Review of Dynamic Models for Catchment and Surface Water Acidification

Technical Report
P246

Review of dynamic models for catchment and surface water acidification

R&D Technical Report P246

Alan Jenkins and Brian Reynolds

Research Contractor:
Institute of Hydrology

Further copies of this report are available from:
Environment Agency R&D Dissemination Centre, c/o
WRc, Frankland Road, Swindon, Wilts SN5 8YF

tel: 01793-865000 fax: 01793-514562 e-mail: publications@wrcplc.co.uk

Publishing Commissioning
Environment Agency
Rivers House
Waterside Drive
Aztec West
Bristol BS32 4UD

Tel: 01454 624400 Fax: 01454 624409

ISBN 1 85705 046 0

Dissemination status
Internal: Release to Regions
External: Released to Public Domain

Statement of Use
The purpose of this document is for use by EA staff and others involved in the management of river catchments, particularly those catchments where land use is primarily agricultural.

Research Contractor
This document was produced under R&D Project P4-019 by:

Institute of Hydrology
Maclean Building
Crowmarsh Gifford
Wallingford, Oxon
OX10 8BB
Tel: 01491 838800 Fax: 01491 692424

Environment Agency's Project Manager
The Environment Agency's Project Leader for R&D Project P4-019 was:
Colin Powlesland, Steel House, 11 Tothill Street, London

R&D Technical Report P246

CONTENTS

EXECUTIVE SUMMARY

The environmental problems associated with acidic deposition have initiated research on which air pollution abatement programmes and legislative controls can be based. This research is aimed at formulating limits for acidic deposition using the critical loads approach to protect the environment. Central to the determination of critical loads has been the development of process-based mathematical descriptions ("dynamic" models) for the mechanisms underlying the relationships between acid deposition and water quality. Since dynamic models take into account long-term processes they offer the only opportunity to understand the processes involved in the spatial and temporal extent of acidification. Such models can be used to address a number of time-related issues concerning acidification including: assessing the environmental consequences of different emission strategies; determining the timescales between achieving critical loads and ecosystem recovery; examining the effect of land-use change, in particular forestry practice, on critical loads; assessing the future behaviour of whole regions to emission reduction policies; coupling with biological models to assess the response and status of organisms in acidified streams and lakes.

This report reviews dynamic process-oriented models of soil and streamwater acidification. In particular, MAGIC and SAFE are used to illustrate the structure and underpinning processes and equations in dynamic models. Data requirements and requisite site parameters are discussed for the models as well as applications to site specific and regional studies, and where available, validation of models with historic data. The report highlights the need for further research to develop MAGIC for both regional and catchment specific applications. Application to specific catchments requires field data describing stream chemistry to adequately quantify the mean annual flux of all major ions. Application to regions requires appropriate data collected at the regional scale to describe the soil, surface water and deposition chemistry characteristics. Further developments in up-scaling procedures are also required.

Key uncertainties identified which require further research include sulphate adsorption/desorption, tree uptake of base cations, nitrogen dynamics, particularly in moorland systems and modelling peat soils. In the case of foresty impacts in the UK, a multi-layer soil model is required. In this respect, the SAFE model can provide additional insight in some circumstances where detailed soil geochemical data is available. Uncertainty in these areas requires more detailed field studies to determine the key controls. Uncertainty in model prediction can be minimised, however, by analysis of a historical surface water chemistry data record for a given site or for surrogate sites within the same region. In terms of regulatory use, the MAGIC model will provide unique information on the long-term acidification status of a catchment or region and is a key tool for assessing emission/deposition scenarios in relation to critical loads.

GLOSSARY OF TERMS AND ACRONYMS

ANC	-	Acid Neutralising Capacity. Defined as sum of base cations minus the sum of acid anions
AWMN	-	Acid Waters Monitoring Network
Base Saturation	-	The percentage of the CEC holding base cations
Baseflow	-	Low flow condition
Carbonate equilibrium	-	The balance between dissolved and gaseous carbon dioxide
CEC	-	Cation Exchange Capacity. Represents the maximum available storage of cations in the soil
CHUM	-	Chemistry of the Uplands Model
CLAG	-	Critical Loads Advisory Group
DOC	-	Dissolved Organic Carbon
DYNAMO	-	EU Project; Dynamic Models to Predict and Scale-up the Impact of Environmental Change on Biogeochemical Cycling
ICP-IM	-	UN-ECE International Co-operation Programme on Integrated Monitoring
LCPD	-	EU Large Combustion Plant Directive
LRTAP	-	Long Range Transboundary Air Pollution
LT50	-	50 day Lethal Toxicity
MAGIC	-	Model of Acidification of Groundwater In Catchments
MAGIC-WAND	-	MAGIC - With Aggregated Nitrogen Dynamics
MIDAS	-	Model of Ion Dynamics and Acidification of Soil
NERC	-	Natural Environment Research Council
pCO_2	-	The partial pressure of carbon dioxide in water
pK	-	Partition coefficient
PROFILE	-	Steady state soil critical loads model
Q	-	River discharge
RAIN	-	Reversing Acidification in Norway
RMSE	-	Root Mean Square Error
SAFE	-	Simulating Acidification in Forest Ecosystems
SMART	-	Simulation Model for Acidifications Regional Trends
Transfer function	-	A time series model
UN-ECE	-	United Nations Economic Commission for Europe
WHAM	-	Windermere Humic Acid Model

1. INTRODUCTION

The link between emissions of gaseous acidic oxides and ecosystem damage through acid rain and dry deposition is now well established. Recognition that emissions undergo long range transport from country to country has resulted in international negotiations and policies on emission reductions. A Sulphur Protocol was developed in 1985 within the framework of the convention on "Long Range Transboundary Air Pollution" (LRTAP) of the United Nations Economic Commission for Europe (UN-ECE). This stated that the participating signatories should reduce their sulphur emissions to at least 30% below the 1980 levels by 1993. It was recognized that this approach was not targeting emission reductions where they were most needed and that an effects based approach was required.

In 1994 the Oslo Protocol on further Reductions in Sulphur Emissions (Second Protocol) was established which incorporated a 'critical load' approach where the critical load 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 our present knowledge*" (Nilsson and Grennfelt 1988). Critical loads can be calculated for a variety of ecosystems and are based upon damage to, or loss of, a target or receptor organism. In the case of soils and freshwaters, for example, sensitive receptors have been identified as tree roots and brown trout, respectively. Critical chemical criteria for the soil or water can then be defined beyond which biological damage will occur. In forest soils a base cation:aluminium molar ratio of 1.0 in the soil solution is a commonly used threshold, whilst an Acid Neutralisation Capacity of zero (ANC=0) is often used for freshwaters (Sverdrup *et al.*, 1990). The Second Sulphur Protocol was designed to reduce acid deposition across UNECE countries with the intention reducing the exceedance of critical load by 60% based on a 150 by 150 km designated grid across Europe.

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 calculations depending on available data; (i) Level 0 or 'empirical critical load' in which critical loads are defined according to best available knowledge often by defining a simple system of classification e.g. the Skokloster classification for soil acidity critical loads where the critical load is based on an allocation of soils to classes as a function of their mineralogy and hence ability to buffer acid inputs (Nilsson and Grennfelt 1988); (ii) Level 1 steady-state mass balance models where the critical load is calculated using a mass balance of sources and sinks of acidity e.g. the Steady-State Water Chemistry model (Sverdrup *et al.* 1990); (iii) Level 2 dynamic models such as MAGIC (Model of Acidification of Groundwater in Catchments) and SAFE (Simulating Acidification in Forested Ecosystem model) which endeavour to simulate the main processes affecting the acidification of soils and freshwaters and thereby predict the time scales of ecosystem response to changing acid deposition inputs. Considerable scientific effort has focused on the development of dynamic models since it is now recognized that these offer the only opportunity to predict the future timing and direction of the response to policy decisions undertaken today.

This document is intended to:

a) Review and summarise the characteristics of existing dynamic acidification models outlining the approaches used, the extent to which dynamic models could be applied to wide regions and the advantages and disadvantages of dynamic versus steady-state models.
b) Identify the key chemical criteria in soils and freshwaters.
c) Examine the use and validity of response curves rather than thresholds.
d) Assess model predictions for different deposition scenarios by means of case studies.
e) Investigate key uncertainties in the model by means of case studies.

2. PROCESSES OF ACIDIFICATION

Before considering the nature and role of dynamic acidification models, the main processes involved in the acidification of soils and waters will be briefly considered.

The process of soil and stream water acidification can be considered in terms of a careful application of the mobile anion concept (Reuss and Johnson 1986). This states simply that as the soil solution must remain electrically neutral, cation leaching must be accompanied by an equivalent amount of anions. Thus for soil acidification to occur, there has to be a source of protons to exchange for base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and a supply of mobile anions (SO_4^{2-}, NO_3^-) to accompany the leached cations. In addition to the effects of externally added strong mineral acids (acid rain), many natural process can also affect the acid-base balance of catchment soils and, ultimately, freshwaters.

2.1 Respiration

Carbon dioxide evolved in the respiration of roots and soil micro-organisms dissolves in the soil solution to form carbonic acid which dissociates to yield protons and bicarbonate anions. Carbonic acid is a weak acid and dissociation is negligible below pH 4.5. Thus, acidification by respiration is self-limiting and relatively unimportant in acid soils. However the high partial pressure of carbon dioxide of the soil atmosphere is important in terms of the pH change induced in soil waters as they degas on entering streams (Cresser and Edwards 1987; Neal 1988a & b)

2.2 Base cation uptake

Plants require base cations for growth, exuding protons from the roots to maintain electrical neutrality. Thus plant growth is an acidifying process which is temporary under conditions where plant death and decay returns the base cations to the soil. If the plants are harvested, as in forestry, permanent depletion of the base cation store will occur. The amount of base cations removed at harvest will depend on tree species, site conditions, timing and type of harvesting (Hornung 1985). Data for a site in north Wales on base poor soils, show that base cation depletion may be quite large relative to soil stores of readily available (exchangeable) base cations after only one forest rotation (Stevens *et al.*, 1988).

2.3 Organic acid production

Decomposition of organic matter leads to the formation of soluble organic acids. These acids are stronger than carbonic acid and can therefore dissociate to give protons and organic anions at a pH below 4.5 (Johnson *et al.*, 1991). The role of organic acids in soil acidification remains an area of debate, depending on soil type and degree of acidification. Even in extremely acid forest soils, organic acids may be the major leaching agent for base cations (Kononova 1966; Reuss and Johnson 1986). However some studies have shown that they are relatively unimportant compared with strong mineral acids (Lee and Hultberg 1990; Westling 1990).

The behaviour of organic acids may be crucial in determining the recovery of some acidified systems following reductions in acid deposition. Krug and Frink (1983) have suggested that increasing organic acid dissociation as acid inputs decline will buffer any pH changes. Critics, however, suggest that the quantitative importance of the organic buffering process cannot be very great due to the low concentrations of organic anions in many soils (de Vries and Breeuwsma 1987). These authors also suggest that the influence of acid deposition on natural hydrogen ion production is small. In podzolised soils, dissolved organic acids are responsible for the chelation and transport of iron and aluminium (Kononova 1966; Ugolini *et al.*, 1977). At Plynlimon, afforestation increased the transport of organically bound iron and aluminium (Hughes *et al.*, 1990). Forest harvesting temporarily mobilized additional aluminium and iron from organic surface horizons by increasing dissolved organic carbon (DOC) concentration in soil water as a result of increased decomposition of organic matter following site disturbance.

The role of naturally occurring organic acids in the acidification of freshwaters has been an area of debate for some time (Glover and Webb 1979; Krug and Frink 1983; Driscoll *et al.*, 1988). This arises for several reasons. Naturally occurring organic acids are a complex mix of species and there are no standard methods available for their determination (Thurman 1985). Measurements of DOC have been used to qualitatively assess the concentration of organic acids, but this measure includes a wide range of forms which vary in their acid-base characteristics. There is evidence that naturally occurring organic acids contain both strong and weak acid functional groups, but the exact dissociation characteristics are hard to quantify (Thurman 1985). Strong acid groups with a dissociation constant (pK_a) less than or equal to 4 will behave similarly to the strong mineral acids and depress the acid neutralizing capacity (ANC) of the water (Driscoll *et al.*, 1989).

Organic acids are important from at least two perspectives. Firstly, recent analyses of episodic stream acidification have indicated that organic acids can make a significant contribution to stream water acidity, particularly where the catchment contains a substantial amount of peat (Kahl *et al.*, 1992; Davies *et al.*, 1992). Secondly, as noted above, organic acid dissociation is linked to the presence of strong mineral acids. The hypothesis proposes that the input of strong mineral acids shifts the balance of acidification away from that caused by naturally occurring organic acids (Krug and Frink 1983; Davis *et al.*, 1985). This hypothesis has received quantitative support from work in North America, in which DOC and organic anion concentrations were negatively correlated with sulphate in low ANC lakes (Driscoll *et al.*, 1989). The significance of the hypothesis is that reductions in strong acid inputs may lead to a shift in balance back to organic acidity. Evidence supporting a role for organic acidity is cited by Skeffington and Brown (1992) where an increase in organic anions has been observed in the Norwegian acid deposition exclusion experiment known as the RAIN (Reversing Acidification In Norway) project (Wright *et al.*, 1986; Wright 1987). The hydrogen ion concentration had altered little in the 5.5 years since the beginning of the experiment despite a reduction in the input of pollution- derived sulphate.

2.4 Sulphate adsorption

Sulphate adsorption is thought to take place on the surfaces of iron and aluminium oxides in soils. These phases are abundant in the B horizons of podzolic soils in Wales (Adams *et al.*, 1987). Sulphate adsorption consumes protons and sulphate thus countering acidification. The process is thought to be concentration-dependent, which means that the capacity of the soil to adsorb sulphate increases with the solution sulphate concentration. The relationship between the adsorbed and the solution sulphate concentration is described as a sulphate adsorption isotherm (Reuss and Johnson 1986). This has important implications, as it means that a soil which is currently in equilibrium with the amount of sulphate it receives can adsorb more sulphate if the input increases. Conversely, a decrease in inputs will cause sulphate to be desorbed until equilibrium is achieved.

This has serious consequences for the reversal of acidification following a reduction in sulphur dioxide emissions. Reversal will be slowed if there is a significant pool of sulphate adsorbed in the soil. There is evidence for sulphate desorption from the Norwegian RAIN acid rain exclusion experiment. After 5 years of acid rain exclusion, outputs of sulphate still exceeded inputs, although concentrations had declined (Wright and Hauhs 1991).

2.5 Nitrogen transformations

The nitrogen cycle is intimately linked with acid-base relationships within the soil. The formation of ammonia during decomposition does not consume or produce protons. During the conversion of ammonia to ammonium ion, one proton is consumed by the protonation of NH_3 to NH_4^+. If this ammonium ion is taken up by a plant, a proton is released, so that the cycle of decomposition followed by ammonium ion uptake has no overall effect on the proton balance.

The microbial conversion of ammonium ion to nitrate is known as nitrification and results in the production of two protons for each NH_4^+ converted to NO_3^-. The fate of this nitrate ion is crucial to the overall effect of the nitrogen cycle on soil acidification. If the nitrate is taken up by plants, then a hydroxyl ion is released and there is no net acidification. If the nitrate is leached, there is an additional acidification equivalent to the production of one proton (Helyar 1976; Reuss and Johnson 1986).

In the absence of nitrate leaching and external inputs of nitrogen, there is no net proton production associated with the nitrogen cycle. The cycle within the plant and the soil is balanced. However, in broad terms, the balance between nitrogen supply and nitrogen uptake will be the main control on nitrate leaching. The form of nitrogen entering the system and the associated anions and cations will have a major influence on the acidifying potential of nitrogen inputs. For temperate forest systems, which have been considered nitrogen limited, nitrate leaching is generally very low. Any increase in nitrate losses above those expected at pristine sites with low nitrogen inputs is therefore taken as sign that the site has become 'nitrogen saturated' (Gundersen 1992). By implication, acidification related to the nitrogen cycle is occurring. Such acidification may manifest itself as increased leaching of inorganic aluminium to surface waters or a reduction in the base cation to aluminium ratio in the soil solution with deleterious consequences for tree health (Ulrich 1990; Runge and Rode 1990).

2.6 Mineral weathering

The supply of base cations from the chemical weathering of soil minerals is an important biogeochemical process determining the availability of plant nutrients and acting to modify soil water chemistry in its' drainage and transmission to surface and groundwaters. As indicated by Jacks (1990), the weathering of minerals in the soil matrix provides the only long term sink for protons. It is also the fundamental process determining the susceptibility of soils to acidification. If the rate of breakdown of soil minerals cannot compensate for the depletion of nutrient base cations by biomass uptake and leaching then it is inevitable that acidification will occur. Therefore research into the impact of acid deposition on natural ecosystems has addressed the issue of base cation release from weathering in some detail. Currently the concept of critical loads which provides a measure of sensitivity of ecosystems to acidification is largely based on the rate of base cation supply from chemical weathering. Unfortunately it is one of the most difficult processes to quantify. The amount of protons consumed by weathering of primary minerals in soils depends on the abundance of weatherable minerals (determined by chemical composition), the rate of weathering and the stoichiometry of the weathering reactions. The weathering rate is also a function of a number of external factors such as:

a) climate - mean annual temperature, rainfall
b) soil hydrology - hydraulic conductivity, permeability
c) physiography - slope, aspect, elevation
d) chemistry - precipitation, throughfall, organic acids, soil pH

At any one site these factors will interact to define the weathering rate.

2.7 Aluminium solubility

The cation exchange complex of acid soils in the UK uplands is dominated by aluminium. For this reason, and because of its toxicity to terrestrial and freshwater biota, the geochemistry of aluminium has been extensively studied. The original concept of inorganic aluminium mobility in acid soils was based on the dissolution of aluminium hydroxide (Gibbsite). As this process consumes protons, it was included in acidification models (Cosby *et al.*, 1985). The formation of aluminium sulphates (e.g. Jurbanite) was also considered to be an important control on aluminium, as well as sulphate chemistry (Nordstrom 1982).

Following detailed analysis of data from a number of Welsh sites, it became clear that the gibbsite and jurbanite equilibrium models were not appropriate, at least not for acid soils in Wales where neither mineral had actually been observed (Reynolds *et al.*, 1988; Neal *et al.*, 1989). At the same time a number of theoretical objections were raised to the way in which aluminium data were analyzed and represented in acidification models (Neal *et al.*, 1987; Neal 1988c).

A number of alternative mechanisms have been proposed for the control of aluminium concentrations in soils and freshwaters. The first of these was an ion exchange mechanism, which was used to describe the increase in soil water aluminium content following afforestation of moorland with Sitka spruce in field and laboratory studies (Reynolds *et al.*, 1988; Adams *et al.*, 1990). Detailed analysis of soil water hydrogen ion - aluminium relationships shows, however, that a simple ion exchange reaction is not adequate, at least in mineral soil horizons (Neal *et al.*, 1990). An alternative hypothesis is that there is no causal link between hydrogen ions and aluminium. In the surface, organic-rich horizons, hydrogen ion fluctuations may be controlled by changes in ionic strength and exchange with sodium while weathering and cycling determine aluminium variations. In the lower soils, aluminium may exchange with cations other than hydrogen ion, whilst hydrogen ion is partially consumed by weathering reactions (Neal *et al.*, 1990). More recently, Berggren and Mulder (1995) have proposed that reactive organically bound aluminium controls the activity of aluminium ions in organic-rich soils typical of much of the UK uplands.

3. THE NATURE AND ROLE OF DYNAMIC MODELS

3.1 The structure of dynamic models

Dynamic models have been developed to predict the acidification of soils, lakes, streams and groundwater specifically accounting for changes through time such as the depletion of element pools in soils and changes in catchment land-use. As such these models explore the dynamic aspects of the response of systems to changes in deposition by seeking to incorporate, to a greater or lesser extent, the key acidification processes outlined above.

Dynamic models aim to address a number of questions in terms of past acidification and future recovery of acidified ecosystems:

i) to identify the regional characteristics that determine critical loads.
ii) to determine the timescales of ecosystem recovery after critical load is achieved.
iii) to determine the consequences for ecosystems of not achieving the critical load.
iv) to examine the effect of land-use, in particular forestry on critical loads and exceedance of critical loads.

v) to determine the interaction between nitrogen and sulphur in the context of critical loads for total acidic deposition.

All dynamic models are a simplified representation of the ecosystems they simulate. Conceptually, the ecosystem is represented in terms of defined pools (e.g. soil cation exchange complex, tree biomass etc.) and the fluxes of matter (dissolved chemicals, water etc.) between these pools. The response time for these two components is very different with changes in fluxes occurring over much shorter timescales than changes in the ecosystem pools (Table 3.1).

Table 3.1 Time scale of chemical processes considered in terrestrial ecosystems.

Process	Flux response time	Pool response time
Soil solution speciation	Instantaneous	Days
Hydrological regimes	Days	Seasonal
Nitrogen dynamics	seasonal	Years
Sulphate absorption	Instantaneous	Decades
Cation exchange	Weeks	Many decades
Nutrient uptake	Seasonal	Rotation period
Chemical weathering	Seasonal	Eons
Soil stratification	Rotation period	Eons

Despite the simplification of reality contained within dynamic models, they are nevertheless complex because they consider a large number of chemical processes simultaneously. In essence, all dynamic acidification models are based on similar components (Figure 3.1). Implemented in its simplest form, a model is a two-compartment representation of a catchment. Atmospheric deposition and mineral weathering products enter the soil compartment and equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream or lake and carbon dioxide is degassed and streamwater chemistry is calculated.

In NW Europe and the USA, the most commonly used dynamic models applied at both catchment and regional scales include MAGIC (Cosby *et al.*, 1985 a,b), MIDAS (Holmberg *et al.*, 1989), SAFE (Sverdrup *et al.*, 1995a), and SMART (Posch *et al.*, 1993). All four models attempt to predict the long-term impact of atmospheric deposition on the chemical composition of soil and the outflowing water using similar basic processes (Table 3.2).

The main features of the models may be summarized as follows, and more detailed case study examples of the application of MAGIC and SAFE are given in Chapters 5 and 6.

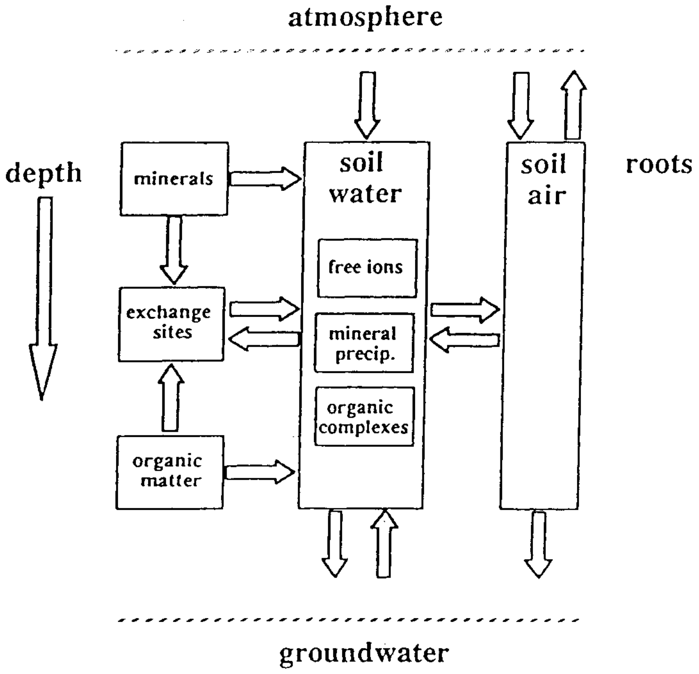


Figure 3.1 Basic components of a dynamic acidification model.

MAGIC (Model of Acidification of Groundwater in Catchments) includes all major cations and anions and reactions involving aluminium, such as hydration and complexation with sulphate and fluoride. MAGIC is the most widely distributed and used dynamic model and has been applied extensively in the UK including the sites in the Acid Waters Monitoring Network (AWMN) (Jenkins *et al.*, 1997).

MIDAS (Model of Ion Dynamics and Acidification of Soil) predicts the rate of change in soil water concentrations of hydrogen ions, aluminium, calcium and magnesium in a one layer mineral soil subject to the deposition of hydrogen ions and base cations. The model has been used to explore the possible paths of acidification and recovery following decreased acid deposition (Holmberg *et al.*, 1989). MIDAS does not predict stream water chemistry, and is used only to predict changes in soil base cations.

SAFE (Simulating Acidification in Forested Ecosystems) is a dynamic geochemical model which calculates chemical weathering release of base cations (calcium, potassium and magnesium) and changes in soil solution chemistry and base saturation (strictly calcium+potassium+magnesium saturation) in response to changes over time in atmospheric deposition, net nutrient uptake, nutrient cycling and hydrology. A steady state soil model called PROFILE (Sverdrup and Warfvinge 1993) is used with the model to calculate final steady state soil conditions which are used as initial input conditions to SAFE. SAFE has been used to model recent and historical soil data from a catchment in the UK (Sverdrup *et al.*, 1995).

Table 3.2 Characteristics of dynamic models. NI signifies that the process is not included in the model.

Process	MAGIC	MIDAS	SAFE	SMART
Al solubility	Equilibrium	Equilibrium	Equilibrium	Equilibrium
Hydrology	Vertical / horizontal	Vertical	Vertical / horizontal	Vertical
Nitrification	NI	NI	Kinetic	Related to ammonium
Sulphate adsorption	Langmuir isotherm	NI	NI	Langmuir isotherm
Cation exchange	Gaines-Thomas equilibrium	Gaines-Thomas equilibrium	Gapon mass transfer	Gaines-Thomas equilibrium
Nutrient uptake	Input	Input	Input	Input
Chemical weathering	Input	Input	Kinetic (PROFILE)	Input
Soil stratification	Two layer	One layer	Multi layer	One layer

SMART (Simulation Model for Acidification's Regional Trends) simulates base saturation, pH, calcium + magnesium, aluminium, ammonium, nitrate, sulphate and bicarbonate in soil solutions. As in the other models it combines a set of equilibrium equations with mass balance equations for the different elements. A simple lake module describing retention of sulphate, nitrate and ammonia has recently been added. A recent example of the application of SMART is given in Kamari *et al.* (1994).

3.2 Dynamic versus steady-state models

The Level 1 or steady-state approach to critical load calculation is based on the application of mass balance equations to calculate the balance between sources and sinks of acidity within a catchment or ecosystem. The net result of this balance is then directly related to the critical load which can be set equal to the pollutant deposition at which the critical chemical value is not transgressed. Mass balance equations have been developed for both soils and freshwater and incorporate both sulphur and nitrogen. Level 1 assessments have the advantage over Level 0 classifications in that they provide a critical load which is directly applicable to ecosystem assessment.

In comparison with dynamic models, the Level 1 approach requires much less data and the equations have generally been formulated in such a way as to use data which can be readily derived from map information either directly or indirectly via simple calculations. Thus, for example, base cation uptake rates by trees can be defined regionally using land cover maps to give the distribution of individual species or woodland types to which are assigned appropriate uptake figures, usually derived from literature values. Combining the information within a Geographical Information System (GIS) allows the mass balance equation to be solved for map units ranging from 1 km squares to 150 km squares. The relative simplicity of the Level 1 approach and generally low data requirements have distinct advantages for regional mapping of critical loads compared to the more 'data hungry' dynamic models particularly at large scales of application. It should be noted however, that whilst availability of GIS and related data manipulation techniques make the Level 1 approach attractive as a management tool at the small catchment scale (1 to 5 km^2 in area), the resolution of the available data becomes the limiting factor in the interpretation of sensitive or exceeded areas. For catchments of this scale, the spatial resolution of the data must be high and downscaling from national maps can give misleading results (Jenkins *et al.*, in press).

The relative simplicity of the Level 1 approach means that they are limited in the information they can provide, since they can only identify sensitive areas and critical loads exceedance but can give no indication of the timescales involved. This is important as systems are dynamic and show different rates of response to changes in deposition. Thus while a future deposition scenario might not result in exceedance of the critical load for particular terrestrial and freshwater ecosystems within a grid square, the rates of recovery might be vastly different.

3.3 Regional Modelling

Progress has already been made towards the regionalization of dynamic models. MAGIC was originally designed for application at the catchment scale and has been extensively applied to sites in America and Europe (Macmillan and Ferrier 1994, Whitehead *et al.*, 1993, Waters and Jenkins 1992, Forti *et al.*, 1994, Jenkins *et al.*, 1997). It has been used to describe, for specific research catchments, the historical onset of acidification in response to increasing acid deposition and to predict future trends in soil and stream water chemistry following a variety of proposed sulphur emission reduction protocols. Site specific applications are concerned with quantification of impacts at a specific location. However, there is now interest in having the capability to assess the future behaviour of surface waters for a whole region, the statistics for which are extremely useful for supporting policy decisions (e.g. in determining the percentage of streams likely to recover under a given deposition scenario).

Two methods of up-scaling the MAGIC model for regional application have been developed (Sefton and Jenkins 1998). The first is a multiple site approach where numerous sites in a region are calibrated and impacts assessed for a particular site or for a whole region. The disadvantage of this method is the intensive data requirements. This methodology has been used in applications in Scotland (Wright *et al.*, 1994). The second method is the use of Monte Carlo techniques whereby input variables are defined as frequency distributions based on observed data describing the region as a whole. This is achieved by defining frequency distributions of spatially variable parameters based upon observed deposition, stream and catchment data across the region. For each of numerous model runs, input parameters are sampled from the distributions and output parameters collected to construct frequency distributions of stream chemistry. This method has been used in Norway and Wales (Hornberger *et al.*, 1989, Jenkins *et al.*, 1990). This approach is limited in that impacts cannot be assessed for a specific location in the region. Rather the results must be interpreted as a shift in the frequency distribution of the model output, be that stream water chemistry or critical load exceedance.

