Coire nan Arr	NG 808422	897	<1
2	Allt a' Mharcaidh	NH 881045	998	2
3	Allt na Coire nan Con	NM 793688	790	50
4	Lochnagar	NO 252859	92	0
5	Loch Chon	NN 421051	1470	51
6	Loch Tinker	NN 445068	112	0
7	Round Loch of Glenhead	NX 445068	95	0
8	Loch Grannoch	NX 542700	1287	70
9	Dargall Lane	NX 449786	210	0
10	Scoat Tarn	NY 159104'	95	0
11	Burnmoor Tarn	NY 184043	226	0
13	Old Lodge	TQ 456294	240	5
14	Narrator Brook	SX 581685	240	0
15	Llyn Llagi	SH 649483	157	0
16	Llyn Cwm Mynach	SH 678238	152	51
17	Afon Hafren	SN 844876	358	50
18	Afon Gwy	SN 824854	210	0
19	Beaghs Burn	D 173297	273	0
20	Bencrom River	J 304245	298	0
21	Blue Lough	J 327252	42	0

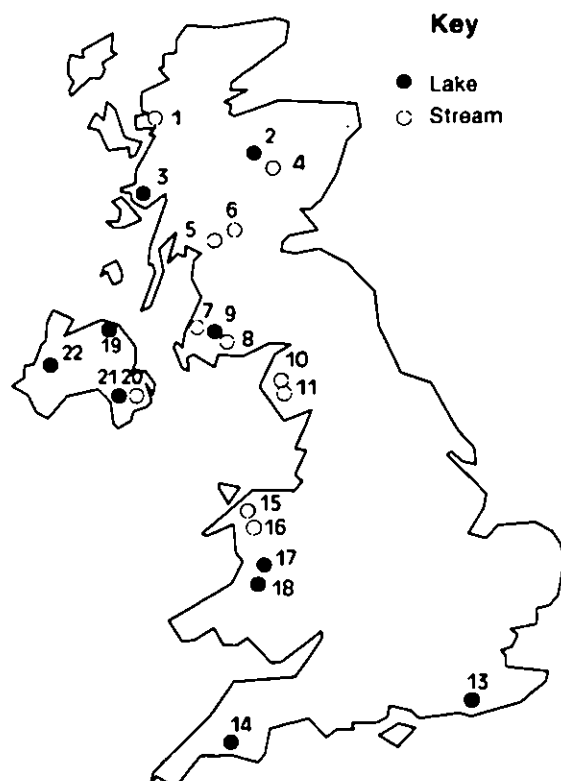
Key

● Lake
○ Stream

Figure 3.1 Location of the AWMN sites.

AWMN sites are forested and this represents the only anthropogenic impact, apart from acid deposition, within the catchments (Figure 3.1). Old Lodge (20% forested) and Narrator Brook (15% forested), are treated as moorland catchments for modelling work as the forest is deciduous and is not considered to have a significant effect on processes such as canopy scavenging. Moreover the forest is assumed to have always been present in the catchment and so annual uptake and decomposition fluxes are assumed to be in balance over long time periods.

Of the 22 sites, 11 streams are sampled monthly and 11 lakes sampled quarterly. Samples are analysed for a full suite of chemical determinands. pH is measured potentiometrically; Ca, Mg, Na, and K by inductively coupled plasma - optical emission spectrophotometry (ICP - OES); NO_3, Cl, and SO_4 by automated colorimetry or ion chromatography (Dionex) and TOC by total carbon analyser (Patrick *et al.*, 1991). Acid neutralising capacity (ANC) is calculated and defined as the sum of base cations (Ca, Mg, Na and K) minus the sum of strong acid anions (SO_4, Cl and NO_3).

Analysis of samples for chemically unstable determinands such as pH, alkalinity, N, phosphorous (P) and Al species is undertaken locally; other species are analysed at the Institute of Hydrology, Wallingford. The performance of each local laboratory is monitored by a programme of analytical quality control administered by WRc plc. The principal objective of the AWMN is to provide a quality chemical and biological database, which in conjunction with the existing ADMN (Figure 3.2) will enable the assessment of trends in surface water chemistry and its biological effects, particularly in relation to future decreased emissions of S and N oxides.

The chemistry of the AWMN (Table 3.1) reflects the combination of geological sensitivity, acid deposition and land-use across the country. Of the 22 sites, 11 have Ca concentrations $\leq$ 50 μeq l[-1] and 18 sites $\leq$ 100 μeq l[-1]. The most acidified sites in the network are situated in the Galloway region of south west Scotland and north and central Wales. Mean pH is < 5.5 at 11 sites and < 5.0 at 5 sites. Acidified sites also have high levels of soluble Al and many of the acidified sites have impoverished fish populations as a result. Although N is not considered in detail here, many sites currently exhibit NO_3 leakage in runoff (Table 3.1). NO_3 concentrations in runoff are > 10 μeq l[-1] at ten sites and NO_3 contributions to total non-marine acid anions is > 10% at 16 sites and > 20% at six sites (Jenkins *et al.*, 1996). Within each region the effects of afforestation are reflected in the more acidified nature of surface waters in the forested catchments relative to nearby moorland sites.

3.1.2 Rainfall runoff data

MAGIC is a flux based model and requires specification of the annual water budget at each site in terms of rainfall, runoff and evapotranspiration (ET). Estimates of rainfall were obtained from the Meteorological Office 20 km × 20 km mean rainfall dataset for the period 1989–92. This gridded dataset, based on approximately 4000 raingauges, provides the most detailed representation of rainfall patterns over the UK and is used by the UK Critical Loads programme (Battarbee *et al.*, 1995).

Site	Name	Grid ref.	AWMN sites
1	Straithvaich Dam	NH 347750	1
2	Allt a' Mharcaidh	NH 876052	2, 4
3	Polloch	NM 792689	3
4	Balquhidder	NN 521206	5, 6
5	Loch Dee	NX 468779	7, 8, 9
6	Bannisdale	NY 515043	10, 11
7	Beddgelert	SH 556518	15, 16
8	Pumlumon	SN 823854	17, 18
9	Barcombe Mills	TQ 437149	13
10	Yarner Wood	SX 786789	14
11	Lough Navar	H 065545	19, 20, 21, 22

Figure 3.2 Location of the Acid Deposition Monitoring Network (ADMN) sites.

Table 3.1 *A WMN mean surface water chemistry for 1988-1994. Units are* log_{10} μeq l^{-1} *for ANC, Ca, NO_3 and Al.*

Site	pH	ANC	Ca	NO₃	Al
1	6.4	40	43	3	2
2	6.4	57	42	1	4
3	5.8	29	58	4	7
4	5.3	2	29	14	4
5	5.5	·18	77	10	7
6	6.1	64	83	2	2
7	4.9	-10	34	5	11
8	4.6	-42	49	15	35
9	5.5	1	50	10	6
10	4.9	-15	33	20	14
11	6.5	59	92	5	1
13	4.6	-56	155	8	27
14	5.6	12	33	7	6
15	5.2	11	60	9	10
16	5.3	11	82	9	13
17	5.3	·1	46	20	19
18	5.4	11	42	9	12
19	5.7	111	105	3	6
20	5.2	7	53	25	22
21	4.7	·20	55	25	42
22	6.5	201	147	2	5

Catchment runoff estimates are not available for the majority of AWMN sites and so runoff is calculated from an estimate of ET and the gridded rainfall data. This study assumes that the ET of high rainfall areas ranges from 10% for a moorland catchment (Jenkins & 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 mature forestry cover (Figure 3.1). Old Lodge, in southern England, is the only lowland site in the AWMN and is situated in a low rainfall and higher temperature area than any of the other sites. A high ET (c. 50%) is required to explain the high concentrations of all ions in streamwater at this site.

3.1.3 Deposition chemistry

Wet deposition of all major ions is routinely measured at 32 sites across the country (Figure 3.2) as part of the secondary network, also known as the ADMN (Devenish, 1986). The network was set up in 1986 by the Department of the Environment (RGAR, 1987; 1990) and is now administered by AEA Technology's National Environmental Technology Centre (NETCEN). The primary network consists of five sites equipped with wet-only collectors, sampled daily. The secondary network consists of 32 sites equipped with bulk deposition collec-. tors sampled, weekly. Although only three sites are co-located with those of the AWMN, most sites are in close proximity (Figures 3.1 and 3.2). The most suitable deposition collector for each AWMN site was determined on the basis of proximity, altitude and sea-salt characteristics (Appendix 2.1).

Rainfall and ion concentrations in rainfall are known to be highly variable with altitude due to orographic enhancement mechanisms (Dore *et al.*, 1992; Fowler *et al.*, 1988). One such mechanism, seeder-feeder scavenging (Bader & Roach, 1977), involves the scavenging of cloud water (feeder cloud) of high ionic
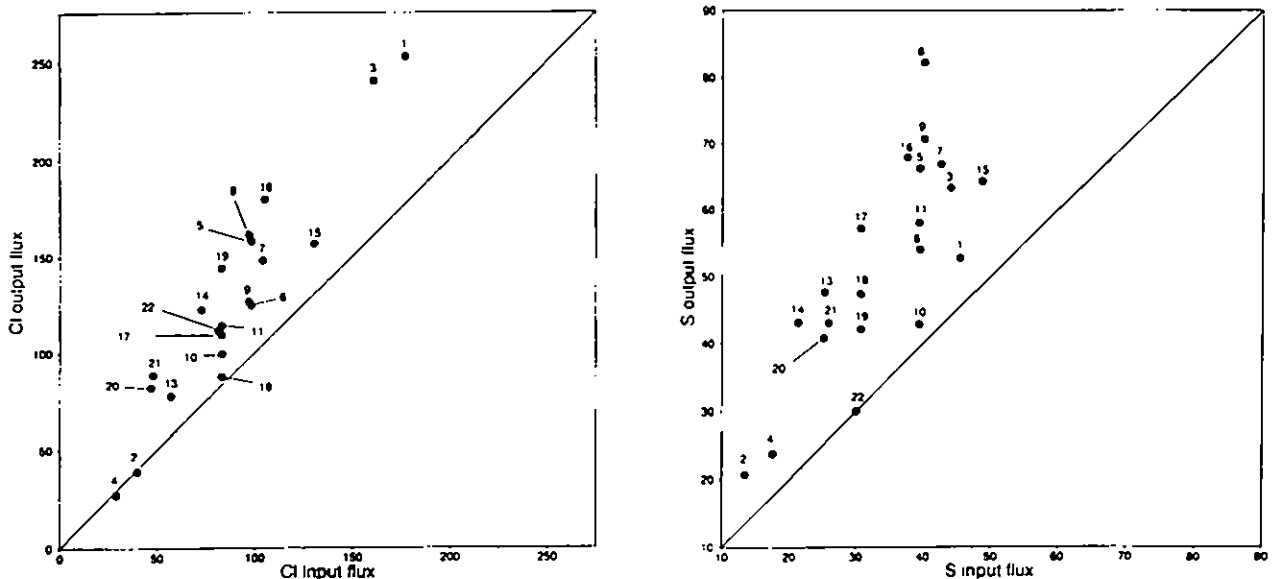

Figure 3.3 *Input - output budgets for a) Cl and b) SO_4 for ADWN wet deposition and A WMN output flux. Units in kg ha⁻¹ yr⁻¹*

concentration at low altitude by droplets of less polluted rain originating from higher elevation (seeder) cloud. The effect of this mechanism on rainfall composition in the UK has been investigated experimentally at Great Dunn Fell in northern England (Fowler et al., 1988). Rainfall volume varied by a factor of 2.0 between altitudes of 250 m and 847 m and wet deposition concentrations of major ions by a factor of 2.2 to 3.1. Wet deposition fluxes at the summit were found to be five times that at 250 m. These results have been repeated elsewhere in northern England and sites in Scotland and form the basis of a model of the seeder-feeder mechanism (Dore et al., 1992). These enhancements of wet deposition are, however, not used in this application of MAGIC since these estimates do not exactly match the observed output fluxes for conservative (Cl) and pseudo-conservative (SO_4) ions. Since MAGIC is based on principals of ion balance, correct simulation of conservative ions is important to the accuracy of model predictions of the non-conservative ions. Instead, 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. At all but two sites some enhancement of inputs is necessary to balance output flux (Figure 3.3).

Cl is not thought to be retained on the exchange complex to any great degree in UK soils and is, therefore, treated as conservative. That is, MAGIC assumes that Cl is in steady state with respect to input-output flux at each time step. This is probably a valid assumption given that none of the AWMN sites has a catchment source of Cl. Using the rainfall and runoff and the Cl concentration in the streamwater, therefore, the required enhancement of Cl input in rainfall, X_{dep}, can be calculated such that;

$$X_{dep} \cdot RF = X_{ur} \cdot RO$$

Where X_{dep} is the total (wet + dry + occult) deposition concentration of Cl (meq m^{-1}), RF is the annual rainfall in m, X_{ur} is the measured Cl concentration in streamwater (meq m^{-3}), and RO is the annual runoff yield in m. Calculated total inputs for Cl match closely the calculated deposition fluxes estimated at 20 × 20 km scale (Figure 3.4). Discrepancies between these estimates are not surprising, however, given that for the UK data, enhancements of deposition are made at 400 km² scale and utilise the mean altitude of the grid square together with the mean forest cover to estimate forest filter deposition (see later) whilst the AWMN catchments range in scale from < 1 to 14 km². The mean characteristics of the 20 × 20 km grid square in which each site is located may poorly reflect the altitude and forest cover of the catchment and so lead to over or underestimation of total 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 (0.86 for Na, 0.019 for K, 0.21 for Mg, 0.04 for Ca and 0.104 for SO_4) such that;

$$BC_{dep} = BC_{wet} + f_{BC} \cdot (X_{dep} - X_{wet})$$

Where BC_{dep} is the total (wet + dry + occult) deposition of base cations, BC_{wet} is the observed wet deposition concentration, f_{BC} is the sea salt fraction, X_{dep} is the total deposition concentration of Cl inferred from the Cl mass balance, and X_{wet} is the observed wet deposition concentration of Cl. This sea salt input is assumed to be constant throughout the hindcast and forecast simulations unless land-use change has occurred (see later).

Since most UK soils are relatively young they have little capacity to adsorb SO_4 and although SO_4 adsorption is included in the model structure, the value of E_{max} is assumed to be low. This effectively causes SO_4 to be in steady state with respect to the balance between input and output at present day since E_{max} has been reached. This pseudo-conservative behaviour enables deposition enhancement for non-marine SO_4 (anthropogenic SO_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 (Appendix 3.2). Again, these additional inputs are reasonably well matched with the national 20 × 20 km enhanced deposition flux data and the output flux from the AWMN (Figure 3.4).

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. Total N deposition is thought to greatly exceed the wet component, particularly for NH_x species (RGAR, 1990) because the biota are actively mining N from the atmosphere. As for SO_4, enhanced wet and dry deposition for NO_x and NH_x is available on a 20 km × 20 km gridded basis for the UK for 1989-92 and this is used directly as a model input. These data are enhanced for the seeder-feeder process but not land-use type and are therefore only appropriate for moorland catchments. Dry and occult deposition of N species are also greatly enhanced by the presence of forestry and have been investigated by Fowler et al., 1989 at Eskdalemuir in Scotland. They found that total N deposition for a fully forested catchment was 2.1 times that of a nearby moorland catchment. For the five forested sites in the AWMN the extra dry and occult deposition of N species has been estimated based on the percentage forest cover within each catchment and using linear interpolation based on the range of values reported by Fowler et al., 1989. The Observed NO_3 concentrations in streamwater are matched by applying a linear uptake function in the soil and water compartments of the model (Section 2.3).
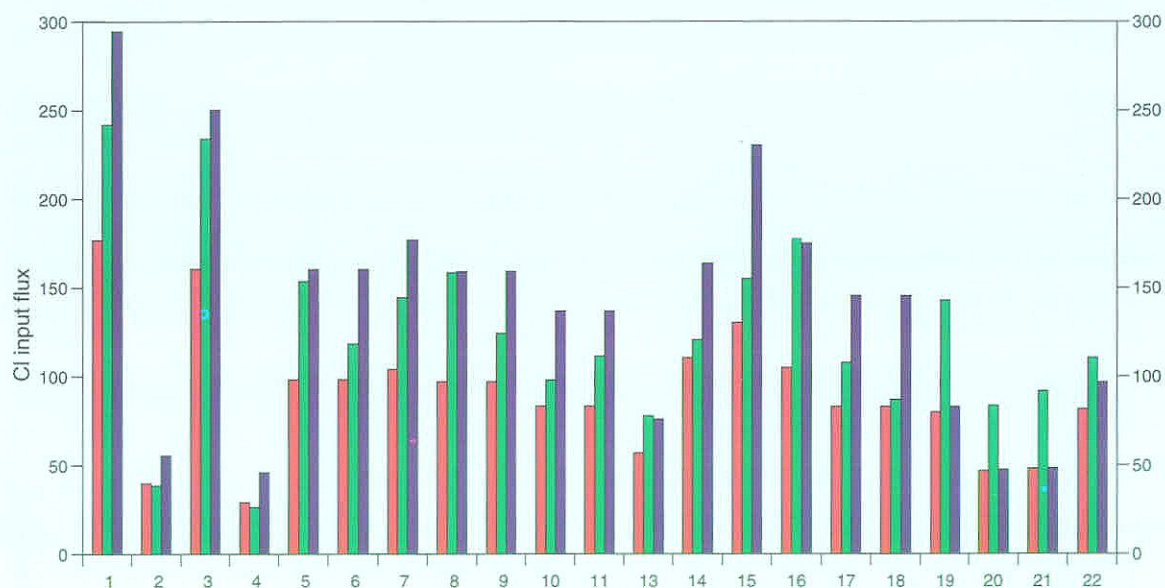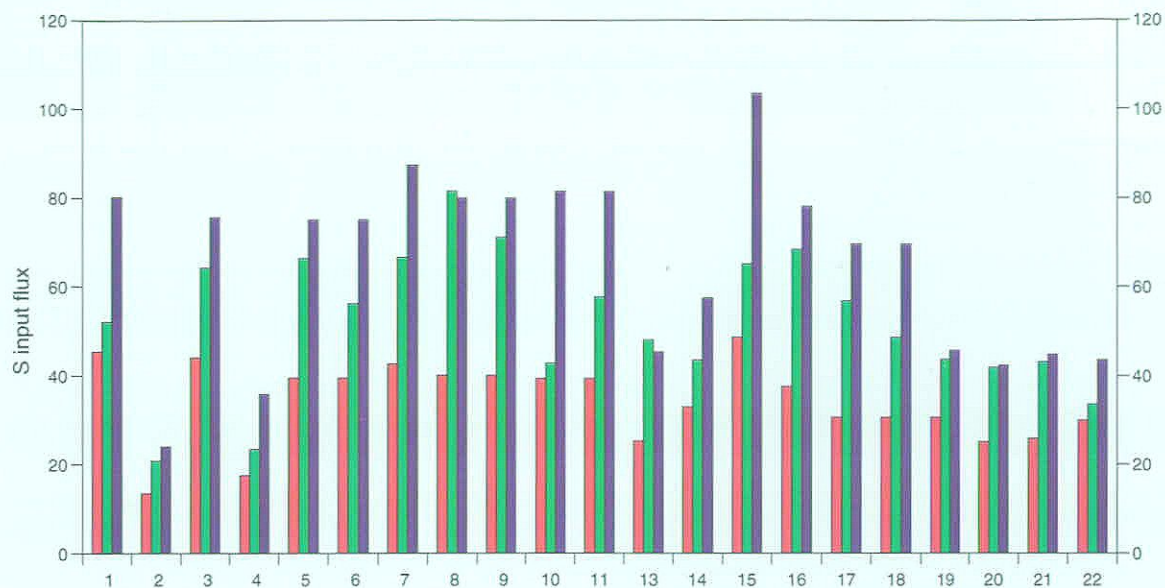
Figure 3.4. *Estimated present day deposition fluxes for a) Cl, and b) SO₄, for ADMN wet deposition (red), MAGIC deposition (green) and seeder-feeder enhanced wet and dry deposition (purple) for the AWMN sites. Units kg ha⁻¹ yr⁻¹.*

The historical trend in wet deposited non-marine SO_4 is assumed to follow the sequence described by the Warren Spring Laboratory (1983, 1987 unpublished data). The early part of the sequence (Figure 3.5) reflects the pattern of increased industrial growth from the onset of industrialisation in the mid to late nineteenth century. Increases in GDP and *per capita* energy consumption accelerated through the 1950s and this is correlated with increased emissions of acidic oxides. Following the Clean Air Acts of 1954 and 1962, the implementation of the "tall stacks" policy combined with increasing industrial activity, emissions increased and hence the deposition of S and N to all areas of the UK and Europe also increased.

