Model of
Acidification of
Groundwaters
In
Catchments
-
With
Aggregated
Nitrogen
Dynamics

Calibration, Validation and Assessment of Nitrogen Deposition Scenarios

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Executive Summary

The workshop on Critical Loads for Nitrogen held in Lokeberg, Sweden in April 1992 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). A dynamic modelling approach can; determine the time dimension between achieving critical loads and ecosystem recovery; determine the consequences of not achieving a critical load; examine the effect of land use change, in particular forestry practice, acting alongside changes in nitrogen deposition; determine the interaction between nitrogen and sulphur in the context of critical loads for total acidic deposition; and, determine the relative importance of changes in the deposition of oxidised and reduced forms of nitrogen.

MAGIC (Model of Acidification of Groundwater In Catchments) is well developed and has been extensively tested and validated but provides limited application with respect to nitrogen as the model allows only for a specified net catchment retention of nitrogen at each time step. MAGIC-WAND (MAGIC-With Aggregated Nitrogen Dynamics) builds directly on MAGIC and allows the main fluxes and transformations of nitrogen to be independently specified at each time-step. MAGIC-WAND has been specifically developed for wide application and scenario assessment. It maintains the sulphur based chemistry dynamics of MAGIC and considers reduced and oxidised nitrogen species. The model requires specification of nitrification, mineralisation, fixation and denitrification rates and changes in these fluxes through time. Plant uptake is non-linear and dependant upon external nitrogen concentrations. A wide range of data describing these rates and fluxes have been reported and are reviewed to aid in model calibration.

The.main sensitivity of the model lies in the selection of the parameters which describe the hyperbolic uptake function. Literature data can provide ranges for these values but specific catchment related values are not obtainable since the model is conceptual. Selection of uptake parameters must reflect catchment vegetation and vegetation change through time. Further observational and experimental work to determine nitrogen fluxes and dynamics at different ecosystems is required to facilitate site specific and regional model applications.

The model is applied to two catchments, one forested and one moorland, in the Galloway Region of SW Scotland. Predictions of future response to different nitrogen deposition scenarios are expressed as ranges, the extremes of which are determined by the parameters selected for the plant uptake function. The model response to inputs of oxidised and reduced forms of nitrogen is assessed. The importance of the 'counter-ion' associated with the nitrogen is stressed. Future work will aim to test the robustness of the model through site applications across Europe, to a variety of land uses and on a regional basis.

1.Background and Introduction

1.1. Determination of Critical Loads

The critical load of a pollutant is defined as: "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988).

The acidifying effects of sulphur and nitrogen deposited from the atmosphere depend on the mobility and retention of the sulphate and nitrate anions once in the ecosystem. Soils in glaciated regions typically have low-to-moderate sulphate adsorption capacities and so sulphate inputs and outputs are generally in steady state (ie., inputs equal outputs). Changes in sulphate deposition rather quickly appear as changes in the sulphate concentration of surface waters. If these sulphate concentrations decline, acid stresses on the soils and surface waters are reduced.

Nitrogen, on the other hand, is generally retained within upland terrestrial systems in the UK, particularly coniferous forests, largely because nitrogen is the growth-limiting nutrient. Chronic elevated deposition of nitrogen, however, can produce quantities of inorganic nitrogen in soils in excess of that needed by the biota for growth. The un-assimilated nitrogen can be leached from soils and appears as nitrate in runoff (excess ammonium is quickly converted to nitrate in forest soils). The term "nitrogen saturation" has been given to this loss of nitrate in runoff. As with the sulphate, nitrate is a mobile strong anion and acts to acidify the soils. Nitrogen saturation, therefore, reduces the critical loads of both nitrogen and sulphur for soil and freshwater systems. Prediction of nitrogen saturation is difficult at best. The processes responsible are difficult to quantify. The best information currently available on the magnitude and timing of nitrogen saturation (or retention) comes from empirical observations.

The amount of sulphur deposition that can be tolerated by a forest soil without harmful effects on the trees is dependent on the amount of nitrogen deposition, and, conversely, the amount of nitrogen deposition that can be tolerated depends on the sulphur deposition. Either the sulphur or nitrogen deposition must be specified first before the critical load and exceedance (either positive or negative) of the other can be calculated. This is the approach used by Henriksen et al. (1993) to calculate exceedances for sulphur and nitrogen for lakes in Finland, Norway and Sweden.

The effects of deposition of sulphur and nitrogen on soil and surface water acidity can be simulated, and the critical load calculated, using models of soil acid-base chemistry. These models are of two basic types: static models based on soil type and mineralogy; and dynamic models which additionally take into account the time-dependent processes involved in soil acidification and recovery (Sverdrup et al., 1990; Frogner et al., 1992). Both types rely on an input-output mass balance approach. Both are, therefore, consistent with the concept of critical load which implies that each receptor (eg. surface water and soils) has an intrinsic capacity to neutralize acid inputs. Static models determine critical loads such that all sources of acidity are balanced by all sources of alkalinity, have no time component (ie. assume equilibrium conditions), assume that acidification is completely reversible and, with respect to nitrogen, assume that ecosystem dynamics which determine nitrogen concentrations will not change in the future. Dynamic models also include processes such as cation exchange, anion adsorption and the role of forest growth and management that result in time-dependency of soil response to acidic inputs.

The development of dynamic modelling approaches enables an assessment of the influence of nitrogen dynamics in the context of nitrogen critical loads per se but more importantly for total acidity given the present and future commitments to nitrogen emissions protocols. That is, given that sulphur emissions reduction protocols are now in place the most important question relates to the potential for nitrogen leaching off-setting the expected reversibility. The specification of a critical load for sulphur in the absence of knowledge of how the nitrogen dynamics within the catchment system might change in the future is, therefore, inappropriate.