A third approach has been used for the SMART model for predicting the chemical response of European forest soils to changes in atmospheric acid inputs (de Vries *et al.*,1994). The model is limited to key processes which are represented in a simplified manner (Table 3.3) with the intention of utilizing data available at regional scales rather than requiring a host of detailed information only found at well instrumented sites. Even with these simplifications, it was necessary to use 'transfer functions' to derive some model input parameters from available regional data sets. Unfortunately, uncertainties involving initial values for some soil

Table 3.3 The processes and process descriptions included in the SMART model (after deVries *et al.*, 1994).

Process	Element	Process description
Rate limited reactions		
Growth uptake	Divalent base cations, ammonium, nitrate	Constant growth
Nitrogen immobilization	Ammonium, nitrate	Proportional to nitrogen deposition
Nitrification	Ammonium, nitrate	Proportional to net ammonium input
Denitrification	Nitrate	Proportional to net nitrate input
Silicate weathering	Aluminium, divalent base cations	Zero order reaction
Equilibrium reactions		
Dissociation / association	Bicarbonate	Carbon dioxide equilibrium equation
Carbonate weathering	Divalent base cations	Carbonate equilibrium equation
Aluminium hydroxide weathering	Aluminium	Gibbsite equilibrium
Cation exchange	Protons, aluminium, divalent base cations	Gaines-Thomas equation

parameters (C/N ratio, soil base saturation) and the weakness of the description of nitrogen dynamics had a major influence on the model predictions.

The additional information gained from dynamic as opposed to steady-state models means that efforts to develop regional applications of dynamic models must continue. The 'quality' of regional predictions compared to site specific applications will be compromised by the lack of data at the appropriate scale. However the use of statistical techniques or the development of transfer functions offers real possibilities for meaningful regionalized dynamic modelling of critical loads and critical load exceedance.

4. PREDICTING THE BIOLOGICAL RESPONSE TO ACIDIFICATION

4.1 Key chemical criteria

The critical loads concept requires the identification of a critical chemical indicator which can be related both to deposition loading and to organism response within the ecosystem. The concept of a critical base cation to aluminium ratio in the soil solution as the critical chemical indicator has been widely used for terrestrial ecosystems within Europe (Posch *et al.,* 1995) whilst a value of the Acid Neutralizing Capacity (ANC) of zero has been used for freshwaters (CLAG 1994).

4.1.1 The base cation to aluminium ratio

The approach most widely used to determine a critical chemical criterion value for the critical load of soil acidity is that linking soil chemical status and plant response via a critical molar base cation to aluminium ratio ($((Ca+Mg+K)/Al_{crit})$ in the soil solution (UNECE 1996). This approach arises mainly from experimental data which have shown that the toxic effects of aluminium on tree roots can be offset to some degree by the presence of base cations in the soil solution (Rengel 1992). The approach was formally developed by Sverdrup and Warfvinge (1993a) and critical values covering a wide range of plant species are reported for a reduction in root growth to 80% of 'normal' under laboratory conditions (Sverdrup and Warfvinge 1993a). The soil solution base cation to aluminium ratio is output either directly or may be calculated as a time series for dynamic acidification models such as MAGIC and SAFE, so that critical loads can be assessed in relation to the transgression of specified values of $(Ca+Mg+K)/Al_{crit}$ for the plants of interest.

Although widely used in European critical loads mapping, the base cation to aluminium ratio response function is not universally accepted and has been subject to some criticism (Hogberg and Jensen 1994; Lokke *et al.*, 1996). In a recent review, Cronan and Grigal (1995) concluded that the calcium to aluminium ratio could provide a useful ecological indicator of "the approximate thresholds beyond which the risk of forest damage from aluminium stress and nutrient imbalances increases". They recommend a more conservative approach compared to that of Sverdrup and colleagues, and suggest that other complementary indicators (e.g. soil base saturation less than 15% of the effective cation exchange capacity) should be used to corroborate observations of calcium to aluminium ratios. Lokke *et al.* (1996) go further, suggesting that the general use of a fixed value for $(Ca+Mg+K)/Al_{crit}$ (usually 1) is not appropriate since base cation to aluminium ratios vary considerably in time and space. They suggest that other indicators, for example ground layer plant species, mycorrizal fungi and soil animals might be considered as alternatives. Nevertheless, no critical threshold has been advanced to replace the BC/Al ratio and so this must be considered the standard approach.

4.1.2 Critical chemical criteria for freshwater

The approach most widely adopted in Europe has been to relate the presence / absence of a selected indicator species to stream or lake water ANC. Whilst the choice of indicator species is subject to debate, brown trout, a fish of major economic and conservation importance, has so far mainly been used. This partly reflects the historical development of the critical loads approach for freshwaters which was based primarily on Scandinavian data (Henriksen *et al.*, 1992). From Scandinavian lakes it was shown that few brown trout populations were damaged where ANC values exceeded 20 :eq l^{-1} but there were no fish present where the ANC was less than -40 :eq l^{-1}. At ANC = 0 :eq l^{-1} there was a 50% chance that brown trout would be present, a finding confirmed by analysis of Welsh regional data (Ormerod 1993).

Brown trout are only one of a number of biological indicators of ecosystem health with respect to acidity. Data from a regional survey of acid streams in Wales showed statistically significant increases in the taxon richness and abundance of stream invertebrates with ANC. An ANC value of 35 :eq l^{-1} was identified as a threshold below which the probability of the occurrence of dippers was significantly reduced and breeding performance was significantly impaired (Ormerod 1993).

Because diatoms are amongst the most sensitive organisms to acid stress, they have been widely used in lake sediments to indicate the onset of acidification i.e. the point at which the critical load was exceeded (Battarbee *et al.*, 1988). Detailed examination of cores from lake beds in the UK has shown that the degree of lake acidification (critical load exceedance) can be related to the calcium content of the water and the sulphur deposition to the site (CLAG 1995). This has allowed a dose-response curve to be developed to predict the acidification status or degree of critical load exceedance for UK freshwaters.

The difference in threshold ANC values for sustaining populations of brown trout and dippers highlights an important problem with threshold chemical criteria set with respect to one organism. Unless the most sensitive component of the ecosystem is selected, damage may occur within the ecosystem before the chosen chemical criterion is transgressed. One solution to this might be to look at community responses rather than single species. Data from the Welsh Acid Waters Survey provide a useful example of this approach in which the biological character of 99 stream sites in four arbitrary classes of ANC (between -250 to 400 :eq l^{-1}) was assessed (Table 4.1). The species richness of mayflies, caddis larvae and total invertebrates all varied significantly between the classes, as did the density of brown trout. In nearly all cases there was a progressive gradation in biological character between classes rather than a step

Table 4.1 Variation with mean ANC of taxon richness of invertebrates and density of brown trout at sites in upland Wales. The values are means (with standard deviation).

ANC category (:eq l^{-1})	Mayflies	Stoneflies	Caddis	All taxa	Trout density
-200 to -50	0 (0)	6.2 (1.2)	3.3 (2.1)	16.2 (4.4)	0.73 (0.5)
-50 to 0	0.5 (1.0)	7.3 (1.9)	4.1 (3.2)	21.6 (9.8)	11.0 (0.8)
0 to 50	1.3 (1.4)	6.9 (1.4)	4.3 (2.4)	27.2 (8.3)	24.3 (0.6)
50 to 450	3.4 (2.2)	7.7 (2.4)	7.1 (5.3)	33.6 (15.3)	39.2 (0.7)

change at any given value of ANC (e.g. ANC=0). Nevertheless, these patterns suggested that biological benefits would accrue from an increase in ANC values from negative to positive.

This analysis is an example of a 'top down' approach to defining critical chemical criteria, in which given chemical values are stipulated and biological characteristics relative to stipulated conditions are assessed. Hence on the basis of fish data we might decide some value of ANC is important (e.g. ANC=0) then determine whether other biological features may or may not be protected.

An alternative is to use a 'bottom up' approach, in which important biological characteristic are first recognized and the chemical conditions required to maintain them are determined. The biological characteristic might be the presence of a species of economic or conservation importance. In the Welsh data set, biological features were related to ANC using regression analysis and the methods described in Ormerod (1995). The taxon richness of mayflies, caddis and all invertebrates increased significantly in each case with ANC (Table 4.2). Thus, for any given ANC, the average number of taxa could be predicted, so that, for example streams with ANC = 0 :eq l^{-1} would on average have 14 fish per100m^2, and at ANC = 40 they would have

Table 4.2 Regression relationships (y=a+b.ANC) between biological characteristics and ANC for Upland Welsh streams.

Parameter	a	b
Mayfly species	1.12	0.017
Caddis species	4.49	0.016
Total taxon richness	24.5	0.074
Trout density	1.18	0.004

24 fish per $100m^2$. This relationship may be inverted so that mean ANC for a given fish density may be determined. An example of the predictive modelling approach is given in Ormerod (1995).

4.2 Response curves

The concept of the critical chemical threshold at which damage to selected ecosystem components can be expected is the cornerstone of ecosystem based emission reduction strategies. The approach is limited in that it gives no idea as to the timescale of the response. For this to be assessed, a dose-response relationship is required.

4.2.1 Response curves for terrestrial systems

The reduction in vegetation growth over time in response to changing base cation to aluminium ratios in the soil solution can also be modelled dynamically using a damage function developed by Sverdrup and Warfvinge (1993a). The damage function uses an ion exchange model to simulate the interaction between base cations and aluminium at the root surface. The ion exchange model is linked to the root damage function via an experimentally determined coefficient (K). Several ion exchange models are available including Gaines-Thomas, Gapon, Vanselow and Unspecific. Of the vegetation species reviewed by Sverdrup and Warfvinge (1993a), the Vanselow and Unspecific models account for the majority of reaction types at plant root surfaces. The details of the model derivations and experimental data used to formulate the damage functions are contained in Sverdrup and Warfvinge (1993a). In summary, the Vanselow model assumes that the root ion exchange matrix is a polydentate, valence specific substrate. Thus for example, three divalent base cations or two aluminium ions can be linked to a hexavalent binding site by double bonds. This means that during the reaction some re-arrangement of the solid phase is required to accommodate the arrangement of binding sites. The damage function (f(BC/Al)) is expressed as:

$$f(BC/Al) = ([BC^{2+}] \, . \, (BC/Al)^2) \, / \, ([BC^{2+}] \, . \, (BC/Al)^2 + Kv) \qquad (4.1)$$

where:

$[BC^{2+}]$ = molar concentration of divalent base cations
(BC/Al) = molar base cation to aluminium ratio
Kv = response coefficient for Vanselow model

In the Unspecific ion exchange model, the reaction is defined as valence unspecific, i.e. the ion exchange matrix is indifferent to the valence of the adsorbing ions and the matrix behaves as a continuum of receptor sites. This implies that when an aluminium ion exchanges for a divalent base cation, the difference in charge is adjusted for by some as yet unknown process. The damage function using the Unspecific model is expressed as:

$$f(BC/Al) = (BC/Al) / ((BC/Al) + Kus) \qquad (4.2)$$

where:

Kus = response coefficient for the Unspecific model

The effect on plant growth is calculated by Sverdrup and Warfvinge (1993b) as a percentage reduction (G) relative to 'normal' growth using the following equations for the Vanselow (4.3) and Unspecific (4.4) ion exchange models :

$$G = 3\ x(uptake)_I\ .\ 100\ .\ ([BC^{2+}]_I\ .\ (BC/Al)_i^2) / ([BC^{2+}]_I\ .\ (BC/Al)_i^2 + Kv) \qquad (4.3)$$

$$G = 3\ x(uptake)_I\ .\ 100\ .\ (BC/Al)_I / ((BC/Al)_I + Kus) \qquad (4.4)$$

where:

$x(uptake)_I$ = the fraction of uptake in soil layer I
$[BC^{2+}]_I$ = molar concentration of divalent base cations in soil layer I
$(BC/Al)_I$ = molar base cation to aluminium ratio in soil layer I

Reaction types and K values for plant species typical of acid upland grassland are shown in Table 4.3.

Table 4.3 Reaction types and Kus values for plant species commonly occurring in acid grassland swards.

Plant species	Reaction type	Kus value	$(Ca+Mg+K)/Al_{crit}$
Juncus squarrosus	Unspecific	0.08	0.3
Deschampsia flexuosa	Unspecific	0.13	0.5
Agrostis capillaris	Unspecific	0.2	1.0
Calluna sp.	Unspecific	0.2	0.8
Holcus lanatus	Unspecific	1.5	8.0

The species in Table 4.3 cover a range of responses (K values range between 0.08 and 1.5) and hence susceptibilities to growth effects as a result of changes in $(Ca+Mg+K)/Al_{crit}$ ratio.

The growth response equations in Table 4.3 have been used in conjunction with output from an application of the SAFE model to a part of the Plynlimon catchments (Reynolds, in press). For the majority of species the predicted growth rate reductions were small following an increase in acid deposition from the mid nineteenth century. The largest growth rate reductions were shown by *Holcus lanatus* where growth declined to about 77% of 'normal' between 1960 and 1970 when acid inputs were at their peak and the soil solution base cation to aluminium ratios were at their lowest. Good recovery to circa 90% of normal growth was predicted as soil water conditions ameliorated following a decline in acid inputs in line with the requirements of the Second Sulphur Protocol.

In principle, therefore, these damage functions can be used either at specific sites or regionally provided predictions of the temporal change in base cation to aluminium ratio in the rooting zone are available and the distribution of plant species is known. Indeed these relationships have already been used to predict the effects of acidification on forest growth in Sweden and to assess the economic implications of growth reductions (Sverdrup *et al.,* 1994). As with all model assessments, the short comings of the techniques must be recognized. The damage functions relating acidification and growth are defined under controlled laboratory conditions, and uncertainties always surround extrapolation of such data to the field situation. The model does not include the anticipated effects of secondary stress factors such as changes in tolerance to frost or drought, nor does it allow for other chemical interactions, for example between aluminium and phosphorus. Sverdrup and Warfvinge (1993a) also point out that there are considerable uncertainties surrounding some of the data used to define the growth relationships.

In view of its central role in critical loads methodology as the link between predicted soil chemistry and plant response (UNECE 1996), it is important that further work should be undertaken to evaluate the $(Ca+Mg+K)/Al_{crit}$ concept. This will require a considerable field effort to determine the critical load, exceedance and degree of damage to the biota at a range of sites. At present, it would seem best, to treat predictions of growth response with caution, as being indicative of likely responses and for comparing responses between species of different 'acid' tolerance.

4.2.2 Response curves for aquatic ecosystems

Empirical models to predict the biological response of freshwater ecosystems to changes in stream acidity have also been developed of which the trout survival and trout density models developed by Ormerod *et al.* (1988) provide good examples. The survival model is based on empirical data from field toxicity trials and predicts a 50 day lethal toxicity (LT50) from a linear regression equation incorporating aluminium concentration:

$$\text{LT50 Days} = 22.2 - 36.2(\text{Al mgl}^{-1}) \qquad (4.5)$$

The trout density model was based on data from 88 Welsh upland streams and relates fish density to filterable aluminium concentration (mgl^{-1}) and total hardness (mgl^{-1} $CaCO_3$):

$$\text{Log}_{10}\,\text{trout density} = -1.69 - 1.58\log(\text{Al}) + 1.13\log(\text{Hardness}) \qquad (4.6)$$

The regression equation 4.6 explained 53% of the variance in the trout density data, and modifications are planned for the model to incorporate other factors such as river habitat characteristics to improve its predictive power (Stevens *et al.*, 1997).

Two important problems have been identified with the application of biological models to assess responses to reductions in acidity (CLAG 1995). The first of these is biological hysteresis in the observed response of biological communities to an improvement in water quality. Following liming of streams at Llyn Brianne there has been no substantial increase in taxon richness even though adequate chemical conditions have been sustained for over five years (Rundle *et al.*, 1995). Factors inhibiting biological recovery may include competition with surviving indigenous fauna, inappropriate food or habitat resources or the inability of colonists to locate the manipulated streams. Whatever the reason, such lag effects are not included in biological models and cause uncertainty in the predictions of biological recovery following reductions in acid deposition (CLAG 1995). The second problem is that of predicting biological change for chemical conditions which lie outside the calibration range of the models. It seems likely that reductions in acid deposition will lead to stream waters which are base poor with moderate pH and low aluminium concentrations (Ormerod *et al.*, 1988; 1990). Such waters were not included in the model calibrations as they are relatively rare in Britain, since acidification has tended to increase base cation concentrations through accelerated leaching whilst ANC has declined (CLAG 1995).

4.3 Effects of acid episodes

So far the models developed for predicting the biological response to acidification in aquatic systems rely on empirical data from experiments and surveys which provide an assessment under ‘average’ conditions. Episodic acidification of surface waters is recognized as causing significant stress and an increased mortality to aquatic organisms. It is currently believed that transient increases in acidity and in the concentration of aluminium, coupled with decreases in calcium concentrations are the major factors determining the biological response to acidic episodes (Baker *et al.*, 1990).

The topic of acid episodes has been examined in some detail in a number of review papers (Kahl *et al.*, 1992; Wigington *et al.*, 1992; Davies *et al.*, 1992) from which it is clear that the factors controlling episodic acidification are complex as they involve interactions between a number of processes. Episodic changes in stream chemistry are ubiquitous, but the degree of chemical change varies because of a number of factors (Wigington *et al.*, 1992). Acid episodes are not symptomatic of chronic acidification. However, the degree to which the catchment is chronically acidified is a factor which determines the severity of the pH depressions and increase in aluminium concentrations. In these circumstances, the catchment becomes conditioned by an increase in the quantity of hydrogen ions and aluminium available for transport during storm events. Baseflow ANC may also be reduced so that lower minimum ANCs are observed during events. With the exception of so called ‘sea-salt’ events, when Na in rainwater exchanges for H^+ on soil exchange sites, initiated by large inputs of neutral salts, a direct influence of rainfall composition on episodic stream chemistry is rarely observed. The result is an acidification of the soil solution and surface waters. Between events, soil exchangeable acidity will be replenished on the cation exchange sites by weathering and exchange reactions initiated by proton donors in the soil. Thus sea-salt events are a transient water quality problem not necessarily linked to soil acidification (Hendershot *et al.*, 1991).

Antecedent hydrological conditions are important in the short-term for determining the chemical availability of sulphate and nitrate during episodes. Freeze-thaw (Edwards *et al.*, 1986), wetting and drying cycles (Reynolds *et al.*, 1992) and seasonality are all important factors governing nitrate response. For sulphate, the duration of dry periods prior to rainfall can be significant (Davies *et al.*, 1992). Antecedent conditions are also important for determining hydrological pathways through and from catchment soils to the stream. The pre-event soil moisture status will be a major factor in determining the major flow routes. In turn, the flow paths taken by storm waters will determine to a large extent what chemical changes occur as water migrates from the soil to the stream (Wigington *et al.*, 1992).

An understanding of flow paths and storm flow generation in catchments is vital to the modelling and prediction of stormflow chemical responses in streams and was identified as priority for research in a review by Davies *et al.* (1992). Modelling approaches to episodic acidification have used physically based runoff models and end member mixing models (Neal *et al.*, 1992, Neal *et al.*, 1990b; Robson and Neal 1990). Mixing models are a technique for exploring the relative contributions of different water sources to streamflow during storm events. In the simplest case, the mixing relationships between two source waters of contrasting chemistry (end members), for example acidic surface soil water and base-rich, alkaline groundwater are modelled. A 'conservative' tracer is used which clearly distinguishes the two water types, such that the concentration of the tracer in the resultant mixture can be calculated as the volume-weighted average of the tracer concentrations in the two source waters. Using ANC as the tracer, this approach has been linked to the MAGIC model to predict future episodic acidification responses for the moorland upper Wye catchment under different acid deposition regimes (Neal *et al.*, 1992).

The modelling approach adopted by Neal *et al.* (1992) can also link to the evaluation of critical loads for freshwaters through the development of duration curves and frequency diagrams for aluminium and hydrogen ion concentrations. This provides an alternative means of estimating critical loads for moving waters to that provided by steady-state modelling.

The separation of the biological effects of acid episodes from those of chronic acidification has proved a perplexing problem for biologists (Reynolds and Ormerod 1993). The difficulties arise because episodic changes are largely a characteristic of surface waters which have relatively low ANC, and hence are also subject to chronic change. Further difficulties arise because there has been a tendency to see acid episodes as toxicological phenomena, causing lethal and sub-lethal responses in individual organisms. This is in contrast to their being seen and understood as ecological phenomena, effecting biological change at the population or community level. Ormerod and Jenkins (1994) have concluded that there was a dearth of general and systematic data on factors influencing the amplitude, duration, frequency and peak concentrations of hydrogen ions or aluminium during episodes. Moreover, whilst there was evidence that fish kills can occur following episodes, and there was experimental evidence of impacts on invertebrates, the real biological impacts of episodes could not be quantified because:

i) biological systems vary in their response to episodes at different levels of organization (individual, species, population, community);

ii) data available on the impacts of episodes have involved either experiments (and hence artefacts) or field data (which lack control, precision and cause-effect knowledge)

iii) biological impacts have been seen largely as ecotoxicological phenomena affecting individuals, rather than ecological phenomena affecting populations or communities;

iv) the effects of single episodes, multiple episodes and chronic acidification are difficult to separate under real field conditions; in particular, spatial trends in mean pH and aluminium concentration are just as strong a correlate with biological status as are measures of episodicity.

At present, the lack of understanding of the biological response to acid episodes adds uncertainty to critical loads assessments and modelling predictions.

5. CRITICAL LOADS FOR PEATS

Critical loads of acidity for mineral soils are set to prevent the depletion of the reserve of exchangeable base cations in the long-term. For this to occur, the supply of base cations to the soil, primarily from mineral weathering and atmospheric deposition must balance base cation depletion by leaching due to acid rain and losses from crop removal (forest harvesting, grazing etc.). A shortcoming of this approach is that it cannot be applied to highly organic ombrotrophic peat soils which, by definition (Clymo 1984), rely solely on atmospheric deposition for their water and nutrient supply. In the absence of a supply of base cations from weathering, alternative approaches to setting critical loads are therefore required. The application of techniques used for mineral soils would result in zero or negative critical loads implying that acidification due to acid deposition was occurring even in areas with background inputs. The purpose of this chapter is to review the current application of the critical loads concept to peats and to assess the options available for dynamic modelling of peat acidification and critical loads. This will be prefaced by a brief introduction to the hydrological and hydrochemical functioning of peats.

5.1 Background

5.1.1 Nomenclature

Peatlands are defined by Burton and Hodgson (1987) as all mire forms, whether actively forming or drained, that retain at least 40 cm thickness of peat material. A number of systems have been developed to classify the range of peatlands occurring in nature, including those based on ecological criteria (Bellamy 1968; Gilman 1994), plant communities (Rodwell 1991) and environmental factors such as hydrology and hydrochemistry (Heathwaite *et al.,* 1993). As a result, confusion tends to arise among non-specialists because different classification terms may be interchanged in the literature to reflect different characteristics of the system under discussion. From the point of view of acid deposition effects, the most sensitive peats are those which depend on rainfall for mineral nutrients and water supply. Such peats are classified as ombrotrophic (Clymo 1984). Because ombrotrophic peats have soil or drainage waters either with a low nutrient and calcium content and / or a high humic acid content they may also be referred to respectively as oligotrophic (low nutrient) or dystrophic (high humic content) peats (Heathwaite *et al.*, 1993).

5.1.2 Peat structure and hydrology

The structure and hence hydrological characteristics of peats are important in determining their chemical response to acid deposition and the related effects on drainage water chemistry. Over time, established peat deposits become differentiated into two morphologically and functionally distinct layers; the acrotelm and the catatelm (Ivanov 1981). The acrotelm, which is the upper layer, is defined by the depth to which the water table falls during a dry summer. In the UK, this is typically 100-150 mm below the surface. The acrotelm has a relatively high hydraulic conductivity and is a zone of intensive gas exchange with the atmosphere. It is therefore the hydrologically, chemically and biologically active part of the peat and is the focus of research into acidification effects and critical loads (Skeffington *et al.*, 1995). The catatelm is the lower peat layer and consists of relatively uniform, more compressed peat which has a low hydraulic conductivity and remains waterlogged throughout the year. An important hydrological feature of peats is the extent to which the water table fluctuates throughout the year as this has a major effect on chemical processes affected by redox status. The shift from aerobic conditions to anaerobic in saturated peats has a major influence on the fate of nitrogen and sulphur compounds with direct implications for peat acidity.

5.1.3 Chemical processes affecting peat acidity

Ombrotrophic peats are widespread in the wetter, upland parts of western Europe where low temperatures and waterlogged conditions inhibit organic matter decomposition. The net result of the complex series of breakdown processes occurring in peats is the production of acidic 'humic substances'. The acidity of these compounds arises from the attached carboxyl and phenolic hydroxyl functional groups. Humic substances derived from peats typically have about double the carboxyl content compared to the quantity of phenolic hydroxyl groups present (Thurman 1985). The carboxyl groups are more acid with pKa values between 2.5 and 4.5 (Tipping and Hurley 1988; Tipping *et al.*, 1990 whilst the phenolic groups are very weakly acidic and typically have pKa values in excess of 7 (Thurman 1985). Therefore, in the absence of complexing agents and metallic cations, the carboxyl functional groups will maintain peat pH values at or below 4. The negative charge on dissociated hydroxyl groups gives peat a cation exchange capacity which, because it relies on the dissociation of hydroxyl groups, is pH dependent. This exchange complex is dominated by hydrogen ions in most peats, except those receiving drainage from mineral soils or groundwater inputs (soligenous mires). In ombrotrophic peats the presence of metallic cations on the exchange complex will be regulated in the long-term by the composition of the rainfall. Ombrotrophic peats will acidify naturally due to the uptake of cations by plants in exchange for hydrogen ions and because of organic acid production arising from the incomplete decomposition of organic matter (McKnight *et al.*, 1985).

The role of the nitrogen cycle in acidification has already been described in outline in Section 2.6. Within peats, the functioning of the nitrogen cycle is controlled to a large extent by the redox conditions which are themselves determined by whether the peat is waterlogged or not. When peat soils are saturated and hence anaerobic, the processes of mineralization (ammonification) and nitrification proceed at much slower rates. Indeed, nitrification may be completely inhibited as the nitrifying bacteria cannot live under anaerobic conditions. Mineralization will proceed more slowly under anaerobic conditions because there are fewer anaerobic decomposers than aerobic ones (Ross 1995). Anaerobic decomposers have a much lower nitrogen immobilisation requirement, however, so that a more rapid release of ammonium occurs than would be anticipated given the relatively low mineralization rates. This often results in a build up of ammonium in the peat accompanied by a small pH increase. The rhizosphere of aerochymous plants, which transfer oxygen via the plant and diffuse it through the roots, can become aerobic microsites where mineralization and nitrification proceed despite the anaerobic status of the bulk peat.

The other nitrogen transformation of importance in peats is denitrification which is the anaerobic, microbially mediated conversion of nitrate to nitrous oxide at pH values <6, or to nitrogen gas at higher pH values (Koskinen and Keeney 1982). Again, water table height is a major control as denitrification rates decline significantly as peats dry out and become aerobic (Freeman *et al.,* 1997). The significance for the peat acidity balance is that denitrification, being a reducing reaction is an alkalinization process (van Breemen *et al.*, 1984).

Peats retain a large store of organic nitrogen which is effectively removed from the nitrogen cycle. Reasons for this are firstly the very low mineralization rates of organic matter and mineral nutrients and secondly, the high C:N ratios of peat which stimulate microbial activity causing microbial immobilisation of nitrogen until the system becomes nitrogen limited (Damman 1988). Nitrogen immobilisation will predominate provided the C:N ratio is greater than 25, below 25 nitrogen mineralization and release is observed (Dowding 1974).

Sulphur transformations are the other major suite of processes which influence the acid-base balance of peats. Dissimilatory reduction of sulphate is a microbially mediated process occurring under waterlogged conditions in which sulphates are reduced to sulphides. Sulphide formation is an alkalinization process leading to the precipitation of iron sulphide (pyrite) or generation of hydrogen sulphide gas if iron is lacking. Under aerobic conditions, sulphides are oxidised to sulphates, a process which generates acidity.

5.2 Response of peats to acid deposition

The ecological effects of acid deposition on peats has been and still remains one of the major neglected areas of acid deposition research (Goreham *et al.*, 1984; Skeffington *et al.*, 1995) and debate continues as to whether acid deposition to peatlands can lead to long-term cation depletion (Ross 1995). The response of peats to acidic inputs is complex involving a suite of processes which determine the sinks and sources of acidity in the system. These include ion exchange, sulphate reduction (Brown 1986) and nitrate assimilation (Yesmin *et al.,* 1996a).