The peak in emissions in the late 1970s was followed by international agreements to curtail the emission of non-marine SO_4 in the early 1980s. This is followed by relatively constant deposition from 1984 through to present day. NO_3 and NH_4 deposition are assumed to have increased since industrialisation in accordance with the estimated NO_x emissions in the UK (DOE, 1983, DOE, 1990). Both NO_3 and NH_4 are assumed to follow the same historical sequence (Figure 3.5). Other ions in deposition are assumed to remain constant throughout the historical reconstruction unless the catchment has undergone a land-use change (see Section 3.1.5).
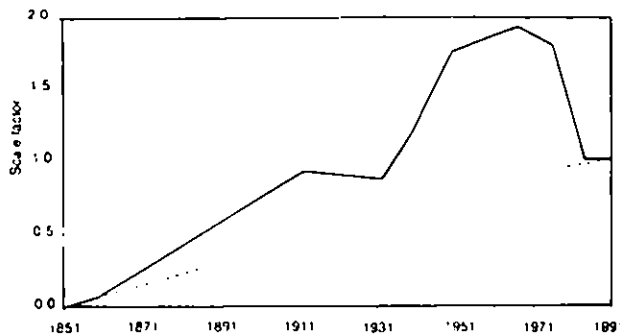
Figure 3.5 *Estimated historical trends in S and N deposition relative to present day deposition flux (i.e. present day deposition flux has a scale factor of 1.0)*

3.1.4 Soils data

Spatial variation in soil properties across a catchment is the direct result of factors relating to changes in altitude, geomorphology, land-use and vegetation type, underlying geology and the presence and spatial distribution of glacial deposits. This spatial variation is particularly important in upland catchments, which often exhibit complex geomorphology and impart a large degree of spatial heterogeneity in soil characteristics. Varying hydrological characteristics of upland soils are mainly governed by relief and give rise to characteristic spatial patterns of soils within the catchment. For example the Allt a' Mharciadh in north east Scotland exhibits spatial soil heterogeneity that is characteristic of the AWMN catchments. At the high altitude rim of the catchment alpine podsols dominate. These grade into podsols and peaty podsols in the middle to lower reaches of the catchment and give way to peats and peaty gleys in the lowest portion of the catchment close to the stream.

MAGIC is not a spatially distributed model and so this variability must be aggregated into one profile that represents both spatial and vertical heterogeneity within the catchment. This process of aggregation, or weighting, was performed sequentially. Firstly the catchment boundary from a 1:50 000 Ordnance Survey map was transfered onto a soils map (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 Macaulay Land Use Research Institute (MLURI) contains soil profile descriptions surveyed at 5 km² scale and soil chemical analyses at 10 km². Soil data for the English and Welsh sites were derived from previous research on the AWMN sites, reports and soil memoirs for specific sites (Lee, 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. This procedure was followed for CEC, BD and exchangeable base cation fractions (EX_a).

For BD the weighting procedure is given as:

$$BD_{profile} = \sum_{i=1,n} BD_i \cdot \frac{d_i}{\sum\limits_{i=1,n} d_i}$$

Where $BD_{profile}$ is the lumped profile bulk density, BD_i is the bulk density in horizon i, d_i is the depth of horizon i and n is the number of soil horizons in the profile. Where no data exist for the BD of each profile, estimates were based on the organic component of the soil. For L, H, and O horizons where loss on ignition (LOI) is between 70 and 100%, BD was assumed to be 300 kg m⁻³; A horizons with LOI between 60 and 69% BD was assumed to be 1000 kg m⁻³; B horizons with LOI between 30 and 59% BD was assumed to be 1200 kg m⁻³; and for C horizons with LOI < 29% BD was assumed to be 1500 kg m⁻³. CEC is weighted by depth and BD for each soil profile, such that:

$$CEC_{profile} = \frac{\sum\limits_{i=1,n} CEC_i \cdot BD_i \cdot d_i}{\sum\limits_{i=1,n} (BD_i \cdot d_i)}$$

and EX_a are weighted by depth, BD and CEC, such that:

$$EX_{profile} = \frac{\sum\limits_{i=1,n} EX_i \cdot BS_i \cdot CEC_i \cdot d_i}{\sum\limits_{i=1,n} (CEC_i \cdot BD_i \cdot d_i)}$$

For catchments with more than one soil type, the profiles were weighted according to the spatial coverage of each soil type in the catchment, such that:

$$V_{catch} = \sum_{i=1,n} V_{profile} \cdot f_i$$

Where V_{catch} is the aggregated soil characteristic for the catchment, $V_{profile}$ is the profile lumped parameter, f is the proportion of catchment dominated by soil type i and n is the number of soil types present. This process then generates one value for each parameter which is both depth and spatially weighted across the catchment for a one layer MAGIC application. Soil base saturation (BS) is calculated as the weighted sum of the individual base exchange fractions.

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3.1.5 Forest growth sequences

The impact of afforestation on acidification of soil and water in geologically sensitive areas has formed the basis of the development of a process-based approach to simulating forest growth within acidification models (Neal et al., 1986; Whitehead et al., 1988a; Cosby et al., 1990). In the UK a determined land management strategy of conifer afforestation implemented in the 1940s has contributed to surface water acidification. Many studies have reported that conifer afforestation enhances the acidity of drainage waters compared with moorland sites (Harriman & Morrison, 1982; Nilsson et al., 1982; Stoner & Gee, 1985). Three processes have been incorporated into MAGIC to simulate the impact of afforestation on acidification of soils and surface water: (i) mineral uptake by growing forests (Miller, 1981); (ii) enhanced dry and occult deposition (Mayer & Ulrich, 1977); (iii) decreased water yield concentrating pollutants in surface waters (Neal et al., 1986; Whitehead et al., 1988a).

Uptake and enhanced deposition are included as extra fluxes that are specified at each time step linked to forest age and percent mature forest cover while discharge is treated as a variable input also 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 driving the processes involved, allows construction of historical sequences and future forecasts of the key driving variables at each site. Two future forestry scenarios are utilised in this study; (i) each stand is assumed to be felled at 50 years age at which time ET, uptake and deposition enhancement are assumed to revert to moorland levels, and; (ii) each stand is felled at 50 years age and immediately re-planted such that the same forest growth assumptions are repeated. Under scenario (i), all catchments revert to moorland after 50 years since this is the maximum age for any forest stand and under scenario (ii) the area and age of forest is identical to present day after 50 years. Scenarios (i) and (ii), therefore, represent best and worst cases, respectively (Figure 3.6d). It is unlikely that the forest will be left to grow beyond maturity given that the forests are classified as commercial crops and for this reason a scenario of "no change" has not been considered.

Catchment runoff yield

Catchment runoff yield is known to be affected by the micro-climate of a forest as a result of the effects of interception loss and increased ET (Kirby et al., 1991). A regional study by Maitland et al. (1990) showed that these losses were consistently higher under conifer plantations relative to deciduous woodland, particularly as annual precipitation declines. At forested sites, runoff yield is assumed to decrease in response to increased ET

from a pre-planting level of 10% (moorland catchments) to 20% at canopy closure. Canopy closure is assumed to be at 20 years age for all stands. At each site, this general pattern is modified with respect to the amount of mature canopy cover in the catchment at each time step (Figure 3.6c).

Plant uptake

The estimation of net nutrient uptake by vegetation is problematic given the difficulties of assessing processes such as crown leaching and below-ground turnover (Miller, 1984). For "even-aged" forests, the greatest demand for soil nutrients occurs early in the life of the crop during crown development (Miller, 1981) and the rapid build-up of foliar biomass (Gimona, 1992). As the forest ages, the rate of accumulation of nutrients on the forest floor and the rate of nutrient uptake becomes broadly similar. Thus the maximum uptake from soils is reached well before the time of maximum stem growth. As the forest matures, nutrients progressively accumulate on the forest floor as organic litter, at a rate broadly proportional to the growth rate of the tree (Miller & Miller, 1976). The nutritional requirement of older trees may be greater than that of younger trees but a larger component is met through recycling of nutrients in litter (Miller, 1981). Older trees recycle a greater proportion of their annual uptake through litter and there is an increasing dependence upon nutrient cycling within the organic horizons. The resultant decrease in soil uptake rate is combined with efficient capture of atmospheric nutrients as the forest matures. This relative pattern of net nutrient demand (uptake flux) from the soil is assumed in the MAGIC simulation of forest growth (Figure 3.6a). Given this general pattern, the uptake fluxes are then modified to account for the age and percent forest cover at each site.

Forest filter deposition

The increased deposition flux attributable to the ability of the tree canopy to filter pollutants from the atmosphere promotes higher output fluxes of the conservative ions. At forested sites, therefore, extra deposition (filter deposition) is required to balance the higher output fluxes of Cl and SO_4 (Appendices 3.1 and 3.2). Since all of the forested sites in the AWMN have a moorland site in close proximity, it is assumed that the present day deposition enhancement (dry + occult deposition) at the moorland site would be the same for the forested site prior to forest growth. The canopy filtering effect promotes deposition in excess of that received at the moorland site. The extra Cl and SO_4 required to balance the observed output flux is added as neutral sea-salt (Section 3.1.3). The time-sequence of increased deposition (Figure 3.4b) is represented as a simple ramp from moorland (zero canopy filtering) to forest at canopy closure (maximum canopy filtering). Again, this general pattern is modified at each site as a function of percent mature forest cover at each time step (Figure 3.6d).
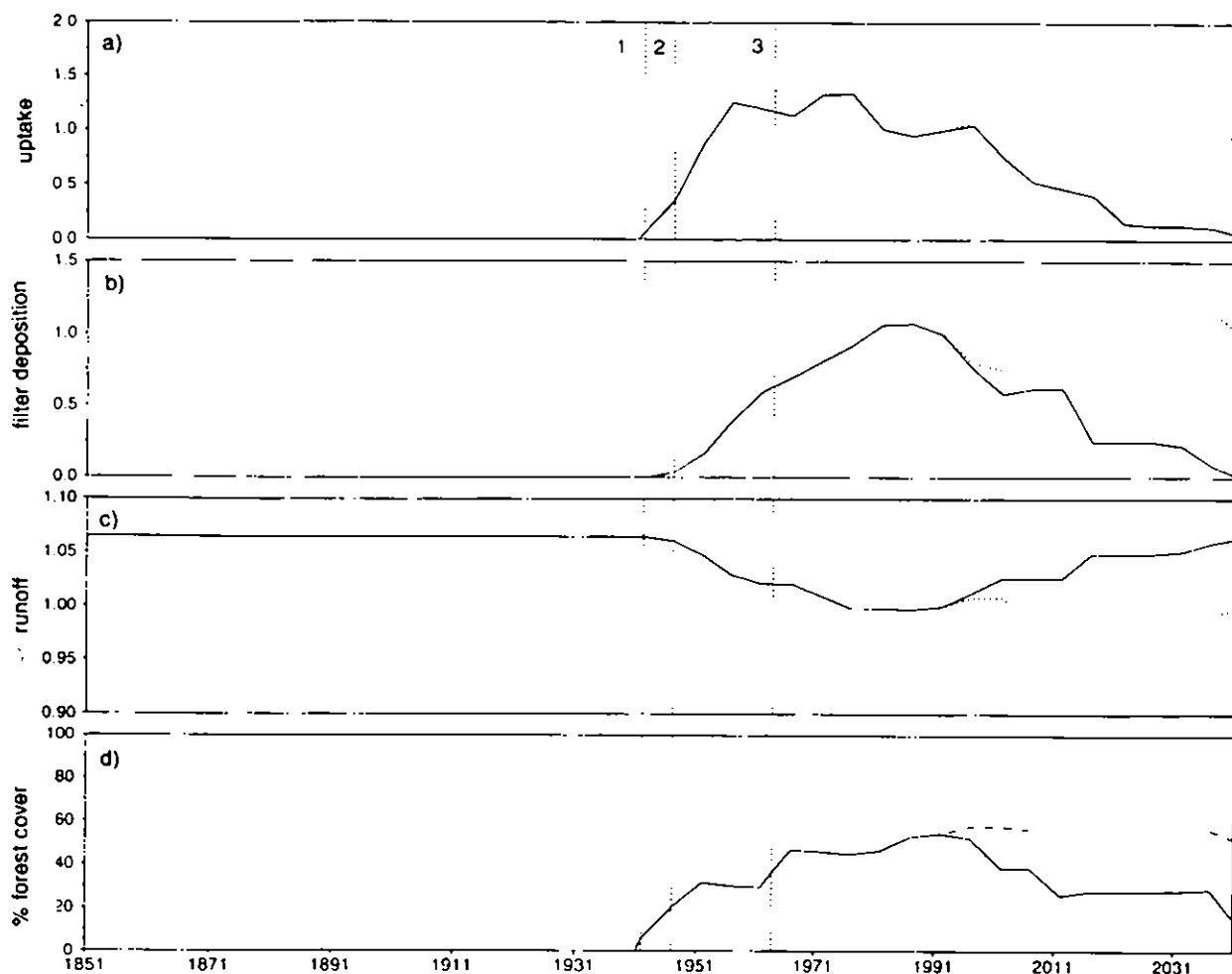
Figure 3.6. *Calculated sequences of a) net forest uptake for Ca, Mg, Na, K, and SO₄ b) forest canopy filter deposition for Ca, Mg, Na, K, NH₄, NO₃, SO₄ and Cl c) catchment discharge and d) change in percentage mature forest cover, for the Afon Hafren. Scale factor equals 1.0 for present day flux. The three planting phases are indicated as 1, 2 and 3. The solid line represents scenario (i) and the dotted line scenario (ii).*

Case study of the Afon Hafren

Forestry Commission stock maps of the Afon Hafren catchment show the first stand was planted in 1942 covering 6.6% of the total catchment area. Subsequently, a further 16% was planted in 1947, a further 12% in 1964 and the final 3% in 1994 (Figure 3.6a). This three stage planting history has a complex and additive effect on the ET, enhanced deposition and ion uptake (Figure 3.6c). Time sequences like this are derived for each site based on the relevant Forestry Commission data.

3.2 Model calibration

The calibration for each site is carried out sequentially. First, the concentrations of the stream Cl and SO₄ are calibrated by adjusting occult and dry deposition of sea salts and gaseous/particulate S

compounds under the assumption that these ions are in approximate steady-state with respect to atmospheric inputs. Next, the NO₃ and NH₄ 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 based on the Rosenbrock (1960) algorithm.

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 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 (Tables 4.1 and 4.2).

The calibrations are performed on simulations run from 1851 to 1991. The historical deposition sequence over the period is estimated by scaling currently observed deposition to a reconstruction of S emissions of the UK (Warren Spring Laboratory 1983, 1987; Figure 3.5). After each historical simulation, the model variables in 1991 are compared to the observed data in 1991, 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.

As a result of uncertainty in the measurement of the fixed parameters in the field, the lumping procedures employed for catchment soils and analytical errors in the target variables, a "fuzzy" optimisation procedure is implemented for the calibration. The procedure consists of multiple calibrations of each model structure using perturbations of the values of the fixed parameters and estimated uncertainties in the target variables.

The size of the perturbations of the fixed parameters is based on known measurement errors of spatial variability of the parameters (Appendix 4.1). The uncertainty in the target variables are estimated as the measurement errors of the variables (5 μeq l^{-1} or 10% for concentrations of surface water base cation concentrations and 0.5 or 10% for soil BS which ever value is the greatest of the two conditions).

Each of the multiple calibrations begins with three initial conditions; (i) a random selection of perturbed values of the fixed parameters; (ii) a random selection of the starting values of the adjustable parameters; and (iii) specification of uncertainty in the target variables. The adjustable parameters are then optimised using the Rosenbrock algorithm to achieve a minimum error fit to the target variables. The optimisation algorithm is stopped and the calibration considered complete when the simulated values of all target variables are within pre-specified uncertainty limits for the observations. This procedure is undertaken a minimum of ten times at each site.

Using the fuzzy optimisation based on multiple calibrations, uncertainty bands for the model simulations can be presented as minimum and maximum values for output variables in any year, derived from the group of successful calibrations. These uncertainty bands encompass the range of variable values simulated, given the specified uncertainty in the fixed parameter values and the measured target variables. Simulation results are plotted as maximum and minimum values through time and the "true" model calibration lies between these lines.

4 Model validation

4.1 Model calibration results

The model was successfully calibrated to all 21 sites - simulated chemistry of soil and surface water is in good agreement with observed concentrations for all ions (Figure 4.1).

The historical simulation of soil and water chemistry is driven by sequences defined for acid deposition and forest growth. The predicted acidification of soil and surface water is indicated by comparing simulated background chemistry with simulated present day chemistry (Figure 4.2). For surface water pH it appears that sites that are currently most acidified have changed most from background with the exception of Old Lodge (site 13), which has the lowest simulated background pH (Figure 4.2a). Those sites that have a simulated background pH
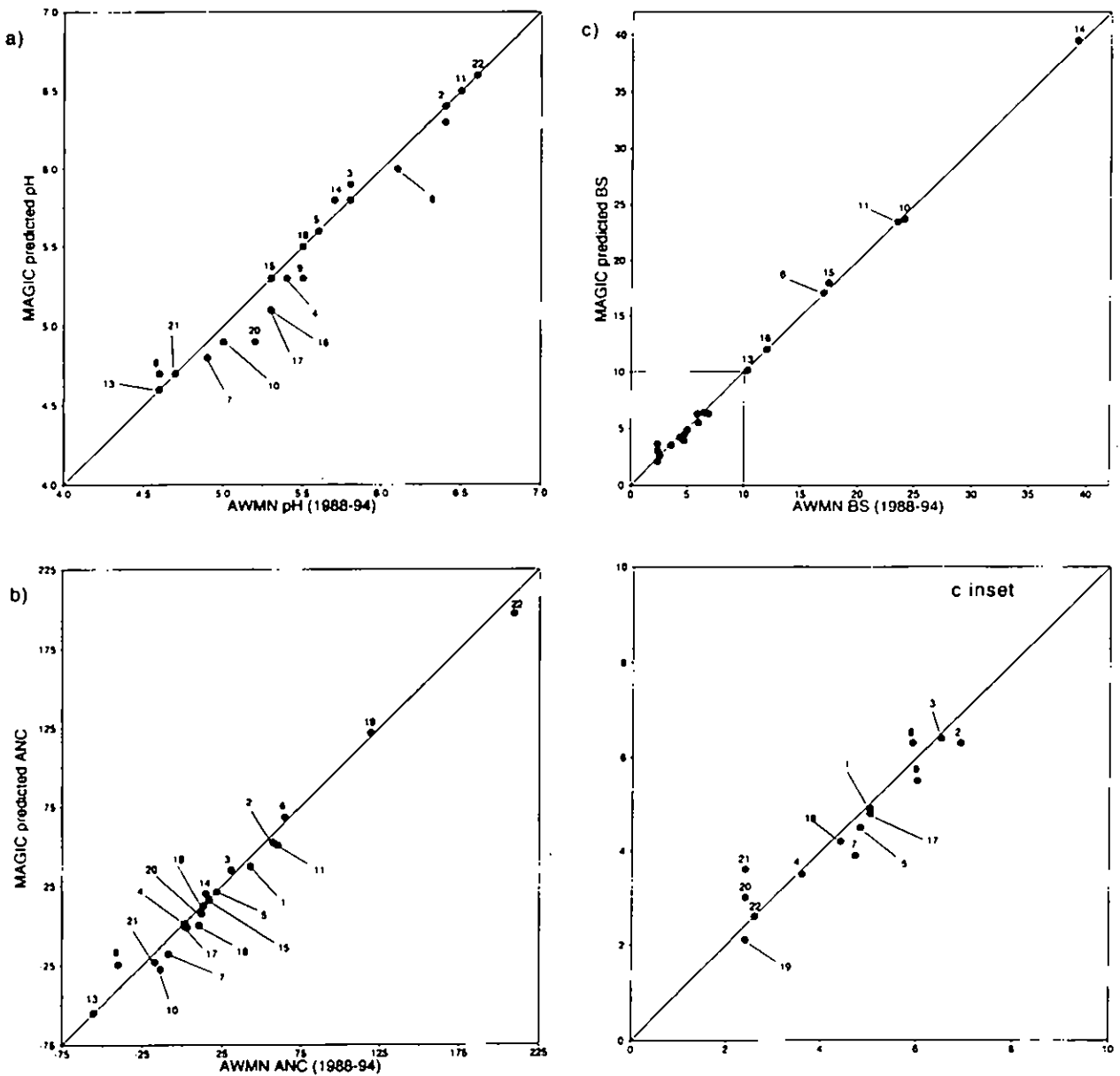
Figure 4.1 Comparison of the MAGIC simulated present day and AWMN (1988 - 94 mean) chemistry for a) surface water pH b) surface water ANC and c) soil BS. Units in log_{10} for pH, $\mu eq\ l^{-1}$ for ANC and % of CEC for soil BS.
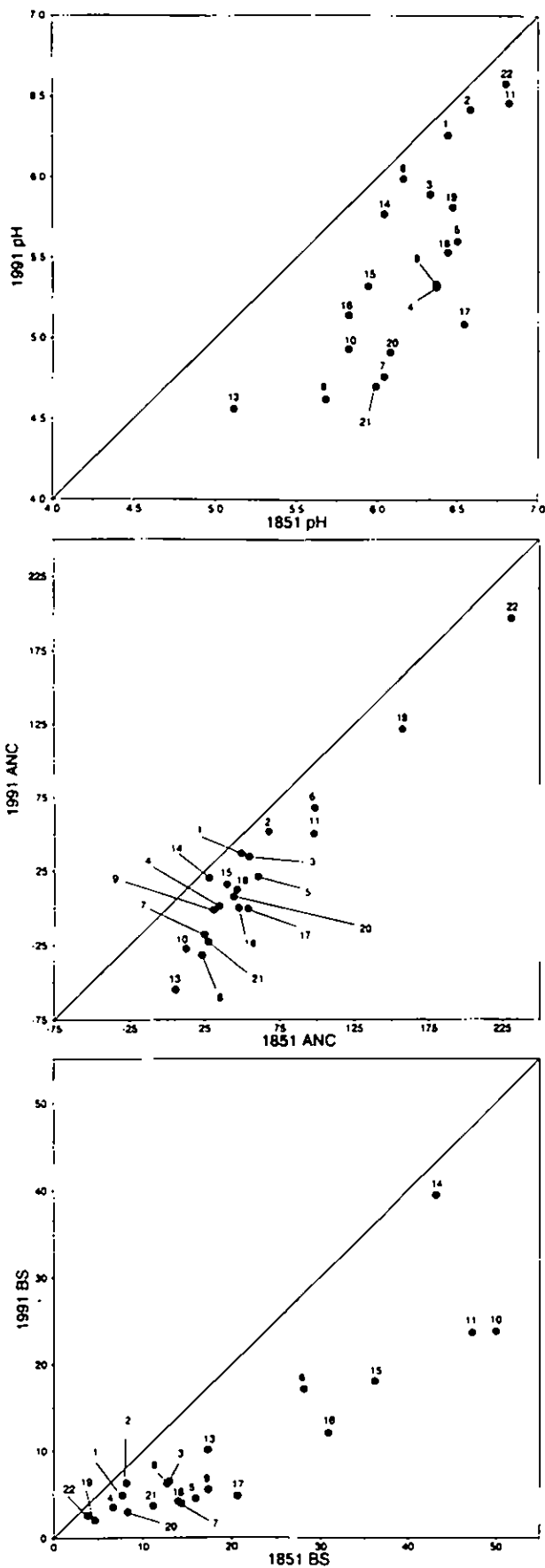
1991 pH

1851 pH

1991 ANC

1851 ANC

1991 BS

1851 BS

> 6.5 are not predicted to have acidified to any great extent up to present day. Currently acidified sites such as Blue Lough (site 21), Round Loch of Glenhead (site 7) and Scoat Tarn (site 10) are predicted to have acidified from a background pH of 6.0 - 6.2 down to 4.7 - 4.9. The two most acidified sites in the AWMN, Old Lodge (site 13) and Loch Grannoch (site 8), both with pH 4.6, are predicted to have acidified the most. Note that the H ion concentration associated with pH is a log scale.