The strength of dynamic model applications in an applied sense is in answering key policy questions such as; What degree, in time and space, of soil and water recovery can we expect from a given emissions reduction strategy ? What level of emissions reduction is necessary to achieve a given level of soil and water recovery within a given time scale ? What are the consequences for soils and surface waters of not achieving a critical load ? What is the potential for nitrogen leaching to off-set the expected recovery from agreed sulphur emissions reductions ? What is the relative impact of decreasing oxidised or reduced forms of nitrogen deposition ?

1.2. Nitrogen Saturation and Breakthrough

Natural or undisturbed ecosystems are commonly nitrogen deficient and retention of nitrogen in the terrestrial portion of these systems is usually almost complete (eg. Likens et al. 1977, Bormann et al. 1977, Vitousek and Howarth 1991, Johnson 1992). While it has been shown that periodic or random disturbances can cause nitrogen "leakage" from forests (eg. Vitousek et al. 1979, Neal et al. 1992), these responses are transient and nearly complete nitrogen retention resumes when the disturbance ceases. Long term inputs of nitrogen from atmospheric deposition, however, may produce a condition of "nitrogen saturation" (eg. Nilsson 1986, Agren and Bosatta 1988, Aber et al. 1989, Stoddard 1994). Nitrogen saturation is characterised by increased and persistent losses of nitrogen (as nitrate or ammonium) in streamflow or groundwater discharge (eg. Aber et al. 1989, van Miegrot et al. 1992, van Miegrot and Johnson 1993). Saturation occurs when the combined inputs of inorganic nitrogen from internal sources (mineralisation and fixation) and external sources (deposition, fertilisation, etc.) exceed the nitrogen uptake capacity of plants and soil microorganisms. Recent experiments indicate that nitrogen saturation can be induced rather quickly with only modest increases in nitrogen inputs (Kahl et al. 1993, Wright and van Breemen in press).

If nitrogen saturation occurs, a number of adverse effects on watershed resources are possible. Nitrate and ammonium are important nutrients for aquatic plants and decreased retention in catchment soils can lead to increased concentrations of these nutrients in surface waters which in turn can lead to eutrophication. Leaching of nitrate to groundwater can lead to concerns over human health if the groundwater resource is exploited. Nitrate is also a strong acid anion and if released to soils and surface waters is effective as an acidifying agent and mobilizer of toxic aluminium (eg. Henriksen and Brakke 1988). Assimilation of ammonium ion in soils or water can also have an acidifying effect. High concentrations of nitrate and ammonium have even been implicated in widespread forest die-back in central Europe (van Breemen and van Dijk 1988).

In the light of the potential effects, reports of increased nitrogen concentrations in recent years in lakes and streams in both North America and Europe should be viewed with some concern (eg. Hauhs et al. 1989, Driscoll et al. 1989, Emmett et al. 1993, Stoddard 1994, Dise and Wright in press). A number of studies have even reported nitrogen losses from aggrading forest ecosystems (eg. van Breemen et al. 1982).

1.3. Lumped Dynamic Models For Catchment Nitrate Leaching

It is apparent that development of sound watershed management strategies, including assessment of critical loads (for both aquatic and terrestrial resources), requires tools for understanding the watershed-level processes and geochemical effects of nitrogen saturation. In particular, mathematical models are required to integrate current understanding of biogeochemical processes affecting nitrogen at all scales within watersheds. The attributes required of such models are;

i) They should be applicable at the watershed scale (ie. state variables in the model should relate to whole system responses - such as water quality or plant productivity - which integrate effects of processes operating at various scales within the watershed).

ii) They should be generalisable to several ecosystem types.

iii) It should be possible to calibrate/evaluate them using catchment scale variables (aggregated soil characteristics; statistical descriptions of terrestrial biota; annual average, seasonal and/or episodic soil and surface water chemical concentrations; survey data; etc.)

iv) They should be amenable to implementation at multiple sites or on a regional basis using, mapped, remotely sensed or surveyed data (ie. model complexity should be maintained at a level consistent with process knowledge while simultaneously recognizing that management needs often require model applications in situations where data are sparse or incomplete).

v) They should be designed with a view to incorporation into a decision making framework (ie. the model can be used to assess alternate control scenarios which in turn requires that potential control variables such as land use patterns, atmospheric deposition, etc., be represented in the model structure).

vi) They should provide a mechanism for coupling the dynamics of nitrogen to the hydrogeochemistry of soils and surface waters.

2. The MAGIC Model

2.1. Model Description

The MAGIC (Model of Acidification of Groundwater In Catchments) model combines a number of key soil chemical processes lumped at the catchment scale to simulate soil and surface water chemistry. MAGIC consists of: 1) soil-soil solution equilibria equations in which the chemical composition of soil solution is assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution and precipitation of aluminum, and dissolution of inorganic carbon; and 2) mass balance equations in which the fluxes of major ions to and from the soil and surface waters are assumed to be governed by atmospheric inputs, mineral weathering, net uptake in biomass, and loss in runoff (Cosby et al. 1985a, 1985b).

MAGIC has been extensively used in a variety of applications at sites in both North America and Europe. Application of MAGIC to the whole-catchment experimental manipulations of the RAIN project shows that this intermediate-complexity lumped model predicts the response of water and soil acidification to large and rapid changes in acid deposition (Wright et al. 1990). These results reinforce other evaluations of MAGIC such as comparison with palaeolimnological reconstructions of lake acidification (Jenkins et al. 1990a) and changes in regional lake chemistry in Wales (Jenkins et al. 1990b). In addition several of the assumptions in MAGIC have been tested experimentally (Grieve 1989). MAGIC is one of several dynamic models included in the UN-ECE Handbook on Mapping Critical Loads (Henriksen et al. 1989) and has been used extensively within the UK Freshwaters Critical Load Programme (Jenkins and Shaw 1993, DOE 1994).