Laboratory evidence for the acidification of dystrophic peats in response to acid rain has come from experiments in Scotland which indicated that laboratory treatment of peats with 'acid rain' solutions increased leaching of base cations as would be anticipated from ion exchange theory (Skiba *et al.*, 1989). Further experiments suggested that the pH of peat had generally declined by about 0.5 units as a result of acid deposition, leading to a drop of 1.1 units in drainage water pH (Skiba and Cresser 1989). The laboratory work was extended into the field by comparing peat pH and base saturation with atmospheric deposition at 123 sites in Scotland. The results showed a regional association of lower base saturation peats with areas of high acid deposition (Skiba *et al.*, 1989). Although statistically significant, the correlations between acidic inputs, pH and base saturation were weak; 5% of the variation in peat pH and 35% of the variation in base saturation was explained by variations in acid deposition (Skeffington *et al.*, 1995). A difference of about 0.55 pH units was observed between areas of highest and lowest acid deposition. From subsequent experiments in which peat samples were equilibrated with solutions containing differing concentrations of calcium, magnesium and hydrogen ions, Smith *et al.* (1993) concluded that the concentrations of calcium and hydrogen ions in incoming rainfall were the predominant influences on the equilibrium pH of the surface layers of dystrophic peats. Thus the authors concluded that one of the major effects of acid deposition on dystrophic peats would be acidification measured as a downward shift in equilibrium peat pH.

In a critique of the Aberdeen experiments, Skeffington *et al.* (1995) pointed out several weaknesses in the approach. In particular, they were critical about of a laboratory equilibration study which included centrifugation, as this may have led to disruption of the peat structure and exposure of new exchange sites. Following experimental work using intact cores, Wilson *et al.* (1995) found that peats did not equilibrate with applied rain solutions. Even if simple ion exchange behaviour was assumed, they concluded that the change in peat chemistry would be very slow because the pool of exchangeable hydrogen ions was very large compared to the atmospheric hydrogen ion flux. The results showed that the response of peat to acid rain was complicated by internal processes affecting the sources and sinks of acidity. There was significant sulphate retention in the higher sulphate treatments which was ascribed to sulphate reduction to hydrogen or iron sulphides, reflecting earlier laboratory (Brown 1986) and field manipulation studies (Urban and Bayley 1986). All the added nitrate was retained whilst there was a net release of ammonium ions. The nitrogen results were in many respects similar to those of Sanger *et al.* (1996) who were also using peat cores and monoliths and who concluded that nitrate retention provided a possible ameliorating mechanism against the acidifying effects of nitrogen deposition.

5.2.1 Ecological responses

The nature of peats and hence their chemical characteristics differ considerably depending on the vegetation from which they were formed and the degree of humification. It follows therefore that any changes in the chemistry of the acrotelm which feedback to the ecosystem as a whole through changes in decomposition rates, nutrient availability and plant species composition, will have a direct influence on future chemical responses. Earlier work on ecological effects of acid deposition on peats concentrated on the exposure of peats to aerially deposited sulphur dioxide. Lee and co-workers demonstrated a number of effects including loss of certain sensitive *Sphagnum* species from peats in the southern Pennines (Ferguson and Lee 1983). Nitrogen deposition may now be responsible for the continuing absence of these species (Lee *et al.*, 1987; Woodin and Farmer 1993) and for the increase in grass cover on otherwise heather dominated peatlands (Yesmin *et al.*, 1996a). In a series of experiments, workers at the University of Aberdeen have also identified a variety of ecological responses to acid deposition including changes to enchytraeid worm populations (Yesmin *et al.*, 1995), damage to mycorrhizae associated with *Calluna* (Yesmin *et al.*, 1996b) and a reduction in decomposition rates (Sanger *et al.*, 1994).

5.3 Steady-state critical loads for dystrophic peats

The method currently used in the UK to calculate the critical load of acidity for dystrophic peats is that developed at Aberdeen University and described by Smith *et al.* (1993). The method relies heavily on the early work described in Section 5.2 and on the assumption that peats behave as a simple ion exchange surface. The basis of the method is a suite of functions relating peat pH to rain pH and calcium concentration. The data for the functions comes from laboratory equilibration studies of peat samples from Glendye in Scotland with solutions containing a range of calcium and hydrogen ion concentrations (Smith 1993). For a given grid square, the functions are used to calculate the pH of peat under pre-industrial (pristine) conditions assuming that pre-industrial rainfall had a pH of 5 and a calcium concentration the same as present day. To do this a simple regression relationship (developed from the experimental data) between peat pH and calcium content at an equilibrating solution (rain) pH of 5 is used. Before solving for pristine peat pH, the calcium concentration in the rainfall for the grid square is adjusted to give an 'effective' calcium concentration which allows for evapotranspiration effects using grid-based rainfall and runoff data. Having calculated the pristine pH, the hydrogen ion load which would shift the pristine pH downwards by an arbitrary 0.2 units has to be calculated. This hydrogen ion load is the critical load for the peat. To do this, the 'effective' rain pH (i.e. rainfall pH adjusted for the effects of evapotranspiration) required to achieve the critical peat pH (pristine pH-0.2 pH units) is calculated from a regression equation relating 'effective' rain pH to peat pH for the 'effective' rainfall calcium concentration of the given grid square. The hydrogen ion load (critical load) is calculated by multiplying the rain pH (back corrected from the 'effective' rain pH) by the rainfall volume for the grid square.

As discussed earlier the Aberdeen method has been criticised in a number of respects by Skeffington *et al.* (1995). The calibration equations relating peat pH, rainfall pH and calcium concentration are derived from a single site. Peats differ in their chemical response depending on the vegetation from which they were formed and the degree of humification. Climatic and land use factors are important. The assumed pristine rainfall conditions are also in doubt, although pre-industrial rainfall pH values are thought to have been c. pH 5.0 (Charlson and Rodhe 1982). There is rather more uncertainty about pre-industrial rainfall calcium concentrations which were probably lower in the absence of widespread intensive agriculture (lime spreading), quarrying and industrial processes. The equilibration procedure includes an initial stage in which the peats are pre-washed with artificial rain at pH 4.0 thereby losing information about the equilibrium relationships of the natural peat. Perhaps the most significant point of debate is the choice of a pH decline of 0.2 units as the criterion for damage. The justification for this in the original methodology is not clear (Smith 1993), being loosely based around observations of declines in surface water pH and effects on *Calluna* growth. The criterion is proposed as provisional and indicative of a level of peat acidification unlikely to cause significant damage (Smith 1993; Smith *et al.,* 1995).

Despite the drawbacks to the Aberdeen method, it remains the only attempt at setting a critical load for dystrophic peats beyond the European practice of placing peats into the lowest critical load class. As yet, Skeffington and co-workers have not published an alternative method although they suggest that a better approach might be to base the critical load on a specified decrease in base saturation, taking account of other processes which generate or consume acidity.

5.4 Setting a biological indicator for acidification damage

One of the current uncertainties in setting critical loads for dystrophic peats is the whole issue of what constitutes damage and the choice of a suitable biological indicator which can be related to chemical conditions in the peat. Although a wide range of biological responses have been recorded (see Section 5.2.1) the precise relationship between the response of a selected indicator organism and peat acidification remains elusive. Indeed, many of the effects observed, for example those on *Sphagnum* in the south Pennines and north Wales involve an interaction between sulphur acidity and nitrogen supply (Lee *et al.,* 1987; 1988) with the added complication of the nutrient enrichment as well as the acidification effects of nitrogen. The main conclusion to arise from the work so far undertaken is that further investigations into the biological consequences of acid deposition on peat ecosystems is required.

One possibility for a critical chemical criterion is to use an adaptation of the critical base cation to aluminium ratio proposed for mineral soils. A critical molar base cation to hydrogen ion ratio in the soil solution has been provisionally proposed for organic and peat soils in the current UNECE critical loads mapping manual (UNECE 1996). The method is applicable to soils with no aluminium or where the aluminium is masked by high (>100 mgl^{-1}) concentrations of dissolved organic carbon. For deciduous trees and ground vegetation, the values for the critical base cation to hydrogen ion ratio are estimated as $0.3.(Ca+Mg+K)/Al_{crit}$, whilst for conifers the value of $(Ca+Mg+K)/Al_{crit}$ is used. The method is largely untested and requires further investigation (UNECE 1996).

5.5 Towards a dynamic model for peat acidification

It is beyond the scope of this project to develop a dynamic model for peat acidification and critical loads assessment. However a number of basic requirements for such a model can be identified from what is known about the hydrochemical functioning of peats. It would be premature to link a peat acidification model directly to a critical loads assessment given the lack of information on biological targets at the present time. Any peat model development should take account of chemical criteria which might be required in the future. These might include critical values of base saturation, peat pH, and base cation to hydrogen ion ratio in the peat soil solution (calculated from the molar concentrations of divalent base cations, potassium and hydrogen ions), all of which are standard outputs from most acidification models. The following are proposed as a series of basic, conceptual building blocks (sub-models) required in the development of a peat acidification model. It is not intended that this list will be exhaustive nor that the details of the algorithms and precise data requirements will be discussed. The intention is to give a steer to possible future work.

5.5.1 Hydrological submodel

The hydrological behaviour of peats is crucial to their chemistry through interactions between water content and redox conditions (Section 5.1.3). The basic components of the hydrological sub-model would have to include:

- rainfall input (from meteorological data)
- evapotranspiration losses (standard equations e.g. Penman, Thornthwaite + meteorological data)
- Flow through the acrotelm (simple application of Darcy's law, or hydrological mass balance assuming conservative water flow or a small amount of exchange with the catatelm)
- Exchange of water with the catatelm (specified exchange rates which might be modified following intensive research in the literature)
- Stream flow or runoff output

An important component will be to capture the behaviour of the water table through controls on water flows and inputs. The operational time-step of the model will partly determine this. Seasonal fluctuations could perhaps be ignored over an annual time step by defining some form of aggregated behaviour. The feedback to chemical response from this approach would need careful consideration.

Flow through the acrotelm is non-ideal and Darcy's law is not really an adequate representation. Peat acrotelms tend to have lower hydraulic conductivity values than would be anticipated for their high porosities (Baird 1995). This may arise because of pore blocking by colloidal particles or gas bubbles. Furthermore, cracks or natural pipes can increase flow and cause bypassing of the peat matrix. These complexities are still the subject of research and modelling would need to take account of new developments as they arose.

5.5.2 Variable charge exchange surfaces

The hydrochemical model WHAM (Windermere Humic Acid Model; Tipping *et al.* 1995) has been developed to predict for organic soils: (i) the net electrical charge on soil solids as a function of pH, (ii) the non-specific binding of metallic cations and ammonium on humic diffuse layers and (iii) the equilibrium solution concentration of base cations, hydrogen ion and aluminium. The model requires site specific soil data as inputs including measurements of extractable cations and organic matter content together with data from batch titrations. The data are used within WHAM to calculate the soil content of active organic matter i.e. humic and fulvic acids. The model can be used in a variety of ways, including predicting the time taken for equilibrium conditions to be reached for a given input water chemistry. The model has been used to analyse the results from the peat core work by Skeffington and co-workers, and could in principle be used to predict critical loads for peats provided a suitable chemical criterion could be established (Tipping, *pers comm.* 1998).

5.5.3 Redox reactions

These important reactions should be included in any model of peatlands especially for sulphur dynamics. The quantitative importance of nitrogen reactions is more difficult to assess. Most experimental data suggest that peats will retain nitrate and this might best be simulated using a simple first order uptake of all incoming nitrate limited by a C:N ratio of 25. At values above 25, complete nitrate retention is assumed and nitrate leaching commences when the C:N drops below 25. Ammonium is more difficult to simulate, but could be included in the non-specific ion binding sub-model (Section 5.5.2) or it could be assumed that any incoming ammonium is converted to organic nitrogen releasing one equivalent of protons for each equivalent of ammonium. Nitrification may not be quantitatively important if the peats were saturated for most of the year.

5.5.4 Nutrient cycling

Modelling a generalised nutrient cycle for peatland systems is likely to be very difficult given the variety of vegetation types which occur. Semi-natural systems with no or very low grazing are often assumed to be in 'steady state' with respect to nutrient cycling ie uptake into biomass is assumed to be balanced by returns in litterfall and canopy leaching. Thus the net removal of nutrients from the soil-plant system is assumed to be very low and equivalent to the nutrients retained in refractory organic matter i.e. the undecomposed residual of plant remains. In aggrading peats, decomposition rates are very low, so that there will be a net loss of nutrients from the soil-plant cycle. Any development of a peat acidification model would need to assess the quantitative importance of nutrient accumulation into peat and this will vary with vegetation type, land management, climate and pollutant input. Thus factors such nutrient loss through heather burning and accounting for shifts in productivity through vegetation change driven by increased nitrogen decomposition would have to be assessed.

5.5.5 The CHUM model

The CHUM model (CHemistry of the Uplands Model; Tipping 1996) simulates soil-water chemical interactions and water flow in upland catchments. The model is specifically designed to take account of the reaction of inorganic chemical species with solid phase and dissolved organic matter using the equilibrium speciation model WHAM (Section 5.5.2) however it also incorporates simple hydrology and nitrogen dynamics (uptake and nitrification). The model is therefore applicable to peats and can be used to predict peat solution and runoff chemistry. At present it does not include redox reactions for either sulphur or nitrogen although these could probably be developed using the hydrological components of the model to predict saturation and hence redox conditions. The disadvantage of the model for critical loads assessments is that because it is designed for application to individual catchments, it is formulated to run at a daily time-step requiring a considerable amount of data to calibrate the model. The options for regionalization have yet to be considered (Tipping, *pers comm.*, 1998).

5.6 Conclusions

It is apparent from this brief review that critical loads assessments for peats and organic soils are less well developed than for mineral soils. In the UK, peat critical loads are based on a steady-state model developed at Aberdeen University. The weaknesses of the model have been criticised in the scientific literature, but at present no alternative model has been proposed. In relation to dynamic modelling, there have been no model developments specifically aimed at critical loads assessments for peats. The CHUM model is probably unique in its formulation to directly simulate the chemistry of organic soils and offers considerable potential for predicting the response of peat and peat water chemistry to changes in acidic inputs. It is, however, designed for catchment-scale applications requiring considerable input data for calibration.

The major area of weakness in the application of the critical loads concept to peats is establishing critical chemical criteria with a biological meaning. The currently used criterion of a decrease in peat pH by 0.2 units is largely arbitrary and is very loosely justified by the Aberdeen group. The use of a critical base cation to hydrogen ion ratio remains untested. The complexity of peat ecosystems and the interactions between sulphur and nitrogen, both as an acidifying agent and as a nutrient, are likely to make this a difficult issue to resolve without further experimental work.

From the perspective of the Agency's requirements for dynamic modelling of critical loads, considerable research and development work is required before a suitable dynamic model is available. Peats are an extremely important upland ecosystem in relation to catchment hydrology, as a wildlife habitat and for regulating fluxes of solutes and gases in the environment (Hughes and Heathwaite 1995). It is estimated that 90% of the once extensive blanket peatlands of northern and western Britain have been lost so that only 125 000 ha remain (Hughes and Heathwaite 1995). Acid deposition poses a threat to the remaining peatlands so that development of techniques for assessing impacts and setting limits to deposition are urgently required.

6. THE MAGIC MODEL

6.1 Introduction

MAGIC is a long-term, process-oriented, hydrochemical model in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving sulphate sorption, cation exchange, dissolution/precipitation/speciation of aluminium and dissolution/ precipitation of inorganic carbon. The flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff. Fluxes to and from a pool of exchangeable base cations in the soil change over time due to changes in atmospheric deposition and the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry.

6.2 Hydrochemical equations

The governing equations in MAGIC are based on a simple set of reactions describing the equilibrium between dissolved and absorbed ions in the soil-soil water system as proposed by Reuss and Johnson (1986). This model has been expanded from their two component calcium-aluminium system to include important cations and anions in catchment soil and surface waters (Cosby *et al.*, 1986) and the effects of forest growth processes (Cosby *et al.*, 1990). MAGIC uses an aggregated approach to modelling whole catchments in that a relatively small number of important soil processes are used to produce catchment response, and spatial heterogeneity of soil properties within the catchment are combined into 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 which 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 (equation 6.1) and divalent base cations (equation 6.2), dissolution and precipitation of inorganic aluminium represented as an equilibrium with a solid phase of aluminium hydroxide (equation 6.3), and dissolution of carbon dioxide (equation 6.4) followed by dissociation to bicarbonate (equation 6.5) and carbonate (equation 6.6);

$$S_{AlNa} = \{Na^+\}^3\ EAl\ /\ \{Al^{3+}\}\ ENa^3 \qquad (6.1)$$

$$S_{AlCa} = \{Ca^{2+}\}^3\ EAl^2\ /\ \{Al^{3+}\}^2\ ECa^3 \qquad (6.2)$$

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 combined set of soil cation exchange reactions for the whole catchment.

$$3H^+ + Al(OH)_3\ (s) = Al^{3+} + 3H_2O \qquad (6.3)$$

$$CO_2\ (g) = CO_2\ (aq) \qquad (6.4)$$

$$CO_2\ (aq) + H_2O = H^+ + HCO_3^- \qquad (6.5)$$

$$HCO_3^- = H^+ + CO_3^{2-} \qquad (6.6)$$

For each of the base cations and strong acid anions in the model a dynamic mass balance equation (equation 6.7) can be written.

$$dXT/dt = Fx + Wx - Q.(X).n \qquad (6.7)$$

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. Hydrogen ions, aluminium and bicarbonate 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) firstly the deposition of strong acid anions, namely sulphate and nitrate, and (ii) the degassing of carbon dioxide as soil water enters the streamwater compartment of the model, and (iii) organic anions. Currently, at the most acidic sites, strong acid anion concentrations provide the main control on pH with alkalinity generation by carbon dioxide 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 bicarbonate has the strongest control over streamwater pH. This degassing of carbon dioxide is controlled in the model by means of a carbon dioxide partial pressure. In the absence of observations the carbon dioxide partial pressure (pCO_2) in UK systems is normally considered to be twenty times atmospheric in the soil compartment reflecting the combined effects of soil microbial and root respiration (Cresser and Edwards 1987) and twice atmospheric in the streamwater compartment (Neal 1988a), thereby generating bicarbonate alkalinity through de-gassing as soil water enters the streamwater. Field measurements are rarely available to describe pCO_2. The carbon dioxide system is temperature dependent.

Organic anions in MAGIC are simulated by specifying the total amount of organic carbon present in soil and surface water and assigning theoretical pK values to monoprotic, diprotic and triprotic anions. 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 (on a weight per volume basis) is the effective charge density of the organic acid. Organic charge is assumed to be the same in both the soil and streamwater compartment of the model and pK values are routinely set at 4.5 for monoprotic, 10.25 for diprotic and 20.5 for triprotic organic acids although these values can be adjusted in the calibration process. This effectively produces a monoprotic acid as the dominant organic acid in both soil and streamwater for those 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 combined physical characteristics of the soil and the sulphate sorption process. The total amount of each base cation in the catchment is the product of the soil depth, 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 chloride, nitrate and fluoride have no adsorbed phase in the model. The relationship of dissolved and sorbed sulphate is assumed to follow a Langmuir isotherm and is concentration dependent (equation 6.8).

$$\text{Total Adsorbed Sulphate} = E_{max} .2.(SO_4^{2-}) / (C + 2.(SO_4^{2-})) \qquad (6.8)$$

where, E_{max} is the maximum soil adsorption capacity (meq kg^{-1}) and C is the half saturation constant (meq m^{-2}).

Sulphate sorption is determined by complexation with iron and aluminium sesquioxides which are common in most upland UK soils but accurate data on sulphate sorption characteristics are generally lacking. Consequently, in the UK situation it is generally assumed that the capability for sulphate adsorption is low. The values that define the Langmuir isotherm are normally set such that sulphate effectively acts in steady state in UK systems, $E_{max} = 0.01$ meq kg^{-1} and C = 1000 meq m^{-2}.

MAGIC contains an extremely simplified representation of the nitrogen cycle involving a net catchment retention at each time step (zero order uptake) to calibrate the simulated against observed nitrate and ammonium concentrations in streamwater. Improved nitrogen processes have been implemented in a new version of MAGIC, MAGIC-WAND (Model of Acidification of Groundwater In Catchments With Aggregated Nitrogen Dynamics) (NRA 1995) and this model is currently being improved.

Whereas standard precipitation and throughfall gauges provide adequate estimates of integrated inputs to catchments and the outputs in runoff are integrated at the catchment outflow, corresponding estimates of soil parameters characteristic for an entire catchment are more difficult to obtain. Key soil parameters required by the model include depth, bulk density (BD), porosity, CEC (measured at soil pH), and the fraction of exchange sites occupied by calcium, magnesium, sodium, and potassium. Values need to be aggregated both spatially and with depth at each catchment to obtain single values for each parameter.

A complete summary of model equations, parameters and inputs are given in Annex 1.

6.3 Data requirements

The input requirements to run the MAGIC model are data describing surface water chemistry, the atmospheric deposition and net uptake-release fluxes for the base cations and strong acid anions, deposition history soil physical and chemical characteristics and land-use history. 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 sulphate, ammonium and nitrate must be corrected for dry deposition of gas, particulates and aerosols. The volume of streamflow from the catchment must also be provided to the model. The model is usually calibrated using average hydrologic conditions i.e. mean annual precipitation and streamflow volume although the model can be set up for monthly timesteps.

6.4 Applications of MAGIC

6.4.1 Critical loads and the response to future emissions scenarios

MAGIC can be used to estimate critical loads by determining a time at which the defined critical soil solution or freshwater chemistry is to be achieved. To estimate critical loads the model is calibrated to a catchment using available soil, water chemistry and land-use data. The model is then used in predictive mode to determine the sulphur deposition required to achieve some pre-defined chemical target at some time in the future. This critical chemistry is usually taken as surface water alkalinity of zero and soil water calcium to aluminium molar ratio of 1.5, but in practice any chemical parameter in the soil-water system may be used to determine a critical load.

An example of this approach to critical load determination is the application to the Allt a'Mharcaidh and the Round Loch of Glenhead (Jenkins 1995). In the Allt a'Mharcaidh (Figure 6.1a) current and past sulphur deposition is not sufficient to depress stream alkalinity below zero or decrease the calcium to aluminium ratio below 1.5 i.e. the critical load is not currently exceeded at this site and so sulphur deposition is increased in the model to achieve alkalinity zero and thereby quantify the critical load. At the Round Loch of Glenhead (Figure 6.1b) present deposition exceeds the critical load for water and so the deposition must be reduced to achieve alkalinity zero, but the soil is not as sensitive.

MAGIC has been applied to 21 sites in the AWMN to assess the recent sulphur emission reduction protocol (Jenkins *et al.*, 1997). Future predictions based on the best available prediction of sulphur deposition following adherence to the Second Sulphur Protocol indicate that there will be some degree of 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 sulphur over the next 50 years at all sites. The predicted response of soil base status over the same time scale, however, is a continuing decline at most sites. The conclusion is that future sulphur deposition under the Second Sulphur Protocol will still exceed the supply of base cations from weathering and lead to further soil acidification at these sites. Maintaining the Second Sulphur 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 sulphur and nitrogen deposition is removed. Detailed results are discussed in Jenkins *et al.*, (1997).

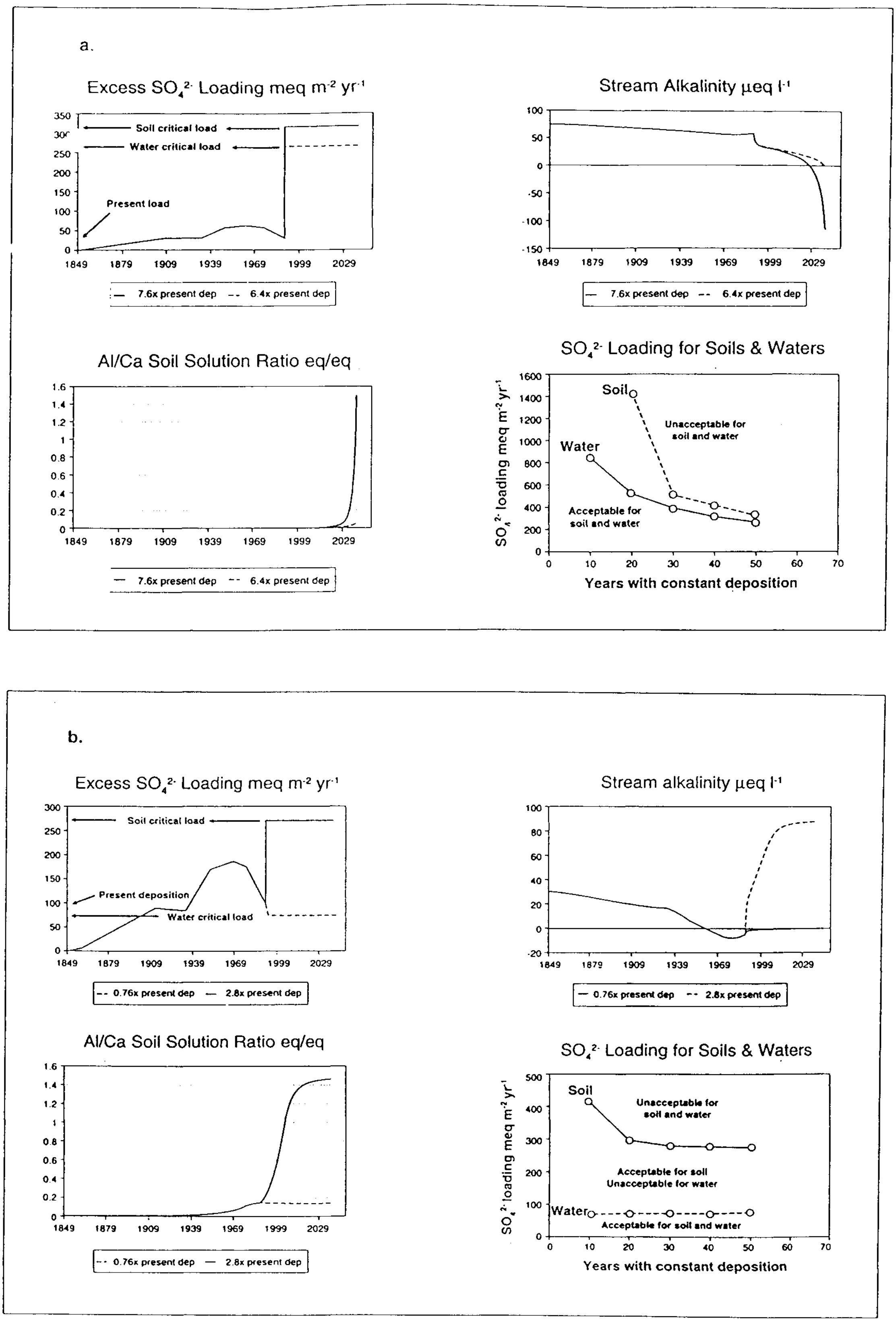


Figure 6.1 **The use of MAGIC to derive target loads for surface waters and soils at a) Allt a'Mharcaidh; and (b) Round Loch of Glenhead.**

6.4.2 Effects of forestry on model predictions

Future land-use policy within a catchment is another important factor in determining the rate of recovery of acid soils and waters. Trees are important as both receptors for indicating the degree of acidification of an ecosystem, and in their role in the soil and water acidification process. They take up base cations during their growth, change the hydrological regime of a catchment by decreasing water outflux, and filter pollutants from the atmosphere increasing the total deposition load (Cosby *et al.*, 1990). 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; (ii) enhanced dry and occult deposition; (iii) decreased water yield concentrating pollutants in surface waters.

MAGIC was applied to the Loch Grannoch AWMN site to investigate the effect of future afforestation policy (Figure 6.2) (Jenkins 1995). Two future land-use scenarios were

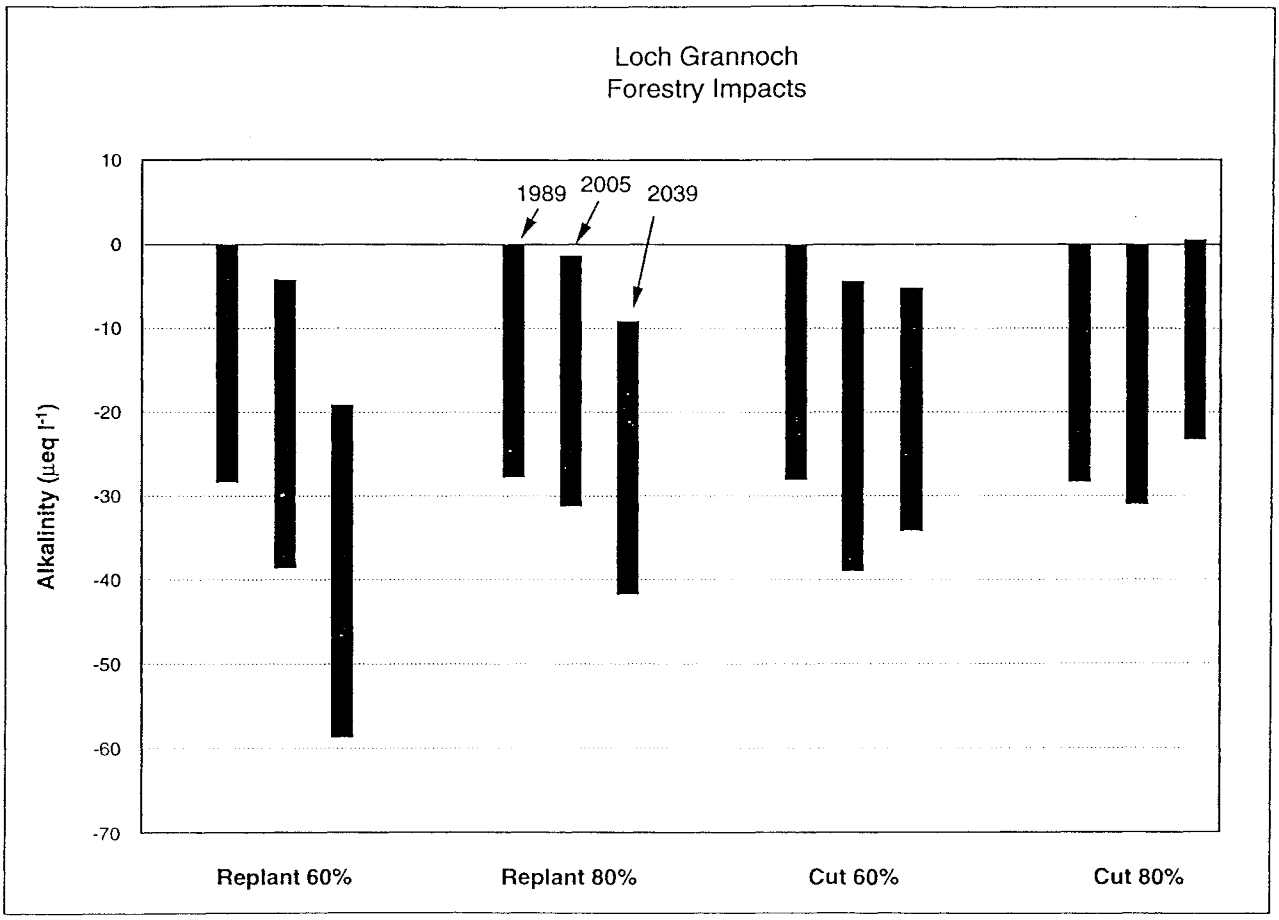


Figure 6.2 MAGIC prediction of surface water alkalinity at Loch Grannoch under two emission scenarios (LCPD and 80% reduction) and two land-use strategies (replanting forest after felling at age 50 years and no replanting after felling).

considered: forest felled and replanted immediately, forest felled with no replanting. The latter option produces the predicted best recovery of water chemistry recovery irrespective of the future emission strategy employed. The calculation of critical loads for soil and freshwater in areas where plantation forestry is a major land-use requires that these impacts be considered. Jenkins *et al.* (1997) discuss the effects of deforestation in greater detail at several other AWMN sites.