The response of forested sites is complicated by land-use change during this period and this contributes to the scatter in this relationship. ANC decrease from background to present day is also generally larger at the most acidic sites although the two well-buffered sites in Northern Ireland, Beaghs Burn (site 19), and Coneyglen Burn (site 22) show considerable ANC reduction (Figure 4.2b). This pattern reflects the base status of the catchment soils and the total S deposition and N leaching over the historical simulation period. This is well demonstrated by the extremely low simulated background and present day BS at these two base poor sites (Figure 4.2c). In general, those sites with the highest observed soil BS are predicted to have lost the most BS with the exception of Narrator Brook (site 14).

Figure 4.2 Comparison to MAGIC simulated background (1851) and MAGIC simulated present day (1988 - 94 mean) chemistry for a) surface water pH b) surface water ANC and c) soil BS. Units in $\log_{10}$ for pH, $\mu eq l^{-1}$ for ANC and % of CEC for soil BS.

Table 4.1 MAGIC present day (1991) optimised soil base cation selectivity coefficients. Units in $\log_{10}$

Site	Ca	Mg	Na	K
1	5.5	5.2	2.6	-1.6
2	5.5	4.8	1.7	-2.5
3	3.9	4.5	1.5	-3.7
4	3.0	4.2	1.7	-3.6
5	4.2	4.5	1.9	-3.8
6	4.9	6.1	1.9	-4.4
7	2.3	2.5	1.0	-3.8
8	1.1	2.4	-0.6	-4.6
9	2.4	2.7	0.4	-3.7
10	-1.5	-0.1	-1.1	-5.5
11	5.2	5.0	1.6	-3.0
13	1.4	3.0	-0.6	-3.8
14	0.6	2.1	-1.4	-5.8
15	1.6	2.1	-1.0	-4.4
16	2.6	2.8	-0.7	-4.6
17	2.2	5.4	0.4	-4.2
18	2.5	5.1	0.3	-3.2
19	8.8	8.5	4.4	-0.5
20	4.0	4.6	1.1	-3.2
21	2.4	3.6	0.8	-4.2
22	11.6	10.8	4.9	0.6

Optimised parameters for base cation weathering and Ca, Mg, Na, and K soil selectivity coefficients are consistent across all sites (Table 4.1 and 4.2). Higher values of base cation selectivity coefficients reflect soils with higher base status and result in greater ion exchange since the process is concentration dependent. There is a good agreement between those sites that have higher base status, those that are predicted to have historically lost base status and those that are predicted to have the highest base cation selectivity coefficients.

Table 4.2 MAGIC present day (1991) optimised soil base cation weathering rates. Units in $\mu eq\ m^{-2}\ yr^{-1}$.

Site	Ca	Mg	Na	K	Total
1	72	10	22	0	104
2	22	0	32	0	54
3	80	1	12	0	93
4	1	4	17	0	22
5	101	4	4	0	109
6	148	48	16	1	213
7	33	1	0	0	34
8	18	0	1	1	20
9	37	1	2	0	40
10	0	2	2	0	4
11	108	25	14	1	148
13	3	0	1	0	4
14	7	0	7	3	17
15	59	0	1	0	60
16	39	0	32	0	71
17	7	39	23	0	69
18	20	29	5	0	54
19	106	51	18	0	175
20	14	0	24	0	38
21	12	1	4	0	17
22	149	116	25	2	292

Analysis of the simulated time-series of pH from background condition to present day shows that the sharpest decline is predicted to have occurred in the period c.1940 to c.1970 (Figure 4.3). This coincides with the period of highest atmospheric emissions (Figure 3.5). In general, the uncertainty limits on simulated pH increase as pH declines towards present day. This results from the uncertainty limits placed on the rainfall-runoff parameter during calibration which causes larger variation in SO_4 concentrations under higher S input. The uncertainty limits closely match observed variation in pH at most sites (Figure 4.3).

4.2 Comparison with diatom reconstructions

There is a strong body of evidence through palaeoecological studies linking the effects of acidic deposition to biological impoverishment of freshwaters (Battarbee et al., 1988; Battarbee & Charles, 1994). The records of diatom floras taken from lake sediment cores provide a record of the timing, rate and magnitude of biological and chemical change that has occurred at sensitive sites throughout Europe and North America. The technique linking biological and chemical change was first developed by Nygaard (1956) and provides the only long term record of lake acidification since the advent of industrialisation in the mid-nineteenth century (Davis et al., 1983). Trends in diatom flora have been strongly correlated with increases in acid deposition, although the role of catchment land-use, primarily plantation forestry in sensitive areas, may also be partly responsible for more recent acidification (Flower et al., 1987).

Sediment cores have been taken from the 11 AWMN lake sites and analysed using standard methods (Battarbee, 1986). Quantitative reconstruction of lake pH is a two stage process i) modern diatom assemblages are modelled against present day lake water chemistry using a modern training dataset; and ii) the historical pH is reconstructed by calibration of the model against diatom assemblages observed in the cores. Diatom-inferred pH (DI-pH) for each core was calculated using a weighted-averaging transfer function based on the Surface Water Acidification Programme (SWAP) modern diatom chemistry dataset (Birks et al., 1990). The dataset contains 167 soft-water lakes representing a variety of biogeochemical conditions in the UK and Scandinavia. The amount of biological change is calculated using detrended canonical correspondence analysis (DCCA) (ter Braak & Prentice, 1988) and the sample dates are calculated using ^{210}Pb dating methods. The SWAP data set suggests that the route mean square error (RMSE) of prediction of DI-pH is approximately 0.32 pH units and reflects all sites in the dataset. This is used as the RMSE for the DI-pH reconstructions at all AWMN sites.

Comparisons of the DI-pH and observed mean pH for the year prior to coring are within one standard error (0.32 pH units) at all sites except Loch Coire nan Arr (site 1), Loch Tinker (site 6) and Lochnagar (site 4) (Figure 4.4a). Of the sites that are greater than one standard error from the observed pH, DI-pH of between 0.4 and 0.6 pH units (Juggins et al., 1996). The first two of these sites are amongst the highest pH sites in the AWMN and indicate a potential problem of bias towards lower pH sites (< 6.0) in the SWAP training set. The diatom flora at Lochnagar (site 4) contains a number of circumneutral species for which the pH tolerance is also less well known and may reflect bias in the SWAP training set (Juggins et al.,1996).
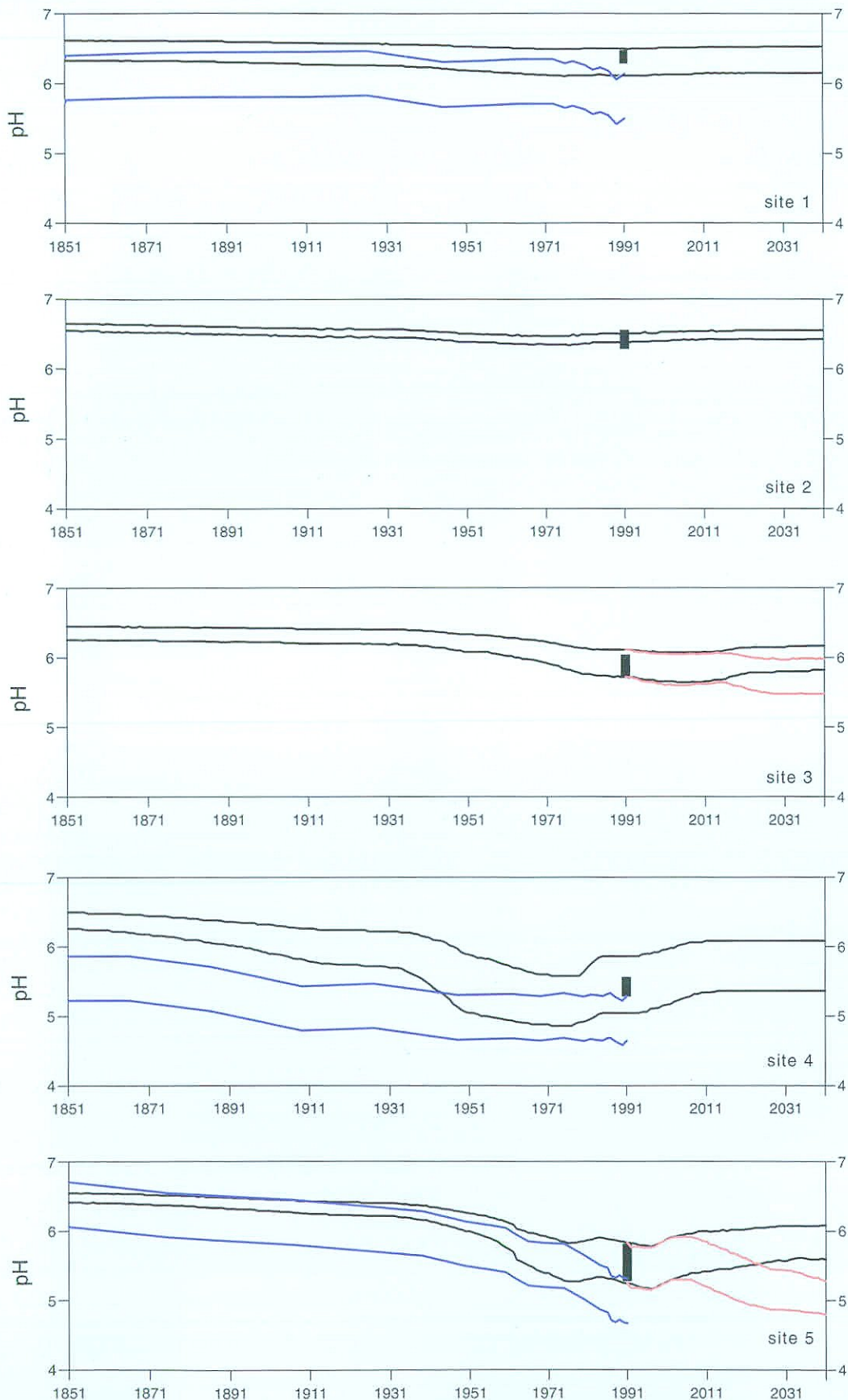
Figure 4.3 *MAGIC simulated minimum and maximum surface water pH from 1851 – 1991 (black lines) compared with diatom inferred lake water pH, ± 1 standard error of the mean (blue lines). Forecast predictions under the Second S Protocol (black line, forested sites = Scenario 1; red line, forested sites = Scenario 2). Solid black bar represents minimum and maximum mean annual pH for the period 1988 – 94. Units in log_{10}.*
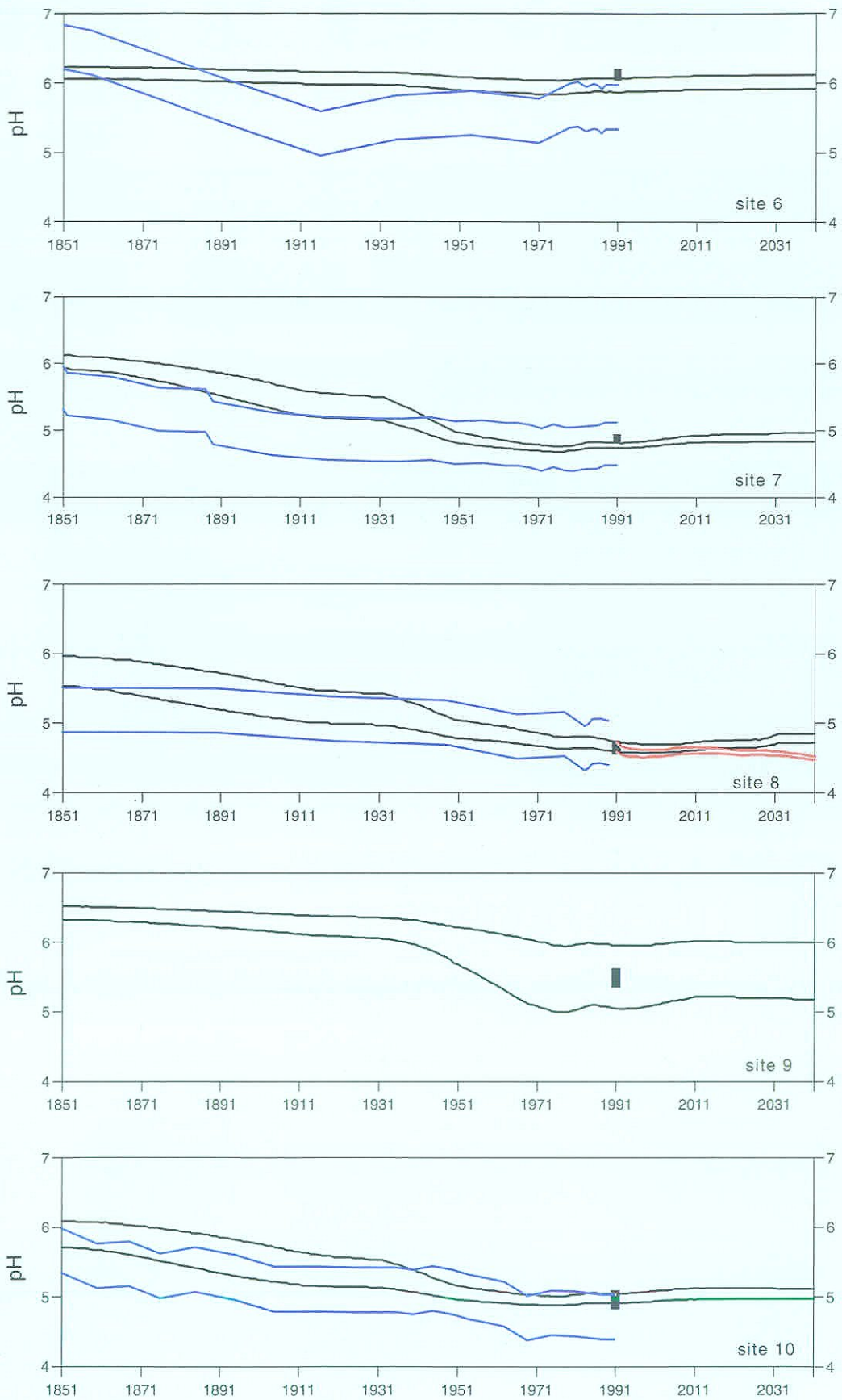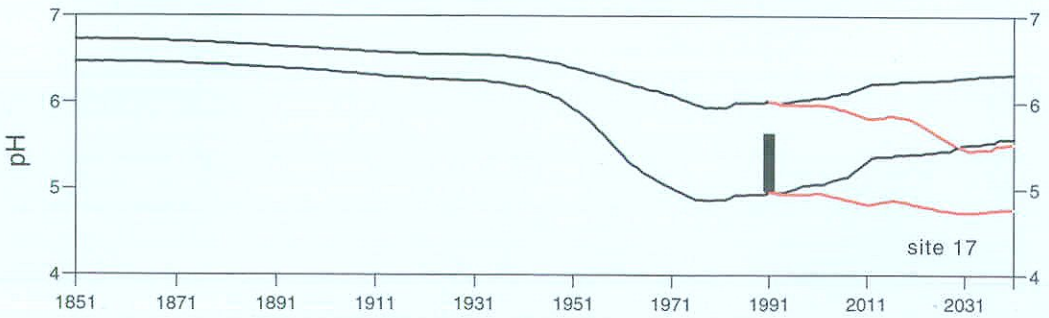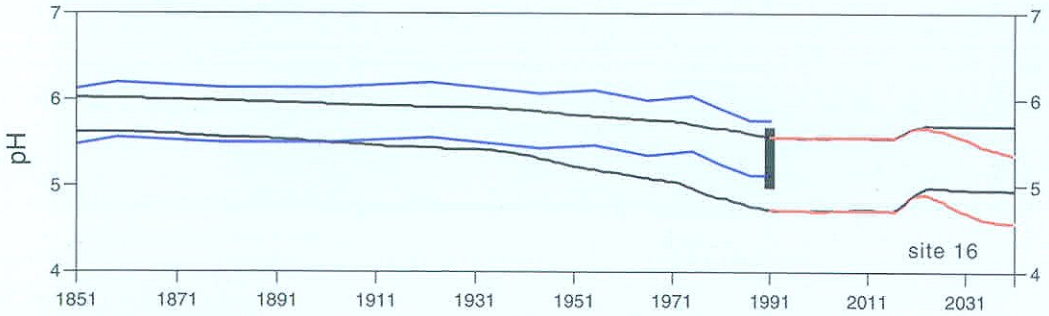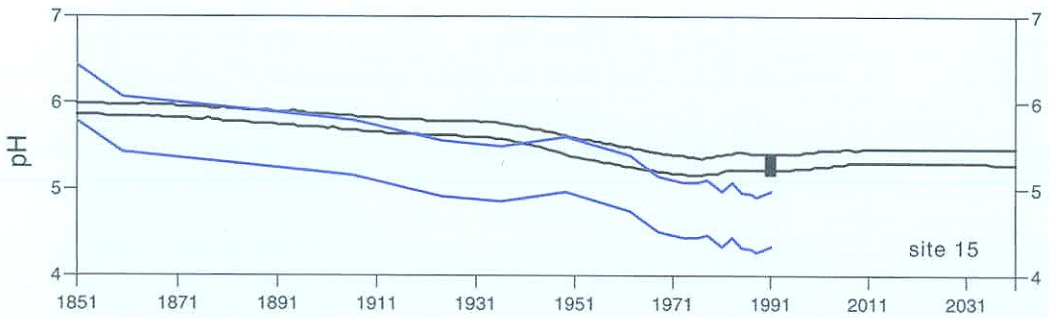
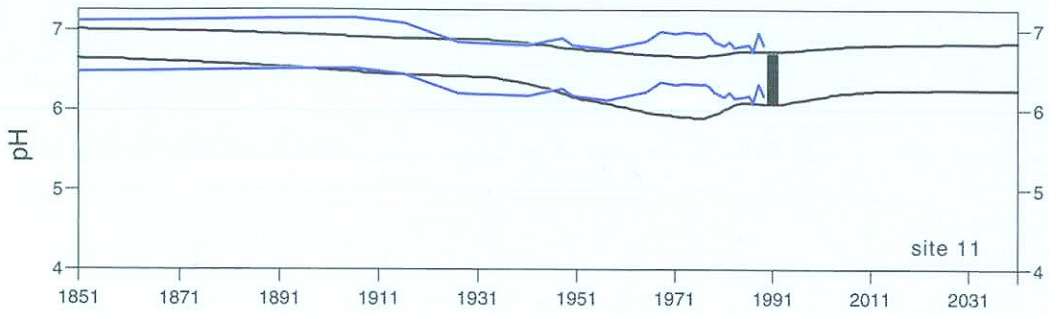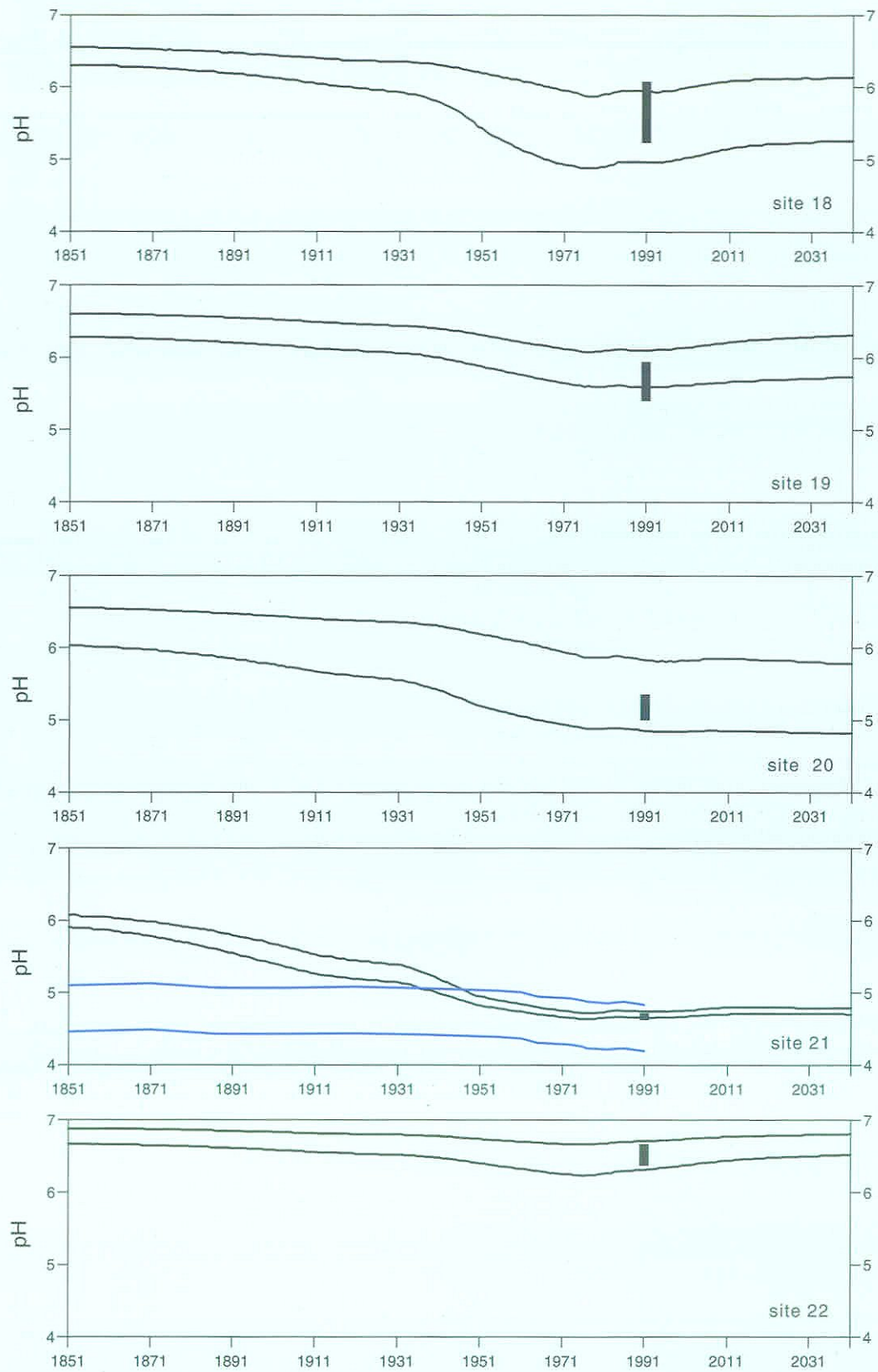**Figure 4.3** *continued*