MAGIC uses a lumped approach in two ways: (1) a myriad of chemical and biological processes active in catchments are aggregated into a few readily-described processes, and (2) the spatial heterogeneity of soil properties within the catchment is lumped to one set of soil parameters. Whereas standard precipitation and throughfall gauges provide adequate estimates of integrated inputs to catchments and the outputs in runoff are integrated at the weir, 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, porosity, cation exchange capacity (measured at soil pH), and the fraction of exchange sites occupied by Ca, Mg, Na, and K. Values need to be aggregated both spatially and with depth at each catchment to obtain single values for each parameter.

MAGIC comprises an extremely simplified representation of nitrogen involving a specified net catchment retention to calibrate simulated nitrogen against observed nitrogen in streamwater. This net retention is the net result of all fluxes and processes of the terrestrial nitrogen cycle. Nitrogen species, NO_3 and NH_4, are treated individually but as a simple net catchment retention described as a zero order equation such that;

$$\text{Net retention} = k\,N$$

Where nitrogen is the external concentration of NO_3 and NH_4 and k is the proportion of N retained at each time step. The value of k is then adjusted to match observed concentrations given a specified input.

The term "retention" as used here is the net result of several sources and sinks of nitrogen within the ecosystem. The terminology used by Henriksen et al. (1993) to calculate exceedances for nitrogen and sulphur in surface waters in the Nordic countries considers the following sources and sinks of nitrogen in terrestrial catchments:

$$N_{le} = N_{dep} - N_{den} - N_{upt} - N_{imm} - N_{exp}$$

where N_{le} is nitrogen leached in runoff from the catchment; N_{dep} is total nitrogen deposition; N_{den} is nitrogen lost by denitrification; N_{upt} is the net uptake of nitrogen by the biomass in the catchment; N_{imm} is the nitrogen immobilized in the soils; and N_{exp} is the export of organic nitrogen out of the catchment in drainage waters. Nitrogen fixation is not considered to be an important source of inorganic nitrogen for forest soils.

Catchment input-output data do not allow discrimination among these components of nitrogen leaching. It can generally be assumed that N_{exp} and N_{den} are low (relative to the other terms) except for wetland systems and so nitrogen retention results primarily from uptake by plants (N_{upt}) and net immobilization by the soils (N_{imm}).

2.2. Critical Loads for Nitrogen Using MAGIC

The MAGIC model has been used to assess the influence of nitrogen deposition on calculated critical loads for sulphur, by varying the net catchment retention of nitrogen (Figure 2.1) indicating the "trade off" between sulphur and nitrogen deposition. Lower sulphur deposition is required to maintain zero alkalinity in surface water in the light of increased nitrogen deposition and assuming a constant catchment nitrogen retention.

This approach has been furthered in southern Norway by representing the net nitrogen retention as a function of nitrogen deposition (Frogner et al. 1994). Input-output data from coniferous forest ecosystems in Europe were used to set empirical "best case" and "worst case" limits for nitrogen retention (Dise and Wright, in press). These data (Figure 2.2) suggest that nitrate leaching from soils is minimal in catchments with nitrogen deposition levels less than 10 kgN/ha/yr (70 meq/m^2/yr); nitrate leaching varies from 0% to 100% of nitrogen deposition in catchments with nitrogen deposition in the range 10-25 kgN/ha/yr (70-175 meq/m^2/yr); nitrate leaching is 50-100% of nitrogen deposition in all catchments with nitrogen deposition more than 25 kgN/ha/yr (175 meq/m^2/yr).

Nitrogen critical loads were evaluated for forest soils in Norway using the dynamic model MAGIC, and the criterion that the Ca/Al ratio in the uppermost 50 cm soil solution should not be less than 1.0 at a point fifty years in the future. Assumptions were made regarding best and