6.5 Validation of MAGIC

Predictions of acidification of soil and water are based on mathematical models of the physical system. It is therefore of great importance for the credibility of model predictions to demonstrate that the models are adequate representations of a system, and that the related algorithms are correct implementations of the models. These two tasks are known as model validation and code verification respectively.

Each of the dynamic models described have undergone internal verification procedures during design, construction, operation and maintenance. Each of the key processes in MAGIC have been harness tested using hand calculations, analytical solutions (where available) and consistency checking (e.g. mass conservation).

Validation of dynamic models requires data for which the model can be calibrated against plus independent data to which the model predictions can be compared. Given the typical timescales of acidification, long time series of data from natural systems are required. Such extended records exist for very few catchments. MAGIC has been applied to several catchments where such long data records have been inferred from diatom abundance in lake sediment cores (Jenkins *et al.*, 1990). This method of validation arises from evidence that trends in diatom flora are strongly correlated with increases in acid deposition (Battarbee *et al.*, 1988). The records of diatom flora taken from lake sediment cores provide a record of timing, rate and magnitude of biological and chemical change that has occurred at sensitive sites throughout Europe and north America.

Sediment cores were also taken from 11 AWMN lake sites and analyzed using standard methods (Battarbee 1986). Lake pH was then reconstructed in two stages. Firstly, modern diatom assemblages were modelled against present day lake water chemistry using a dataset covering biochemical conditions in 167 softwater lakes in the UK and Scandinavia. The historical pH was then reconstructed by calibrations of the model against diatom assemblages observed in the cores. Diatom-inferred pH (Di-pH) is then calculated for each core using the methods outlined in Jenkins *et al.* (1997). Figure 6.3a shows that Di-pH and observed mean pH for the one 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). Of the sites that are greater than one standard error from the observed pH, there is a consistent underestimate of the Di-pH of between 0.4-0.6 pH units. The first of these two sites are amongst the highest pH sites in the AWMN and indicates a potential problem of bias towards lower pH sites (pH<6.0) in the chemistry dataset. The diatom flora at Lochnagar (site 4) contains a number of circumneutral species for which pH tolerance is less well known and may reflect bias in the dataset (Juggins *et al.*, in press). Comparison of Di-pH for 1850 and simulated MAGIC pH in Figure 6.3b indicates a poor match. Given that the Di-pH for 1850 at Blue Lough (site 21) is clearly too low and that sites 4 and 6 show a poor match between observed and Di-pH 1990, however, a generally consistent relationship exists between the rest of the sites.

Both the above methods contain uncertainties and the inconsistency between Di-pH 1991 and observed mean pH decreases confidence in the Di-pH reconstruction methodology. However, the two methods produce close models at several sites suggesting both confidence in the model and the potential of the methodology behind the diatom reconstruction technique.

The model in Monte Carlo mode was applied to data from a 1974 survey of 464 lakes in southern Norway (Cosby *et al.*, 1989). The results showed that a significant acidification had occurred in the decades preceding the survey. Model projections for the 12 years following the survey suggest that only minor changes in water quality occurred over that period (Figure 6.4). These predictions were corroborated by a re-survey of some of the lakes in 1986.

A survey of 50 lochs in the Galloway area, south western Scotland conducted in 1979 and repeated in 1988 revealed major changes in water chemistry (Wright *et al.*, 1994). These changes were corroborated by regular measurements at several of these lochs during that period. These two data sets separated in time by 9 years and covering a period of relatively large and rapid change in acid deposition presented an ideal opportunity for validation of the model. MAGIC was applied and successfully reproduced the major changes in water chemistry observed over the period 1979-1988. Both calibration to the 1979 data with prediction of 1988, and calibration to the 1988 data with reconstruction of 1979 gave close fits to the observations. The model has also been applied to 77 sites in Wales and calibration to 1995 data hindcast to 1984 data show a good match (Sefton and Jenkins, 1998).

MAGIC, SAFE and SMART have recently been used in a joint modelling exercise as part of the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP-IM), part of the Effects Monitoring Strategy under the UN-ECE LRTAP convention (Wilkinson and Jenkins, 1996). The models were applied to 6 selected ICP-IM sites: the Afon Hafren (Wales), Birkenes (Norway), Forellenbach (Denmark), Gårdsjön (Sweden), Prades Sor (Spain) and Hietjarvi (Finland). Of these sites, those in Wales, Norway and Sweden are currently acidified and the site in Spain is acidifying. The models were calibrated to the present-day observed conditions using consistent input data, model parameters and historical deposition scenarios for the sites. The calibrated models were used to predict the long-term acidification of soils and runoff water given different scenarios of future deposition of sulphur and nitrogen based on agreed measures for emission reductions. The dynamic response of possible critical load exceedances were assessed. Model results were compared and uncertainties assessed.

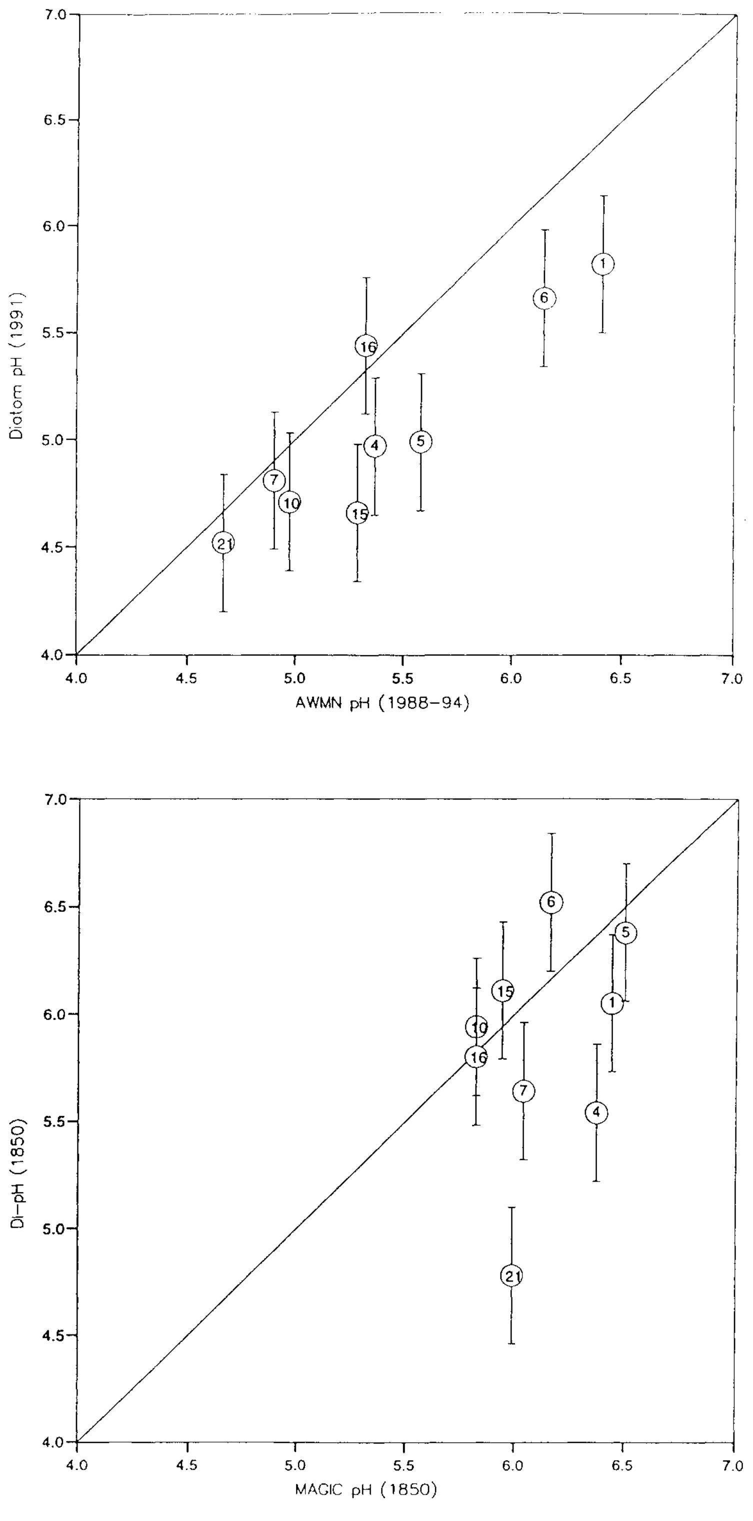


Figure 6.3 **Comparisons of diatom modelled pH reconstructions for; (a) Observed AWMN mean surface water pH (1988-94) versus diatom reconstructed pH (1991); (b) Di-pH versus MAGIC background reconstructed pH (1850). Error bars represent the RMSE of 0.32 pH units for all sites.**

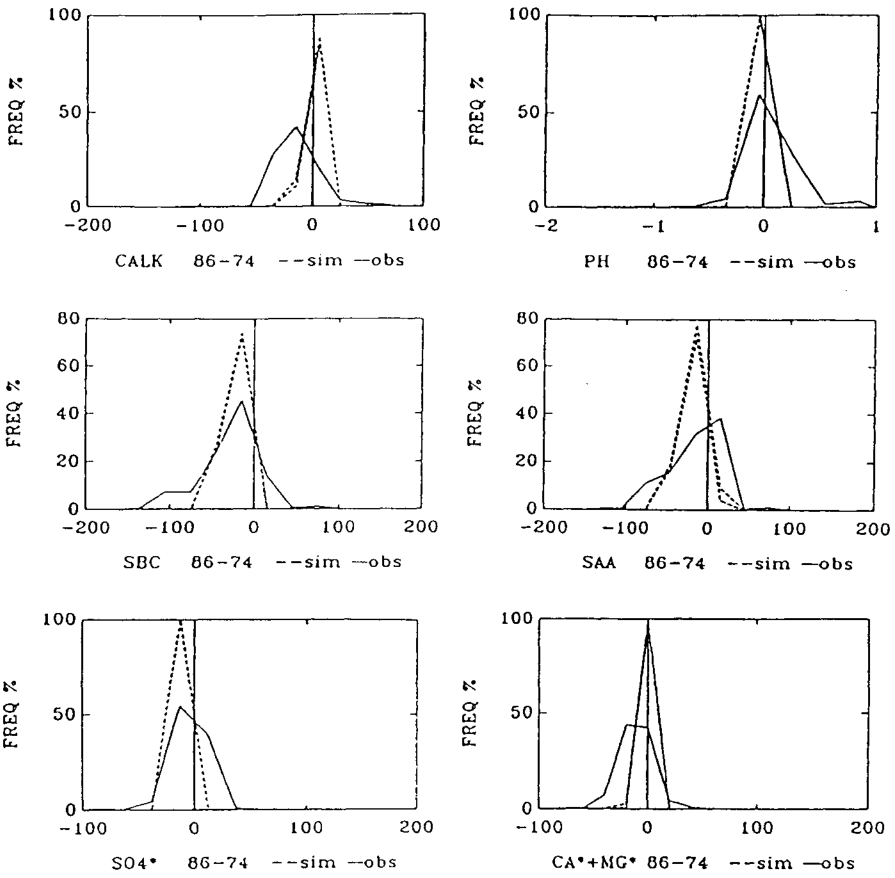


Figure 6.4 **Frequency distributions of observed (solid line) and simulated (dashed lines) changes in water quality variables between 1974 and 1986.**

For acidifying deposition 3 future scenarios were employed (Table 6.1). In each scenario base cation, chloride, ammonium and ammonia depositions were kept at present levels. Figure 6.5 gives an example of the simulated values for soil base saturation for scenarios A-C for two of the sites. Base saturation being a measure for soil acidification. Detailed results are given in Forsius *et al.* (in preparation). The calibrated models give consistent results for historical base saturation in 1900. At all sites the model results indicate a slight decrease in base saturation until present day. The predicted response at each site is dependent on the future deposition scenario. Scenario B where 'Maximum Feasible Reductions', for sulphur emissions and a 30% reduction for NO_x emissions were assumed, resulted in many cases in a stabilization in the soil acidification. The only clear exceptions were the MAGIC and SMART simulations for the Afon Hafren where continued soil acidification was predicted. The A scenario (Second Sulphur Protocol for sulphur and present level for nitrogen emissions 'Best Prediction') resulted in a slower response than the B scenario though emission reduction for sulphur was still sufficient to stop continued soil acidification with, again, the Afon Hafren being the exception.

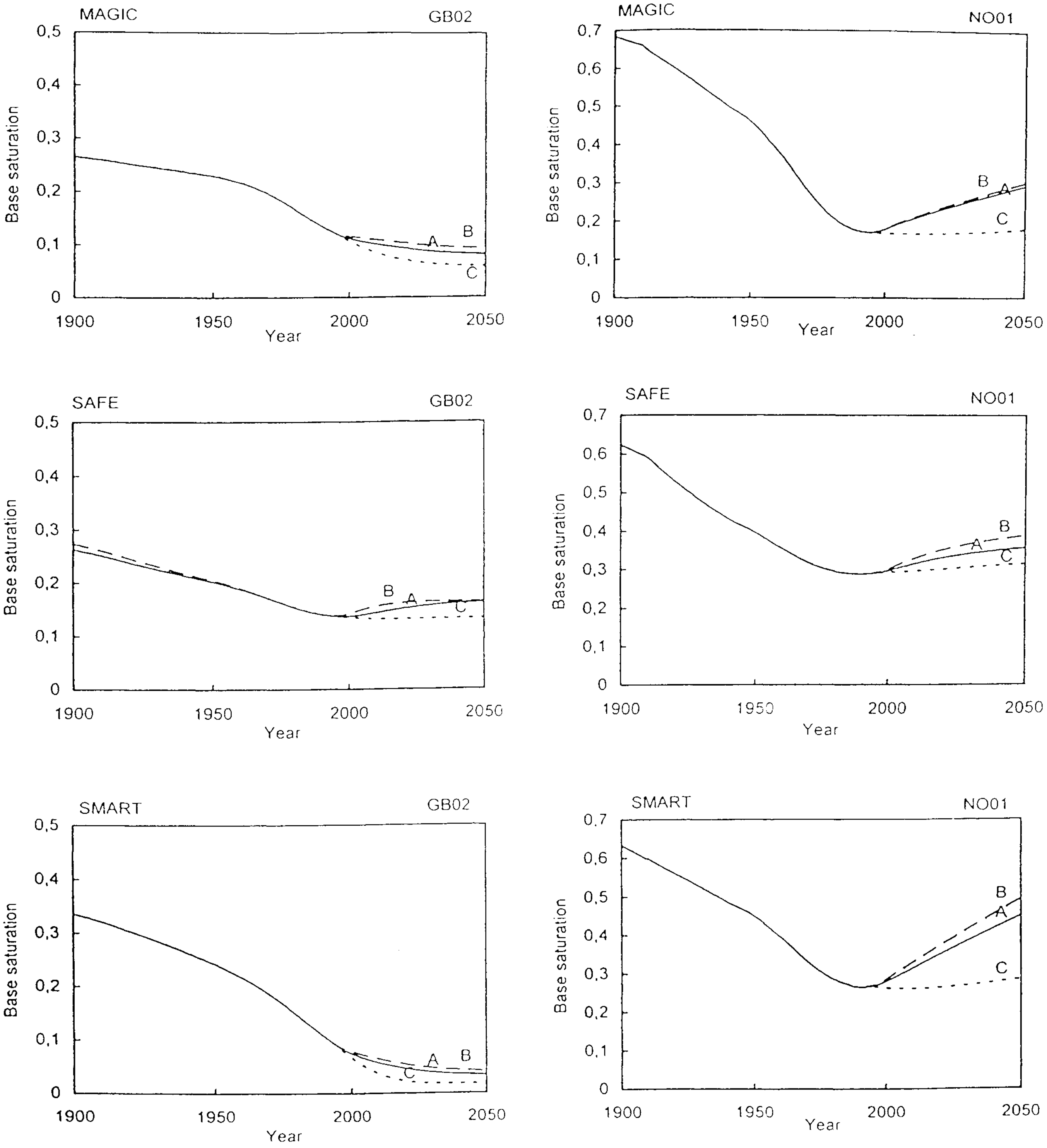


Figure 6.5 **Simulated soil base saturation (fraction) for GB02 Afon Hafren and N001 Birkenes using three dynamic models and scenarios A-C.**

Table 6.1 **The three scenarios employed in the model intercomparison exercise, roughly representing the possible range of future acidifying deposition.**

Scenario	SO_2	NO_x	NH_y
A best prediction	Second sulphur protocol	Present level	Present level
B lower limit	Maximum feasible reductions	-30% from present level	Present level
C upper limit	Present level	Present level	Present level

The three models gave in most cases consistent trends. The same result was also obtained in a previous study (Warfwinge *et al.*, 1992). Although the models contain in many cases similar process descriptions there are still important differences in the model structure (e.g. in the estimation in weathering rates). The similarity of predictions lends confidence to the use of such models for scenario assessments and other policy oriented work.

6.6 Uncertainty and sensitivity analysis for MAGIC

Models are simplifications of a real system regardless of their complexity, i.e. no model is ever completely correct in terms of reproducing reality. Hence uncertainty is inherent in every model. Application of a model to assess acidification of a catchment is a complex process and involves significant uncertainties that have to be assessed. Uncertainty analysis involves determining the uncertainty in model predictions that results from imprecisely known input variables, and sensitivity analysis involves determining the contribution of individual input variables to the uncertainty in model predictions. Reasons for performing an uncertainty/sensitivity analysis are to determine if the uncertainty in a predicted quantity falls within a specified set of boundaries (e.g. critical loads for a catchment) and to provide guidance on the investment of research efforts to reduce uncertainty. Sampling based uncertainty/sensitivity analysis procedures also provide a powerful tool for model verification.

6.6.1 Uncertainty analysis

There are several formal approaches to uncertainty analysis. Of these approaches, Monte Carlo analysis is the most widely used. Monte Carlo simulations were carried out for the MAGIC model applied to the White Oak Run Catchment, Virginia (Hornberger *et al.*, 1986). Simulations were carried out by randomly selecting a set of parameter values from within the designated ranges (Table 6.2) and integrating equation 6.7 for sulphate from 1844 to 1984 using this set of values. Each simulation run was then classified either as producing acceptable results (i.e. simulated stream sulphate concentrations matched observations made in the study area in 1982) or as not producing acceptable results. This procedure was repeated many times to give an accumulation of acceptable and unacceptable values. The distribution of parameter values associated with the acceptable results was compared with the distribution of parameter values associated with the unacceptable results. If the two distributions were not statistically different, the parameter is unimportant for simulating the designated behaviour; if the two distributions differ significantly the parameter is important.

Table 6.2 Range of MAGIC parameter values used in uncertainty analysis.

Parameter	Definition	Minimum-maximum values	Units
	Physical parameters		
P	Porosity	0.25-0.50	fraction
D	Soil depth	0.3-1.7	m
Q	Discharge	0.3-0.9	m yr^{-1}
E_{mx}	Maximum capacity	1-15	meq kg^{-1}
C	Half saturation	50-350	meq m^{-3}
	Deposition parameters		
DF	Dry deposition factor	1.4-2.0	- -
C_B	1844 sulphate concentration in precipitation	3-9	meq m^{-3}
	Slopes of deposition curve		
S_1	1880-1925	0.0-0.01	yr^{-1}
S_2	1925-1945	0.005-0.020	yr^{-1}
S_3	1945-1965	0.009-0.033	yr^{-1}
S_4	1965-1975	0.009-0.033	yr^{-1}

Both catchment physical and deposition parameter values were selected independently from rectangular distributions with the limits described in Table 6.2. One thousand Monte Carlo simulations were run for three different cases. For the first case a known deposition sequence was specified and only the catchment physical parameters were selected randomly (case I). Second, the catchment physical parameters were fixed at values selected as appropriate for the catchment (Cosby *et al.*, 1985c) and the deposition parameters selected randomly (case II). For case III, both deposition and physical parameters were randomly selected. For each case, a simulation was categorized as being acceptable if the simulated stream sulphate concentration in 1982 was between 55 and 110 meq m^{-3}, the range of measured concentrations for the study area (Dise 1984).

The resulting distribution of simulated stream sulphate concentrations in 1982 for case III was very broad (Figure 6.6). The range of simulated concentrations was 23 to 349 meq m^{-3}, whereas the range of measured concentrations was 55 and 110 meq m^{-3}. Both the mean and variance of the distribution of simulated concentrations increased with time in the Monte Carlo analysis (Figure 6.7). The initial mean sulphate concentration was low and variability was due only to uncertainties in C_B and DF. As deposition increased through time, the simulated mean sulphate concentration increased. The variance of the simulated concentrations also increased because of uncertainties in the deposition sequence and the physical/chemical parameters controlling the dynamic behaviour of the model. Initially the distribution of acceptable simulations was similar to that of all Monte Carlo realizations. Beyond the early part of this century, however, many of the simulations diverged widely from the track of the acceptable simulations (Figure 6.7). In case III, 385 of the 1000 simulations produced 1982 sulphate concentrations between 55 and 110 meq m^{-3}.

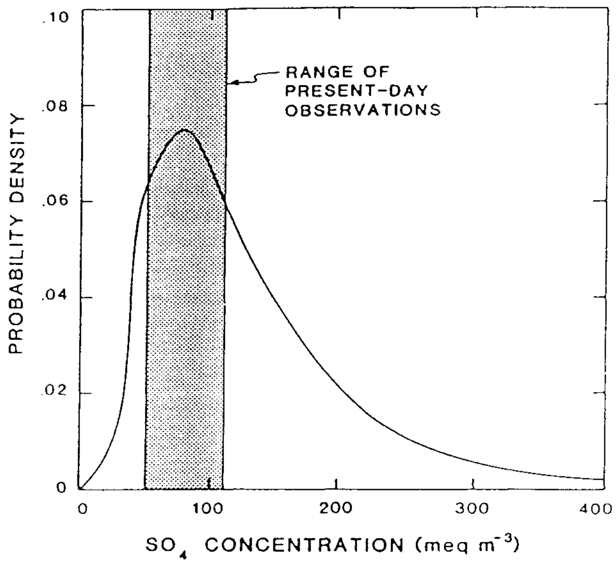


Figure 6.6 Distribution of stream sulphate concentrations in 1982 resulting from the Monte Carlo simulations.

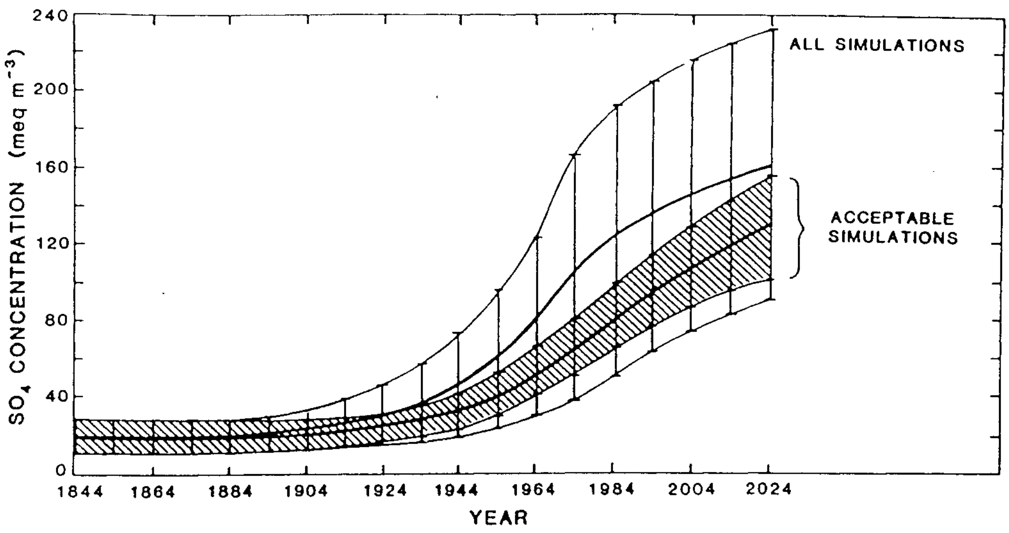


Figure 6.7 **Temporal evolution of simulated sulphate concentrations. Bold lines are mean concentrations; vertical lines show one standard deviation about the mean. Results for simulations in the acceptable range are shaded.**

For the majority of the applications of MAGIC in the UK to date, sulphur adsorption by catchment soils is assumed to be negligible. This assumption is made necessary because of: (i) a lack of detailed sulphur input and output fluxes at most sites to enable quantification of net sulphur retention, and (ii) a lack of information describing the sulphur adsorption characteristics of UK soils. The net effect of this assumption (Figure 6.8) is that predicted recovery from acidification is potentially optimistic. An assessment of the uncertainty associated with the assumptions made with respect to SO_4 adsorption is given in Annex 2 which details a series of uncertainty tests on the MAGIC model undertaken as part of this research project. In essence, it is necessary to have a minimum of 5 years streamwater chemistry record for a given site in order to constrain the calibration and narrow the uncertainty indicated in Figure 6.8. For the example of the Afon Hafren, documented in Figure 6.8, the predicted steep decline between 1950 and 1991 was not observed during the period 1980-1991.

There is increasing evidence that soils continue to leach sulphate at high levels for many years following substantial decreases in sulphur inputs. In this case, the recovery from acidification will be delayed in time. There exists a clear need for further examination of the degree and nature of sulphur adsorption and desorption in soils of the UK. In the meantime, applications of the model should continue to assume no sulphate adsorption and future predictions must be interpreted with respect to these representing a 'best case' scenario.

A further key uncertainty at forested sites is the specification of net plant uptake fluxes for base cations. The growing trees consume base cations through their roots and some proportion of these are transferred back to the soil surface each year as litterfall and through fall. Net uptake represents the residual of these fluxes which is retained within the tree biomass and removed from the catchment at felling and so the cations are removed from the system. Crucial to modelling the future acidification response of forested catchments, therefore, is the specification of the source of the base cations. In a one soil-layer model, uptake by trees has little acidification effect in the soil water or surface water since the total pool of base cations in the soil is extremely large relative to the total net uptake flux over the life of the forest. If, on the other hand, two soil layers are incorporated in the model structure, the specification of the source of the base cations for net uptake is crucial; if all uptake is from the upper soil, the relatively low total cation pool is rapidly depleted and future acidification occurs, particularly under a second rotation forest (Figure 6.9). By contrast, if net uptake is assumed to derive from the lower soil, an acidification response is not predicted. The basis of this analysis is given in Annex 2. Further work to determine the correct parameterisation of net uptake flux for forested catchments is required. Until this research is undertaken, it is recommended that a single soil layer structure is the best option and the predictions assumed to represent a 'best case'. In any case, soils data describing two layers are seldom available for model applications.