site 11

site 13

site 14

site 15

site 16

site 17

24
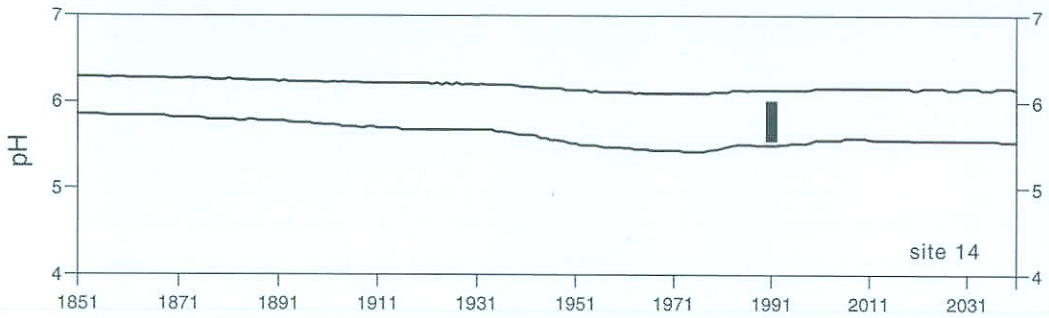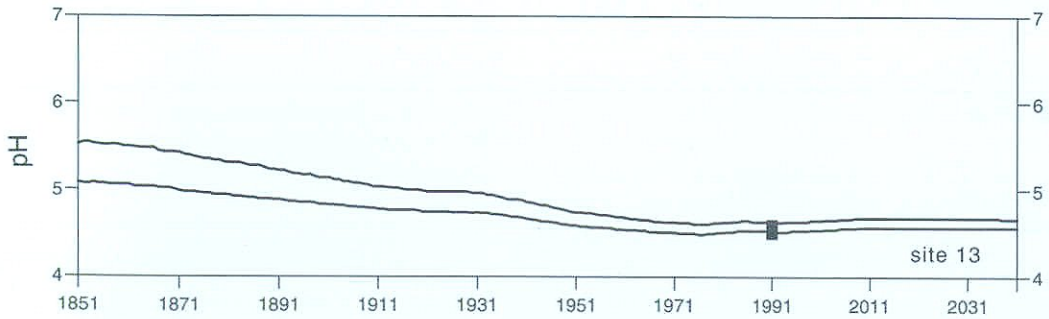
Comparison of DI-pH for 1850 and simulated MAGIC 1850 pH demonstrates a poor match (Figure 4.4b). The DI-pH for 1850 at Blue Lough (site 21) is clearly too low and sites 4 and 6 show a poor match between observed and DI-pH 1990. A generally consistent relationship exists between the rest of the sites. With respect to the timing of the change, the two methods also generally agree that an accelerated decrease in water pH occurred in the period 1940 – 70 (Figure 4.3).
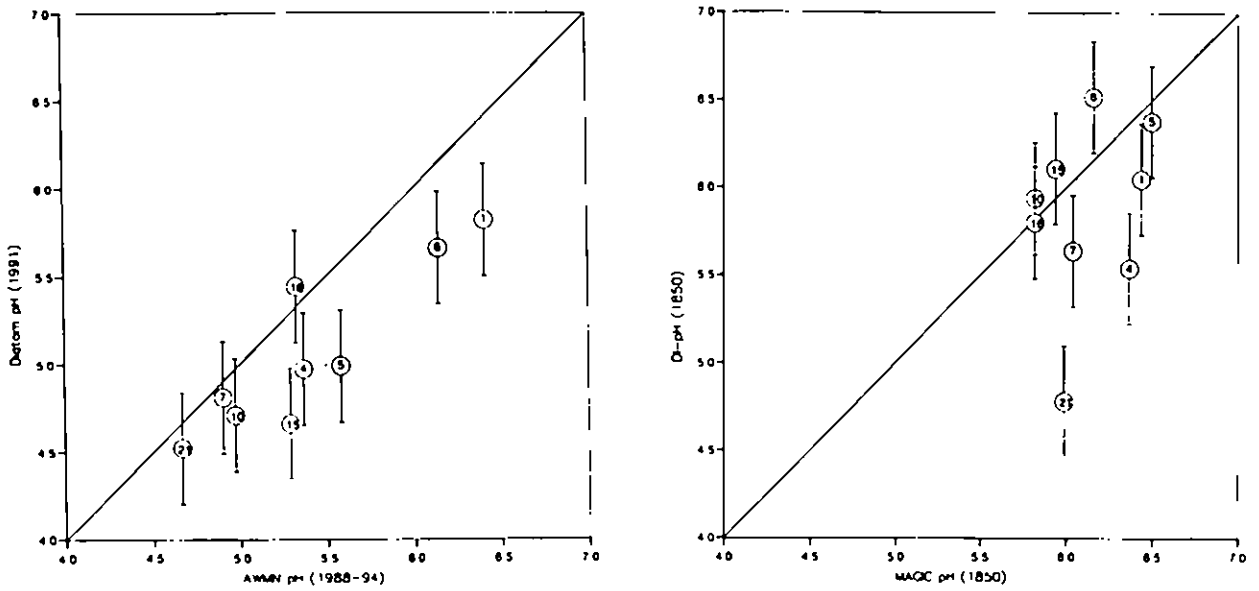
Figure 4.4 *Comparisons of diatom modelled pH reconstructions for a) observed A WMN mean surface water pH (1988 - 94) versus diatom reconstructed pH (1991) b) DI-pH versus MAGIC background reconstructed pH (1851). Error bars represent the RMSE of 0.32 pH units for all sites.*

The comparison of MAGIC reconstructed pH from background or pre-acidification conditions with independent diatom evidence represents the only means of validation of both techniques since no time series of water chemistry exist for such a long period. The uncertainties in both approaches are large and the inconsistency between DI-pH 1991 and observed mean pH decreases confidence in the DI-pH reconstruction. Nevertheless, the two methods produce close matches at several sites thereby increasing the confidence in the predictive capability of the MAGIC model.

5 Predicted response to the 'Second S Protocol'

The ratification of the Second S Protocol in June 1994 has committed the UK to reducing national S emissions by 70% by the year 2005 and 80% by the year 2010. These reductions in non-marine S deposition are unlikely to translate to equivalent reductions in deposition at the AWMN catchments which are mostly situated in the high altitude, western side of the UK and many are situated some distance upwind of major point source emissions. The crucial questions in terms of recovery of the most acidified sites are "where?" and "by how much?" will these reductions take place to meet the agreed targets.

The development of atmospheric transport and deposition models has enabled high emission sources to be targeted and allows an informed decision as to which sources have the greatest impact in areas sensitive to acidification. One such model is the Hull Acid Rain Model (HARM).

5.1 The Hull Acid Rain Model (HARM)

The HARM model (Metcalfe et al., 1989; Metcalfe & Whyatt, 1995) is a source-receptor deposition model developed from the Harwell Trajectory Model (HTM, Derwent et al., 1988). The model is a receptor-oriented lagrangian model that incorporates the chemistry of major ions contributing to acid deposition, namely SO_2, NO_x, NH_x and HCl. The model is driven by a simple representation of meteorology and operates at a spatial resolution of 20 km × 20 km. The model shows a reasonable agreement between modelled present day deposition and measured S deposition (Figure 5.1). Present day estimates are based on measured wet deposition from the ADMN and modelled seeder-feeder wet, dry and occult deposition (Fowler et al., 1988; 1995).
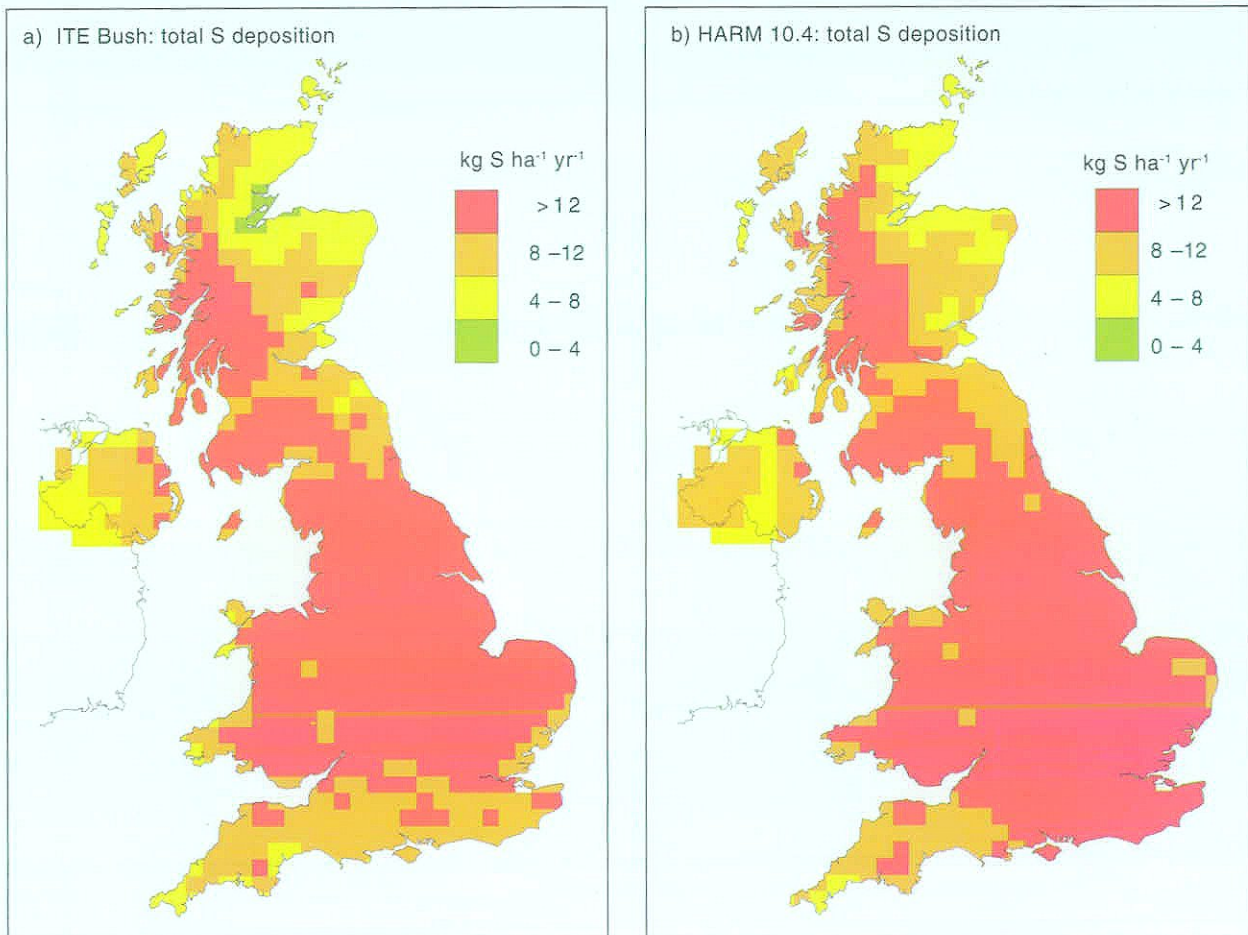

Figure 5.1 (a and b) *S deposition for a) observed present day (1989 – 92) b) HARM predicted present day.*
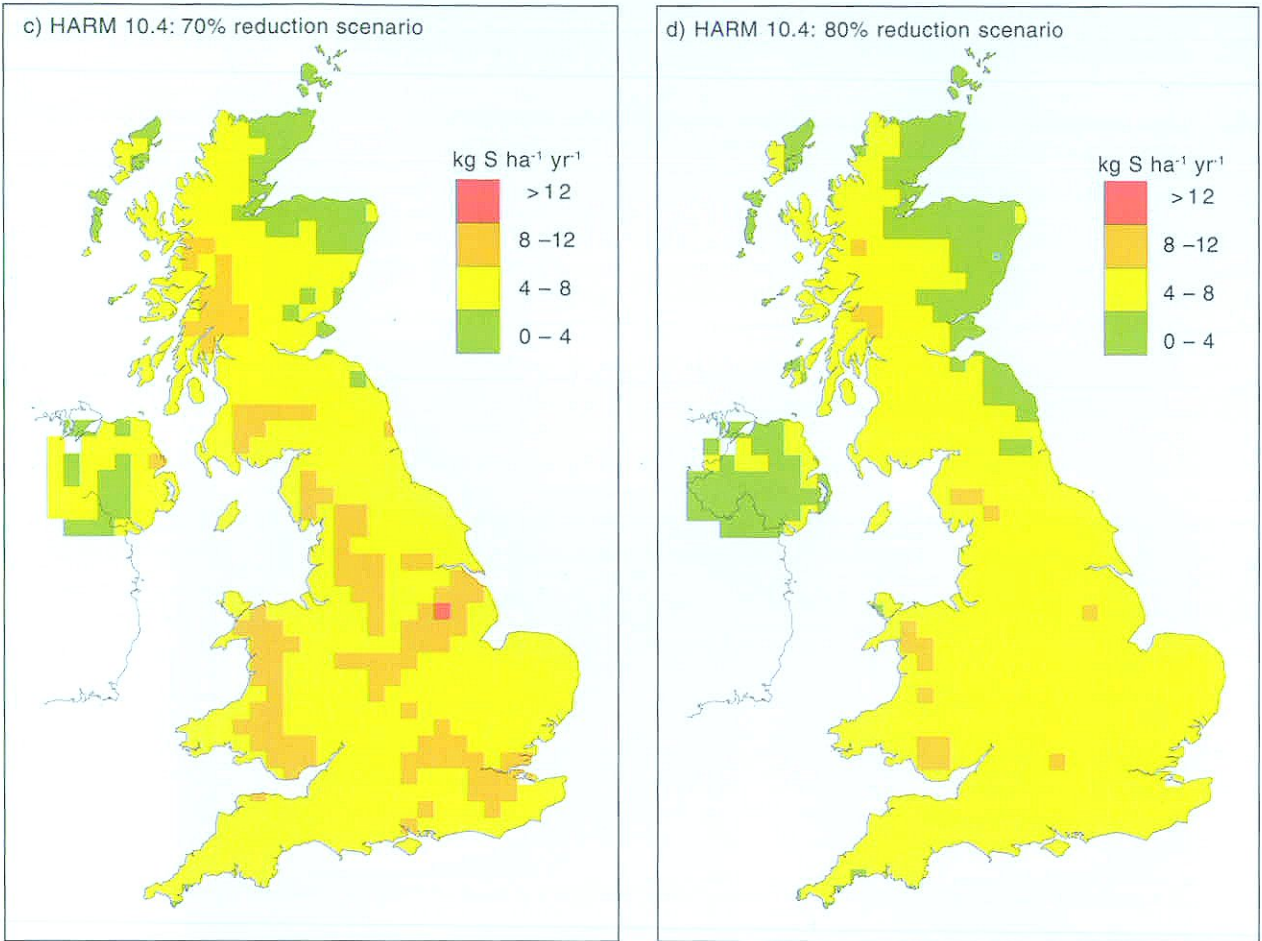
27

Figure 5.1 (c and d) *c) HARM predicted 2005 and d) HARM predicted 2010. Units in kg ha⁻¹ yr⁻¹.*
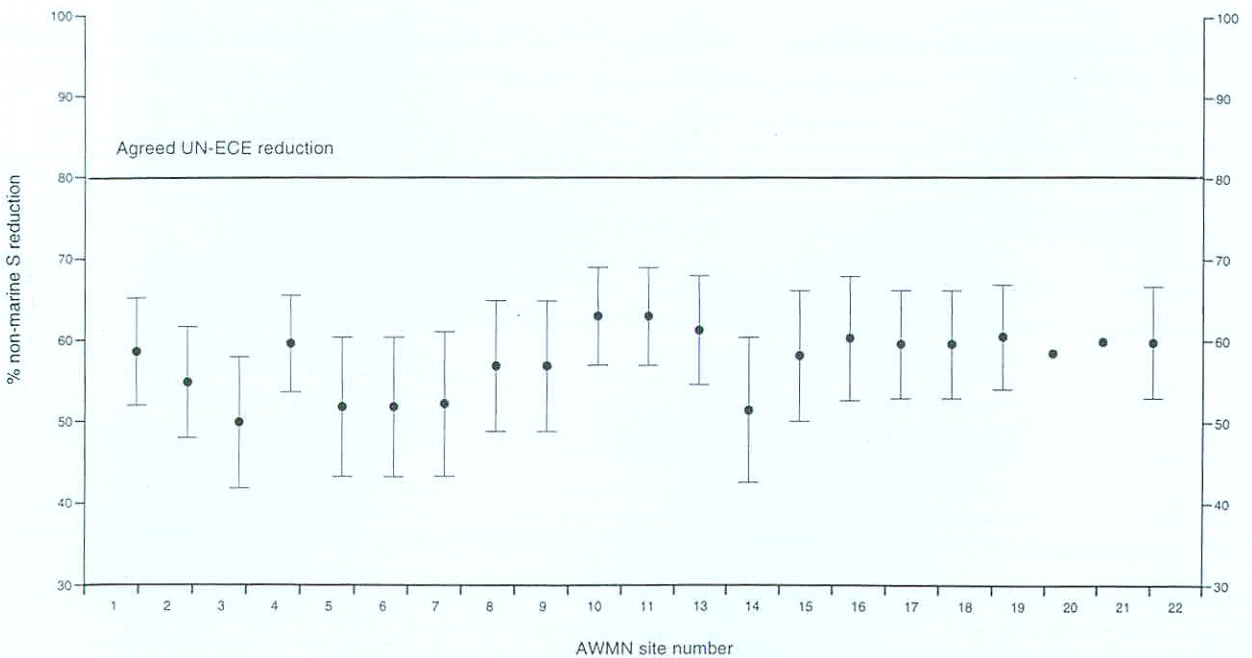*Courtesy of Dr Sarah Metcalfe (University of Edinburgh).*

Figure 5.2 *Agreed emission reduction from the Second S Protocol (dotted line), HARM predicted mean deposition reductions (solid circle) and ± 1 SD estimates (tails) for the 20 × 20 km grid squares encompassing AWMN sites.*

Using HARM modelled present day non-marine S deposition and predicted deposition for the years 2005 and 2010 a forecast sequence has been set up for each AWMN site to assess the likely soil and water chemistry response to the protocol. For these applications, the percentage change between HARM simulated present day and predicted 2010 deposition are used to modify the present day deposition used in the MAGIC calibration. Present day modelled deposition does not closely match that required by MAGIC to fit observed surface water chemistry. The present day deposition used in MAGIC, however, is well within the uncertainty limits defined for both HARM and the deposition enhancement model (Smith *et al.*, 1995).

In applying HARM, the agreed emissions reductions are achieved by targeting high emission sources, mainly power stations, fuel switching to gas and low S coal, and flue gas desulphurisation (Table 5.1).