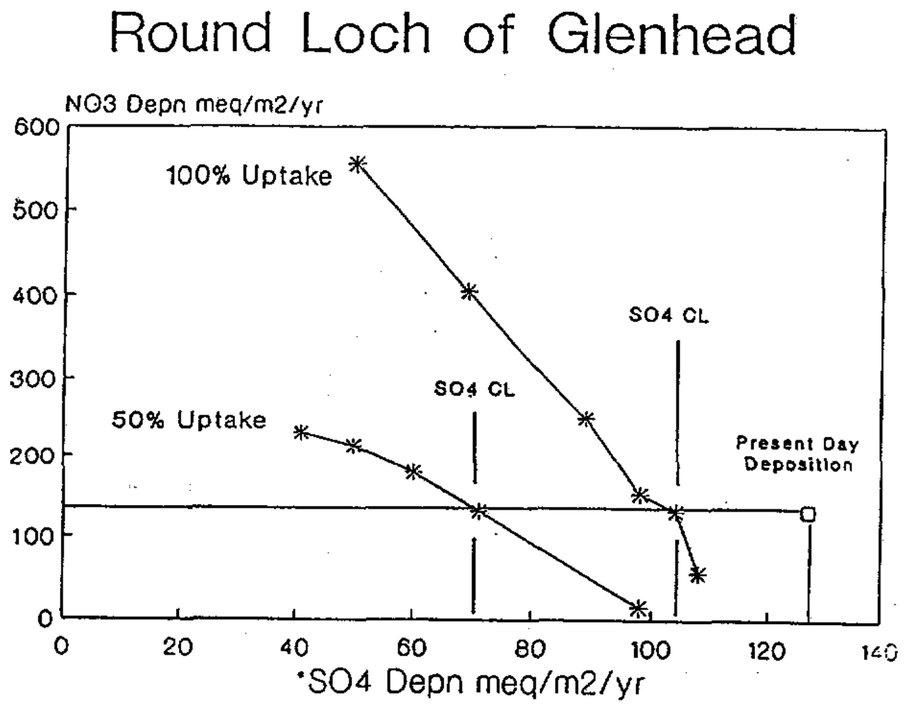

Figure 2.1. MAGIC predictions of critical loads for surface water based on achieving alkalinity zero by 2039. Presently, NO_3 concentrations in surface waters are low reflecting only direct input to the lake itself (100% immobilisation within the terrestrial catchment) and the present S critical load of c. 105 meq m^{-2} yr^{-1} is calculated under this assumption. If NO_3 deposition increases, SO_4 critical load decreases to maintain zero alkalinity. If NO_3 immobilisation in the terrestrial catchment decreases to 50%, at the present level of NO_3 deposition the S critical load would fall to c. 70 meq m^{-2} yr^{-1} to achieve zero alkalinity.

worse case future scenarios of sulphur deposition and nitrogen retention. These evaluations show that the assumptions regarding decreases in nitrogen retention in soils (future nitrogen saturation) are of great importance in determining the nitrogen critical load to these soils and can have a large effect upon the magnitude of the calculated critical loads. Surprisingly, alternate assumptions about future sulphur deposition scenarios (20 and 60% reductions) appear to have smaller effects on the calculated nitrogen critical loads.

These results strongly suggest that more information regarding the magnitude of nitrogen retention and the processes controlling cycling in forested ecosystems is of utmost importance for the specification of nitrogen critical loads. A more explicit representation of the N cycle is also required to address the potential implications of land use change (Figure 2.3), in particular,the observed change in net nitrogen retention as a function of forest age (Emmett et al. 1993) and to assess the relative effects of reduced and oxidised forms of nitrogen deposition.

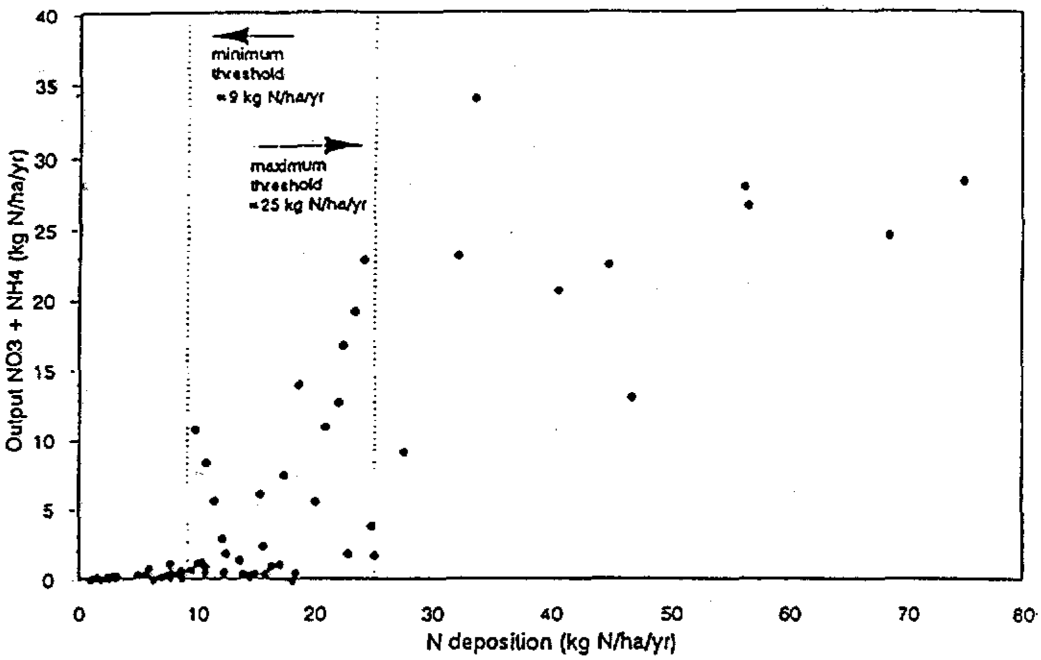

Figure 2.2. Comparison of N deposition and output fluxes for several sites across Europe (from Dise and Wright, In Press).