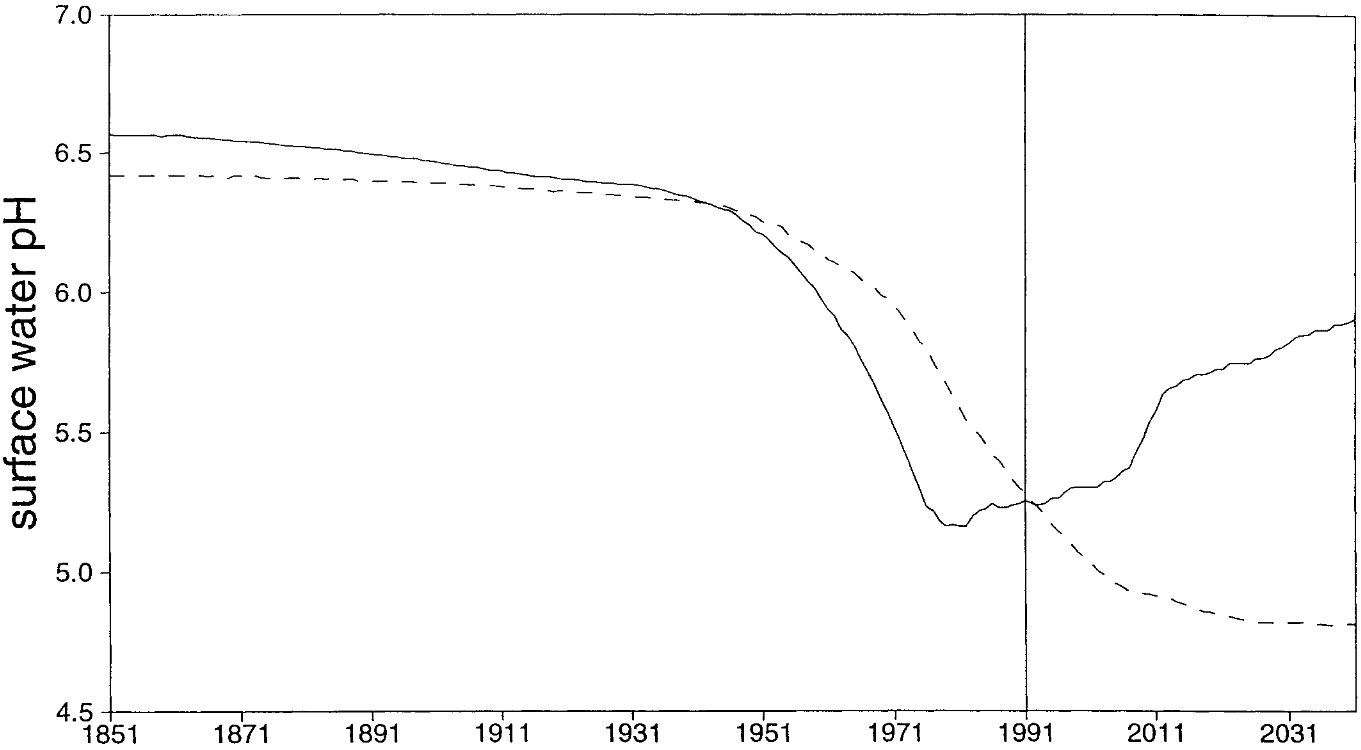


Figure 6.8 **MAGIC predictions at Plynlimon (Afon Hafren) under the second sulphur protocol emission reduction scenario; comparison of outputs with and without sulphate adsorption. Solid line represents the model with no sulphur adsorption and dashed line includes a high degree of sulphur adsorption.**

Perhaps the key uncertainly regarding future surface water acidification response in the UK is the catchment retention of nitrogen compounds.

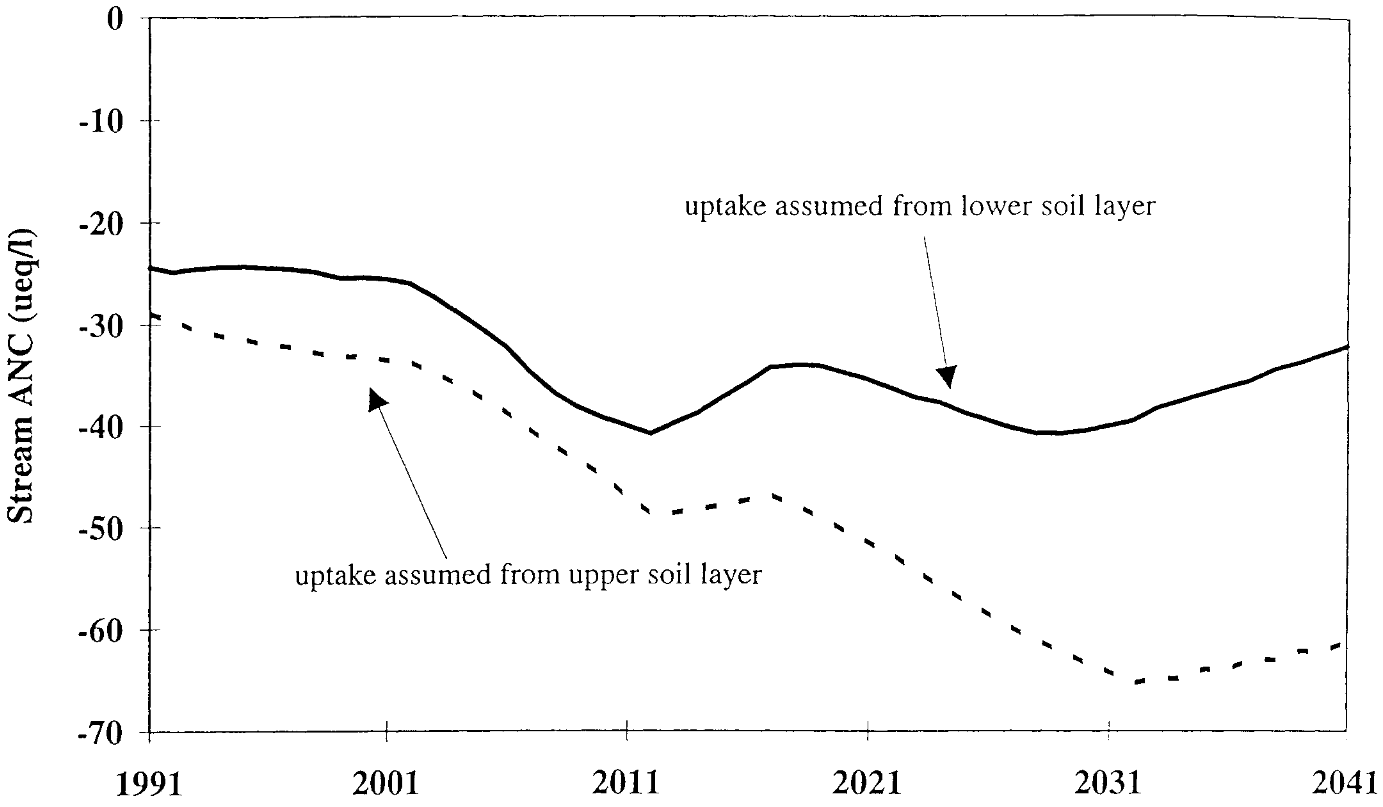


Figure 6.9 **MAGIC predictions at Plynlimon (Afon Hafren) assuming reduced sulphur deposition and second rotation forestry contrasting the response of assuming net base cation uptake from upper and lower soil layers.**

Nitrogen (N) is generally retained within terrestrial systems, largely because N is the growth-limiting nutrient (Tamm 1992). Chronic elevated deposition of N as oxidised (NOx) or reduced (NHy) species, however, can produce quantities of inorganic N in soils in excess of that needed by the biota for growth (Agren 1983; Aber *et al.*, 1989). The unassimilated N can lead to eutrophication and/or acidification in soils and can be leached from soils to appear as NO_3 in runoff potentially promoting eutrophication and/or acidification in surface waters. Excess ammonium (NH_4) is quickly converted to nitrate in forest soils, and so rarely contributes to N leaching except under conditions of extremely high N deposition (Bobbink *et al.*, 1992). The term 'nitrogen saturation' has been used to describe the situation whereby the supply of inorganic N exceeds the biotic (plant and microbial) requirement and is manifest through increased leaching of inorganic N below the rooting zone (Aber *et al.*, 1989). Prediction of N saturation is difficult at best and the processes responsible are difficult to

Prediction of N saturation is difficult at best and the processes responsible are difficult to quantify but NO_3 leaching to surface waters may be indicative of N saturation. The best information currently available on the magnitude and timing of N saturation (or retention) comes from empirical observations (Westling 1991; Emmett *et al.*, 1993 Dise and Wright 1995).

International agreements aimed at reducing emissions of S and N have been negotiated under the auspices of the UNECE Convention on Long Range Transboundary Air Pollution since the mid 1980s. The most recent agreement, the Second S Protocol signed in Oslo in 1995, was based on the concept of critical loads (Posch *et al.*, 1995) and called for reductions in UK emissions to 70% of 1980 levels by 2005 and further to 80% of 1980 levels by 2010. Agreement on levels of N emissions is yet to be negotiated. It is clear, however, that the amount of S deposition that can be tolerated by catchment systems without harmful effects on aquatic biota is dependent on the amount of N deposition, and vice versa (Henriksen *et al.*, 1993). The specification of a critical load for S, therefore, in the absence of knowledge of how the N dynamics within the catchment system might change in the future, is inappropriate.

The development of dynamic modelling approaches enables an assessment of the influence of N dynamics in the context of total acidity. That is, given that protocols for S emission reductions are now in place, the most important question relates to the potential for N leaching to offset the expected reversibility. The importance of dynamic models in this context was recognised at a UNECE sponsored workshop on critical loads for N held in Lokeberg, Sweden, in April 1992, where it was identified that, "Strong efforts should be made to develop and test dynamic models for assessing the consequences of the exceedance of critical loads" (Grennfelt and Thornelof 1992).

The strength of dynamic model applications in an applied sense is in answering the key policy question “What is the potential for N leaching to offset the expected recovery from agreed S emissions reductions?”

MAGIC-WAND represents an extension to the MAGIC model to incorporate the major N fluxes and changes in fluxes through time (Figure 6.10). The N dynamics are fully coupled to the existing S driven model. The model structure is designed to enable assessment of future surface water chemistry response to a given N deposition scenario. Assumptions relating to the uptake capabilities of the vegetation and future land use change and the sensitivity of a catchment or region to these components can also be assessed.

Initially, the model incorporated specification of the net mineralisation flux of N and plant uptake was calculated as a concentration dependant hyperbolic function. This is fully described in Jenkins *et al.* (1997), and Jenkins and Renshaw (1995).

Further development of the model has now been undertaken in the light of difficulty on obtaining data to describe the net nitrogen mineralisation flux. At the heart of the new model lies the assumption that the net retention/release (or immobilisation/mineralisation) of incoming inorganic N in the soil is determined by the C : N ratio of the top soil layer. Such a relationship has been proposed by Gunderson *et al.* (1997) following an assessment of N leaching and soil C : N ratios across a range of forested sites in Europe (Figure 6.11) such that at N rich sites most of the incoming N is leached whilst at low N sites all of the incoming N is immobilised.

The model solution at each time step is sequential; the net plant uptake requirement for N, specific at each time-step (uptake-litterfall), is satisfied; second, the fraction of remaining N immobilised by the soil is determined by the soil N pool size relative to the (constant) soil C pool. The soil N pool is incremented accordingly and the remaining N, if any, is leached to the streamwater. If nitrification is assumed to be complete, it is not necessary to distinguish between deposition and plant uptake of NH_4 or NO_3 and any N leached is in the oxidised form.

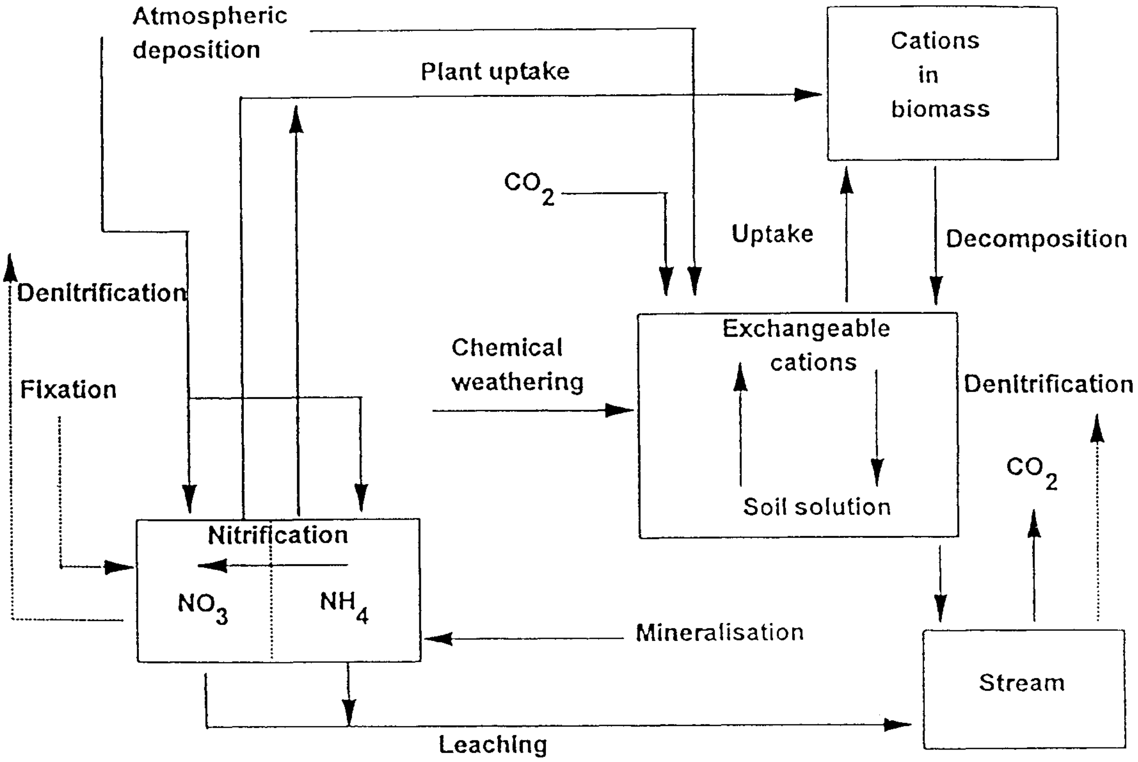


Figure 6.10 **Schematic of the catchment N stores and fluxes in MAGIC-WAND**

Application of the model to Plynlimon (Afon Hafren) shows the potential for severe acidification beyond current levels in the future as nitrogen breakthrough occurs and promotes elevated nitrate concentrations in the stream (Figure 6.12). This renewed acidification, illustrated as a decrease in ANC, is predicted to occur under deposition scenarios that describe a worst case of nitrogen deposition (20% decrease from present day) and a best case of nitrogen deposition (c. 60% decrease) combined with currently agreed sulphur reductions under the Second Sulphur Protocol. In addition to the uncertainty in the catchment response to future N deposition, there exists uncertainty in the calibration of MAGIC-WAND (Annex 2). Again, the uncertainty can best be reduced if a historical stream chemistry record is available at a given site. Work is now in progress to determine whether regional N dynamics can be identified to alleviate the problem of historical data record.

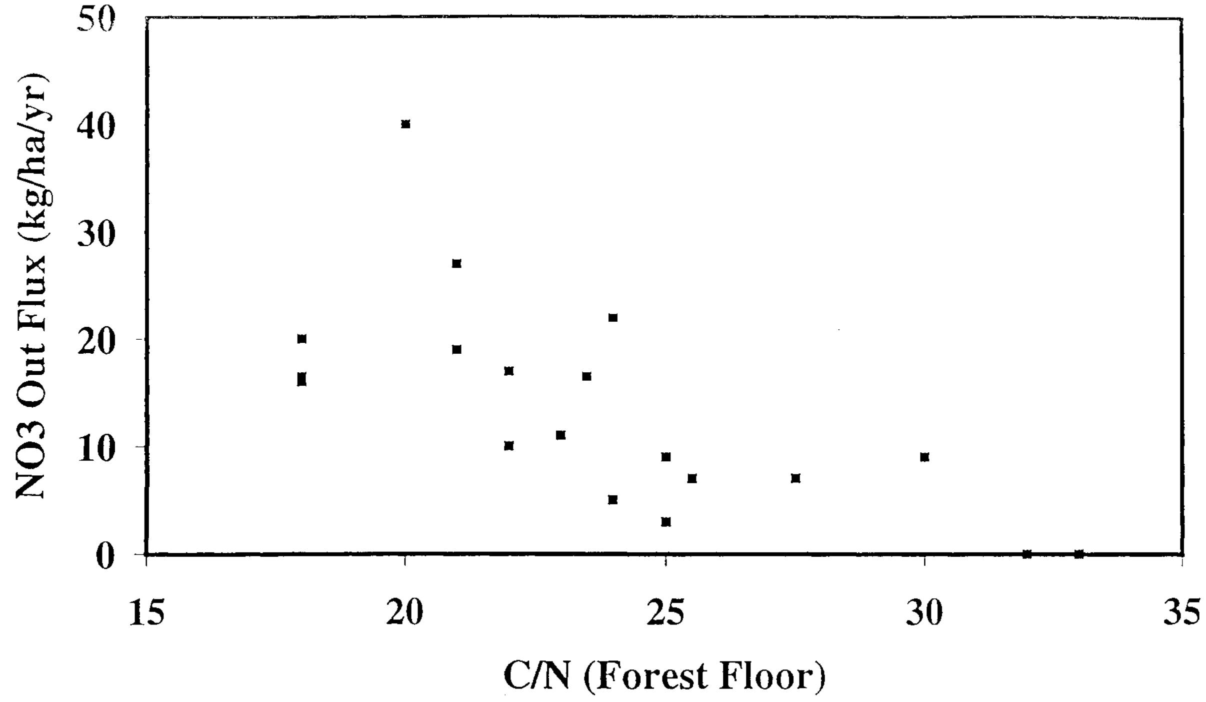


Figure 6.11 **Observed relationship between organic layer C : N status and nitrogen leaching relative to deposition (after Gundersen *et al.* 1997).**

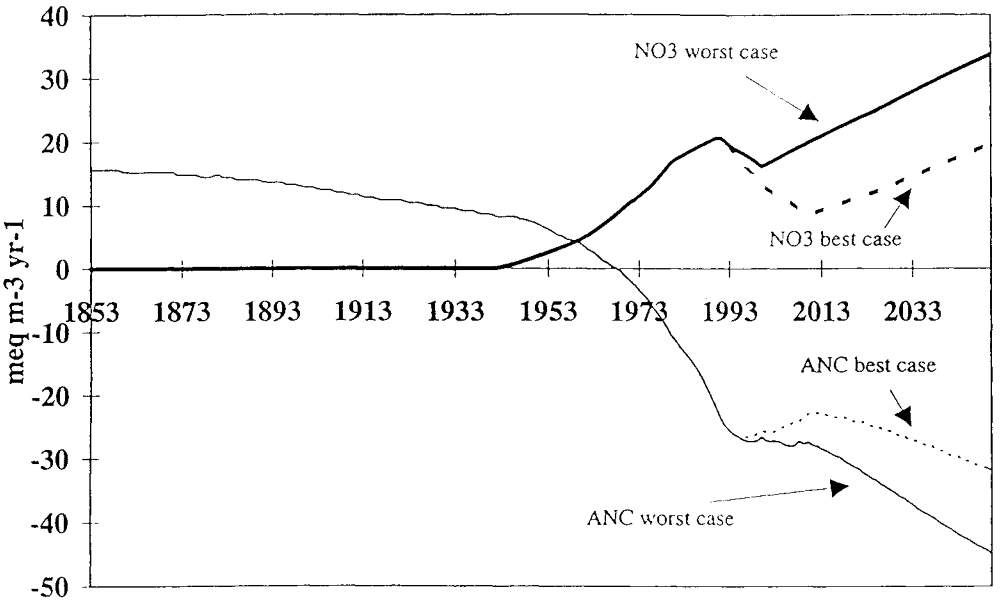


Figure 6.12 **The predicted response of nitrate leaching and ANC at Afon Hafren assuming a best case nitrogen deposition scenario (dotted lines) and a worst case (solid lines) combined with currently agreed sulphur reductions.**

The simulations, however, assume that the existing forest cover remains unchanged at this site and this is unlikely. In reality, the forest will be felled within the next 5 years and re-planted immediately. This new forest will have a significantly higher demand for N and so will reduce NO_3 leaching to the stream. The development of MAGICWAND and coupling to more detailed nitrogen and carbon cycling models continues but the model as it currently exists provides a unique tool for assessing the impacts of coupled nitrogen and sulphur deposition scenarios at single sites across the UK although the application requires soil carbon and nitrogen data which can only be obtained by field sampling.

6.6.2 Sensitivity analysis

A traditional sensitivity analysis in which parameters are varied individually about a nominal value has not been used with MAGIC. The paucity of continuous time series data means that running such an uncertainty analysis would not reflect true model performance. Instead the parameter values from the Monte Carlo simulations were subject to a statistical analysis to determine the sensitive characteristics of the model over the full range of possible parameter values. Three sensitivity classes were selected based on the Kolmogorov-Smirnov two-sample statistic $d_{m,n}$: insensitive for $d_{m,n}<0.125$, moderately sensitive for $0.125<d_{m,n}<0.25$ and sensitive for $d_{m,n}>0.25$. A value of $d_{m,n}=0.125$ corresponds approximately to a significance level of 0.999 for 1000 Monte Carlo simulations.

Using this criteria, in all three cases, the model was found to be sensitive to several parameters (Table 6.3). For case I, E_{mx} was the most sensitive parameter with D and Q moderately sensitive. This is consistent with the results of Cosby *et al.* (1986) who showed that E_{mx} was more important than C in determining model behaviour. The sensitivity analysis also showed that soil porosity was much less important in controlling the response of sulphate concentration than soil depth since it had more influence on the total adsorption capacity of the system. For case II, the critical parameters were the first slope value S_1 and the dry deposition factor DF. This implied that for a catchment with fixed physical parameters the total loading of sulphur determined whether acceptable results can be obtained. When all parameters were included as in case III the system was sensitive to the physical parameters, in particular the maximum adsorption capacity E_{mx} for which the $d_{m,n}$ value was greater than 0.25.

Model sensitivity guides the calibration process for each application and the use of a "fuzzy" optimisation procedure attempts to encompass uncertainly in measured catchment parameter valves and sensitivity in internal model parameters.

Calibrations for a site are carried out sequentially. First, the concentrations of stream chloride and sulphate are calibrated by adjusting occult and dry deposition of sea salts and gaseous/particulate sulphur compounds under the assumption that these ions are in approximate steady-state with respect to atmospheric inputs. Next, the nitrate and ammonium concentrations are calibrated by adjusting first-order uptake functions to match observed surface water concentrations. Finally, the base cations concentrations are calibrated using an optimisation procedure based on Rosenbrock (1960) algorithm.

Table 6.3 Sensitivity of parameters used in MAGIC based on the two-sample Kolmogorov-Smirnov statistic $d_{m,n}$, where n is the number of acceptable simulations and m the number of unacceptable simulations (* indicates insensitive $d_{m,n} < 0.125$;H indicates moderately sensitive $0.125 < d_{m,n} < 0.25$;I indicates sensitive $d_{m,n} > 0.25$).

Parameter	Case I (n=464, m= 536)	Case II (n=640, m=360)	Case III (n=385,m=615)
P	*		*
D	H		H
Q	H		H
E_{MX}	I		I
C	*		*
DF		I	*
C_B		H	*
S_1		I	*
S_2		H	H
S_3		H	*
S_4		*	*

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 calcium, magnesium, sodium, potassium and soil exchangeable fractions of calcium, magnesium, sodium, potassium (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 calibration procedure. Base cation weathering rates and base cation selectivity coefficients for the soils are not directly measurable and are considered as "adjustable" model parameters to be optimised in the calibration procedure.

The calibrations are performed on simulations run from pre-acidification conditions to present day. The historical deposition sequence over the period is estimated by scaling currently observed deposition to a reconstruction of sulphur emissions. After each historical simulation, the model variables are compared to observed data, the adjustable parameters are modified as necessary to improve the fit and the historical simulation is re-run. The procedure is repeated until no further improvement in the fit is achieved.

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 perturbations of the fixed parameters is based on measurement errors of spatial variability of the parameters. The uncertainty in the target variables are estimated as the measurement errors of the variables (5μeq l^{-1} or 10% for concentrations of surface water base cation concentrations and 0.5 or 10% for soil base saturation 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 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 the 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.

7. THE SAFE MODEL

7.1 Introduction

The SAFE (Simulating Acidification in Forest Ecosystems) model is a dynamic geochemical model which calculates weathering release of base cations (calcium+magnesium+potassium) and changes in soil solution chemistry and base saturation (strictly calcium+magnesium+potassium saturation) in response to changes over time in atmospheric deposition, net nutrient uptake, nutrient cycling and hydrology (Warfvinge *et al.*, 1993; Jonsson 1994). SAFE was developed in the Chemical Engineering Department of Lund University in Sweden and is essentially the dynamic counterpart of the PROFILE model (Sverdrup and Warfvinge 1993b). Both models share the same weathering rate sub-model which uses measurable soil properties such as soil texture, mineralogy, soil moisture conditions and percolation to calculate weathering rates. Thus SAFE and PROFILE differ and percolation to calculate weathering rates. Thus SAFE and PROFILE differ from other comparable soil chemistry models in that the weathering rate is calculated from independent physical and chemical properties of the soil system and the application of transition state theory as applied to silicate minerals.

7.2 Model structure and processes

SAFE is based on a conceptual model of a forest soil and incorporates the following chemical sub-systems:

- Leaching and accumulation of dissolved chemical components
- Solution equilibrium reactions involving carbon dioxide, aluminium and organic acids
- Silicate weathering reactions
- Cation exchange reactions
- Uptake and reactions of nitrogen compounds
- Biological uptake and cycling of base cations

Within SAFE and PROFILE, the soil profile is divided into several layers which correspond to the natural soil horizons. Each soil layer is treated as a perfectly mixed-tank reactor. Water is allowed to percolate in specified quantities between the soil horizons as there is no soil hydrological sub-model within SAFE to link percolation rates with soil hydrological properties (e.g. rainfall, soil moisture tensions). However, runoff from the soil will be less than precipitation so that uptake by plant roots (expressed as a percentage of incoming precipitation) must be specified for each soil layer in accordance with root distribution.

7.2.1 Solution reactions

Within the model, soil solution buffering is controlled by the carbon dioxide-bicarbonate system, acid-base reactions of a simple monovalent organic acid and an aluminium sub-model. The partial pressure of carbon dioxide is specified for each layer and the dissolution of carbon dioxide and protolysis reactions are defined in the model. Inorganic aluminium concentrations are modelled by assuming that soil water concentrations of trivalent aluminium ions are controlled by equilibrium with the mineral gibbsite. This approach is acknowledged as controversial and an alternative is currently under development (Jonsson 1994 Alveteg *et al.*, 1995). Soil water concentrations of dissolved organic carbon are specified as input. Whilst DOC participates in the formation of weak monovalent organic acids, it does not enter complexation reactions with aluminium.

7.2.2 Weathering

Mineral weathering within SAFE relies on the hypothesis that the surface reactions of minerals following universal rate laws, based on transition state theory, even though the chemical environment of the mineral may vary. Recent work on the PROFILE model has questioned the dissolution reactions are poorly understood and dissolution rates will be affected by variations in the chemical composition of the minerals as well as by the presence of structural defects. In contrast, transition state theory is most appropriate to systems which are chemically and structurally homogeneous. Hodson and Langan (1996) were, however, unable to quantify what effect this departure from ideal conditions might have on predicted weathering rates. The weathering rate for the soil profile is the sum of the dissolution rates for the individual minerals. Dissolution rates increase in response to increasing concentrations of hydrogen ions, organic acids and higher partial pressures of carbon dioxide. Dissolution rates are inhibited by the accumulation of weathering products such as inorganic aluminium and base cations through complexation on active sites (Sverdrup 1990). Temperature dependence of weathering reactions is expressed using an Arrehenius equation. Soil moisture saturation is used to estimate the fraction of the exposed mineral surface area in contact with water and thus able to participate in weathering reactions. The weathering of secondary minerals is represented by the dissolution of vermiculite.

7.2.3 Cation exchange

The SAFE model calculates cation exchange reactions as reversible chemical reactions which are rate limited by the transport of base cations through the soil solution. A Gapon exchange equation is used to model the base cation concentration at the exchange surface. The nutrient base cations (calcium+magnesium+potassium) are modelled as a combined divalent component. This is not a true representation of the potassium exchange reaction, but the model=s authors consider that this introduces only a small error given that the Gapon equation regards the exchange surface as monovalent. The model=s authors argue that this simplification is a necessary compromise between the exact representation of reaction mechanisms, model complexity and the useful predictive capability of the model.

7.2.4 Nitrogen

Nitrification is the only biological process modelled within SAFE using a kinetic expression. Nitrogen uptake is specified as a maximum annual figure distributed through the soil profile and SAFE assumes that ammonium is taken up preferentially. Nitrate is taken up only if there is insufficient ammonium to satisfy plant requirements, thus nitrification and nitrate uptake can not occur simultaneously. Denitrification is not included in the model. SAFE was originally designed for application to recently developed soils in glaciated regions. For this reason, it does not include sulphate adsorption reactions.

7.2.5 Base cation cycling

SAFE does not include any processes to describe the uptake and cycling of nutrients within the soil-plant system. The components of a simplified nutrient cycle must therefore be specified for each time step of the model. Nutrient cycling is considered with respect to inputs and outputs from the soil where:

$$TI = Wd + Dd + Ce + Lf + Nm \quad (7.1)$$

$$TO = Nu + Ce + Lf \quad (7.2)$$

where:

TI = Total input
Wd = Wet deposition
Dd = Dry deposition
Ce = Canopy exchange
Lf = Litter fall
Nm = et mineralization
TO = total output
Nu = net uptake (uptake into growth of stems, branches and coarse roots)

All terms are in meq m^{-2} $year^{-1}$.