Table 5.1 *Targeting of S sources within UK utilities used to attain the emissions reduction set by the Second S Protocol.*

Source type	% reduction	Base year
ESI & oil refineries	82	1980
Industrial	60	1991
Domestic	6	1991
Overall reduction	70	1980
80% scenario for 2010		
ESI & oil refineries	88	1980
Industrial	60	1991
Domestic	45	1991
Overall reduction	80	1980

HARM predicts S deposition at 20 × 20 km grid scale across the UK. Figure 5.2 shows how the agreed 80% reduction in S emissions by the year 2010 is predicted to translate to deposition reduction at each of the AWMN sites. In all cases the deposition reductions fall short of the agreed emissions reduction as a result of the remote locations of many of the sites relative to high emission sources. Uncertainty estimates of deposition predictions from HARM (± 1 standard deviation), based on 100 × 100 km grid squares, were generated by Monte Carlo analysis and are used in MAGIC forecast predictions to provide upper and lower estimates of mean soil and streamwater chemistry. All 20 × 20 km grid cells that lie beneath each of the 100 × 100 km grid cells are assumed to have the same standard deviation. Uncertainty estimates are not available for the Bencrom River and Blue Lough in south east Northern Ireland as these two sites fall outside the 100 × 100 km grid for this region.

5.2 Predicted response of soils and surface waters

MAGIC predictions have been made at all of the 21 AWMN sites using the appropriate HARM predicted deposition reduction for non-marine S (Figure 5.3). These forecasts assume that the predicted deposition reduction to 2010 is held constant for a further 30 years. No changes in land-use are assumed at the moorland sites during the forecast and Scenario 1 (clearfelling) is assumed for the five forested sites. The effects of land-use change at the forested sites is discussed in detail in Section 5.3.

The predicted response within 50 years is generally a small recovery in acid status of surface water but the agreed reductions are not adequate to effect a significant pH recovery in acid sensitive surface waters in the UK. Furthermore, soil BS is predicted to continue to decline at the majority of sites indicating that S deposition is still greater than base cation supply from weathering. The consequence of this in the longer term is that this recovery will not be sustained and surface water will re-acidify in the future (Figure 5.4).

An assessment of the likely medium to long term response has been attempted under four scenarios of reduced acidic deposition.

Scenario 1: Second S Protocol (red).

Scenario 2: Second S Protocol, remove all N deposition (green)

Scenario 3: all non-marine S removed from present deposition, N held constant at current level (light blue).

Scenario 4: all non-marine S and N removed from present deposition (purple).

The model was run for 150 years under each scenario assuming no changes in catchment land-use at the moorland sites and clearfelling at the forested sites (one rotation).

Under Scenario 1 the long-term recovery in streamwater ANC does not approach simulated background (Figure 5.4) despite reductions in non-marine S deposition of the order of c. 50 – 60% at all sites. Predicted responses fall into two categories:
i) sites that demonstrate a sustained long term recovery in ANC (sites 1, 2, 3, 5, 6, 7, 8, 11, 16, 17, 18, 19 and 22)
ii) sites that show short term recovery followed by continued acidification as a consequence of continued soil acidification (sites 4, 9, 10, 13, 14, 15, 20 and 21). The inadequacy of the Second S Protocol to promote long term recovery at these sites prompts the question "what level of reductions in acidic deposition (both S and N) will be required to initiate long term recovery?".
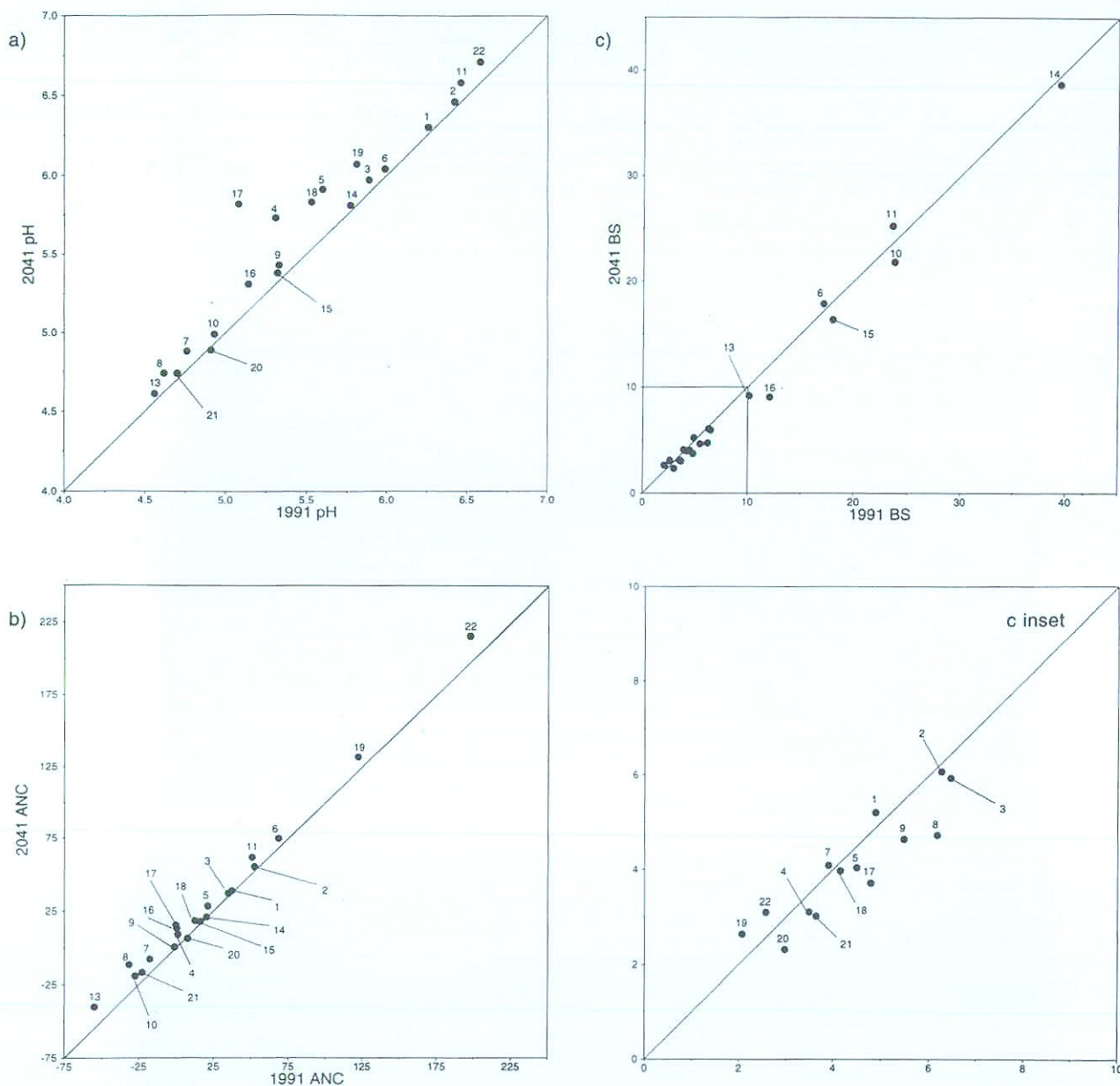
Figure 5.3 *MAGIC predicted change from present day (1991) to 2041 a) surface water pH b) surface water ANC and c) soil BS at the AWMN sites. Units in log_{10} for pH, $\mu eq\ l^{-1}$ for ANC and % of CEC for soil BS.*

Clearly, the model suggests that more drastic measures may be needed to reverse the acidification that has occurred at the most sensitive sites. Sites showing long term deterioration under Scenario 1 and currently leaking N are predicted to recover under Scenario 2. This indicates the importance of N deposition in both the current acidification status and in the potential for future recovery at these sites. Old Lodge (site 13) and Narrator Brook (site 14) are the only two sites that show continued deterioration in surface water ANC under Scenario 2, although N leakage at these sites is only small and its contribution to acidification status is minimal. Sites that are currently leaking only small amounts of N show limited response to reductions in N deposition.

Forecasts under Scenario 3 suggest that recovery is more pronounced, in terms of achieving background ANC, if all non-marine S is removed from deposition. This is not surprising given that non-marine S is the primary cause of acidification at these sites. There are, however, a number of the more acidified sites that do not recover in the long term. These are also sites where NO_3 concentrations in surface water is high relative to non-marine SO_4 concentration (Jenkins *et al.*, 1996). Under Scenario 4, all sites recover towards background ANC but the return to background conditions is predicted to take several hundreds of years. Clearly the time to recovery under this scenario reflects the current acidification status, soil base status and weathering rate at the individual sites.
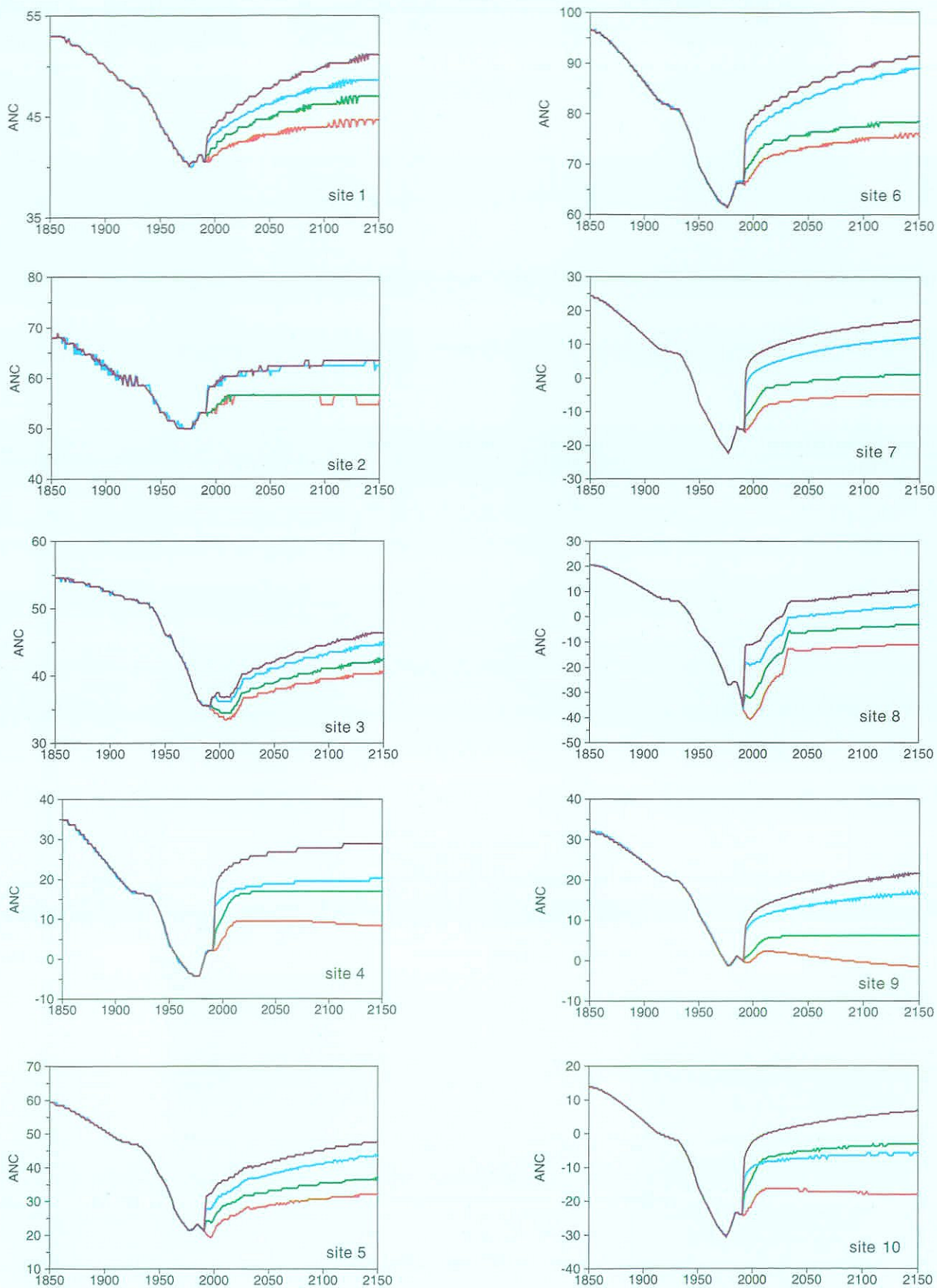
Figure 5.4. *Long term response of surface water ANC from 1850 to 2150. Forecast scenarios from 1991 to 2150 represent four alternative acid deposition scenarios. Scenario 1 (red), Scenario 2 (green), Scenario 3 (light blue), Scenario 4 (purple). Units in μeq l⁻¹.*
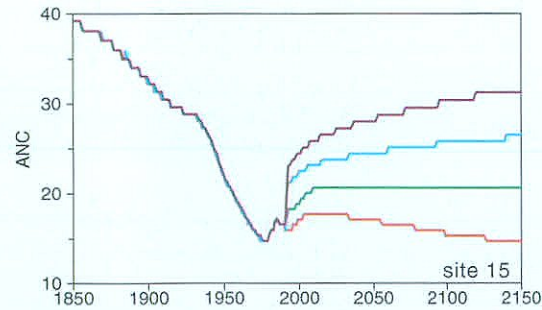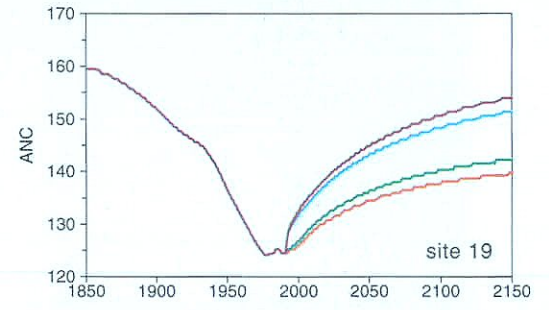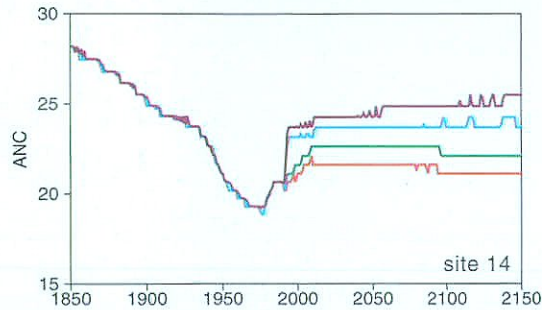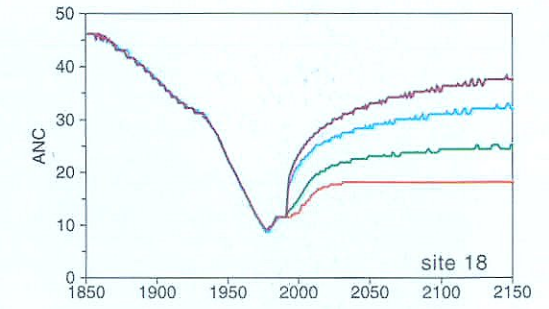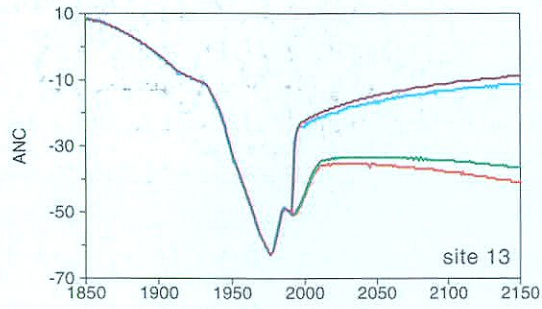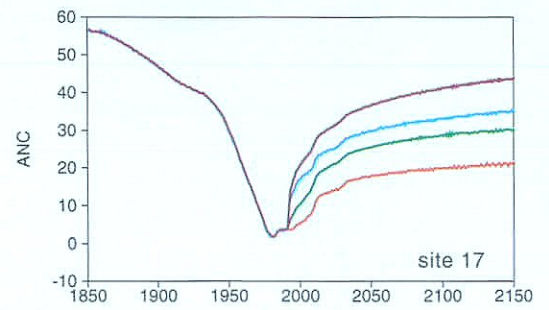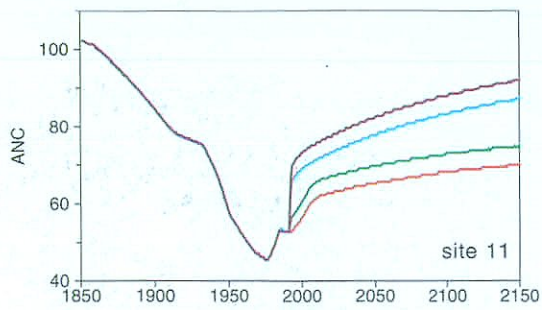
Figure 5.4 continued
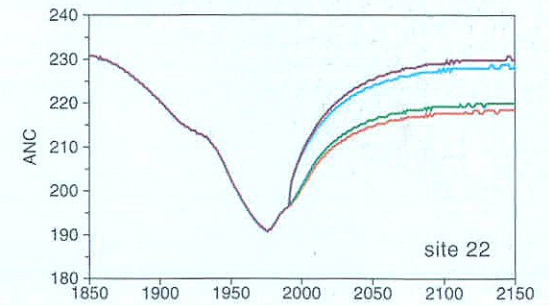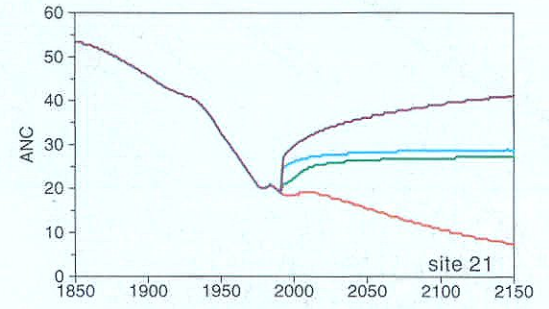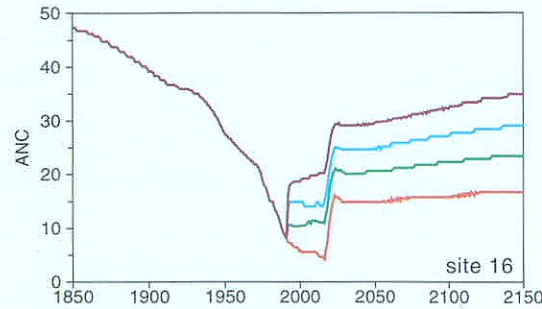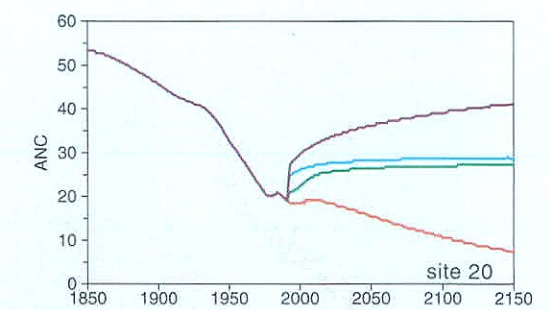
5.3 Effects of land-use change

Five of the 21 AWMN sites are forested, ranging from
about 42% at Allt Coire nan Con to 78% at Llyn Cwm
Mynach. Two scenarios have been used to assess the
most likely future forest management strategies:
i) cut all of the forest at 50 years of age with no further
replanting, and
ii) cut at 50 years of age and replant immediately. These
two scenarios combined with the agreed S reduction
cause responses that differ markedly from site to site in
response to the extent and timing of forest plantation.

At Allt Coire nan Con (site 3), the relatively large
reduction in S deposition (Figure 5.2) promotes little
pH recovery (Figure 4.3) until the forest is removed
whereupon a sustained increase in pH is achieved. On
planting a second rotation, however, further
acidification is predicted (Figures 4.3c and 5). At Loch
Chon (site 5), the response to emission reduction
(Scenario 1) is delayed because large areas of forest do
not reach maturity until after 2010. This leads to a
slight increase in SO_4 concentration in the stream, hence
an initial decrease in pH due to increased filter
deposition and reduced runoff. This is followed by a
recovery in pH as the SO_4 deposition reductions take
effect and the recovery is sustained (Figure 5.3e). With a
second rotation forest (Scenario 2) further acidification is
predicted. A similar response is predicted at the Afon
Hafren (site 17), no net recovery is observed under
Scenario 2 but a sustained pH recovery is predicted
without re-planting (Scenario 1).

In the Galloway region of south west Scotland a
comparison of the predicted historical and future
behaviour at a forested and non-forested site
exemplifies the land-use impact (Figure 5.3 and Figure
4.3). At both the Round Loch of Glenhead
(moorland — site 7) and Loch Grannoch (forested —
site 8) the hindcast reconstructions are similar until the
1960s when the model predicts a sharp increase in
acidification at the forested site. This corresponds with
the period of extensive forest planting. The forecast
response at the moorland site is a recovery in
streamwater pH whereas at the forested site no recovery
is predicted to occur until the forest is removed.