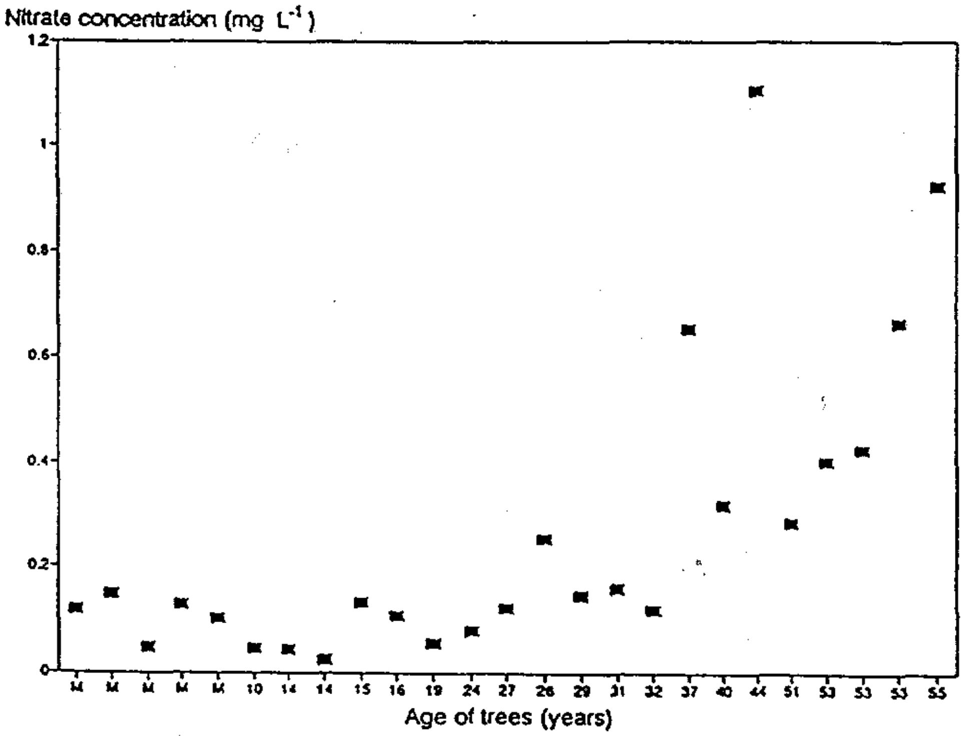

Figure 2.3. Nitrate concentrations in streams draining catchments under forests of different ages in Wales (from Emmett et al. 1993)

3. The MAGIC-WAND Model

3.1. Model Description

MAGIC-WAND (MAGIC With Aggregated Nitrogen Dynamics) represents an extension to the MAGIC model to incorporate the major nitrogen fluxes and changes in fluxes through time (Figure 3.1). The nitrogen dynamics are fully coupled to the existing sulphur driven model. The model structure is designed to enable assessment of future surface water chemistry response to a given nitrogen 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.

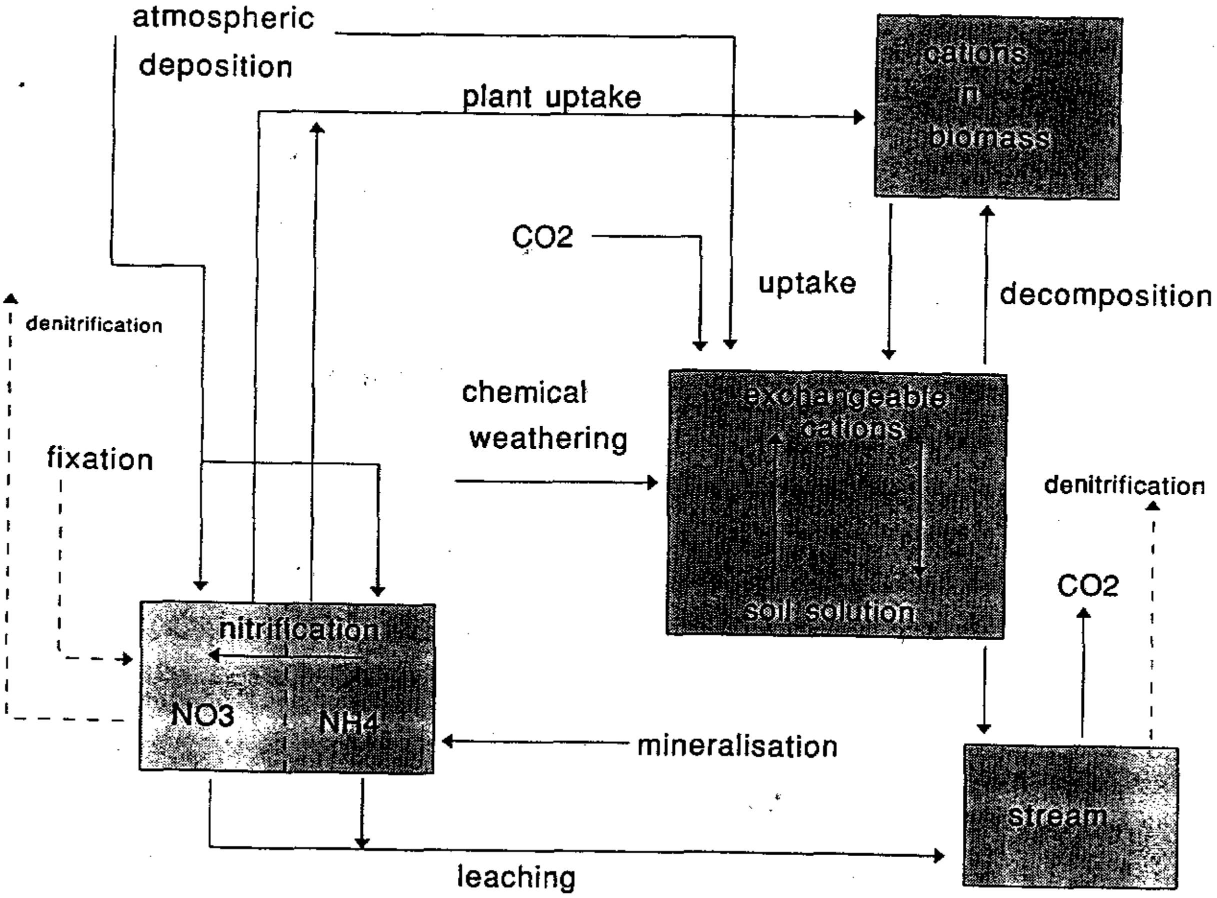

Figure 3.1. Schematic of the flows and stores in MAGIC-WAND.

MAGIC-WAND maintains the full sulphur based chemistry of MAGIC and considers two species of inorganic nitrogen, nitrate (NO_3) and ammonium (NH_4). Both species are assumed to be present only in solution in soil water. The model explicitly incorporates the major terrestrial fluxes of nitrogen, such that;

NO_3 leaching = deposition + nitrification + external addition - uptake - denitrification

and

NH_4 leaching = deposition + external addition + mineralisation - nitrification - uptake

If the net result of these fluxes is positive (surplus NO_3 and/or NH_4) leaching to surface waters occurs.