Canopy exchange is calculated as the difference between throughfall and (wet + dry) deposition. Litter fall is the leachable nutrient content of falling needles or leaves. Net mineralization is the net supply or accumulation of nutrients from the soil organic phase and essentially represents the change in the soil organic matter nutrient pool.

7.3 Model initialization

SAFE requires specified initial conditions at the starting point of the model run. To ensure that SAFE simulations result from changes in external (e.g. acid deposition) or internal (e.g. nutrient cycling) loadings, the model is initiated under steady state conditions (Sverdrup *et al.*, 1995b). Formerly this was achieved as an initial >external= step using the PROFILE model, but this stage is now incorporated as an initialization routine within the SAFE >package=. An important feature of the current versions of the model (e.g. SAFE v. 0.0B9) is that it calibrates to known values of base saturation. Any number of values may be used as calibration points within the time period of the model run. Having achieved a successful calibration, the model then develops a hindcast of soil solution chemistry and base saturation back from the calibration points to the starting date of the input time-series. It also predicts forward to the end of the input time-series.

7.4 Application of SAFE

As with any dynamic process model, SAFE is only a representation of a very complex reality and is subject to a variety of limitations in terms of process representation, data requirements and assumptions. Practical experience of SAFE has indicated that there are some key aspects of the model which must be carefully considered during application to a site and subsequent interpretation of results.

7.4.1 Data requirements

Essentially, SAFE requires two types of data set. One relates to the specific physical and mineralogical characteristics of the site and the other is the set of time series data for atmospheric deposition and nutrient cycling. The availability of these data (or meaningful surrogates from the literature) is an important constraint on the application of the model at any site.

7.4.2 Site parameters

Table 7.1 shows the range of soil data required for application of the model to a soil profile at Plynlimon in mid-Wales.

Whilst initially, the list looks quite daunting, the parameters can be subdivided into those which:

i) can be measured relatively easily at the site (horizon thickness, DOC concentration, soil temperature)
ii) can be reliably estimated from a knowledge of the site and plant root distribution (inflow, percolation, base cation uptake, nitrogen uptake)
iii) can be readily obtained from the literature (pCO_2, pKGibbsite, DOC concentration)

iv) which require careful measurement or are difficult to estimate (soil mineralogy, bulk density, exposed surface area, soil moisture content).

Items falling into category (iv) are likely to place practical constraints on the application of the model. Ideally, the model requires a surface-area weighted soil mineralogy which should be determined for the soil of interest. This is an expensive, time-consuming and probably impractical task. Mineralogical data are usually determined on a percentage by weight basis for the fine earth fraction (<2mm particle size) and not relative to surface area. Percent by weight data are generally used in applications of both PROFILE and SAFE. In Scotland, the mineralogy of the major groups of soil forming parent materials has already been determined and weathering rates have been calculated using PROFILE (Langan *et al.*, 1995). Within England and Wales data are gradually becoming available under the DETR critical loads programme which will provide quantitative mineralogy for a number of the acid sensitive soil-parent material combinations. The mineralogical constraint will, therefore, soon be overcome. Sensitivity analysis of the model shows that, depending on the soil and parent material, soil mineralogy is an important component in relation to predictive uncertainty (Jonsson 1994; Zak *et al.*, 1997).

Table 7.1 Input data for individual soil layers (Oh, Eag, Bs C) at Plynlimon.

Parameter	Unit	Oh	Eag	Bs	C
Horizon thickness	m	0.07	0.06	0.16	0.02
Bulk density	kg m^{-3}	769	921	862	862
pCO_2	x ambient	7.5	10	17.5	20
Inflow	% of precipitation	100	85	80	75
Percolation	% of precipitation	85	80	75	75
Ca+Mg+K uptake	% of total max	85	10	5	0
N uptake	% of total	85	10	5	0
DOC	mg l^{-1}	9.5	6.0	3.7	2.3
pK Gibbsite		6.5	7.5	8.5	9.5
Exposed surface area	m^2m^{-3}	le3	3.27e6	2.81e6	3.37e5
CEC	keq kg^{-1}	60.9e-6	66.9e-6	41.3e-6	22.1e-6
Mineral	% of total				
Plagioclase feldspar		0.0	1.0	1.0	1.0
Muscovite		0.0	58.3	56.6	33.9
Chlorite		0.0	0.1	11.1	12.3
Vermiculite		0.0	0.8	0.2	0.1

The remaining items in category (iv) present rather more difficulties. As discussed earlier, weathering rate is highly dependent on the degree of wetting of the exposed mineral surface area as this determines the amount of mineral available for dissolution. Wetted surface area is calculated as a function of the exposed surface area of mineral and the soil moisture saturation. The latter is a function of the volumetric soil moisture content and the bulk density.

Model simulations are sensitive to variations in the value of the exposed mineral surface area (Jonsson 1994; Zak *et al.*, 1997). Exact measurement of mineral surface area (Aw) is extremely time consuming and costly. As an alternative it may be calculated from particle size data using the relationship between soil particle size and surface area proposed by Sverdrup *et al.* (1990), whereby:

$$Aw = (0.3 * Xsand + 2.2 * Xsilt + 8.0 * Xclay) * \Delta bulk \qquad (7.3)$$

$$\mathrm{Xcoarse} + \mathrm{Xsand} + \mathrm{Xsilt} + \mathrm{Xclay} = 1 \tag{7.4}$$

where

Δ bulk = bulk density
The size fractions are classified as:

Coarse	> 2000 :m
Sand	63-2000 :m
Silt	2-63 :m
Clay	< 2 :m

These are relatively easy to measure from samples collected on site and some data are available from Soil Survey memoirs which can allow more regionalized applications of the model. However, there is evidence from recent work that the equation used to calculate Aw places a major mathematical constraint on model predictions in that an upper limit is imposed on the value of Aw which may be underestimated by a factor of 100% (Hodson *et al.*, in press (a)).

Sensitivity analysis of PROFILE has indicated that soil moisture saturation is an important term contributing to uncertainty in weathering rate predictions (Jonsson 1994; Zak *et al.*, 1997). It depends on both volumetric soil moisture content and bulk density. The latter can be determined in the field using standard methods (e.g. Avery and Bascombe 1974) although measurements in stoney soils can present considerable problems. Nevertheless, accuracy is important as bulk density influences two of the main parameters (surface area and moisture saturation) which determine the weathering rate. In particular, the relationship between soil moisture saturation and bulk density is progressive, so that variation at high bulk density values has a proportionally greater effect on model predictions than variations at low bulk density values (Jonsson 1994). Volumetric soil moisture data are usually available from well characterized sites, and can be extrapolated from soil classifications (Sverdrup *et al.,* 1990). However, varying soil moisture content between 0.2 and 0.4 m^3_{water} / m^3_{soil} (the range of recommended default values) can lead to a 120% variation in weathering rates (Hodson *et al.*, in press (b)). Whilst this can be understood in terms of an increase in wetted mineral surface area and hence larger reaction surface, soil drainage characteristics exert a major control on soil moisture conditions and external climatic variability can cause wide variations in moisture status over the course of a year.

7.4.3 Time series variables

In common with all dynamic models, there is a requirement for time series data to drive the SAFE model. The availability of historical deposition scenarios is crucial to the success of the model in simulating changes in soil chemistry over time. This is a well recognized problem from applications of MAGIC and other dynamic acidification models and would benefit from a concerted effort to define historical deposition reconstructions on a regional basis within the UK.

SAFE also requires time-series data for net nutrient uptake and nutrient cycling parameters. These can be constructed from literature values and a knowledge of the nutrient dynamics of the ecosystem (e.g. Sverdrup *et al.*, 1995a), although this procedure is quite time consuming. For example, in forest systems, the time series has to take account of factors such as the changing nutrient demand of the crop with increasing age as well feedbacks through changes in net mineralization rates and litter inputs. The group in Lund have developed a nutrient cycling >front end= to SAFE for a forest ecosystem based on European data for Norway spruce. This has yet to be evaluated for UK plantation forest conditions. Two particular aspects of the nutrient cycling time series which need consideration in the UK context are a) the transition from semi-natural moorland vegetation to plantation forest and b) the representation of successive forest rotations. A useful development for the more widespread use of SAFE in the UK would be to set up appropriate templates for the nutrient cycling time series for ecosystems developed on acid sensitive soils (e.g. plantation Sitka spruce, heather moorland, semi-natural acid grassland).

7.5 Uncertainties in predicting critical loads using SAFE

Predictions of soil solution base cation to aluminium ratios are subject to uncertainty within the SAFE and PROFILE models. Sensitivity analyses of the PROFILE model have shown that predictions of base cation to aluminium ratios are sensitive to the value assigned to pKGibbsite (Goulding and Blake 1993; Zak *et al.*, 1997) and by analogy, the same will be true for SAFE. Indeed the value of the Gibbsite equilibrium constant generally has a strong forcing effect on calculated soil chemistry in the models which employ it. Its utility is open to question in that the gibbsite mineral is not found in acidic European temperate soils and the gibbsite equilibrium model does not effectively represent the equilibrium dynamics of aluminium in acid soils (Neal *et al.*, 1989; Andersen *et al.*,1990). Estimates of field values for pKGibbsite are acknowledged as problematic (Sverdrup *et al.*,1990) and work is ongoing in the development of alternative approaches to the gibbsite equilibrium model for incorporation within PROFILE and SAFE (Alveteg *et al.*,1995).

7.6 Scope for site-specific and regional modelling using SAFE

The SAFE model can be readily applied to specific, well characterized sites provided that certain basic data requirements can be met. Of these, the most important are soil mineralogy, bulk density and an estimate of volumetric moisture content. In principle the model can be applied regionally or to a series of less well characterized sites using extrapolated data and published defaults (e.g. Sverdrup *et al.*, 1990). At present it is not possible to say how the quality of predictions will be affected by using generalized data and more extensive sensitivity testing would be useful in order to identify a minimum set of parameters which must be known with reasonable accuracy. Some progress has been made towards this objective for the PROFILE model (e.g. Hodson and Langan 1996) and some major potential short-comings have been identified. Despite these reservations, PROFILE is able to predict successfully weathering rates which are in broad agreement with those derived from other methods (Langan *et al.*, 1996; Hodson and Langan 1996).

Whilst a times series of nutrient cycling input parameters can be developed for specific sites from >scratch=, it would be useful to develop methodologies to simplify this procedure. This could be achieved by constructing some generalized representative templates which can be adapted to specific sites. In this respect, the forest nutrient cycle >front end= developed by the Lund group should be evaluated under UK conditions. Forestry in the UK differs in many respects from that in other parts of Europe, not least in that the main species is Sitka rather than Norway spruce. A further development might be to consider linking SAFE to nutrient cycling models, although these are often data demanding and therefore of limited regional applicability.

SAFE was developed to simulate mineral soils and in principle the model can be run on organic soils by setting the mineral content to zero, and relying on the atmospheric inputs, solution chemistry and ion exchange reactions to determine soil solution chemistry. Critical loads could then be calculated using the base cation to hydrogen ion ratio rather than the $(Ca+Mg+K)/Al_{crit}$ ratio (UNECE 1996). The validity of this approach needs further investigation, since the model processes may be inappropriate to organic exchange surfaces (where surface charge exhibits a strong pH dependency) and where solution acidity is dominated by organic acids.

The SAFE model can be used to simulate stream water chemistry in that the percolate leaving the deepest soil horizon can be degassed to atmospheric pCO_2 values and mixed with water of specified DOC concentration. This is an unrealistic representation of the situation encountered in most UK upland streams where there is a baseflow component which is mixed with varying amounts of soil derived runoff depending on flow conditions. It would however, be interesting to explore possibilities for developing SAFE in relation to more realistic surface water simulations by using it to predict soil runoff chemistry under different land use / deposition scenarios. These runoff waters could then be mixed with a specified baseflow chemistry to predict stream water chemistry under a variety of flow conditions.

The SAFE model has a limited capability to handle nitrogen deposition and cycling and can thus be used to simulate the effects of changing N deposition to the terrestrial environment. Again, the limitations of the model must be appreciated in relation to the reliability of model predictions. As with other dynamic models historic time trends for the atmospheric deposition of nitrogen and base cations remain an ongoing uncertainty.

8. CRITIQUE OF DYNAMIC MODELS

Each dynamic model has an individual structure, or a different representation of a process, and utilise data which have been collated using different techniques. Each model will have different limitations. There are, however, some uncertainties which apply to all:

1. The aggregating or ‘lumping’ approach presents considerable conceptual problems and is a source of model uncertainty where data is sparse. All catchments exhibit strong heterogeneity in physical and chemical characteristics. This is incorporated in models in two ways:

   i) it is assumed that several chemical processes can be represented by simpler conceptualizations (process aggregation), for instance only the Al^{3+} species is involved in cation exchange between soil and soil water. If appreciable exchange of other aluminium complexes occurs, this combined approach may be unable to simulate that behaviour.

   ii) Chemical and physical characteristics across a catchment are assumed to be uniform (spatial aggregation). This assumption ignores any heterogeneity that may be present within the soil layers within a catchment. Also, localized differences in chemical properties and maxima and minima in acidification values will be smoothed out.

2. Most dynamic models are developed to look at long term effects and as such use average hydrologic conditions of mean annual precipitation and stream flow volume and cannot simulate short term hydrological effects. However, in MAGIC if time steps shorter than 1 year are used the model may be driven by partitioning the annual precipitation and streamflow into smaller segments and weighting each segment according to the within year variation of precipitation and the stream hydrograph. This enables the strong seasonal response, particularly in NO_3 streamwater concentrations, to be incorporated. Further work is required to introduce uncertainty around the simulated annual means which represent maximum and minimum concentrations associated with high and low flows.

3. Uncertainties in models currently arise from a lack of detailed understanding of several processes. These processes are not important at every site, but a lack of knowledge of any one process limits the interpretation of model predictions on a regional scale or when predicting responses of several areas. These include:

   i) the dynamics of the production, transport and consumption of organic matter within the systems.
   ii) the acid/base behaviour of dissolved organic material.
   iii) the dynamics of aluminium dissolution, transport and precipitation.
   iv) the complexation of inorganic aluminum with dissolved organic material (this is especially important for simulating biological toxicity).
   v) the functioning of the nitrogen cycle particularly with respect to the disruption of the cycle leading to increased leaching and mobility of nitrate.
   vi) the dynamics of forest growth with respect to the effects on the acid/base status of the soil (particular attention needs to be given to the effects of deforestation on soil processes).

   vii) sulphate adsorption/desorption.

Of these processes, (i) to (iv) do not contribute to uncertainty in predicted surface water ANC concentrations as they do not affect the processes that control the base cation or strong acid anion concentrations. In soils, however, aluminium is a key determinand in the critical loads methodology and in surface waters, aluminium is the most important toxic fraction. It is important, therefore, that these uncertainties are quantified. The processes (v) to (vii) are extremely important to model uncertainty with respect to surface water ANC and as such were the subject of more detailed study (Annex 2). The conclusion of this study indicates that the uncertainty can be considerably reduced if an historical surface water chemistry is available for a site or for similar sites within a region.

4. Uncertainties in deposition input data for the models, including:

   i) total (bulk+dry+occult) deposition estimates for S, NO_x, NH_4 and base cations.
   ii) the historical deposition trends for specific sites or regions.
   iii) the current rates of increase or decline in deposition.

Despite these uncertainties and limitations, dynamic models provide a unique tool for catchment management in relation to changes in atmospheric acidic deposition and land-use change. They provide the only tool for assessing the timing of hydrochemical response and this ability alone emphasises their capability above ‘equilibrium’ based critical load concepts.

Of the dynamic models available, MAGIC is considered to be the most useful to the EA in terms of:

i) it has been extensively tested against long-term and experimental data under a wide variety of geo-physical settings
ii) it requires a level of data input which is consistent with readily available information for most small catchments in the UK
iii) it is relatively easy and quick to calibrate and so amenable to extensive uncertainty analysis to give maximum and minimum predictions for a given site
iv) there is considerable expertise and experience available in its calibration and application in the UK.

Of course, any model application is only as good as the data used for parameterisation and calibration and it is data quality and availability that determines the applicability of MAGIC for catchment management and for input to decisions regarding regulation of emission sources. At small catchment scale (<10 km^2) adequate soil and water chemistry data should be available and if not, this can be collected quickly (within a few weeks) but the lack of historical data presents a potential problem in model calibration unless data from nearby sites can be used as a surrogate. At this scale, accurate specification of catchment input flux may provide another uncertainty in the model application. At regional scale, water chemistry data describing the annual output flux of ions is rarely available since regional water chemistry surveys are usually based on single water samples and this represents the key uncertainty in model calibration. This problem may be overcome by the use of Monte Carlo techniques or a multiple site, fuzzy optimisation approach. A research programme (DYNAMO) is currently underway to develop methods to scale-up hydrochemical models, including MAGIC, funded by the EU and IH.

In conclusion, it is clear that dynamic models, and in particular the MAGIC model, have a key role in a regulatory framework. They are well tested against historical pH reconstructions from lake sediment diatoms, catchment manipulation experiments and long-term monitoring data.

They are relatively simple to calibrate and require a minimum of observed data to produce future predictions which are qualitatively useful, for example in scenario analysis. Given an historical data record for a given site, the predictions are subject to less uncertainty and can be interpreted quantitatively. They are the only tools available with which to determine the potential response of soil and surface water to a change in atmospheric acidic deposition and as such they have considerable utility over the steady-state critical loads methodologies.

9. DISCUSSION AND FUTURE RECOMMENDATIONS

Dynamic models provide the only opportunity to determine the likely future response of soil and stream water chemistry to changes in deposition of sulphur and nitrogen. They are therefore needed to complement steady state techniques for critical load calculations. This document has highlighted the usefulness of the MAGIC model as a tool for calculating critical loads under different emission strategies. The feasibility of scaling up the model from site specific to regional scales has been proven, this enables statistics for future behaviour of surface waters for the region as a whole to be estimated which is useful for policy decisions. The model has been used to examine effects of land-use, in particular forest growth processes, on the acidification process and the rate of recovery at forested sites. Output from MAGIC has been linked using simple empirical relationships to relate biological status in aquatic systems to their chemistry, and the use of a diatom model has shown some potential for model validation.

For this research project, a series of analyses of MAGIC were undertaken to explore the key uncertainties in the model representation of S dynamics, forest uptake and N dynamics. Annex 2 serves as a summarised project record and documents the new research carried out.

There are several areas in which further research is planned in MAGIC and several other dynamic models, including:

i) An improvement in the description of nitrogen processes in the model is required although this can only follow development of a more detailed understanding of the nitrogen biogeochemistry of catchment systems and in particular moorland/grassland areas. The processes controlling nitrogen leakage from terrestrial ecosystems is currently being implemented in an enhanced version of the model MAGIC-WAND (Model of Acidification of Groundwater In Catchments With Aggregated Nitrogen Dynamics) in which nitrification, plant uptake, mineralization and denitrification are considered.

ii) Whilst the development of acidification in response to sulphur deposition is relatively well understood in terms of the chemistry of soil and aquatic systems, the biological interactions and eventual biological effects (on flora and fauna) are less certain and need to be investigated. This, however, is a limitation of current biological research which potentially limits the interpretation of model predictions and does not contribute to uncertainty in the dynamic models themselves. The biological impact of acidification due to high nitrate levels on the ecosystem is less well known and also needs to be assessed.

iii) Because of the observed seasonal variation of some acidification processes (e.g. nitrogen leaching), and the effect of episodic events, particularly on the biological status of surface waters (De Walle *et al.*, 1994), it would be appropriate to develop the model to run on a monthly timescale. This requires more detailed temporal data and the development and incorporation of a hydrological model to determine flow pathways and soil moisture. Such a development is currently the focus of a research programme within the NERC Environmental Diagnostics Programme.

iv) Long term data monitoring programmes need to be established at sensitive key catchments. These data could be used to calibrate, validate and apply models for critical load assessment. Wide scale assessment of soil base chemistry and carbon and nitrogen status is also desirable to facilitate model application and to reduce uncertainty.

v) Dynamic models need to take greater account of acidification processes in soil layers, in particular the sensitive upper organic horizons upon which soil critical load maps are based (Hornung *et al.*, 1995). One layer soil models with aggregated properties are inadequate for such studies. 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.

vi) Some of the model processes in the long-term will be affected by climate change. Synergistic effects between atmospheric deposition and climate change should therefore be considered in future model development and scenario assessment.

vii) There exists a clear need to develop the concept of critical loads for peat soils in the light of criticism relating to current empirical models. With respect to dynamic models, considerable research is required in relation to hydrological modelling, organic matter charge characteristics, redox reactions and nutrient cycling. Detailed plot and catchment models such as WHAM and CHUM represent a step towards the development of a generally applicable modelling tool but require significant input data.

viii) The importance of regional model applications within a regulatory framework demands that up-scaling procedures continue to be developed. Clearly, the uncertainty in regional model predictions will be higher compared to site specific predictions as a result of the data availability at appropriate space and time scales. The development of statistical techniques and methods of simulating chemistry of 'whole' river systems offer significant steps forward in regional scenario assessments.

ix) Since dynamic models offer an opportunity to assess the time development of soil and water chemistry in response to changes in atmospheric deposition, the use of critical 'thresholds' in the critical loads framework is inappropriate (for example, BC/Al ratio = 1 or ANC = 0) since these imply step changes in biological response. No other thresholds have been advanced in this respect and this remains a key requirement. An alternative approach involving plant growth response has been incorporated within the SAFE model but this is not well developed or tested. Nevertheless, in some circumstances where detailed soil geochemical and nutrient cycling information is available, SAFE is a more appropriate model to assess different responses between species than MAGIC.

x) There is a general lack of understanding of the biological response to acid episodes which adds uncertainty to critical load assessments. Furthermore, the MAGIC and SAFE models operate on annual time-step and so do not explicitly incorporate episodic chemistry changes. This is a key area for future development.

With respect to use of dynamic models for regulatory control, the MAGIC model can provide unique information on the soil and water acidity response to a change in atmospheric acidic deposition. With minimal data collection, the model can be calibrated and used for scenario analysis in a qualitative manner, i.e. to determine the relative impacts of different emission control strategies. At most sites, model predictions could be improved by constraining the calibration using surrogate data from similar sites within the region. At a regional scale, data for calibration is rarely available and a comprehensive soil and water sampling study would be required. This is made attractive, however, by the potential to incorporate statistical uncertainty analysis within the model application and interpretation of results. The model requires a detailed knowledge of soil and surface water biogeochemistry and has a high potential for incorrect or inappropriate usage in terms of calibration and prediction.

Current developments are aimed at improving the chemical process representation within the model to reduce prediction uncertainty and improving the methods of regional application. A further improvement will be the incorporation of seasonal and high/low flow effects. In its current form, however, MAGIC provides a tool for advising on long-term acidification status, particularly at those sites where change in deposition of sulphur is anticipated. As a tool for assessing nitrogen deposition, the existing model provides only a qualitative output which nevertheless can provide important information with respect to comparison of different N emission scenarios, for example, the relative difference in ecosystem impact can be assessed against the cost of implementing each scenario.

10. REFERENCES

Adams, W.A., Karim, M.I. and Gafoor, S.N. (1987) Composition and properties of poorly ordered minerals in Welsh soils. 1. Composition. *Journal of Soil Science* 38, 85-93.

Adams, W.A., Ali, A.Y. and Lewis, P.J. (1990) Release of cationic aluminium from acidic soils into drainage water and relationships with landuse. *Journal of Soil Science* 41: 255-268.

Alveteg, M., Sverdrup, H. and Warfvinge, P. (1995) Developing a kinetic alternative in modelling soil aluminium. *Water Air and Soil Pollution* 79: 377-389.

Andersen, S., Christophersen, N., Mulder, J., Seip, H.M. and Vogt, R.D. (1990) Aluminium solubility in the various soil horizons on an acidified catchment. In: *The Surface Waters Acidification Programme*, ed. B.J. Mason, pp 155-159, Cambridge University Press.

Avery, B.W. and Bascomb, C.L. (eds) (1974) *Soil Survey Laboratory Methods*. Technical

Monograph 6, Soil Survey, Harpenden.

Baird, A.J. (1995) Hydrological investigations of soil water and groundwater processes in wetlands. In: Heathewaite, A.L. and Hughes, J.M.R., Hydrology and Hydrochemistry of British Wetlands, Wiley, Chichester, pp. 111-129.

Baker, J.P. *et al.* (1990) *Biological Effects of Changes in Surface Water Acid-base Chemistry.* National Acid Precipitation Assessment Program, State of Science/Technology Report, Washington DC.

Battarbee, R.W. (1986) Diatom analysis. In: *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. and Stevenson, A.C. (1988) *Lake Acidification in the UK 1800-1986: Evidence from the Analysis of Lake Sediments.* ENSIS Publishing, London.

Bellamy, D.J. (1968) An ecological approach to the classification of the lowland mires of Europe. Proceedings of the 3rd International Peat Congress, Quebec, pp. 74-79.

Berggren, D. and Mulder, J. (1995) The role of organic matter in controlling aluminium solubility in acidic mineral soil horizons. *Geochimica et Cosmochimica Acta* 59: 4167-4180.
Brown, K.A. (1986) Formation of organic sulphur in UK anaerobic peat. Soil Biology and Biochemistry 18: 131-140.

Burton, R.G.O. and Hodgson, J.M. (eds) (1987) Lowland Peat in England and Wales. Soil Survey Special Survey No. 15, Soil Survey, Harpenden.

Charlson, R.L. and Rodhe, H. (1982) Factors controlling the acidity of natural rainwater. Nature 295: 683-685.

CLAG (1994) *Critical Loads of Acidity in the United Kingdom.* Critical Loads Advisory Group Summary Report, Institute of Terrestrial Ecology, Edinburgh.

CLAG (1995) *Critical Loads of Acid Deposition for United Kingdom Freshwaters.* Critical Loads Advisory Group, Sub-group Report on Freshwaters, Department of the Environment, London.

Clymo, R.S. (1984) Sphagnum-dominated peat bog: a naturally acidic ecosystem. Philosophical Transactions of the Royal Society of London, B305: 487-499.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N. (1985a) Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resources Research* 121: 1591-1601.

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

Cosby, B.J., Wright, R.F, Hornberger, G.M. and Galloway, J.N. (1985b) Modelling the effects of acid deposition: estimation of the effects of long-term water quality responses in a small forested catchment. *Water Resources Research* 21, 1291-1301.

Cosby, B.J., Hornberger, G.M, Galloway, J.N. and Wright, R.F. (1985c) Freshwater acidification from atmospheric deposition of sulphuric acid: a quantitative model. *Environmental Science and Technology* 19, 1145-1149.

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

Cosby, B.J., Hornberger, G.M. and Wright, R.F. (1989) Estimating time delays and extent of regional de-acidification in southern Norway in response to several deposition scenarios. In: *Regional Acidification Models.* (eds) Kamari, J., Brakke, D.F., Jenkins, A., Norton, S.A. and Wright, R.F. Springer Verlag.

Cosby, B.J., Jenkins, A., Ferrier, R.C., Walker, T.A.B. and Miller, J.D. (1990) Modelling stream acidification in afforested catchments: long term reconstructions at two sites in Central Scotland. *Journal of Hydrology* 120, 140-162.

Cresser, M. and Edwards, A. (1987) *Acidification of Waters.* Cambridge University Press, Cambridge.

Cronan, C.S. and Grigal, D.F. (1995) Use of calcium/aluminium ratios as indicators of stress in forest ecosystems. *Journal of Environmental Quality* 24: 209-226.

Damman, A.W.H. (1988) Regulation of nitrogen removal and retention in Sphagnum bogs and other peatlands. Oikos 51:291-305.

Davis, R.B., Anderson, D.S. and Berge, F. (1985) Palaeolimnological evidence that lake acidification is accompanied by loss of organic matter. *Nature* 316: 436-438

Davies, T.D. *et al.* (1992) Acidic episodes in surface waters in Europe. *Journal of Hydrology* 132: 25-69.

de Vries, W. and Breeuwsma, A. (1987) The relation between soil acidification and element cycling. *Water Air and Soil Pollution* 35: 293-310.

de Vries, W., Reinds, G.J., Posch, M. and Kamara, J. (1994) Simulation of soil response to acidic deposition scanarios in Europe. *Water Air and Soil Pollution* 78: 215-246.

de Walle, D.R., Swistick, B.R. and Sharpe, W.E. (1994) Episodic flow-duration analysis: a method of assessing toxic exposure of brook trout (*Salvelinus fontinalis*) to episodic increases in aluminium. JOURNAL??

Dise, N.B. (1984) *A Synoptic Survey of Headwater Streams in Shenandoah National Park, Virginia to Evaluate Sensitivity to Acidification by Acid Deposition.* M.Sc thesis, Department of Environmental Science, University of Virginia, Charlottesville.

Dowding, P. (1974) Nutrient losses from litter on IBP tundra sites. In: Holding, A.J., Heal, O.W., McLean, S.F. and Flanagan, P.W. (eds) Soil Organisms and Decomposition in Tundra. International Biological Programme, Tundra Biome. Tundra Biome Steering Committee, Stockholm, Sweden, pp. 363-373.

Driscoll, C.T., Johnson, N.M., Likens, G.E. and Feller, M.C. (1988) Effects of acidic deposition on the chemistry of headwater streams: a comparison between Hubbard Brook, New Hampshire and Jamieson Creek, British Columbia. *Water Resources Research* 24: 195-200.

Driscoll, C.T., Likens, G.E., Hedin, L.O., Eaton, J.S. and Bormann, E.H. (1989) Changes in the chemistry of surface waters. *Environmental Science and Technology* 23: 137-142.