Figure 5.5 (right) MAGIC predicted change (1991 -
2041) in a) surface water pH b) surface water ANC
and c) soil BS; under alternative forest management
strategies. Scenario 1 (open circles) and Scenario 2 (solid
circles). Units in log_{10} for pH, μeq l^{-1} for ANC and % of
CEC for soil BS.
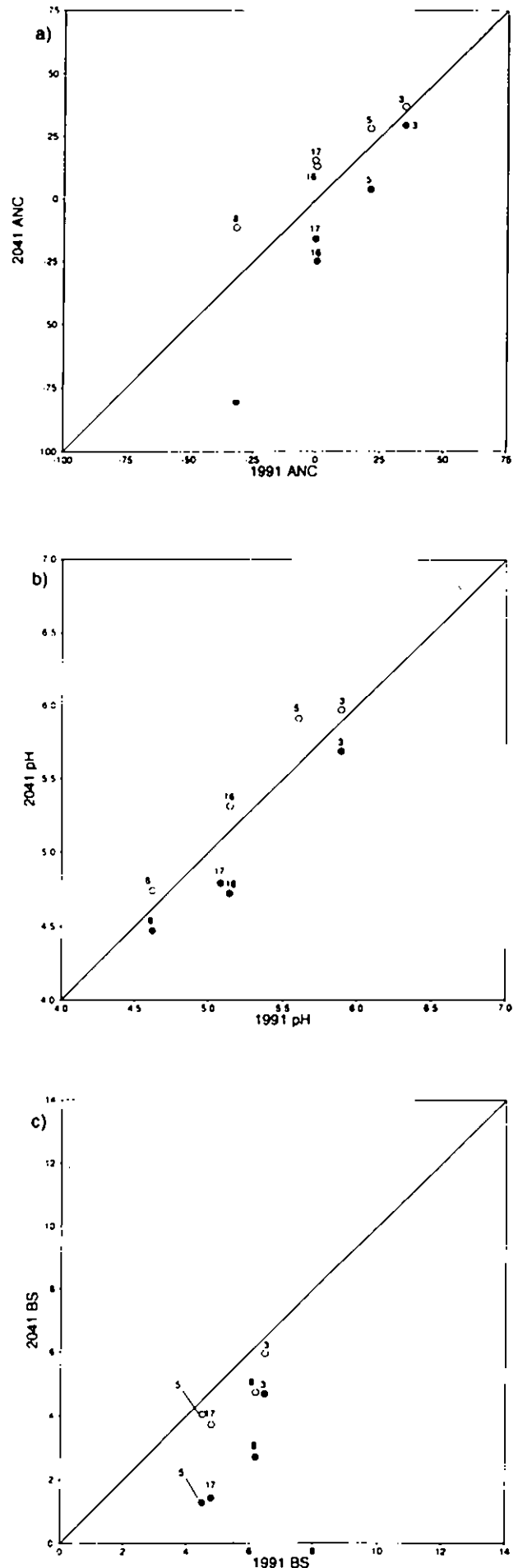
In general, if forest is removed and no further planting is undertaken, surface water ANC and pH are predicted to recover at all sites (Figure 5.4). Soil BS on the other hand continues to decrease indicating that incoming S is still greater than cation supply from weathering. This long term loss of base cations from the soil cannot be sustained in the long term and further surface water acidification will occur at these sites in the longer term. Clearly, a second rotation forest, with its base cation uptake requirements, exerts an additional stress on soil base cation supply and so tends to exacerbate this longer term problem.

A comparison between the two forest scenarios at the five sites for streamwater pH, ANC and soil BS indicates that the response of each site appears to reflect the current acid status rather than the extent of afforestation at each site. The most acidic sites show increased acidification under Scenario 2 and this is particularly evident for Loch Grannoch (site 8), Llyn Cwm Mynach (site 16) and the Afon Hafren (site 17). Allt na Coire nan Con (site 3) is the least acidic of the forested sites and surface water pH and ANC is predicted to decrease only marginally even under Scenario 2. Figure 4.2 indicates that this site has historically not acidified to any great degree and that the growth of the forest has had little or no acidification effect. The MAGIC hindcast pH reconstruction and diatom reconstruction at this site indicate that atmospheric deposition rather than forest growth has been the main cause of historical acidification at this site.

6 Critical loads

A critical load is an intrinsic catchment property that equates to the long term base cation weathering rate. It is assumed to be time independent when calculated under steady state conditions but may change if weathering rate changes, perhaps in response to climate change. Critical loads can be calculated for various compartments of the ecosystem, mainly soils, surface waters and vegetation, although the methods of calculation differ. For negotiation of the Second S Protocol, critical loads were calculated using empirical and steady state mass balance techniques (see Section 1.2). A critical load derived from a dynamic model differs from a critical load based on steady state approaches by incorporating time-dependent processes, such as cation exchange, SO_4 adsorption and plant uptake, which influence soil and streamwater chemistry. The dynamic modelling approach to critical load calculation also provides a more conservative method of calculation, since recovery over a predetermined time scale is inherent in the calculation, and also leads to generally higher critical load exceedance. Dynamic modelling approaches were not adopted by the UN-ECE in the development of the Second S Protocol but the relevance of dynamic models to the future assessment of the protocol has been emphasised (Kleemola & Forsius, 1996).

6.1 MAGIC critical loads

A critical load as calculated using MAGIC should be interpreted as a "Target Load". It represents the level of S deposition that is necessary to attain a pre-defined environmental quality variable at a given point in the future. Present steady state models are time invariant and the time to recovery is, therefore, irrelevant to the calculation. Clearly, a critical load for S deposition may be achieved relatively quickly but the recovery to a specified "target chemistry" may take many decades.

MAGIC calculates a critical load, in this case for total S deposition, by adjusting present day non-marine S deposition and running the model forward in time. The deposition change, whether an increase or decrease, is assumed to be undertaken at present day as a step change and held constant for the given time period. At acidified sites this provides an overestimate of the critical load since the emission reduction cannot be achieved so quickly. The water quality variable, e.g. surface water ANC, is then compared with the target to be achieved (ANC_{lim}). ANC_{lim} is the critical ANC required to protect a defined biological target within the ecosystem. The model then uses an iteration procedure to obtain the level of S deposition required to reach the chemical target at the specified point in the future. This

deposition then becomes the critical load for S. Critical loads based on a 50-year timescale are used here since this represents an economically justifiable time frame over which such reductions can be achieved.

Current critical loads for S deposition based on the SSWC method are based on a chemical target for surface waters of $ANC_{lim} = 0$ μeq l^{-1} (Sverdrup et al., 1990). This has been defined as the ANC at which there exists a 50% probability of survival of salmonid fisheries in lakes in the UK. An ANC_{lim} of 0 μeq l^{-1} has been adopted by the UK for the national mapping of critical loads for surface waters (Harriman et al. 1995a). In other European countries different values have been adopted based on empirical relationships between present day lake water chemistry and the presence or absence of fish populations (Henriksen, 1980; 1992). Norway for example has adopted an ANC_{lim} of 20 μeq l^{-1} and Finland 50 μeq l^{-1}.

The choice of ANC_{lim} and the timescale to recovery, therefore, determine the critical load and a considerable debate is ongoing concerning the correct value for ANC_{lim} in the UK. Recent evidence suggests that for Scottish fisheries, sites with a mean surface water ANC ≤ 0 μeq l^{-1} are currently almost all fishless, although sites that have mean ANC ≥ 0, yet suffer from periodic fluctuations below 0 μeq l^{-1}, have relatively healthy fish populations (Harriman et al., 1995b). Diatom-based pH studies suggest that for many Scottish lake sites the change in diatom flora occurred at ANC = 20 μeq l^{-1} and suggest that for low TOC waters, a value of ANC_{lim} of 20 μeq l^{-1} should be adopted, increasing to 50 μeq l^{-1} for high TOC waters. In this respect ANC = 0 μeq l^{-1} appears to be too low for protecting salmonid fishery status in the UK. This implies that critical loads for surface waters may be too high and the amount of critical load exceedance is being underestimated. Most of the AWMN sites exhibit relatively low TOC concentrations ranging from 1-5 mg l^{-1} (two sites in Northern Ireland, Beaghs Burn and Coneyglen Burn exhibiting TOC concentrations between 7 - 10 mg l^{-1}). For this reason, an alternative ANC_{lim} of 20 μeq l^{-1}, has been adopted for this work.

The importance of the choice of ANC_{lim} is well demonstrated by the model (Figure 6.1). Taking a 50 year recovery timescale, at three sites: Old Lodge (site 13), Loch Grannoch (site 8) and Scoat Tarn (site 10), a critical load could not be calculated. This implies that even if all non-marine S deposition were to be removed immediately, surface water ANC would not recover to 0 μeq l^{-1} within 50 years. Similarly, if ANC_{lim} is set to 20 μeq l^{-1}, 7 of the 21 sites would not recover within 50 years.
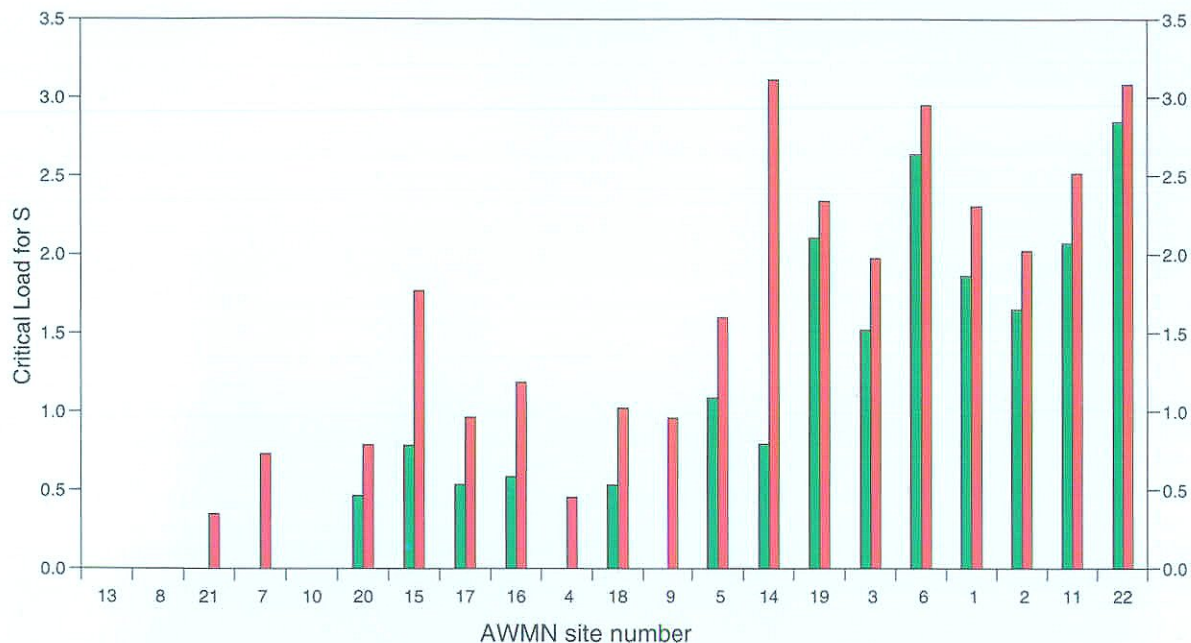
Figure 6.1 *MAGIC critical loads for surface water ANC_{lim} 0 (red) and 20 µeq l^{-1}(green). Sites are ordered by increasing mean surface water pH for the period 1988 – 94. Note that for some sites a critical load cannot be calculated for a given ANC_{lim} or a 50 year time-scale. Units in keq ha^{-1} yr^{-1}.*

6.2 Critical load exceedance

The critical load represents the threshold above which damage is likely to occur if deposition exceeds that level. Critical load exceedance (deposition greater than the critical load), therefore, provides us with a quantitative estimate of ecosystem damage against which emission reduction strategies can be assessed.

The critical load for ANC_{lim} = 0 and a 50-year timescale shows no relationship with current deposition (Figure 6.2). Those sites where the critical load is exceeded are those that are currently acidified (pH < 5.5), including Dargall Lane (site 9) and Round Loch of Glenhead (site 7) in the Galloway region of south west Scotland, Llyn Cwm Mynach (site 16) and the Afon Hafren (site 17) in Wales and Blue Lough (site 21) in Northern Ireland. At the Afon Gwy (site 18) in central Wales, Lochnagar (site 4) in north east Scotland and Bencrom River (site 20) in Northern Ireland (all presently acidified) current S deposition is at the critical load for surface waters.

Figure 6.2 *MAGIC critical loads calculated for ANC_{lim} = 0 and recovery timescale of 50 years (units in keq ha^{-1} yr^{-1}). Note that those sites above the line are currently exceeded.*

6.3 Time dependence of critical loads

The time dependence of critical loads, that is, the chosen timescale of recovery to ANC_{lim}, can only be assessed using dynamic models. Although critical loads presented earlier are based on a 50 year recovery timescale, in practice, any time scale can be chosen (Figure 6.3).
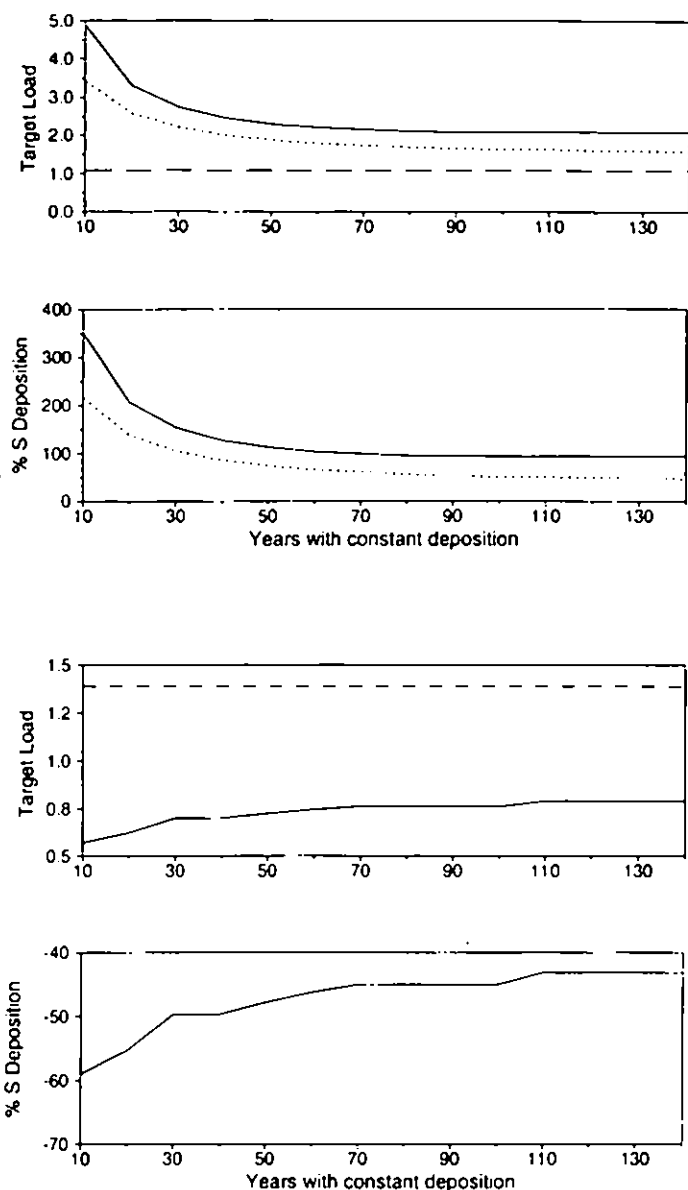
Figure 6.3 Time dependence of critical loads for S deposition for a) Loch Coire nan Arr and b) Round Loch of Glenhead. The X-axis represents the timescale of recovery to ANC_{lim}. Dashed line shows present day deposition. Units in keq ha^{-1} yr^{-1} for ANC_{lim} = 0 (solid line) and 20 μeq l^{-1} (dotted line).

Those sites that are not currently acidified and characterised by having high positive ANC and high pH (ANC = 20 - 70 μeq l^{-1} and pH ≥ 6.0) behave in a similar way to Loch Coire nan Arr (Figure 6.3a). In this case, the deposition of non-marine S must be increased to force the streamwater ANC down to either ANC_{lim} = 0 or 20 μeq l^{-1} and so the critical load is always greater than the current S deposition. The critical load required to depress surface water ANC to the ANC_{lim} is higher if the time over which ANC_{lim} is to be achieved is shorter (i.e. two times higher if the ANC_{lim} is to be achieved in

10 years as opposed to 50 years). This characteristic behaviour reflects the well-buffered nature of the soils and surface waters in these catchments. For an ANC_{lim} of 20 μeq l^{-1}, consistently lower S loads are required. For acidified sites, such as the Round Loch of Glenhead (Figure 6.3b), the time dependence is the opposite to that of non-acidified sites. At these sites, current S deposition exceeds the critical load and surface water ANC is currently less than 0 μeq l^{-1}. Lower S deposition is required, therefore, if ANC is to recover to 0 μeq l^{-1}. This S deposition must also be lower if the timescale to recovery is chosen to be shorter. In the case of the Round Loch of Glenhead the critical load increases from 0.55 to 0.75 keq ha^{-1} yr^{-1} with time to recovery of 10 to 140 years, respectively. This corresponds to deposition reductions for non-marine S, required to achieve the ANC_{lim}, of -60% over 10 years and -45% over 140 years. A critical load could not be calculated for an ANC_{lim} of 20 μeq l^{-1} at the Round Loch of Glenhead even if the timescale to recovery was set to 140 years. Critical loads for ANC_{lim} 0 or 20 μeq l^{-1} could not be calculated for Loch Grannoch (site 8), Scoat Tarn (site 10) and Old Lodge (site 13) over any time scale up to 140 years.

Comparison of the Level I (Henriksen model) and the Level II approach (MAGIC) to critical load calculation shows a pattern that reflects the different assumptions made in the steady state and dynamic models (Figure 6.4). In general, at acidified sites the MAGIC critical load is lower or equal to the Henriksen model. Alternatively, at sites with high critical loads (unacidified) MAGIC critical loads are consistently higher than the Henriksen model. The unacidified sites are characterised by well-buffered water chemistry with high pH and alkalinity, influenced by soils which retain a high acid buffering capacity. To deplete this store of base cations will either take many years of acid deposition at a relatively low S loading, i.e. as described by the equilibrium concept assumed in the empirical critical load, or 50 years of a higher critical load, i.e. as described by MAGIC. Acidified sites, on the other hand, are characterised by low pH and low, or in many cases negative, alkalinity and have soils with low BS. At these sites the MAGIC critical load is lower than the empirical critical load since these systems require longer than 50 years to recover and the base cation store in the catchment soils, which has been depleted due to many years of acidic deposition and forest growth, must be replenished by weathering inputs before surface water recovery can occur.

6.4 Effects of land-use change

The effect of forestry on surface water chemistry is to promote lower pH and ANC than at moorland catchments with similar deposition (Section 5.4). The mechanisms behind this effect are also reflected in the calculation of critical loads (Nisbet et al., 1995). At forested sites that are not acidified now (e.g. Allt na

Coire nan Con (site 3)) there is little difference in critical loads calculated under the two different forest management strategies for a given ANC_{lim}. Indeed, in this case it is the ANC_{lim} which determines the critical load rather than the future forestry scenario (Figure 6.5). Loch Chon (site 5), Llyn Cwm Mynach (site 16) and Afon Hafren (site 17), on the other hand, show an appreciable difference between the critical load calculated under Scenario 1 (clearfelling) and Scenario 2 (forest rotation) for a given ANC_{lim} and in this case both the ANC_{lim} and future forestry policy are important. Under both cases of ANC_{lim} the critical loads are 25 – 50% lower with replanting than with clearfelling as a result of the acidifying effect of the forest. A critical load could not be calculated for an ANC_{lim} of 20 eq l^{-1} under the scenario of forest rotation at Afon Hafren (site 17) and Llyn Cwm Mynach (site 16) indicating that to achieve future recovery in surface water acidity a second rotation forest should not be undertaken. At Loch Grannoch (site 8), no recovery is predicted within 50-years, whatever the future forestry strategy.
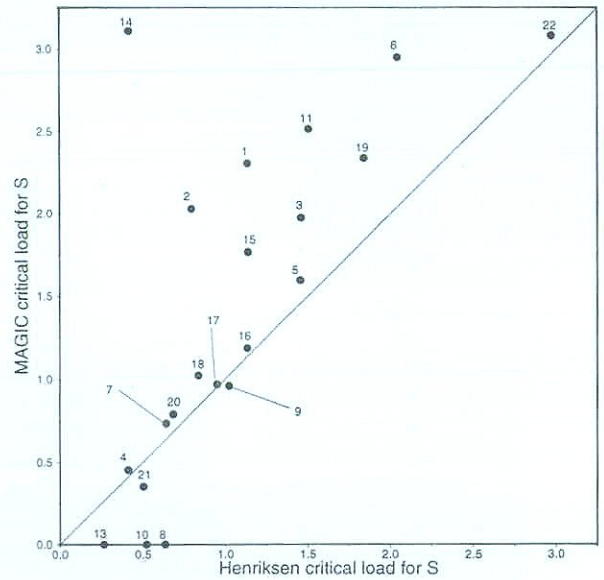
Figure 6.4 *Comparison of Henriksen critical load and MAGIC critical load based on a 50-year recovery timescale and ANC_{lim} = 0. Forested sites are assumed to be clearfelled with no replanting. Units in keq ha^{-1} yr^{-1}.*
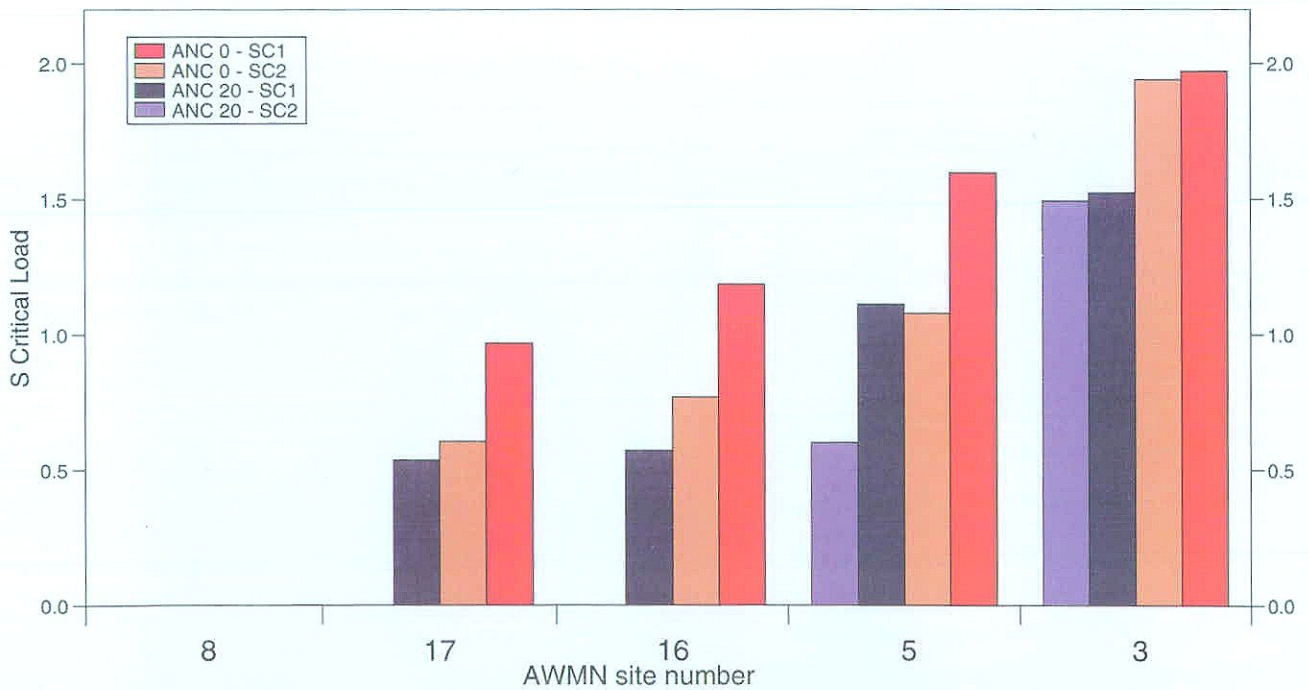
Figure 6.5 *Comparison of forest management strategies on surface water critical loads for the five AWMN forested sites for Scenario 1 (SC1 – clearfelling) and Scenario 2 (SC2 – forest rotation) for ANC_{lim} = 0 and 20 μeq l^{-1}.*

7 Discussion and conclusions

MAGIC was applied to 21 sites in the AWMN. The results were used to calibrate a chemical database that included the best available soils and deposition data at each site. It allowed an independent model validation against diatom data, dynamic assessment of critical loads, assessment of the recent S emission reduction protocol and the impacts of afforestation. It also provided an assessment of the combined effects of acidic deposition and land-use change.