Nitrogen inputs to the system are in the form of inorganic nitrogen added to the soil solution. The primary inputs are **atmospheric deposition** and mineralisation. **Mineralisation** in the model represents the release of inorganic N that was formerly bound in organic matter. The mineralisation product is NH_4. Provision is also made for in the model for other inputs such as **fertilisation** or nitrogen **fixation** (external additions). Time series of all inputs of inorganic nitrogen must be specified a priori. Inputs are fluxes and have units of meq/m^2/year of either NO_3 or NH_4.

Nitrogen losses from the model system are as inorganic nitrogen. The primary output is in hydrologic runoff from the soils. The runoff fluxes are calculated as the product of the simulated concentrations of NO_3 and/or NH_4 at any time step and the hydrologic discharge at that time. Provision is also made in the model for other losses of inorganic nitrogen such as **denitrification** from soil or surface water. The magnitude and timing of these additional outputs of N may be specified a priori or they may be keyed to external NO_3 or NH_4 concentrations using first order reaction kinetics.

The **nitrification** process (microbial mediated transformation of NH_4 to NO_3) is represented in the model by a first order reaction. The rate of loss of NH_4 (equal to the rate of production of NO_3) is given by the product of a rate constant and the concentration of NH_4 at each time step, such that;

$$d(NH_4)/dt = - Kn * (NH_4)$$

where, (NH_4) is the concentration of NH_4 in soil solution (meq/m^3) and Kn is a rate constant (/year).

Plant uptake is modelled as a non-linear process that depends upon the concentration of available NO_3 or NH_4. The equation is hyperbolic (a typical Michaelis - Menten uptake process representation) such that;

$$d(N)/dt = K_{max} * ((N) / (Ks + (N)))$$

where, (N) is the concentration of either NO_3 or NH_4, K_{max} is the maximum uptake rate ($meq/m^3/yr$) and K_s is the half-saturation constant of the reaction (meq/m^3).

The same uptake parameters are assumed for both NO_3 and NH_4 so there can be no differential or preferential uptake of either form of inorganic nitrogen. The values of K_{max} and K_s can be varied through time a priori, to represent the characteristics of a changing or damaged vegetation.

The process equations are solved sequentially at each time step such that the NH_4 deposition flux, mineralisation flux and external additions are added to the soil water NH_4 concentration from the previous time step. The required fraction transformed by nitrification is then subtracted first, followed by the calculated uptake flux. The resulting soil water concentration (if any NH_4 remains) is then available for leaching at a rate dependant upon the hydrologic turnover of the catchment. The NO_3 deposition flux, external additions and the input from nitrification of NH_4 are then added to the soil water NO_3 from the previous time step. From this pool is first subtracted the uptake flux and then losses through denitrification. The resulting soil water pool is then available for leaching, again dependant upon the catchment hydrologic turnover. Further losses of NO_3 by denitrification from surface water are then accounted for.

3.2. Model Parameterisation

Calibration of the nitrogen dynamics requires selection of values for the rate constants and to describe the uptake function. The values of these parameters must provide for a good match between present day simulated and observed (and historical if known) surface water NO_3 and NH_4 concentrations. Measurement of rate coefficients is, however, difficult in the field and in any case, can only usually be made at plot scale whereas MAGIC-WAND requires catchment average values. On the other hand, a large number of plot studies of nitrogen dynamics have been carried out in a wide range of environments (Table 3.1). The most pragmatic approach, therefore, is to utilise literature derived 'ranges' for parameter values and thereby introduce some degree of uncertainty into the model predictions.

3.2.1. Mineralisation

Mineralisation and immobilisation are biologically mediated processes and rates depend upon temperature and soil moisture, the soil microbial population and its characteristics and the carbon and nitrogen status of the substrate. Microbial activity tends to increase with temperature and with soil water matric potential, thereby increasing mineralisation and immobilisation rates, although at extremely high matric potentials (>-60 bar) the microbial population would be adversely affected.

Conventional measurement techniques involving litterbag analysis cannot separately quantify the two processes and simply provide rates of net mineralisation i.e. the surplus NH_4 from microbial transformation of organic nitrogen following microbial uptake of NH_4. It has been reported, however, that gross mineralisation tends to be 3 - 5 times net mineralisation in most soils with relatively low organic matter content.

Source	Coniferous Forest	Deciduous Forest	Grassland
Batey 1982			140 - 430
Melilo 1981		710 - 770	
Gosz 1981	210 - 360		
Emmett et al. In Press (Sitka, N.Wales)	490 - 645		
MLURI (BFS, Scot.)	240		
MLURI (Nutrient poor, Scot.)	230		
MLURI (Mixed Forest, Scot.)	350		
MLURI (Spruce, Germany)	515		

Table 3.1. Reported net mineralisation rates (meq N m^{-2} yr^{-1})

In MAGIC-WAND the amount of NH_4 produced as net mineralisation at each time step must be specified together with any change in this flux through time. This can be further modified on a monthly basis if seasonal changes in mineralisation rates are required.

3.2.2. Nitrification

Nitrification is a biologically mediated process and the rate of reaction depends mainly upon the size, nature and activity of the nitrifying population but there is little evidence that in (forest) soils, nitrification is inhibited by lack of nitrifiers. Specific site conditions, however, may curtail the size and activity of the nitrifying population. Spatial and temporal variability in nitrification rate is due to temperature, soil moisture, vegetation cover and type, topography, litter quality and nitrogen availability. Low soil pH is no longer thought to inhibit nitrification in most ecosystems.

Published nitrification rates for a variety of environments indicate that nitrification is rapid and that the turnover of the NH_4 pool in some forest soils can be less than one day. In most UK waters NH_4 is not detected implying that the combination of plant uptake and nitrification processes remove all NH_4 from the system.

In MAGIC-WAND, the rate of nitrification must be specified as the number of times the available NH_4 pool in the soil is turned over each year. This can be further modified to account for seasonal changes induced by temperature and moisture influences.