Edwards, A.C., Creasey, J. and Cresser, M.S. (1986) Soil freezing effects on upland stream solute chemistry. *Water Research* 20: 831-834.

Ferguson, P. and Lee, J. (1983) The growth of Sphagnum species in the southern Pennines. Journal of Bryology 12: 579-586.

Forsius, M., Alveteg, M., Jenkins, A., Johansson, M., Kleemola, S., Lukewille, A., Posch, M., Sverdrup, H. and Walse, C. (1996) Dynamic model applications for assessing the effects of SO_2 and NO_x reduction strategies on ICP Integrated Monitoring Sites in Europe. Tema Nord, Nordic Council of Ministers, Copenhagen (in preparation).

Forti, M.C., Neal, C. and Jenkins, A. (1994) Modelling perspective of the deforestation impact in streamwater quality of small preserved forest areas in the Amazonian rainforest. *Water, Air and Soil Pollution* 79,325-337.

Freeman, C., Lock, M.A., Hughes, S. and Teynolds, B. (1997 Nitrous oxide emissions and the use of wetlands for water quality amelioration. Environmental Science and Technology 31: 2438-2440.

Gilman, K. (1994) Hydrology and Wetland Conservation. Wiley, Chichester.

Giusti, L. (1992) Chemical weathering and element mobilities at Loch Dee, Scotland. *Proceedings of the Loch Dee Symposium* held on 8-9th December 1992. 71-82.

Glover, G.M. and Webb, A.H. (1979) Weak and strong acids in surface waters in the Tovdal region of southern Norway. *Water Research* 13: 781-783.

Goreham, E., Bayley, S.E. and Schindler, D.W. (1984) Ecological effects of acid deposition upon peatlands: A neglected field in "Acid Rain" research. Canadian Journal of Fisheries and Aquatic Sciences 41: 1256-1268.

Goulding, K.W.T. and Blake, L. (1993) Testing the PROFILE model on long-term data. In: *Critical Loads: Concept and Applications*, eds M. Hornung and R.A. Skeffington, pp.68-73, ITE Symposium No. 28, HMSO, London.

Gundersen, P. (1992) Mass balance methods for establishing critical loads for nitrogen deposition with respect to acidification and eutrophication in terrestrial ecosytems, including groundwater. *Background Document to UN-ECE Workshop "Critical Loads for Nitrogen"*, Lokeberg, Sweden, 6-10 April 1992.

Heathewaite, A.L., Gottlich, K.H., Burmeister, E.G., Kaule, G. and Grospietsh, Th. (1993) Mires: definitions and form. In: Heathewaite, A.L. and Gottlich, K.H. (eds), Mires: Process, Exploitation and Conservation, Wiley, Chichester.

Helyar, K.R. (1976) Nitrogen cycling and soil acidification. *Journal of Australian Institute of Agricultural Sciences*, December 1976, 217-221.

Hendershot, W.H., Warfvinge, P., Courchesne. F. and Sverdrup, H.U. (1991) The mobile anion concept - Time for a reappraisal? *Journal of Environmental Quality* 20: 505-509.

Henriksen, A. (1980) Acidification of Freshwaters - a large scale titration. In: (eds) D. Drablos and A. Tollan. *Ecological Impact of Acid Precipitation*. SNSF-Project, As, Norway, 383p.

Henriksen, A., Kamari, J., Posch, M. and Wilander, A. (1992) Critical loads of acidity: Nordic surface water. *Ambio* 21: 356-363.

Hodson, M.E. and Langan, S.J. (1996) An appraisal of the use of the PROFILE model to calculate mineral weathering rates. In: *4th International Symposium on the Geochemistry of the Earth=s Surface, Conference Proceedings* ed. S.H. Bottrell, pp 581-586, Leeds University.

Hodson, M.E., Langan, S.J. and Wilson, M.J. in press (a) A critical evaluation of the use of the PROFILE model in calculating mineral weathering rates. *Water Air and Soil Pollution.*

Hodson, M.E., Langan, S.J. and Wilson, M.J. in press (b) A sensitivity analysis of the PROFILE model in relation to the calculation of soil weathering rates. Applied Geochemistry.

Hogberg, P. and Jensen, P. (1994) Aluminium and uptake of base cations by tree roots: A critique of the model proposed by Sverdrup *et al. Water Air and Soil Pollution* 75: 121-125.

Holmberg, M., Hari, P. and Nissinen, A. (1989) A model of ion dynamics and acidification of soil: application to historical soil chemistry data of Sweden. In: *Regional Acidification Models*. (eds.) Kamari, J., Brakke, D.F., Jenkins, A., Norton, S.A. and Wright, R.F. Springer Verlag.

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. *Water Resources Research* 22, 1293-1302.

Hornberger, G.M., Cosby, B.J., and Wright, R.W. (1989) Historical reconstructions and future forecasts of regional surface water acidification in southernmost Norway. *Water Resources Research* 25, 9, 2009-2018.

Hornung, M. (1985) Acidification of soils by trees and forests. *Soil Use and Management* 1: 24-28.

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.

Hughes, J.M.R. and Heathewaite, A.L. (1995) Introduction. In: Heathewaite, A.L. and Hughes, J.M.R., Hydrology and Hydrochemistry of British Wetlands, Wiley, Chichester, pp. 1-8.

Hughes, S., Reynolds, B. and Roberts, J.D. (1990) The influence of land management on concentrations of dissolved organic carbon and its effects on the mobilization of aluminium and iron in podzol soils in Mid-Wales. *Soil Use and Management* 6: 137-144.

Ivanov, K.E. (1981) Water Movement in Mirelands. Translated by A.Thompson and H.A.P. Ingram, Academic Press, London.

Jacks, G. (1990) Mineral weathering studies in Scandinavia. In: *The Surface Waters Acidification Programme*, edited by B.J. Mason, 221-222, Cambridge University Press, Cambridge.

Jenkins, A., Whitehead, P.G., Musgrove, T.J. and Cosby, B.J. (1990) A regional model of acidification in Wales. *Journal of Hydrology* 116, 403-416.

Jenkins, A. (1995) Dynamic modelling of chemical responses for future changes in acid deposition and land-use. In: *Critical Loads of Acid Deposition of UK Freshwaters*. Report of the Critical Loads Advisory Group, sub-group on freshwaters for the UK Department of Energy.

Jenkins, A. and Renshaw, M. (1995) *Model of Acidification of Groundwaters In Catchments With Aggregated Nitrogen Dynamics (MAGIC-WAND).* National Rivers Authority R&D Note 468.

Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C.E.M., Ferrier, R. and Swingewood, P. (1997) *Modelling Surface Water acidification in the UK.* Institute of Hydrology Report 131.

Jenkins, A., Coric, S., Reynolds, B., Curtis, C. and Renshaw, M. in press. Critical loads for soils and freshwaters; A comparison of methods at the Plynlimon catchments. *Hydrology and Earth Systems Sciences.*

Johnson, D.W., Cresser, M.S., Nilsson, S.I., Turner, J., Ulrich, B., Binkley, D., and Cole, D.W. (1991) Soil changes in forest ecosystems: evidence for and probable causes. *Proceedings of the Royal Society of Edinburgh* 97B: 81-116.

Jonsson, C. (1994) *Modelling Acidification and Nutrient Supply in Forest Soil.* Reports in Ecology and Environmental Engineering 1:(1994), Department of Chemical Engineering II, Lund University, Sweden.

Juggins, S., Flower, R.J. and Battarbee, R.W. In Press. Palaeolimnological evidence for recent chemical and biological changes in the UK Acid Waters Monitoring Network sites. *Freshwater Biology.*

Kamari, J., Posch, M., Kahkonen, A.M. and Johansson, M. (1994) Modelling potential long-term responses of a small catchment in Lapland to changes in sulphur deposition. *Science of the Total Environment* 160/161, 687-701.

Kahl, J.S. *et al.* (1992) Mechanisms of episodic acidification in low-order streams in Maine, USA. *Environmental Pollution* 78: 37-44.

Kononova, M.M. (1966) *Soil Organic Matter.* Pergamon Press, New York.

Koskinen, W.C. and Keeney, D.R. (1982) Effect of pH on the rate of gaseous products of denitrification in a silt loam soil. Soil Science Society America, Journal 46: 1165-1167.

Krug, E.C. and Frink, C.R. (1983) Acid rain on acid soil: a new perspective. *Science* 221: 520-525.

Langan, S.J., Sverdrup, H.U. and Coull, M. (1995) The calculation of base cation release from the chemical weathering of Scottish soils using the PROFILE model. *Water Air and Soil Pollution* 85: 2497-2502.

Langan, S.J., Reynolds, B. and Bain, D.C. (1996) The calculation of base cation release from mineral weathering in soils derived from Palaeozoic greywackes and shales in upland UK. *Geoderma* 69: 275-285.

Lee, J.A., Press, M.C., Woodin, S. and Ferguson, P. (1987) Responses to acidic deposition in ombrotrophic mires in the UK. In: Hutchinson, T.C. and Meema, K.M. (eds) Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems. NATO ASI Series Vol. G16, Springer-Verlag, Berlin, pp. 549-560.

Lee, Y.H. and Hultberg, H. (1990) Studies of strong and weak acid speciation in freshwaters in experimental forested catchments. In: *The Surface Waters Acidification Programme*, edited by B.J. Mason, 183-192, Cambridge University Press, Cambridge.

Lokke, H., Bak, J., Falkengren-Grerup, U., Finaly, R., Ilvesniemi, H., Nygaard, P.H. and Starr, M. (1996) Critical loads of acidic deposition for forest soils: Is the current approach adequate? *Ambio* 25: 510-516.

MacMillan, D.C. and Ferrier, R.C. (1994) A big economic model for estimating the benefits of acid rain abatement for salmon fishing: a case study in south west Scotland. *Journal of Environmental Planning and Management* 37, 2, 131-144.

McKnight, D., Thurman, E., Wershaw, R. and Hemond, H. (1985) Biogeochemistry of aquatic substances in Thoreau's Bog, Concord Massachusetts. Ecology 66: 1339-1352.

Neal, C., Skeffington, R.A., Williams, R. and Roberts, D.J. (1987) Aluminium solubility controls in acid waters: the need for a reappraisal. *Earth and Planetary Science Letters* 86: 113-119.
Neal, C. (1988a) Determination of dissolved CO_2 in upland stream water. *Journal of Hydrology* 99: 127-142.

Neal, C. (1988b) pCO_2 variations in streamwaters draining an acidic and acid sensitive spruce forested catchment in mid-Wales. *Science of the Total Environment* 76: 279-283.

Neal, C. (1988c) Aluminium solubility relationships in acid waters; a practical example of the need for a radical reappraisal. *Journal of Hydrology* 104: 141-159.

Neal, C., Reynolds, B., Stevens, P. and Hornung, M. (1989) Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales. *Journal of Hydrology* 106: 155-175.

Neal, C., Reynolds, B., Stevens, P.A., Hornung, M. and Brown, S. (1990a) Dissolved inorganic aluminium in acid stream and soil waters in Wales. In: *Acid Waters in Wales*, edited by R.W. Edwards, A.S. Gee and J.H. Stoner, 173-188, Kluwer, Dordrecht.

Neal, C., Robson, A.J. and Smith, C.J. (1990b) Acid Neutralisation Capacity variations for Hafren forest streams: Inferences for hydrological processes. *Journal of Hydrology* 121: 85-101.

Neal, C., Robson, A., Reynolds, B. and Jenkins, A. (1992) Prediction of future short-term stream chemistry - a modelling approach. *Journal of Hydrology* 130: 87-103.

Nilsson, S.I., Miller, H.G. and Miller, J.D. (1982) Forest growth as a possible cause of soil and water acidification: An examination of the concepts. *Oikos* 39: 40-49.

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

Nordstrom, D.K. (1982) The effect of sulphate on aluminium concentrations in natural waters: some stability relations in the system Al_2 O_3-SO_4-H_2O at 298K. *Geochimica Cosmochimica Acta* 46: 681-692.

Ormerod, S.J., Weatherley, N.S., Varallo, P.V. and Whitehead, P.G. (1988) Preliminary empirical models of the historical and future impact of acidification on the ecology of Welsh streams. *Freshwater Biology* 20: 127-140.

Ormerod, S.J., Weatherley, N.S., Merritt, W.J., Gee, A.S. and Whitehead, P.G. (1990) Restoring acidified streams in upland Wales: a modelling comparison of the chemical and biological effects of liming and reduction in sulphate deposition. *Environmental Pollution* 64: 67-85.

Ormerod, S.J. (1993) Assessing critical loads of ANC for stream organisms using empirical data. In: *Critical Loads: Concepts and Applications.* (eds M. Hornung and R.A. Skeffington), ITE Symposium No. 28, pp. 115-118, HMSO, London.

Ormerod, S.J. and Jenkins, A. (1994) The Biological Effects of Acid Episodes. *Acidification of Freshwater Ecosystems: Implications for the Future.* (Eds C.E.W. Steinberg and R.F. Wright), p.259-272. John Wiley & Sons Ltd.

Ormerod, S.J. (1995) Modelling biological responses, present and future. In: Critical loads of acid deposition of UK freshwaters. *Report of the Critical Loads Advisory Group*, sub-group on freshwaters for the UK Department of Energy.

Patrick, S.T., Monteith, D.T. and Jenkins, A. (1995) *The United Kingdom Acid Waters Monitoring Network. Analysis and Interpretation of Results.* ENSIS Publishing, London.

Posch, M., Reinds, G.J. and 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.

Posch, M., de Smet, P.A.M., Hettelingh, J-P., Downing, R.J. (eds) (1995) *Calculation and Mapping of Critical Thresholds in Europe.* CCE Status Report (1995), RIVM, Bilthoven, The Netherlands.

Rengel, Z. (1992) Role of calcium in aluminium toxicity. *New Phytologist* 121: 499-513.

Reuss, J.O. and Johnson, D.W. (1986) Acid deposition and the acidification of soils and waters. Springer Verlag, Berlin, 1-119.

Reynolds, B., Neal, C., Hornung, M., Hughes, S. and Stevens, P.A. (1988) Impact of afforestation on the soil solution chemistry of stagnopodzols in Mid-Wales. *Water Air and Soil Pollution* 38: 55-70.

Reynolds, B., Emmett, B.A. and Woods, C. (1992) Variations in streamwater nitrate concentrations and nitrogen budgets over 10 years in a headwater catchment in mid-Wales. *Journal of Hydrology* 136: 155-175.

Reynolds, B. and Ormerod, S.J. (1993) *A Review of the Impact of Current and Future Acid Deposition in Wales.* Institute of Terrestrial Ecology, Bangor.

Reynolds, B. in press. Predicting soil acidification trends at Plynlimon using the SAFE model. *Hydrology and Earth Systems Sciences.*

Robson, A.J. and Neal, C. (1990) Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales. *Journal of Hydrology* 116: 345-365.

Rodwell, J.S. (ed.) (1991) British Plant Communities, Vol. 2. Mires and Heaths. Cambridge University Press, Cambridge.

Ross, S.M. (1995) Overview of the hydrochemistry and solute processes in British wetlands. In: Heathewaite, A.L. and Hughes, J.M.R., Hydrology and Hydrochemistry of British Wetlands, Wiley, Chichester, 133-181.

Rundle, S.D., Weatherley, N.S. and Ormerod, S.J. (1995) The effects of catchment liming on the chemistry and biology of upland Welsh streams: Testing predictions from empirical models. *Freshwater Biology* 34: 165-175.

Runge, M. and Rode, M.W. (1990) Effects of soil acidity on plant associations. In: *Soil Acidity,* edited by B Ulrich and ME Sumner, Springer-Verlag, Berlin.

Sanger, L.J., Billett, M.F. and Cresser, M.S. (1994) The effects of acidity on carbon fluxes from ombrotrophic peat. Chemistry and Ecology 8: 249-264.

Sanger, L.J., Billett, M.F. and Cresser, M.S. (1996) The effect of precipitation chemistry upon anion and cation fluxes from the surface layer of ombrotrophic mires in the UK. Journal of Applied Ecology 33: 754-772.

Sefton, C.E.M. and Jenkins, A. (1998) A regional application of the MAGIC model in Wales: calibration and assessment of future recovery using a Monte-Carlo approach. *Hydrology and Earth System Sciences* 2 (4): 521-531.

Skeffington, R.A. and Brown, D.J.A. (1992) Timescales of recovery from acidification: Implications of current knowledge for aquatic organisms. *Environmental Pollution* 77: 227-234.

Skeffington, R.A., Wilson, E.J., Immirzi, P. and Maltby, E. (1995) Setting a critical load for dystrophic peat. In: Heathewaite, A.L. and Hughes, J.M.R., Hydrology and Hydrochemistry of British Wetlands, Wiley, Chichester, pp. 183-198.

Skiba, U. and Cresser, M.S. (1989) Prediction of long-term effects of rainwater acidity on peat and associated drainage water chemistry in upland areas. Water Research 23: 1477-1482.

Skiba, U., Cresser, M.S., Derwent, R.G. and Futty, D.W. (1989) Peat acidification in Scotland. Nature 337: 68-69.

Smith, C.M.S. (1993) Assessment of Critical Loads of Acidity for Selected UK Upland Organic Soils. Unpublished PhD Thesis, University of Aberdeen.

Smith, C.M.S., Cresser, M.S. and Mitchell, R.D.J. (1993) Sensitivity to acid deposition of dystrophic peat in Great Britain. Ambio 22: 22-26.

Stevens, P.A., Adamson, J.K., Anderson, M.A. and Hornung, M. (1988) Effects of clearfelling on surface water quality and site nutrient status. In: *Ecological Change in the Uplands*, Special Publication Number 27 of the British Ecological Society, edited by M.B. Usher and D.B.A. Thompson, 289-293, Blackwell, Oxford.

Stevens, P.A., Ormerod, S.J. and Reynolds, B. (1997) *Final Report on the Acid Waters Survey for Wales. Volume 1 Main Text.* Institute of Terrestrial Ecology, Bangor.

Sverdrup, H. and 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. (1990) *The Kinetics of Base Cation Release due to Chemical Weathering.* Lund University Press.

Sverdrup, H., de Vries, W. and 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, Federal Republic of Germany.

Sverdrup, H. and Warfvinge, P. (1993a) *The Effect of Soil Acidification on the Growth of Trees, Grass and Herbs as Expressed by the (Ca+Mg+K)/Al Ratio.* Reports in Ecology and Environmental Engineering 2:1993, Department of Chemical Engineering II, Lund University, Sweden.

Sverdrup, H. and Warfvinge, P. (1993b) Calculating field weathering rates using a mechanistic geochemical model - PROFILE. *Journal of Applied Geochemistry*, 8, 273-283.

Sverdrup, H., Warfvinge, P. and Nihlgard, B. (1994) Assessment of soil acidification effects on forest growth in Sweden. *Water Air and Soil Pollution* 78: 1-36.

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

Sverdrup, H., Alveteg, M., Langan, S. and Paces, T. (1995b) Biogeochemical modelling of small catchments using PROFILE and SAFE. In: *Solute Modelling in Catchment Systems*, ed. S.T. Trudgill, pp. 75-89, Wiley, Chichester.

Thurman, E.M. (1985) *Organic Geochemistry of Natural Waters.* Nihoff/Junk Publishers, Dordrecht, Netherlands.

Tipping, E. and Hurley, M.A. (1988) A model of solid-solution interactions in acid organic soils based on the complexation properties of humic substances. Journal of Soil Science 39: 505-519.

Tipping, E., Reddy, M.M. and Hurley, M.A. (1990) Modelling electrostatic and heterogeneity effects on proton dissociation from humic substances. Environmental Science and Technology 24: 1700-1705.

Tipping, E., Berggren, D., Mulder, J. and Woof, C. (1995) Modelling the solid-solution distributions of protons, aluminium, base cations and humic substances in acid soils. European Journal of Soil Science 46: 77-94.

Tipping, E. (1996) CHUM: a hydrochemical model for upland catchments. Journal of Hydrology 174: 305-330.

Ugolini, F.C., Minden, R., Dawson, H. and Zachara, J. (1977) An example of soil processes in the Abies amabilis zone of Central Cascades, Washington. *Soil Science* 124: 291-302.

Ulrich, B. (1990) Waldsterben: Forest decline in West Germany. *Environmental Science and Technology* 24: 436-441.

UNECE (1996) Mapping Critical Levels/Loads UNECE Convention on Long-range Transboundary Air Pollution, Federal Environmental Agency, Berlin.

UNECE (1996) *Manual on Methodologies for Mapping Critical Loads/Levels.* Draft Manual of the UNECE Task Force on Mapping.

Urban, N.R. and Bayley, S.E. (1986) The acid-base balance of peatlands: a short-term perspective. Water Air and Soil Pollution 30: 791-800.

van Breemen, N., Driscoll, C.T. and Mulder, J. (1984) Acidic deposition and internal proton sources in acidification of soils and waters. Nature 307: 599-604.

Wilson, E.J., Skeffington, R.A., Maltby, E., Immirzi, P., Swanson, C. and Proctor, M. (1995) Towards a new method of setting a critical load of acidity for ombrotrophic peat. Water Air and Soil Pollution 85: 2491-2496.

Warfvinge, P., Holmberg, M., Posch, M. and Wright, R.F. (1992) The use of dynamic models to set target loads. *Ambio 21*, 5, 369-376.

Warfvinge, P., Falkengren-Grerup, U. and Sverdrup, H. (1993) Modelling long-term base cation supply in acidified forest stands. *Environmental Pollution* 80: 1-14.

Waters, D. and Jenkins, A. (1992) Impacts of afforestation on water quality trends in two catchments in mid-Wales. *Environmental Pollution* 77, 2/3, 167-172.

Westling, O. (1990) Strong and organic acid in the runoff from peat and woodland. In: *The Surface Waters Acidification Programme*, edited by B.J. Mason, 137-147, Cambridge University Press, Cambridge.

Whitehead, P.G., Black, V., Jenkins, A., Wright, R.F. and Cosby, B.J. (1993) Modelling acidification at Beacon Hill - a low rainfall, high pollutant deposition site in central England. *Environmental Pollution* 79, 3, 277-281.

Wigington, P.J., Davies, T.D., Tranter, M. and Eshleman, K.N. (1992) Comparison of episodic acidification in Canada, Europe and the United States. *Environmental Pollution* 78: 29-35.

Wilkinson, J. and Jenkins, A. (1996) International Cooperative Programme on Integrated Figure 6 Simulated soil base saturation (fraction) for GB02 Afon Hafren and N001 Birkenes using three dynamic models and scenarios A-C. Monitoring of Air Pollution Effects on Ecosystems. Report of the UK Focal Point to DoE.

Woodin, S.J. and Farmer, A.M. (1993) Impacts of sulphur and nitrogen deposition on sites and species of nature conservation importance in Great Britain. Biological Conservation 63: 23-30.

Wright, R.F. *et al.* (1986) Project RAIN: Changing acid deposition to whole catchments. *Water, Air and Soil Pollution* 30: 47-64.

Wright, R.F. (1987) RAIN Project: Results after two years of treatment. In: *Reversibility of Acidification*, edited by H Barth, 14-29, Elsevier, London.

Wright, R.F. and Hauhs, M. (1991) Reversibility of acidification: soils and surface waters. *Proceedings of the Royal Society of Edinburgh* 97B: 169-191.

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

Yesmin, L., Fitzpatrick, E.A. and Cresser, M.S. (1995) Evidence for atmospheric deposition impacts on the enchytraeid worm population of UK upland ombrotrophic peats. Chemistry and Ecology 11: 193-205.

Yesmin, L., Gammack, S.M. and Cresser, M.S. (1996a) Medium-term response of peat drainage water to changes in nitrogen deposition from the atmosphere. Water Research 30: 2171-2177.

Yesmin, L., Gammack, S.M. and Cresser, M.S. (1996b) Changes in N concentrations of peat and its associated vegetation over 12 months in response to increased deposition of ammonium sulfate or nitric acid. Science of the Total Environment 177: 281-290.

Yesmin, L., Gammack, S.M. and Cresser, M.S. (1996c) Effects of atmospheric nitrogen deposition on ericoid mycorrhizal infection of Calluna vulgaris growing in peat soils. Applied Soil Ecology 4: 49-60.

Zak, S.K., Beven, K. and Reynolds, B. (1997) Uncertainty in the estimation of critical loads: a practical methodology. *Water Air and Soil Pollution* 98: 297-316.

ANNEX 1.

Summary of equations, parameters and inputs for the MAGIC model.

Equilibrium Equations

Soil Water Cation Exchange Reactions

1. $E_{Al} + E_{Ca} + E_{Mg} + E_K + E_{Na} = 1$

2. $BS = E_{Ca} + E_{Mg} + E_K + E_{Na} = 1 - E_{Al}$

3. $\frac{\{Ca^{2+}\}^3 E_{Al}{}^2}{\{Al^{3+}\}^2 E_{Ca}{}^3} = S_{AlCa}$

4. $\frac{\{Na^+\}^2 E_{Ca}}{\{Ca^{2+}\} E_{Na}{}^2} = S_{CaNa}$

5. $\frac{\{Na^+\}^2 E_{Mg}}{\{Mg^{2+}\} E_{Na}{}^2} = S_{MgNa}$

6. $\frac{\{Na^+\} E_K}{\{K^+\} E_{Na}} = S_{KNa}$

Inorganic Aluminum Reactions

7. $\frac{\{Al^{3+}\}}{\{H^+\}^3} = K_{Al}$

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

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

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

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

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

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

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

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

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

17. $\frac{\{ALF_6{}^{3-}\}}{\{Al^{3+}\}\{F^-\}^6} = K_{Al_{10}}$

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

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

Inorganic Carbon Reactions

20. $\frac{\{CO_2(aq)\}}{P_{CO2}} = K_{CO2_1}$

21. $\frac{\{HCO_3{}^-\}\{H^+\}}{\{CO_2(aq)\}} = K_{CO2_2}$

22. $\frac{\{CO_3{}^{2-}\}\{H^+\}}{\{HCO_3{}^-\}} = K_{CO2_3}$

Dissociation of Water and Ionic Balance

23. $\{H^+\}\{OH^-\} = K_w$

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

Mass Balance Equations

1. $dCa_T/dt = F_{Ca} + W_{Ca} - Q*2*(Ca^{2+})$
2. $dMg_T/dt = F_{Mg} + W_{Mg} - Q*2*(Mg^{2+})$
3. $dNa_T/dt = F_{Na} + W_{Na} - Q*(Na^+)$
4. $dK_T/dt = F_K + W_K - Q*(K^+)$
5. $dSO_{4T}/dt = F_{SO4} + W_{SO4} - Q*2*((SO_4{}^{2-}) + (Al(SO_4)^+) + 2(Al(SO_4)_2{}^-))$
6. $dCl_T/dt = F_{Cl} + W_{Cl} - Q*(Cl^-)$
7. $dNO_{3T}/dt = F_{NO3} + W_{NO3} - Q*(NO_3{}^-)$
8. $dF_T/dt = F_F + W_F - Q*((F^-) + (AlF^{2+}) + 2(AlF_2{}^+) + 3(AlF_3{}^0) + 4(AlF_4{}^-) + 5(AlF_5{}^{2-}) + 6(AlF_6{}^{3-}))$

Definitions

Sulfate adsorption
1. $E_S = E_{mx}*2(SO_4{}^{2-})/(C + 2(SO_4{}^{2-}))$

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

Total ion amounts
3. $Ca_T = SP*CEC*E_{Ca} + 2*V*(Ca^{2+})$
4. $Mg_T = SP*CEC*E_{Mg} + 2*V*(Mg^{2+})$
5. $Na_T = SP*CEC*E_{Na} + V*(Na^+)$
6. $K_T = SP*CEC*E_K + V*(K^+)$
7. $SO_{4T} = SP*E_S + 2*V*((SO_4{}^{2-}) + (Al(SO_4)^+) + 2(Al(SO_4)_2{}^-))$
8. $F_T = V*((F^-) + (AlF^{2+}) + 2(AlF_2{}^+) + 3(AlF_3{}^0) + 4(AlF_4{}^-) + 5(AlF_5{}^{2-}) + 6(AlF_6{}^{3-}))$
9. $Cl_T = V*(Cl^-)$
10. $NO_{3T} = V*(NO_3{}^-)$

Sums of aqueous base cation and strong acid anion concentrations
11. $SBC = 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+)$
12. $SSA = 2(SO_4{}^{2-}) + (Cl^-) + (NO_3{}^-) + (F^-)$

Variables

Base cations: (Ca^{2+}), (Mg^{2+}), (Na^+), (K^+)
Strong acid anions: (Cl^-), (F^-), $(NO_3{}^-)$, $(SO_4{}^{2-})$
Inorganic aluminum 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 sulfate: E_S
Alkalinity: Alk
Sums of base cations and strong acid anions: SBC, SSA

Parameters

Thermodynamic equilibrium constants (functions of temperature):

K_{Al_1}, K_{Al_2}, K_{Al_3}, K_{Al_4}, K_{Al_5}, K_{Al_6}, K_{Al_7}, K_{Al_8}, K_{Al_9}, $K_{Al_{10}}$, $K_{Al_{11}}$, $K_{Al_{12}}$, K_{CO2_1}, K_{CO2_2}, K_{CO2_3}, K_w

Lumped Parameters (Functions of Catchments)

Selectivity coefficients: S_{AlCa}, S_{CaNa}, S_{MgNa}, S_{KNa}
Aluminum solubility constant: K_{Al}
Soil chemical properties: C, E_{mx}, CEC
Soil physical properties: SP, V

Inputs (Functions of Time)

Streamflow: Q
Atmospheric deposition: F_{Ca}, F_{Mg}, F_{Na}, F_K, F_{SO4}, F_{Cl}, F_{NO3}, F_F
Net uptake and release in soils: W_{Ca}, W_{Mg}, W_{Na}, W_K, W_{SO4}, W_{Cl}, W_{NO3}, W_F
Partial pressure CO_2: p_{CO2}

ANNEX 2.