The AWMN provides a unique collection of headwater catchments which span a range of S deposition, sensitivity to acidification and degree of afforestation. The successful calibration of the model to this wide range of catchment physicochemical conditions demonstrates the portability of the model. The comparison of model pH reconstructions with independently measured diatom pH reconstructions increases confidence in future model predictions.

Future predictions based on the best available prediction of S deposition following adherence to the Second S Protocol indicate that there will be some surface water pH and ANC recovery at the most acidified sites. This is in response to deposition reductions of c. 50 – 60% in non-marine S over the next 50 years at all sites. The predicted response of soil base status over the same time scale, however, continues to decline at most sites. The conclusion is that future S deposition under the Second S Protocol will still exceed the supply of base cations from weathering and lead to further soil acidification at these sites. Maintaining the Second S Protocol deposition for over 100 years produces little further recovery at presently acidified sites. Indeed many sites show renewed acidification in the longer term following full implementation of the protocol in 2010. Long term predictions at non-acidified sites, over the next 150 years, indicate that recovery to pre-industrial "pristine" status will be slow even if all anthropogenic S and N deposition were removed.

The model predictions reported here are based upon the assumptions made on distributed S emission reduction in the application of the HARM model. If the UK government adopts an approach whereby a market in pollution permits is established to encourage cost-effective investment in cutting S emissions, future water chemistry at these sites may differ to the predictions. The calibrated suite of catchments provides an ideal tool to assess the impact of trading permits between high and low emission utilities to meet the agreed national targets.

Future recovery of soils and surface waters is complicated by changing land-use at forested sites. A conservative assumption of land-use change involving the removal of mature forest with no replanting, combined with the Second S Protocol S emission reduction, results in model predictions that suggest recovery at all forested sites.

Recovery in surface water ANC under this scenario appears to be related to current acid status, in that sites showing the greatest recovery are currently more acidified. There is no clear relationship between percentage forest cover in the catchment and the degree of recovery.

Under a more realistic scenario, assuming forest rotation at 50 years i.e. planting a second rotation forest, the model predicts enhanced acidification at all sites with deterioration in surface water ANC over the next 50 years. The degree of acidification also appears to be related to the current acid status rather than the degree of forest cover. The predicted acidification effect of forest growth supports the current ethos that forests only have an acidifying effect in areas receiving high levels of acidic deposition and/or at currently acidified sites. The predictions further indicate that plantation forestry should be avoided in areas that are sensitive to acidification. Current Forestry Commission policy, however, would suggest that forest rotation is a more realistic scenario. This implies a pessimistic picture for the future acidification status of these sites even if the reductions under the Second S Protocol are implemented.

Decreased N deposition is potentially important at many sites if reductions in S, beyond those already agreed under the Second S Protocol, are not possible. This is especially relevant at sites where increased NO_3 concentrations in surface water are already reported. The degree to which further recovery can be achieved by cutting N or S (in excess of the requirement of the Second S Protocol) is site specific and depends on the relative inputs of N and S and the current N leakage from the terrestrial system.

Estimates of S critical loads for surface waters are related to the base cation weathering rate so reflect current acid status. MAGIC critical loads are calculated as the deposition of S required to produce an ANC_{lim} (biologically relevant chemistry) within a given time scale. The most acidified sites have surface water critical loads less than 1.0 keq ha^{-1} yr^{-1} and current non-marine S deposition exceeds this level. MAGIC-calculated critical loads for surface waters are closely related to those calculated using the Henriksen empirical model. MAGIC critical loads show a greater number of sites exceeding the critical load and the degree of exceedance is greater at acidified sites. This reflects the dynamic nature of the model. MAGIC critical loads are likely to be overestimates because the deposition reductions cannot be achieved immediately. The effect of land-use on critical load calculation reflects the forest growth processes that enhance the acidification of soils and surface waters. Consequently calculated critical loads are lower under a re-planting scenario.

8 Further research requirements

The application of MAGIC to sites in the AWMN has provided a unique assessment of the current acidification status and predicted future response of surface waters in the UK.

Estimates of critical loads for surface waters reflect site sensitivity and land-use and the future predictions of soil and streamwater chemistry suggest that recovery of the most acidified sites may take longer than anticipated. There is a need to make dynamic model estimates of critical loads for soils, more importantly the sensitive upper organic horizons on which soil critical loads maps are based (Hornung et al., 1995). The current one layer model is inadequate for this purpose because of the aggregation of the profile. The development of a model with two soil layers (organic and mineral) will enable calculation of critical loads for the top soil layer and also predictions of response of both layers to changing acid deposition and land-use.

The effects of episodic acidification are particularly relevant to the biological status of surface waters (Davies et al., 1992; DeWalle et al., 1994), particularly with respect to the survival of salmonid fisheries (Harriman et al. 1995b). The headwater stream sites in the AWMN have a flashy response to rainfall and are characterised by large seasonal changes in pH and ANC.

The prediction of episodic acidification, therefore, would be an important and useful development for the determination of future acidic emissions strategy. This requires that the temporal resolution of the model be changed from an annual time step to at least a seasonal one.

Until recently the problem of acidification of surface waters has concentrated on the effects of S as the acidifying anion. The importance of N deposition is now being considered and estimates of critical loads for N have been mapped across Europe (Grennfelt & Thornelof, 1992). Concentrations of NO_3 in surface waters already make a significant contribution to acidification at the AWMN sites (Jenkins et al., 1996). Furthermore, increasing concentrations of NO_3 in surface waters have been reported throughout Europe (Henriksen & Brakke, 1988) and there is an urgent need to develop process based dynamic models to calculate critical loads for N and predict the responses of changing N deposition and land-use.

The extrapolation of site applications of the model to larger regions is also desirable to enable more effective economic assessment of the impact of acidic emission reduction strategies.

Such a scaling-up procedure will need to draw upon the model parameter sensitivities assessed here.

Acknowledgements

References

Bader, M. J. & Roach, W.T. 1977. Orographic rainfall in warm sectors of depressions. *Q. J. Royal Met. Soc.* 103, 269-280.

Battarbee, R.W. 1986. Diatom analysis. *Handbook of Holocene palaeohydrology and palaeoecology* (Ed.) B.E. Berglund. 527-570. John Wiley and Sons. Chichester.

Battarbee, R.W., Anderson, N. J., Appelby, P.G., Flower, R.J., Fritz, S.C., Haworth, E.Y., Higgitt, S., Jones, V. J. Munro, M.A.R., Natkanski, J., Oldfield, F., Patrick, S.T., Richardson, N.G., Rippey, B. & Stevenson, A.C. 1988. Lake acidification in the UK 1800-1986: evidence from the analysis of lake sediments. ENSIS Publishing, London.

Battarbee, R.W., Allott, T.E.H., Kreiser, A.M. & Juggins, S. 1993. Setting critical loads for UK surface waters: the diatom model. In: (Eds.) M. Hornung & R.A. Skeffington. *Critical loads: concepts and applications.* ITE Symposium No. 28. HMSO, London, UK. 99-102.

Battarbee, R.W. & Charles, D.F. 1994. Lake acidification and the role of paleolimnology. *Acidification of freshwater ecosystems: implications for the future.* (Eds.) E.W. Steinberg & R.F. Wright. 51-65. John Wiley and Sons, Chichester, UK.

Battarbee, R.W. 1995. Critical loads of acid deposition for United Kingdom freshwaters. (Ed.) R.W. Battarbee. UK Critical Loads Advisory Group.

Birks, H.J.B., Line, J.M., Juggins, S., Stevenson, A.C. & ter Braak, C.J.F. 1990a. Diatoms and pH reconstructions. *Phil. Trans. Royal Soc. Lon.*, B327, 263-278.

Bormann, F.H., Likens, G.E. & Mellilo, J.M. 1977. Nitrogen budget for an aggrading northern hardwood forest ecosystem. *Science*, 196, 981-983.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. & Wright, R.F. 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water. Res.*, 21, 51-63.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. & Wright, R.F. 1985b. Time scales of acidification: a quantitative model for estimating freshwater acidification. *Environ. Sci. Technol.*, 19, 1144-1149.

Cosby, B.J., Hornberger, G.M., Wright, R.F, & Galloway, J.N. 1986. Modelling the effects of acid deposition: control of long term sulphate dynamics by soil sulphate adsorption. *Water.Res. Research*, 22, 1283-1291.

Cosby, B.J., Jenkins, A., Ferrier, R.C., Walker., T.A.B, & Miller, J.D. 1990. Modelling stream acidification in afforested catchments: long term reconstructions at two sites in central Scotland. *J. Hydrol.*, 120, 140-162.

Davis, R.B., Norton, S.A., Hess, C.T. & Brakke, D.F. 1983. Palaeolimnological reconstruction of the effects of atmospheric deposition of acids and heavy metals on the chemistry and biology of lakes in New England and Norway. *Hydrobiologia*, 103, 113-124.

Davies, T.D., Tranter, M., Wigington, P.J. & Eshleman, K.N. 1992. Acidic episodes in surface waters in Europe. *J. Hydrol.*, 132, 25-69.

Department of the Environment (DOE). 1983. Acid deposition in the United Kingdom. Warren Spring Laboratory, Stevenage, UK.

Department of the Environment (DOE). 1990. Acid deposition in the United Kingdom 1986-1988. HMSO, London. UK.

Department of the Environment (DOE). 1994. Critical loads of acidity in the United Kingdom. ITE, Penicuik, Scotland.

Department of the Environment (DOE). 1995. Critical loads of acid deposition for United Kingdom Freshwaters. ITE, Penicuik, Scotland.

Department of the Environment (DOE) and Forestry Commission. 1991. Forests and surface water acidification. Forestry Commission, Edinburgh, UK.

Derwent, R.G., Dollard, G.J. and Metcalfe, S.E. 1988. On the N budget for the United Kingdom and North West Europe. *Q. J. Royal Met. Soc.*, 114, 1127-1152.

Devenish, M. 1986. The United Kingdom precipitation composition networks. LR 584 (AP). Warren Spring Laboratory, Stevenage, UK.

deWalle, D.R., Swistick, B.R. & Sharpe, W.E. 1994. Episodic flow-duration analysis: a method of assessing toxic exposure of brook trout (*Salvelinus fontinalis*) to episodic increases in aluminium.[published where?]

Dore, A.J., Chourlton, T.W. & Fowler, D. 1992. An improved wet deposition map of the United Kingdom incorporating the seeder-feeder effect over mountainous terrain. *Atmos. Env.*, 26A, 1375-1381.

Finnish Environment Institute. 1996. International co-operative programme on integrated monitoring of air pollution effects on ecosystems. 5th Annual Report. (Eds.) S. Kleemola & M. Forsius. 10-24.

Fowler, D., Cape, J.N., Leith, I.D., Choularton, T.W., Gay, M.J. & Jones, A. 1988. The influence of altitude on rainfall composition at Great Dun Fell. *Atmos. Environ.* 22. 1355-1362.

Fowler, D., Leith, I.D., Smith, R.I., Chourlton, T.W., Inglis, D. & Campbell, G. Atmospheric inputs of acidity, S and N in the UK. 1995. In: Battarbee (Ed.). *Acid rain and its impacts: the critical loads debate*, 43-51. Ensis Publishing. London.

Flower, R.J., Battarbee, R.W. & Appelby, P.G. 1987. The recent palaeolimnology of acid lakes in Galloway, south west Scotland: diatom analysis, pH trends, and the role of afforestation. *J. Ecol.*, 75, 797-824.

Fowler, D., Cape, J.N., Leith, I.D., Chourlton, T.W., Gay, M.J. & Jones, A. 1988. The influence of altitude on the rainfall composition at Great Dunn Fell. *Atmos. Environ.*, 22, 1355-1362.

Fowler, D., Cape, J.N. & Unsworth, M.H. 1989. Deposition of atmospheric pollutants on forests. *Phil. Trans. Royal Soc. Lond.*, B324, 247-265.

Galloway, J.N., Anderson, D.S., Church, M.R., Cronan, C.S., Davis, R.B., Dillon, P.J., Driscoll, C.T., Norton, S.A., Schafran, G.C. 1984. Effects on aquatic chemistry. In: *The acidic deposition phenomenon and its effects: critical assessment review papers.* Volume 2. EPA-600/8-83-016bF, PB85-100048, Washington, DC. U.S. Environmental Protection Agency, Office of Research and Development, 197p.

Gimona, A. 1992. The use of two mathematical models to assess the influence of different factors in acidification processes in two small forested catchments. MSc Thesis.

Giusti, L. 1992. Chemical weathering and element mobilities at Loch Dee, Scotland. Proceedings of the Loch Dee symposium, 8-9th December 1992. 71-82.

Grennfelt, P. & Thornelof, E. (Eds.). 1992. Critical loads for N — a workshop report. Nordic Council of Ministers. Copenhagen, Denmark.

Grieve, I.C. 1989. A laboratory test of the soil chemical submodels of two models of catchment acidification. *Hydrol. Proc.*, 3, 339-346.

Haines, T.A. 1986. Fish population trends in response to surface water acidification. In: *Acid deposition, long term trends*, National Academy Press, Washington DC. 300-334.

Harriman, R. & Morrison, B. 1982. Forestry, fisheries and acid rain in Scotland. *Scott. For.*, 36, 89-95.

Harriman, R., Allott, T.E.H., Battarbee, R.W. & Curtis, C. 1995a. Critical loads for UK freshwaters. In: *Critical loads of acid deposition for United Kingdom freshwaters.* (Ed.) R.W. Battarbee. UK Critical Loads Advisory Group.

Harriman, R., Bridcut, E.E. & Anderson, H. 1995b. The relationship between salmonoid fish densities and critical ANC at exceeded and non-exceeded stream sites in Scotland. *Water, Air and Soil Pollution*, 85, 2455-2460.

Hendry, G.R., Galloway, J.N., Norton, S.A., Schofield C.L., Shaffer, P.W. & Burns, D.A. 1980. Geological and hydrochemical sensitivity of the Eastern United States to acid precipitation. Rep. EPA-600/3-80-024, U.S. Environment Protection Agency, Washington D.C.

Henriksen, A. 1980. Acidification of Freshwaters — a large scale titration. In:*Ecological impact of acid precipitation.*(Eds.) D.Drablos & A.Tollan. SNSF-Project, As, Norway. 383pp.

Henriksen, A., Sverdrup, H. and de Vries, W. 1989. Mapping critical loads: a guidance to the criteria, calculations, data collection and mapping of critical loads. Miljorapport 1990:14. Nordic Council of Ministers. Copenhagen.

Henriksen, A. & Brakke, D.F. 1988. Increasing contributions of nitrogen to the acidity of surface waters in Norway. *Water, Air and Soil Pollution*, 42, 183-201.

Henriksen, A., Kamari, J., Posch, M. & Wilander, A. 1992. Critical loads of acidity: Nordic surface waters. *Ambio.*, 21, 356-363.

Hornberger, G.M., Cosby, B.J, and Galloway, J.N. 1986. Modelling the effects of acid deposition: uncertainty and spatial variability of long term sulphate dynamics in a region. *Wat. Res.*, 22, 1293-1302.

Hornung, M., Bull, K.R., Cresser, M., Hall, J., Loveland, P.J., Langan, S.J., Reynolds, B. and Robertson, W.H. 1995. Mapping critical loads for soils in Great Britain. In: (Ed.) R.W. Battarbee. *Acid rain and its impacts: the critical loads debate*, 43-51. Ensis Publishing, London.

Jenkins, A., Ferrier, R.C., Walker, T.A.B. & Whitehead, P.G. 1988. A modelling study of long-term acidification at an upland Scottish catchment. *Water, Air and Soil Pollution*, 40, 275-291.

Jenkins, A. & Cosby, B.J. 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. In: *Regional acidification models.* (Eds.) J. Kamari, D.F. Brakke, A. Jenkins, S.A. Norton & R.F. Wright. Springer Verlag.

Jenkins, A., Whitehead, P.G., Cosby B.J. & Birks, H.J. 1990a. Modelling long term acidification: a comparison with diatom reconstructions and the implications for reversibility. *Phil. Trans. Royal Soc. Lon.*, B327, 435-440.

Jenkins, A., Whitehead, P.G., Musgrove, T.J. & Cosby, B.J. 1990b. A regional model of acidification in Wales. *J. Hydrol.*, 116, 403-416.

Jenkins, A., Cosby, B.J., Ferrier, R.C., Walker., T.A.B, & Miller, J.D. 1990c. Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. *J. Hydrol.*, 120, 163-181.

Jenkins, A. & Shaw, C. 1993. Comparison of empirical and dynamic model approaches for surface waters. In: (Eds.) M. Hornung & R.A. Skeffington. Critical loads: concepts and applications. ITE Symposium No. 28. HMSO, London.

Jenkins, A., Renshaw, M. & Boorman, D. 1996. The UK Acid Waters Monitoring Network: an assessment of chemistry data, 1988-93. *Fresh. Biol.*, 36, 1, 169-178.

Juggins, S., Flower, R.J. & Battarbee, R.W. 1996. Palaeolimnological evidence for recent chemical and biological changes in the UK Acid Waters Monitoring Network sites. Fresh. Biol. 36, 1, 203-219.

Kirby, C., Newson, M.D. & Gilman, K. 1991. Plynlimon research; the first two decades. Report

No. 109, Institute of Hydrology, Wallingford, UK.

Lea, J.W. 1975. Soils in Powys 1. Soil Survey and Land Research.Centre. Cranfield University, UK.

Likens, G.E., Wright, R.F., Galloway, J.N. & Butler, T.J. 1979. Acid Rain. *Sci. Am.*, 241, 43-51.

Maitland, P.S., Newson, M.D. & Best, G.A. 1990. The impact of afforestation and forestry practice on freshwater habitats. *Nature Conservancy Council focus on nature conservation No. 23*. Nature Conservancy Council, Peterborough, UK.

Mayer, R. & Ulrich, B. 1977. Acidity of precipitation as influenced by the filtering of atmospheric S and N compounds — its role in the element balance and effect on soil. *Water, Air and Soil Pollution*, 7, 409-416.

Metcalfe, S.E., Atkins., D.H. & Derwent, R.G. 1989. Acid deposition modelling and the interpretation of the United Kingdom Secondary Precipitation Network data. *Atmos. Environ.*, 23, 2033-2052.

Metcalfe, S.E. & Whyatt, J.D. 1995. Modelling future acid deposition with HARM In: *Acid rain and its impact: the critical loads debate*, (Ed.) R.W.Battarbee. 27-36. ENSIS Publishing, London.

Miller, H.G. & Miller, J.D. 1976. Effects of N supply on net primary production in corsican pine. *J. Appl. Ecol.* 13, 249-256.

Miller, H.G. 1981. Forest fertilisation some guiding concepts. *Forestry.* 54, 157-167.

Miller, H.G. 1984. Dynamics of nutrient cycling in plantation ecosystems. In: *Nutrition of plantation forests.* (Eds.) G.D. Bowen & E.K.S. Nambiar. Academic Press, London. 53-78.

Muniz, I.P. 1991. Freshwater acidification: its effects on species and communities of freshwater microbes, plants and animals. *Proc. Royal. Soc. Edin.*, 97b, 227-254.

Murlis, J. 1995. Critical loads: the policy background. In: *Acid rain and its impact: the critical loads debate*, (Ed.) R.W. Battarbee. 27-36. ENSIS Publishing, London.