3.2.3. Denitrification

Denitrification is a microbial mediated process and is dependant on soil moisture, temperature, organic carbon supply and the available nitrogen pool. The soil water control is crucial and at matric potentials of greater than -1 bar the process is insignificant. Denitrification need only be considered if bogs or wetlands are present in the catchment although in lake systems this can be an important process which decreases NO_3 concentrations to very low levels.

In MAGIC-WAND, the loss of NO_3 through denitrification must be specified as a flux at each time step together with any changes through time. This can be further modified on a monthly basis to account for possible seasonal changes.

3.2.4. Fixation

Biological nitrogen fixation is a self-regulated process induced or inhibited by changes in the levels of inorganic nitrogen but is influenced by environmental factors such as temperature, pH, oxygen supply, levels of moisture and mineral nutrients and sources and availability of energy. Estimates of nitrogen fixation range from < 1 - 10 kg nitrogen ha^{-1} yr^{-1} for unimproved grassland (Woodmansee et al. 1981, Batey 1982), from 0.3 to 12 kg nitrogen ha^{-1} yr^{-1} in deciduous forests (Melilo 1981) and from 0.4 to 28, with typical values between 5 and 10, kg n ha^{-1} yr^{-1} for coniferous forests (Gosz 1981).

In MAGIC-WAND, the addition of NO_3 through nitrogen fixation must be specified as a flux at each time step together with any changes through time. This can be further modified on a monthly basis to account for possible seasonal changes.

3.2.5. Plant Uptake

It is generally accepted that tree roots can take up both inorganic NH_4 and NO_3, although the relative abundance of each ion in soil solution may determine a preferential uptake response if more of both nitrogen forms are made available. Measured plant uptakes show a wide range both between different vegetation types, such as grassland and forest, and between ecosystems under the same vegetation (Table 3.2). The various features of an ecosystem which can influence the rate of plant uptake include; soil and soil solution processes, in particular the available N; the size, location and length of roots and root hairs, including presence and type of mycorrhizal association; specific chemical and biochemical reactions at the soil solution - root interface and within the root, including selectivity between NO_3 and NH_4, reduction of NO_3 within the plant, presence of inhibitory agents and translocation processes; nitrogen requirements of the plant, including rate of primary production, nutrition and maturity of the plant and rate of internal recycling once nitrogen has been taken up. In forest ecosystems, for example, the reasons for the wide range of uptake rates include; rate of production; availability of nitrogen in the soil; duration of needle retention by conifer species; translocation of nitrogen back to living tissue at the time of senescence, and; age or maturity of the trees.

Source	Coniferous Forest	Deciduous Forest	Grassland
Gosz 1981	215 - 360		
Melilo 1981		515 - 1100	
Woodmansee et al. 1981			460
Batey 1982			140 - 430

Table 3.2. Reported plant uptake rates (meq N m^{-2} yr^{-1})

Within MAGIC-WAND the same hyperbolic function is used to describe uptake of both NH_4 and NO_3. The two parameters required to describe this function, maximum uptake rate (K_{max}) and half saturation or slope ($K_{1/2}$), cannot be measured in reality. It is possible to set reasonable values for these parameters, however, by adhering to a loose set of rules;

(i) If nitrogen concentrations in surface waters are low then the maximum uptake rate should be greater than the sum of the external nitrogen sources.

(ii) If NO_3 is leaking from a site then either maximum uptake rate is less than the sum of external inputs or the half saturation constant is high, that is, the slope of the uptake function to the maximum rate is very low. Both will produce an nitrogen breakthrough to match the observation.

(iii) The half saturation constant cannot be too high as to cause historical breakthrough at a site where this does not presently, and so is unlikely historically, to occur.

The uptake function is the single most important process in MAGIC-WAND for producing nitrogen breakthrough in response to increased inorganic nitrogen inputs or from vegetation ageing and so a reasonable range of values should be used for each application to provide a range of responses. Figure 3.2 shows examples of the sensitivity of the uptake function to different values of K_{max} and $K_{1/2}$. The model requires K_{max} to be specified at each time step and this can be modified to account for ecosystem disturbances or seasonal uptake dynamics.

4. Assessing Sensitivity to Nitrogen Dynamics

4.1. Sensitivity to Uptake Parameters

Sensitivity of MAGIC-WAND to nitrogen dynamics is essentially a function of the interaction between the plant uptake response and the total nitrogen inputs to the system (external concentration). The selection of the parameters describing the plant uptake function is crucial to the degree and timing of nitrogen breakthrough (Figure 4.1). A high value of K_{max} assumes that the plants will be able to utilise higher inputs of nitrogen and so breakthrough will be delayed in time (Figure 4.1a) or, if k_{max} is set sufficiently high relative to total inputs, will never occur. $K_{1/2}$ determines the amount of nitrogen which is taken up by the plants for a given external concentration. If this is set to a low value, maximum plant uptake occurs at relatively low nitrogen inputs and no leakage of nitrogen can occur unless inputs exceed K_{max}. If $K_{1/2}$ is set to a high value, maximum uptake will not be achieved despite high nitrogen inputs to the