Sensitivity analysis in relation to key uncertainties identified

Background

The review of dynamic modelling completed for this study highlighted three key uncertainties in the model structure and calibration; sulphate adsorption/desorption (page 43); catchment transformations and fluxes of N (page 45); and, the impact of afforestation on the base cation uptake flux (page 43). These uncertainties were qualitatively assessed using three case studies whereby the MAGIC model was calibrated to the Afon Hafren catchment. This annex describes the calibration methodology, the assumptions employed, the model structures used for each case study and the main results.

The Afon Hafren Catchment

The Afon Hafren is located in the Cambrian Mountains of mid-Wales and forms the headwaters of the River Severn. The catchment area is 358 ha; soils comprise a mixture of podsols and peat and the bedrock geology is Ordovician grits and Silurian mudstones and shales. Fifty per cent of the catchment is planted with conifers, primarily Sitka and Norway Spruce. Planting took place mainly between 1948-50 and 1963-64. Moorland grasses and *Calluna* occupy the remainder of the catchment and are utilised for rough grazing.

The stream chemistry is acidic with mean pH of 5.27 and calcium of 0.96 mg l^{-1}. Both sulphate and nitrate concentrations are high compared with other sites in the UK Acid Waters Monitoring Network (Patrick *et al.* 1995).

The basis of each of the case studies carried out is the MAGIC model application to the Afon Hafren developed as part of an attempt to calibrate a model for all of the UK Acid Waters Monitoring Network sites using a consistent methodology. This calibrated suite of models has been used extensively for testing scenarios of S and N deposition in advance of the negotiations for the 2nd Nitrogen Protocol and the proposed EU Acidification Strategy. The calibrated parameter values and fixed parameter input values used for this 'base model' are given in Table A2.1.

Table A2.1 Fixed parameter values used and calibrated parameter values derived for the Afon Hafren 'base model'.

Fixed parameters

Rainfall	1704 mm
Runoff	1436 mm
Soil Depth	0.88 m
Bulk Density	1134 kgm^{-3}
Cation Exchange Capacity	70 meq kg^{-1}

Calibrated parameters

Ca weathering	7 meq m^{-2} yr^{-1}
Mg weathering	39 meq m^{-2} yr^{-1}
Na weathering	23 meq^{-2} yr^{-1}
K weathering	0

Ca selectivity coefficient	2.2 ($\log_{10}$)
Mg selectivity coefficient	5.4 ($\log_{10}$)
Na selectivity coefficient	0.4 ($\log_{10}$)
K selectivity coefficient	-4.2 ($\log_{10}$)

Sensitivity Case Studies

1. Sulphate adsorption/desorption

There is currently no direct evidence in the UK for sulphate input flux exceeding stream output flux to indicate sulphate retention within catchment soils. In general, estimates of wet deposition are considerably lower than calculated stream output fluxes and the difference is assumed to represent dry and gaseous deposition of sulphur. This situation masks two important considerations: (I) the estimated total sulphur input could be too low and so many systems may be currently retaining sulphur, and; (II) at sites currently in steady-state with respect to sulphur input and output, considerable sulphur retention may have occurred in the past and is available for future desorption under suitable conditions.

In MAGIC, sulphur retention is assumed to follow a non-linear isotherm which relates soil adsorbed S to the soil-water concentration of S (Section 6.2, page 32). The relationship requires specification of two parameters (Figure A2.1) defined as the maximum S adsorption capacity (effectively defines the upper 'plateau' of the isotherm) and the half saturation constant (effectively defines the slope of the isotherm below the 'plateau'). Since these values are required for the aggregated soils of the catchment, field sampling and laboratory determination of the parameters does not necessarily provide the required values. As a result, and given that estimated S inputs are always lower than S outputs, it is generally assumed in the UK that the maximum S adsorption capacity is negligible and so the model maintains a steady state between S input and output throughout the simulation.

Model Calibration

For this exercise, two models were calibrated to the Afon Hafren; these models maintained consistent base cation weathering fluxes and ion-exchange selectivity coefficients and soil characteristics differed only in terms of the values used for the maximum S adsorption capacity and the S half-saturation constant such that (Figure A2.1):

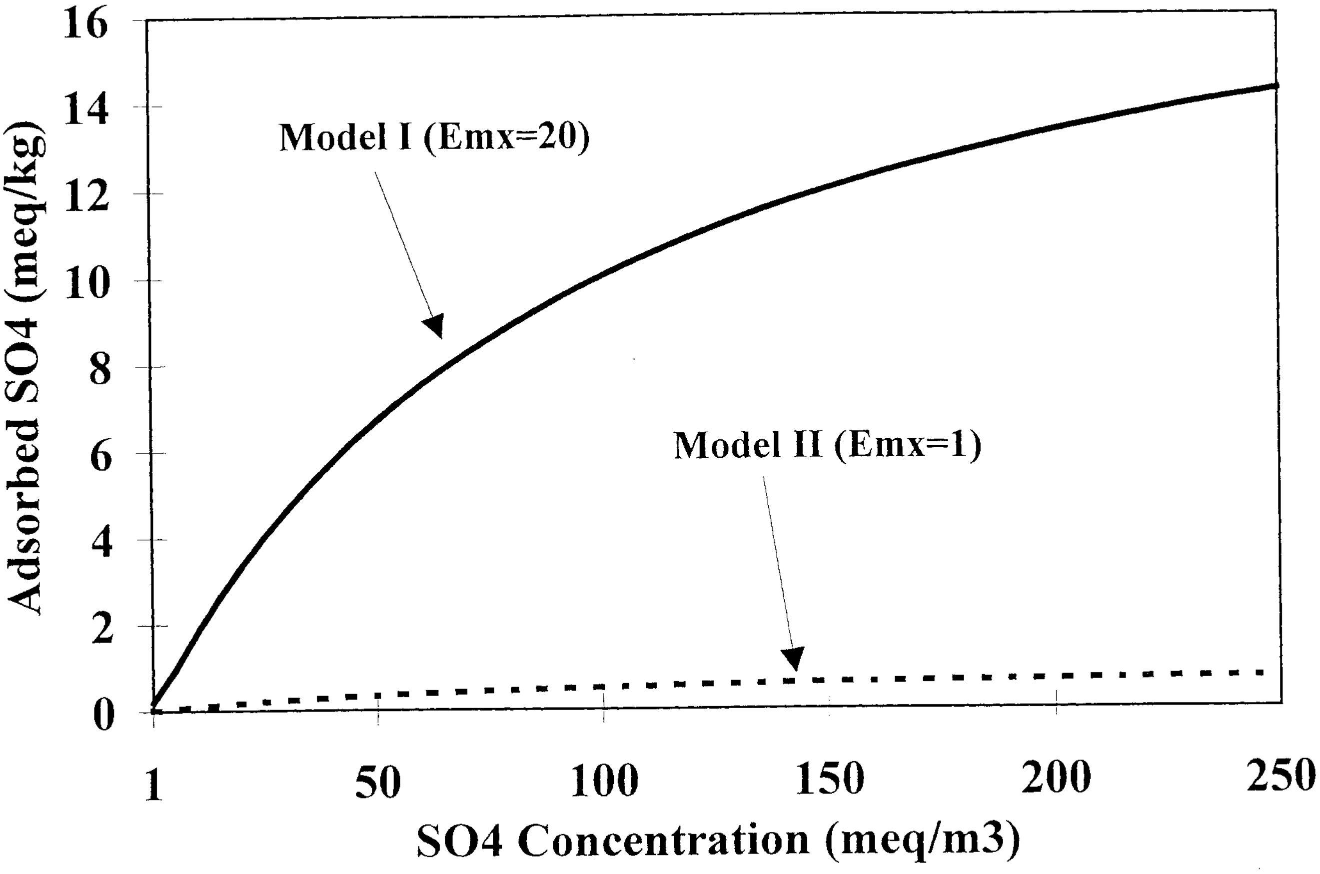


Figure A2.1 Sulphate adsorption isotherms used in the two model calibrations. Model I allows very high adsorption and desorbs S over a long time period as S deposition is reduced. Model II allows little S adsorption and output closely matches changes in input flux.

Model I - calibrated with no S adsorption capacity (maximum capacity = 0.01 meq kg^{-1})

Model II - calibrated with very large S adsorption capacity (maximum capacity = 20 meq kg^{-1} and half saturation constant = 1000 meq m^{-3})

Results and Implication

Each model can be calibrated to present day observed stream and soil chemistry (Figure 6.8). Both the historical reconstruction and the future prediction of streamwater pH, however, differ markedly. This difference represents a considerable uncertainty in the model application. On the other hand, more than 10 years of stream chemistry data exist for the Afon Hafren which confirm that the sharp decline in pH between 1985 and present day has not occurred. This historical data shows a small recovery in pH which matches the predicted pH from Model I (no S adsorption).

Whilst the lack of available evidence of S adsorption in the UK presents a potentially large uncertainty in the model predictions, this uncertainty can be minimised by drawing on a longer period of data record to test the calibration. Data availability, therefore, represents the main constraint to model uncertainty over S adsorption and model applications to sites with data describing less than 5 years stream chemistry data should be interpreted with caution. It should, however, be possible to infer stream chemistry characteristics or soil chemistry characteristics from other sites within a similar region.

2. Base Cation Uptake by Forests

Specification of annual uptake flux of base cations for individual site applications is problematical since there exists no direct method for measuring in the field. This is characteristically achieved through a combination of determining base cation composition of the tree at maturity and derivation of annual biomass increase by physical measurements during the forest life-cycle (or extrapolating from different age trees under similar nutritional and climatic conditions). These estimates for growth are summarised as forestry yield tables. In conjunction with knowledge of the area of forest, its age and Yield Class within a catchment, therefore, the annual base cation fluxes (meq m^{-2}) can be estimated and input to the model. The key uncertainty then becomes the specification of the source of the base cations in the soil.

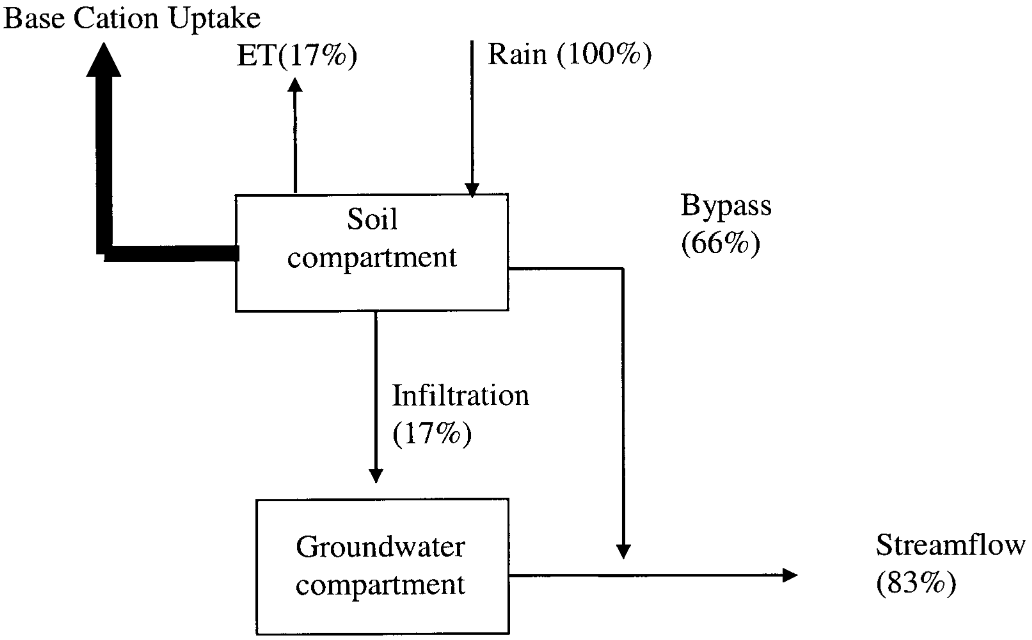
Conventionally, a two-soil layer structure is calibrated to a catchment if detailed soil physco-chemical data is available. The structure of the model is assumed to represent: (i) an upper 'organic' soil compartment where base cation exchange is the dominant process and weathering of primary minerals is assumed to be low; and, (ii) a lower 'mineral' (groundwater) layer where weathering of base cations is the dominant process and ion-exchange is trivial. The streamwater is further assumed to represent a mix of water from these two compartments with water from the soil compartment dominating storm flows and water from the groundwater compartment dominating baseflows.

Casual observation of the depth of tree roots in the field (following blow-down, for example) indicates that rooting depth is shallow but the possibility that the roots can access lower layers is a key uncertainty in model predictions (Section 6.6.1, page 44).

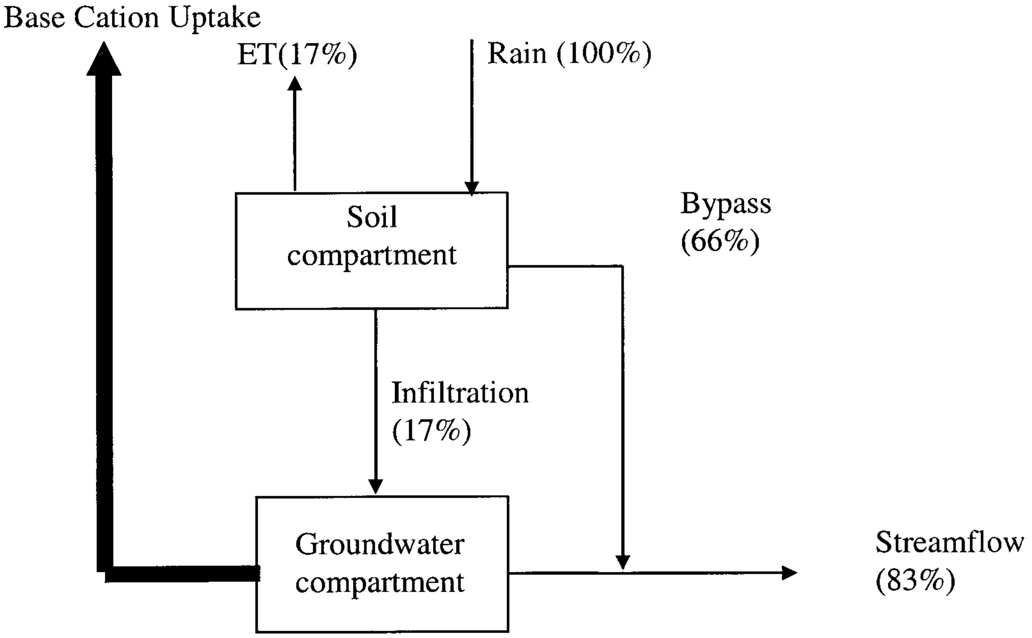
Model Calibration

For this study, 2 models were calibrated to the Afon Hafren. Each was a 2-soil layer structure with the upper layer calibrated to mean high flow chemistry and to measured soil base-cation characteristics and the lower layer calibrated to mean baseflow chemistry and assuming zero cation exchange capacity. Weathering inputs were assumed to be predominantly to the lower layer (90%). Flow routing through the 2 layers was calculated on the basis of the high flow, baseflow and mean stream ANC such that 80% of the rainfall bypassed the lower layer. The calibrated models were used to predict streamwater ANC in the future assuming a decrease in S deposition in line with agreements under the 2nd S Protocol and assuming that each forest 'stand' would be felled at age 50 years and immediately replanted to cover an identical area of the catchment. The two models differed as follows (Figure A2.2):

Figure A2.2 The two-layer model structures used to test uncertainty to tree uptake of base cations. The percentages relate to the flow following the indicated pathway.



Model 1: All base cation uptake assumed to be derived from the soil compartment



Model 2: All base cation uptake assumed to be derived from the groundwater compartment

In reality, these two models represent the 2 extreme possibilities which bound the uncertainty associated with this mechanism.

Results and Implication

Both model structures calibrate approximately, within 5 ueq l^{-1}, to present day observed stream ANC (Figure 6.9, page 46) although a perfect match could not be obtained. The 2 model structures as defined are extremely sensitive to small changes in parameter values as a result of the assumptions regarding weathering and ion exchange and a more consistent match between the 2 models could not be obtained within the time available. With further effort the 1992 ANC could be matched exactly by both model structures.

The future predictions from the two models, however, differ markedly, with a pronounced increase in acidification occurring under model 1 (all base cation uptake from the soil compartment). This results from the continued decline of the soil exchangeable base cation store as a result of continued S deposition and tree requirement. More work is required to determine the ability of the tree roots to access the groundwater compartment and on the recharge of the soil compartment base cation store from the groundwater compartment by hydrological mixing processes within the catchment.

3. Terrestrial Nitrogen Transformations

The response of terrestrial and aquatic ecosystems to continued high deposition of N probably represents the key uncertainty in predicting the future acidification status of surface waters and soils. Nitrogen is generally retained within terrestrial systems but chronic elevated deposition fluxes of oxidised and reduced N can lead to 'nitrogen saturation' and breakthrough leading to elevated nitrate concentrations in surface waters and, thereby, increasing acidity and decreasing ANC. Our current understanding of the biogeochemistry of this process is derived from empirical observation and experimental manipulation which links N saturation to the carbon:nitrogen status of the soil litter layer. This understanding is based only on data from forested ecosystems.

MAGIC-WAND has been developed over the last few years to incorporate the major controls on N fluxes and changes in N fluxes through time. These dynamics are fully coupled to the existing S driven model (MAGIC). The model assumes that N leaching to surface waters is a function of total inorganic N deposition, plant uptake demand for N, soil uptake or immobilisation of N and nitrification of reduced to oxidised N. Denitrification and N fixation can also be specified. At the heart of the model lies the assumption that the net retention/release of incoming inorganic N (or immobilisation/mineralisation) in the soil is determined by the C/N ratio of the top soil layer. Such a relationship has been proposed by Gundersen *et al* (1997) following an assessment of N leaching and soil C/N ratios across a range of forested sites in Europe (Figure A2.3) such that at N rich sites most of the incoming N is leached whilst at low N sites all of the incoming N is immobilised.

The model solution at each time step is sequential; first, the net plant uptake requirement for N, specified at each time-step (uptake-litterfall), is satisfied; second, the fraction of remaining N immobilised by the soil is determined by the soil N pool size relative to the (constant) soil C pool (Figure A2.3). The soil N pool is incremented accordingly and the remaining N, if any, is leached to the streamwater. If nitrification is assumed to be complete, it is not necessary to distinguish between deposition and plant uptake of NH_4 or NO_3 and any N leached is in the oxidised form.

The key uncertainties with this model formulation (which in itself is limited by our current conceptual understanding of the system) lie in the determination of soil C:N status, essentially a soil sampling problem, and the calibration of the relationship between soil C:N and N leaching relative to N input for an individual site. With existing data limitations, this case study attempts to assess the latter as a calibration uncertainty.

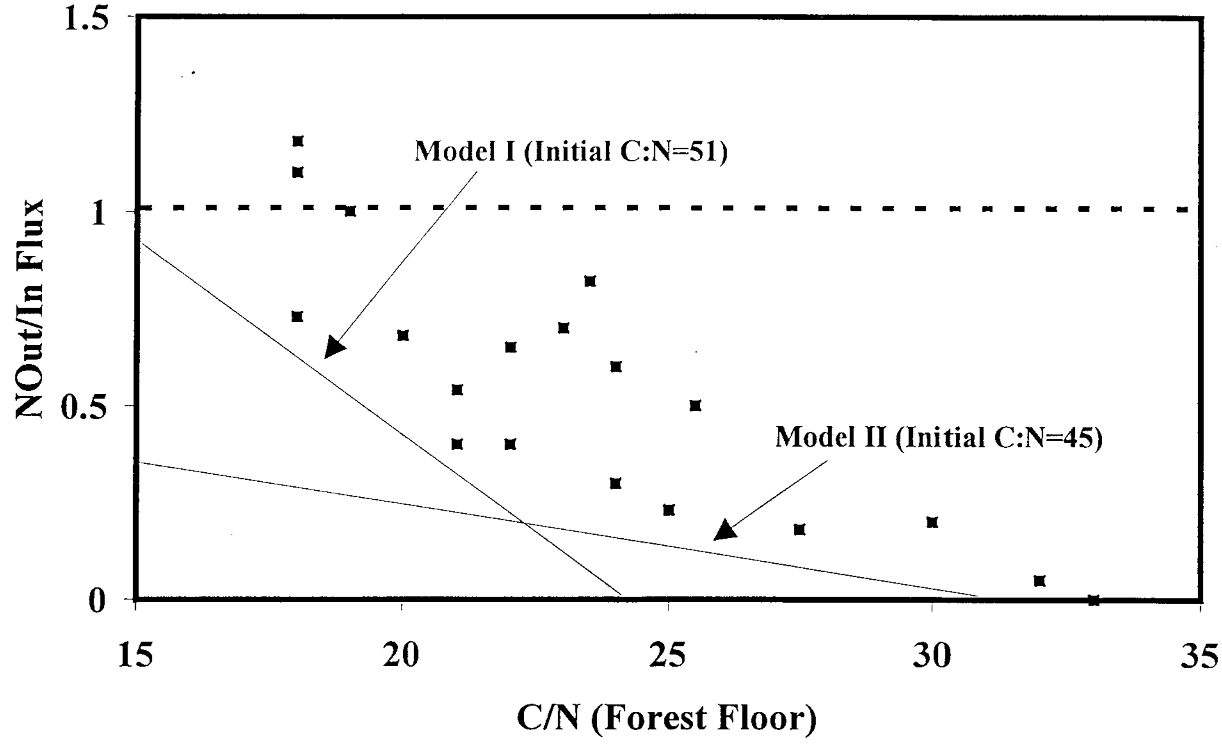


Figure A2.3 The calibrated soil C:N to N leaching curves for the two models. The points define the data of Gundersen *et al* (in press).

Model Calibration

For this case study, the calibrated 'base model' for the Afon Hafren was utilised in MAGIC-WAND and a best estimate of soil C pool and soil C:N status was obtained from available soil samples. Denitrification and N fixation were assumed to be zero. Two calibration methods were then employed:

Model (I) - uses a specified slope for the C:N to N leaching relationship (defined as the slope of the line of best fit to the data presented by Gundersen *et al.* (in press) (see Figure A2.3) and adjusts the intercept (C:N ratio at which N leaching becomes greater than zero) and initial N pool to match observed present day stream NO_3 concentrations and present day observed soil C:N.

Model (II) - uses a specified intercept (defined from the data presented by Gundersen *et al.* (in press) (see Figure A2.3) and adjusts the slope of the C:N to N leaching relationship and initial N pool to match observed present day streamwater NO_3 concentration and soil C:N.

For neither of the 2 models does the calibrated C:N to N leaching curve fit closely to the data observed in forest soils (Gundersen *et al.*, in press). This probably reflects the importance of denitrification at the site; this process is subsumed within the calibrated relationship and no observed data are available. Both calibrated models are then run forward in time to predict streamwater ANC concentrations in response to a c.50% decrease in total N deposition by 2010 and a decrease in S deposition in line with the agreement under the 2nd S Protocol.

Results and Implication

For both models, historical ANC declines rapidly to a minimum in the 1970's, coinciding with the period of peak S deposition flux, and then recovers to present level as S deposition declines over the last 20 years (Figure A2.4). For NO_3, historical concentrations are zero in both models but these diverge from c.1950. The models converge again at present day since both were calibrated to match present day observed ANC and NO_3.

For Model II, NO_3 begins to leak from the soil in 1951 but the increase is gradual to present day. This model predicts a stabilisation of N leakage into the future under the reduced N deposition and since future S deposition is also assumed to decrease the streamwater ANC is predicted to recover significantly. Conversely, for Model II, NO_3 leakage does not occur until 1980 but, thereafter, the increase in concentration is rapid and is predicted to continue into the future with decreased N deposition. The resulting decrease in streamwater ANC occurs despite decreased S deposition.

The uncertainty regarding N dynamics arises out of a conceptual uncertainty in defining and describing the key catchment processes determining N leakage and from uncertainty in measured soil parameters. For example, soil C:N may vary widely over a catchment but often only 1 or 2 soil samples have been taken. This uncertainty is currently being assessed through an intensive sampling effort at catchment scale to identify C:N variation in space. The uncertainty examined here represents a calibration uncertainty which can be minimised with reference to a longer time period of data. There is no observed increasing trend in stream NO_3 concentrations between 1980 and 1990 and so Model I appears to be inappropriate. Instead, the historical record indicates a stable concentration indicating that Model II is more appropriate.

Conclusions

1. Uncertainty in model calibration is minimised when historical streamwater chemistry trends are available to further constrain the calibration. A minimum of 5 years record is required to achieve this constraint.

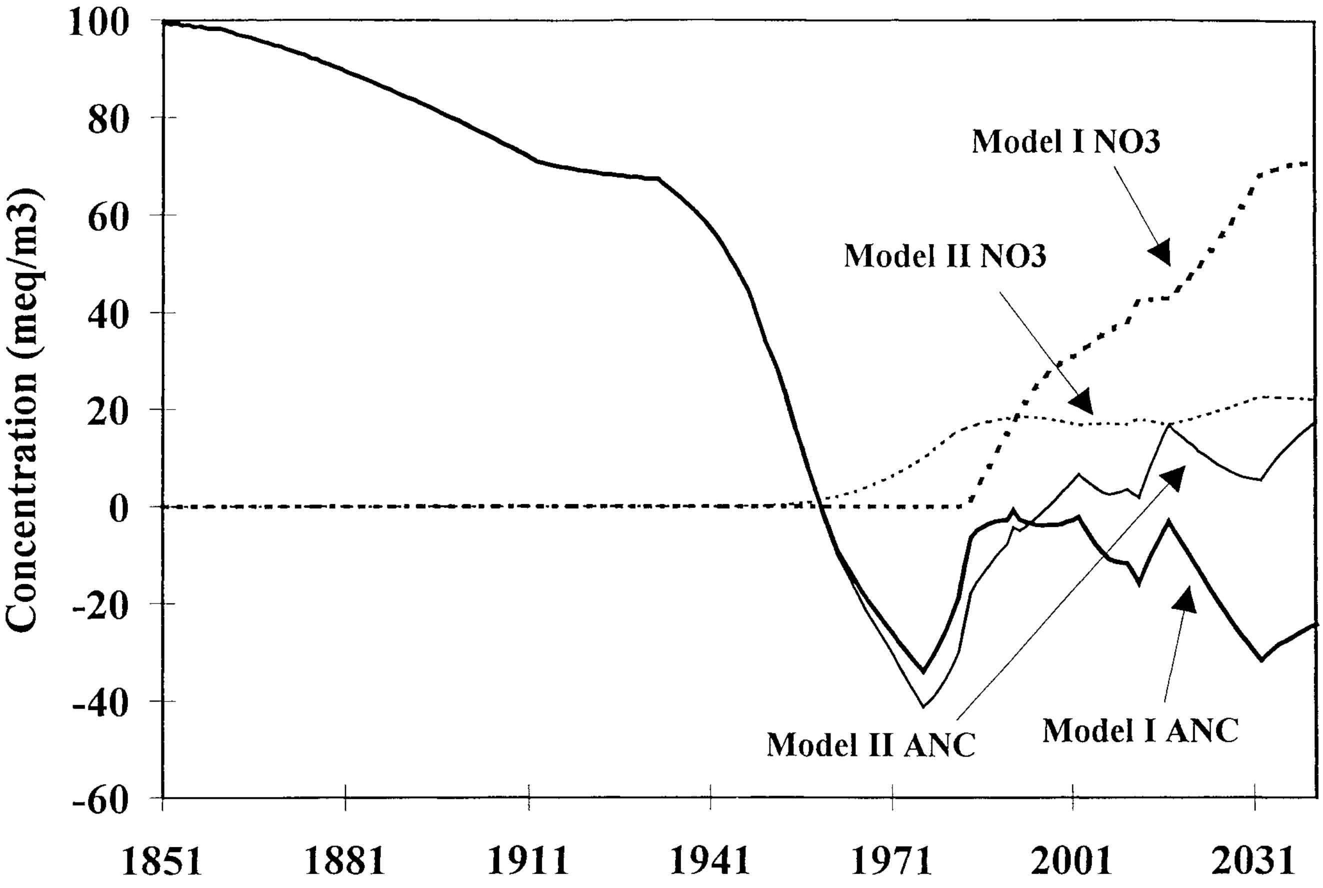


Figure A2.4 **Predicted change in stream NO_3 and ANC using the two different calibration techniques. Note that both successfully match present day concentrations but historical and future behaviour differ markedly.**

2. Data from a single point in time is rarely sufficient to adequately constrain the model calibration and so wide uncertainty in model predictions results. The prediction from such calibrations should be interpreted cautiously to provide qualitative trends rather than quantitative levels.

3. Where stream chemistry data for a single time-step (1 year) are all that is available, it is often possible to infer behaviour from nearby sites with a long-term record. In regional mode, the problem becomes less significant provided the sites cover a wide range of behaviour and the model parameters remain unbiased.

4. The greatest uncertainty lies in the predictions of future N leakage and improvement of our conceptual understanding of the biogeochemical system will be required to improve the model structure. In the meantime, results should be interpreted qualitatively.