Neal, C., Whitehead, P.G., Neale, R. & Cosby, B.J. 1986. Modelling the effects of acidic deposition and conifer afforestation on stream acidity in the British uplands. *J. Hydrol.*, 86, 15-26.

Nilsson, J. & Grennfelt, P. 1988. Critical loads for S and N. Nordic Council of Ministers, Copenhagen. 418p.

Nilsson, S.I., Miller, H.G. & Miller, J.D. 1982. Forest growth as a possible cause of soil and surface water acidification: an example of the concepts. *Oikos*, 39, 40-49.

Nisbet, T.R., Fowler, D. & Smith, R.I. 1995. Use of the critical loads approach to quantify the impact of afforestation on surface water acidification. In: *Acid rain and its impact: the critical loads debate.* (Ed.) R.W. Battarbee. ENSIS Publishing, London.

Nygaard, G. 1956. Ancient and recent flora of diatoms and chrysophyceae in lake gribso. *Folia. Limnological Scandinavia*, 8, 32-94.

Patrick, S.T., Juggins, S., Waters, D. & Jenkins, A. 1991. The United Kingdom Acid Waters

Monitoring Network. Site description and methodology report. ENSIS Publishing, London.

Posch, M., Reinds, G.J. & de Vries, W. 1993. SMART — Simulation Model for Acidification's Regional Trends: model description and users manual. Mimeograph series of the National Board of Waters and Environment 477, Helsinki, Finland.

Reuss, J.O. 1980. Chemical and biological relationships relevant to the effect of acid rainfall on the soil-plant system. *Water, Air and Soil Pollution*, 7, 461-478.

Reuss, J.O. 1983. Simulation of the soil nutrient calcium-aluminium exchange system for the effect of acid precipitation on soils. *J. Env. Qual.*, 12, 591-595.

Reuss, J.O. & Johnson, D.W. 1985. Effects of soil processes on the acidification of water by acid deposition. *J. Env. Qual.*, 14, 26-31.

RGAR. 1987. Acid deposition in the United Kingdom 1981-1985. UK Review Group on Acid Rain. Second report. Department of the Environment, London.

RGAR. 1990. Acid deposition in the United Kingdom 1986-1988. UK Review Group on Acid Rain. Third report. Department of the Environment, London.

Robson, A., Jenkins, A. & Neal, C. 1991. Towards predicting episodic changes in stream water chemistry. *J. Hydrol.*, 125, 161-174.

Rosenbrock, H.H. 1960. *J. Computing*, 3, 175.

Rudeforth, C.C., Hartnup, R., Lea, J.W., Thompson, T.R.E. & Wright, P.S. 1984. Soils and their use in Wales. Bulletin No.11. Lawes Agricultural Trust.

Singh, B.R. 1984. Sulphate sorption by acid forest soils. 1. Sulphate adsorption isotherms and comparison of different adsorption equations in describing sulphate adsorption. *Soil. Sci.*, 138, 189-197.

Smith, R.I., Hall, J.R. & Howard, D.C. 1995. Estimating uncertainty in the current critical loads exceedance maps. *Water, Air and Soil Pollution*, 85, 2503-2508.

Stoner, J.H. & Gee, A.S. 1985. Effects of forestry on water quality and fish in Welsh rivers and lakes. *J. Inst. Water Eng. Sci.*, 39, 27-45.

Sverdrup, H. & Warfvinge, P. 1988. Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model. *Water, Air and Soil Pollution*, 38, 387-408

Sverdrup, H., de Vries, W. & Henriksen, A. 1990. Mapping critical loads — guidance to criteria, methods and examples for mapping critical loads and areas where they have been exceeded, Task force on mapping — UN-ECE, Umweltbundesamt, Berlin, Germany.

Sverdrup, H., Warfvinge, P., Blake, L. & Goulding, K. 1995. Modelling recent and historic soil data from the Rothamsted experimental station, UK, using SAFE. *Agriculture Ecosystems and Environment*, 53, 161-177.

ter Braak, C.J.F. & Prentice, I.C. 1988. A theory of gradient analysis. *Advances in Ecological Research*, 18, 271-313.

Turner, J., Johnson, D.W. & Lambert, M. J. 1980. S cycling in a douglas-fir forest and its modification by N applications. *Ecol. Plant.*, 15, 27-35.

Vollenveider, R.A. 1968. OECD Technical report DAS/SCI 27.

Warren Spring Laboratory, 1983. Acid deposition in the United Kingdom. Warren Spring Laboratory, Stevenage.

Warren Spring Laboratory, 1987. Acid deposition in the United Kingdom 1981-1985. Warren Spring Laboratory, Stevenage.

Waters, D. & Jenkins, A. 1991. Impacts of afforestation on water quality trends in upland catchments. In: International conference on acidic deposition, its nature and impacts, Glasgow, 1990, Royal Society of Edinburgh.

Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., Cosby, B.J. & Parcois, P. 1988a. Modelling long-term stream acidification trends in upland Wales at Plynlimon. *Hydrol. Process.*, 2, 357-368.

Whitehead, P.G., Bird, S., Hornung, M., Cosby, B.J., Neal, C. & Parcois, P. 1988b. Stream acidification trends in the Welsh uplands — modelling study of the Llyn Brianne catchments. *J. Hydrol.*, 101, 191-212.

Wright, R.F. & Haughs, M. 1991. Reversibility of acidification: soils and surface waters. *Proc. Royal Soc. Edin.*, B97, 169-193.

Wright, R.F., Cosby, B.J., Ferrier, R.C. Jenkins, A., Bulger, A.J. & Harriman, R. 1994. Changes in acidification of lochs in Galloway, south western Scotland, 1979-1988: the MAGIC model used to evaluate the role of afforestation, calculate critical loads, and predict fish status. *J. Hydrol.*, 161, 257-285.

Appendix 1

Detailed chemical equations in MAGIC

Equilibrium Equations

Soil water cation exchange reactions

$$E_{Al} + E_{Ca} + E_{Mg} + E_K + E_{Na} = 1 \qquad (1)$$

$$BS = E_{Ca} + E_{Mg} + E_{Na} + E_K = 1 - E_{Al} \qquad (2)$$

$$\frac{\{Ca^{2+}\}^3 \, E_{Al}^2}{\{Al^{3+}\}^2 \, E_{Ca}^3} = S_{AlCa} \qquad (3)$$

$$\frac{\{Na^+\}^2 \, E_{Ca}}{\{Ca^{2+}\} \, E_{Na}^2} = S_{CaNa} \qquad (4)$$

$$\frac{\{Na^+\}^2 \, E_{Mg}}{\{Mg^{2+}\} \, E_{Na}^2} = S_{MgNa} \qquad (5)$$

$$\frac{\{Na^+\}_2 \, E_K}{\{K^+\} \, E_{Na}} = S_{KNa} \qquad (6)$$

Inorganic aluminum reactions

$$\frac{\{Al^{3+}\}}{\{H^+\}^3} = K_{Al} \qquad (7)$$

$$\frac{\{Al(OH)^{2+}\}\{H^+\}}{\{Al^{3+}\}} = K_{Al_1} \qquad (8)$$

$$\frac{\{Al(OH)^+{}_2\}\{H^+\}^2}{\{Al^{3+}\}} = K_{Al_2} \qquad (9)$$

$$\frac{\{Al(OH)^0{}_3\}\{H^+\}^3}{\{Al^{3+}\}} = K_{Al_3} \qquad (10)$$

$$\frac{\{Al(OH)^-{}_4\}\{H^+\}^4}{\{Al^{3+}\}} = K_{Al_4} \qquad (11)$$

$$\frac{\{AlF^{2+}\}}{\{Al^{3+}\}\{F^-\}} = K_{Al_5} \qquad (12)$$

$$\frac{\{AlF_2^+\}}{\{Al^{3+}\}\{F^-\}^2} = K_{Al_6} \qquad (13)$$

$$\frac{\{AlF_3^0\}}{\{Al^{3+}\}\{F^-\}^3} = K_{Al_7} \qquad (14)$$

$$\frac{\{AlF_4^-\}}{\{Al^{3+}\}\{F^-\}^4} = K_{Al_8} \qquad (15)$$

$$\frac{\{AlF_5^{2-}\}}{\{Al^{3+}\}\{F^-\}^5} = K_{Al_9} \qquad (16)$$

$$\frac{\{AlF_6^{3-}\}}{\{Al^{3+}\}\{F^-\}^6} = K_{Al_{10}} \qquad (17)$$

$$\frac{\{Al(SO_4)^+\}}{\{Al^{3+}\}\{SO_4^{2-}\}} = K_{Al_{11}} \qquad (18)$$

$$\frac{\{Al(SO_4)_2^-\}}{\{Al^{3+}\}\{SO_4^{2-}\}^2} = K_{Al_{12}} \qquad (19)$$

Inorganic carbon reactions

$$\frac{\{CO_2(aq)\}}{P_{CO_2}} = K_{CO_{2_1}} \qquad (20)$$

$$\frac{\{HCO_3^-\}\{H^+\}}{\{CO_2(aq)\}} = K_{CO_{2_2}} \qquad (21)$$

$$\frac{\{CO_3^{2-}\}\{H^+\}}{\{HCO_3^-\}} = K_{CO_{2_3}} \qquad (22)$$

Dissociation of water and ionic balance

$$\{H^+\}\{OH\} = K_w \tag{23}$$

$$(H^+) - (OH) + 2(Ca^{2+}) + 2(Mg^{2+}) + (K^+) +$$
$$(Na^+) + 3(Al^{3+}) + 2(Al(OH)^{2+}) + Al(OH)_2^+)$$
$$- (Al(OH)_4) - 2(AlF^{2+}) + (AlF_2^+) - (AlF_4^-)$$
$$- 2(AlF_5^{2-}) - 3(AlF_6^{3-}) + (Al(SO_4)^+) - (AlSO_4)_2^-)$$
$$- (Cl) - (F) - (NO_3) - 2(SO_4^{2-}) - (HCO_3)$$
$$- 2(CO_3^{2-}) = 0 \tag{24}$$

Mass balance equations

$$dCa_t/dt = F_{Ca} + W_{Ca} - Q*2*(Ca^{2+}) \tag{1}$$

$$dMg_t/dt = F_{Mg} + W_{Mg} - Q*2*(Mg^{2+}) \tag{2}$$

$$dNa_t/dt = F_{Na} + W_{Na} - Q*(Na^+) \tag{3}$$

$$dK_t/dt = F_K + W_K - Q*(K^+) \tag{4}$$

$$dSO_{4t}/dt = F_{SO_4} + W_{SO_4} - Q*2*$$
$$((SO_4^{2-}) + (Al(SO_4)^+) + 2(Al(SO_4)_2^-)) \tag{5}$$

$$dCl_t/dt = F_{Cl} + W_{Cl} - Q*(Cl) \tag{6}$$

$$dNO_{3t}/dt = F_{NO_3} + W_{NO_3} \tag{7}$$

$$dF_t/dt = F_F + W_F - Q*((F)) + (AlF^{2+})$$
$$+ 2(AlF_2^+) + 3(AlF_3^0) + 4(AlF_4^-)$$
$$+ 5(AlF_5^{2-}) + 6(AlF_6^{3-})) \tag{8}$$

Definitions

Sulphate adsorbtion

$$E_S = E_{max} *2(SO_4^{2-})/(C + 2(SO_4^{2-})) \tag{1}$$

Alkalinity

$$Alk = (HCO_3) + 2(CO_3^{2-}) + (OH) - (H^+) - 3(Al^{3+})$$
$$- 2(Al(OH)^{2+}) - (Al(OH)_2^+) + (Al(OH)_4) - 3$$
$$(AlF^{2+}) - 3(AlF_2^+) - 3(AlF_3^0) - 3(AlF_4^-) - 3(AlF_5^{2-})$$
$$- 3(AlF_6^{3-}) - 3(Al(SO_4)^+) - 3(Al(SO_4)_2^-) \tag{2}$$

Total ion ammounts

$$Ca_t = SP*CEC*E_{Ca} + 2*V*(Ca^{2+}) \tag{3}$$

$$Mg_t = SP*CEC*E_{Mg} + 2*V*(Mg^{2+}) \tag{4}$$

$$Na_t = SP*CEC*E_{Na} + V*(Na^+) \tag{5}$$

$$K_t = SP*CEC*E_K + V*(K^+) \tag{6}$$

$$SO_{4t} = SP*E_S + 2*V*((SO_4^{2-}) + (Al(SO_4)^+)$$
$$+ 2(Al(SO_4)_2^-)) \tag{7}$$

$$Ft = V*((F) + (AlF^{2+}) + (AlF_2^+) + 3(AlF_3^0)$$
$$+ 4(AlF_4^-) + 5(AlF_5^{2-}) + 6(AlF_6^{3-})) \tag{8}$$

$$Cl_t = V*(Cl) \tag{9}$$

$$NO_{3t} = V*(NO_3) \tag{10}$$

Sums of aqueous base cation and strong acid anion concentrations

$$SBC = 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) \quad (11)$$

$$SSA = 2(SO_4^{2-}) + (Cl^-) + (NO_3^-) + (F^-) \quad (12)$$

Variables

Base cations: (Ca^{2+}), (Mg^{2+}), (Na^+), (K^+)

Stong acid anions: (Cl^-), (F^-), (NO_3^-), (SO_4^{2-})

Inorganic aluminium species: (Al^{3+}) $(Al(OH)^{2+})$, $(Al(OH)_2^+)$ $Al(OH)_3^0$, $(Al(OH)_4^-)$, (AlF^{2+}), (AlF_2^+), (AlF_3), (AlF_4^-) (AlF_5^{2-}), (AlF_6^{3-}), $(Al(SO_4)^+)$, $(Al(SO_4)_2^-)$

Inorganic carbon species: $(CO_2(aq))$, (HCO_3^-), (CO_3^{2-})

Dissociation of water: (H^+), (OH^-)

Exchangeable cation fractions: E_{Ca}, E_{Mg}, E_K, E_{Na}, E_{Al}

Base saturation: BS
Total ion amounts: Ca_t, Mg_t, Na_t, K_t, SO_{4t}, Cl_t, NO_{3t}, F_t

Adsorbed suphate: Es

Alkalinity: Alk

sums of base cations and strong acid anions: SBC, SSA

Parameters

Thermodynamic equilibrium constants (functions of temperature):

KAl_1, KAl_2, KAl_3, KAl_4, KAl_5, KAl_6, KAl_7, KAl_8, KAl_9, KAl_{10}, KAl_{11}, KAl_{12}, K_{CO_1}, K_{CO_2}, K_{CO_3}

Lumped parameters (functions of catchments)

selectivity coefficients: S_{AlCa}, S_{CaNa}, S_{MgNa}, S_{KNa}

aluminium solubility constant: K_{Al}

soil chemical properties: C, E_{Mai}, CEC

soil physical properties: SP, V

Inputs (functions of time)

Streamflow: Q
Atmospheric deposition: F_{Ca}, F_{Mg}, F_{Na}, F_K, F_{SO_4}, F_{Cl}, F_{NO_3}, F_F

Net uptake and release in soils: W_{Ca}, W_{Mg}, W_{Na}, W_K, W_{SO_4}, W_C, W_{NO_3}, W_F

Partial pressure: CO_2: P_{CO_2}

Braces denote activities and parentheses denote molar concentrations. An extended Debye-Huckel expression was used to convert molar concentrations to activities. Units of other variables, parameters, and inputs are given in the text.

Appendix 2

20 km gridded Meterological Office rainfall for the period 1989 – 92 and modelled runoff based on percentage forestry for A WMN sites. Units in mm yr[1].

Site	Rainfall	Runoff
1	2928	2632
2	1095	0975
3	2518	2160
4	928	835
5	2335	1936
6	2335	2102
7	2223	2001
8	2012	1686
9	2012	1811
10	1616	1454
11	1616	1454
13	760	380
14	1367	1230
15	2436	2192
16	1973	1622
17	1704	1436
18	1704	1534
19	1327	1194
20	1015	914
21	1038	934
22	1341	1200

Appendix 3

Appendix 3.1 *MAGIC present day (1991) deposition of chloride (Total Cl, set equal to output flux), ADMN wet deposited chloride from the nearest collector (Wet Cl) and predicted filter deposition (Filter Cl = Total Cl -Wet Cl) for A WMN sites. Units in meq m⁻²yr⁻¹.*

Appendix 3.2 *MAGIC present day (1991) deposition of chloride (Total Cl set equal to output flux) ADMN wet deposited chloride from the nearest collector (Wet Cl) and predicted filter deposition (Filter Cl = Total Cl - Wet Cl) for A WMN sites. Units in meq m⁻² yr⁻¹.*

Site	Total Cl	Wet Cl	Filter Cl	% Filter
1	723	496	227	31
2	108	94	14	12
3	684	426	258	37
4	74	79	0	0
5	446	267	178	40
6	340	267	73	21
7	424	294	130	30
8	458	266	192	41
9	362	266	96	26
10	28	63	42	14
11	326	243	83	25
12	325	145	179	55
13	223	158	64	28
14	347	233	113	32
15	458	363	94	20
16	520	294	226	43
17	310	191	118	38
18	250	191	59	23
19	402	148	253	62
20	227	113	113	49
21	249	116	132	53
22	317	316	1	0

Site	Total SO₄	Wet SO₄	Filter SO₄	% Filter
1	108	88	20	18
2	42	28	13	32
3	133	75	57	43
4	50	24	25	51
5	140	85	54	39
6	109	85	24	22
7	140	91	48	34
8	169	82	86	51
9	148	82	66	44
10	88	90	0	0
11	121	90	30	25
13	104	47	57	54
14	88	58	30	33
15	136	92	43	32
16	142	75	64	47
17	117	54	62	53
18	98	54	44	44
19	86	42	45	50
20	86	32	53	62
21	92	33	59	63
22	63	50	12	19

Appendix 3.3 *(right) MAGIC present day (1991) deposition of total, wet and forest filter N for A WMN sites. Wet N is taken as seeder-feeder enhanced moorland total N. Filter N is based on the percentage forest cover and work by Fowler et al., 1989. Units in meq m⁻²yr⁻¹.*

Site	Total N	Wet N	Filter N	% Filter
1	92	92	0	0
2	62	62	0	0
3	164	112	52	32
4	93	93	0	0
5	281	158	123	44
6	158	158	0	0
7	175	175	0	0
8	266	158	108	41
9	158	158	0	0
10	157	157	0	0
11	157	157	0	0
13	161	161	0	0
14	97	97	0	0
15	187	187	0	0
16	307	165	142	46
17	342	210	132	39
18	210	210	0	0
19	108	108	0	0
20	80	80	0	0
21	91	91	0	0
22	86	86	0	0

Appendix 4

Appendix 4.1 *Soil depth, bulk density and cation exchange capacity (CEC) used for MAGIC calibrations to A WMN sites. Units in m for soil depth, kg m⁻³ for bulk density and meq m⁻³ for CEC.*

Appendix 4.2 *MAGIC present day (1991) optimised exchangeable base cation fractions for the A WMN sites. Units expressed as percentage of the CEC.*

Site	Depth	Bulk density	CEC	Site	ECa	Emg	ENa	Ek	% BS
1	0.82	1046	105	1	1.42	2.45	0.68	0.38	4.93
2	1.03	830	183	2	1.99	2.71	0.87	0.66	6.23
3	0.84	914	132	3	2.37	1.86	1.09	1.10	6.42
4	1.09	1000	127	4	1.63	0.80	0.29	0.64	3.36
5	0.96	985	119	5	2.05	1.08	0.54	0.78	4.45
6	0.81	1068	59	6	9.17	2.33	0.99	4.58	17.07
7	0.87	623	159	7	1.21	1.43	0.49	0.61	3.74
8	1.10	907	174	8	2.09	1.07	1.66	1.29	6.11
9	1.32	1081	70	9	2.21	1.91	1.01	0.64	5.77
10	0.33	624	113	10	13.46	6.94	1.97	1.64	24.01
11	0.36	591	141	11	10.53	8.95	1.89	2.27	23.64
13	1.00	1409	83	13	4.23	1.18	3.14	1.59	10.14
14	1.79	1033	96	14	13.22	8.71	8.27	8.90	39.10
15	0.88	795	74	15	7.47	4.95	3.76	1.45	17.63
16	0.89	796	85	16	3.37	3.24	4.20	1.22	12.03
17	0.88	1134	70	17	2.64	0.19	1.15	0.57	4.55
18	0.84	1122	78	18	2.53	0.33	0.98	0.41	4.25
19	0.46	572	497	19	0.67	0.87	0.30	0.24	2.08
20	0.48	487	618	20	0.88	0.67	0.81	0.48	2.84
21	0.40	733	316	21	1.41	0.58	0.84	0.81	3.64
22	0.42	668	361	22	0.69	1.08	0.49	0.25	2.51

Appendix 5

Appendix 5 Present day (1991) forest mineral uptake for Ca, Mg, Na, K, and SO for the five forested sites in the AWMN. Units expressed in meq m³ yr¹.

Site	Ca	Mg	Na	K	SO$_4$
3	16.1	8.4	2.0	9.5	1.4
5	37.2	19.3	4.6	21.8	3.2
8	63.2	32.7	7.8	37.0	5.4
16	56.1	29.1	6.9	32.9	4.8
17	29.3	15.2	3.6	17.2	4.8

Appendix 6

Percentage NO_3 in the soil compartment of the MAGIC model required to balance surface water NO_3 concentrations in the AWMN (1988 — 94 mean).

Site	NO_3 uptake
1	83
2	92
3	83
4	74
5	84
6	100
7	93
8	76
9	67
10	47
11	95
12	37
13	95
14	69
15	71
16	69
17	63
18	74
19	89
20	32
21	37
22	92