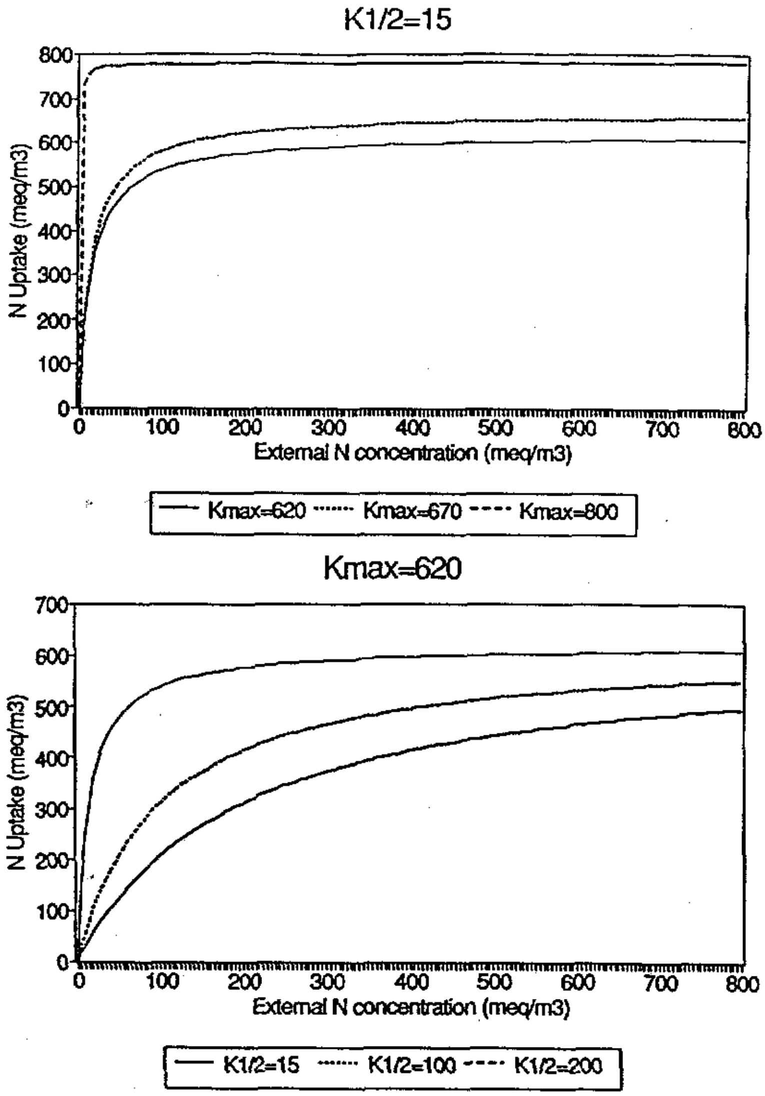

Figure 3.2. The non-linear uptake function. $K_{1/2}$ (a) and K_{max} (b) determine the rate and amount of N uptake for a given external N concentration.

system and some proportion of that input will leak. The proportion is dependant upon the value of $K_{1/2}$ (Figure 4.1b).

Following breakthrough, NO_3 is treated as a mobile anion within the model and so the nitrogen dynamics, in particular the sensitivity to K_{max}, influence the acid status of a site. The example in Figure 4.2 assumes that SO_4 deposition will decrease linearly to 30% of present level by 2010, in line with the agreed UNECE protocol. If nitrogen deposition is held constant for the same period and K_{max} is set such that it is greater than total inputs then NO_3 will not leak and a recovery is predicted in soil base saturation, stream pH and alkalinity. If, however, nitrogen deposition is assumed to double over the period both soil and water continues to acidify at a rate which is determined by the value of K_{max} (NB. $K_{1/2}$ is held constant at 15 in all cases).

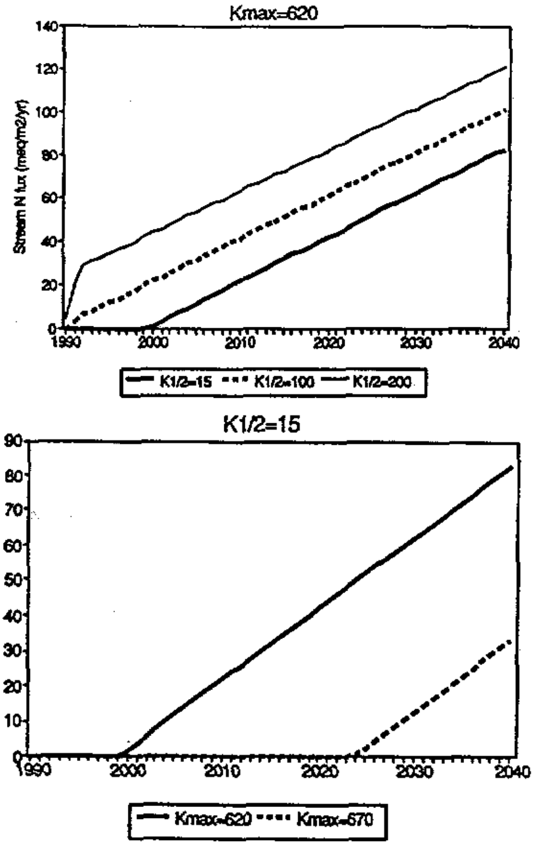

Figure 4.1. The relationship between timing and magnitude of N output flux and K_{max} (a) and $K_{1/2}$ (b) parameters of the uptake function.

4.2. Sensitivity to Uptake, Mineralisation and Deposition

The potential for future nitrogen breakthrough in a catchment system depends not only on the total nitrogen deposition but also on the internal nitrogen cycle within the catchment. The model can be used to assess future nitrogen deposition scenarios in conjunction with changing uptake characteristics associated with forest growth, vegetation change or vegetation damage. Figure 4.3 shows schematically four scenarios ranging from a best to worst case;

(i) a 70% decrease in sulphur deposition by 2010 and no change in nitrogen deposition, mineralisation or uptake (K_{max} = 620 meq/m^2/yr, $K_{1/2}$ =15 meq/m^2/yr^1) characteristics (best case).

(ii) a 70% decrease in sulphur deposition by 2010, a linear increase in nitrogen deposition over 50 years to double present day levels and no change in nitrogen mineralisation or nitrogen uptake characteristics.

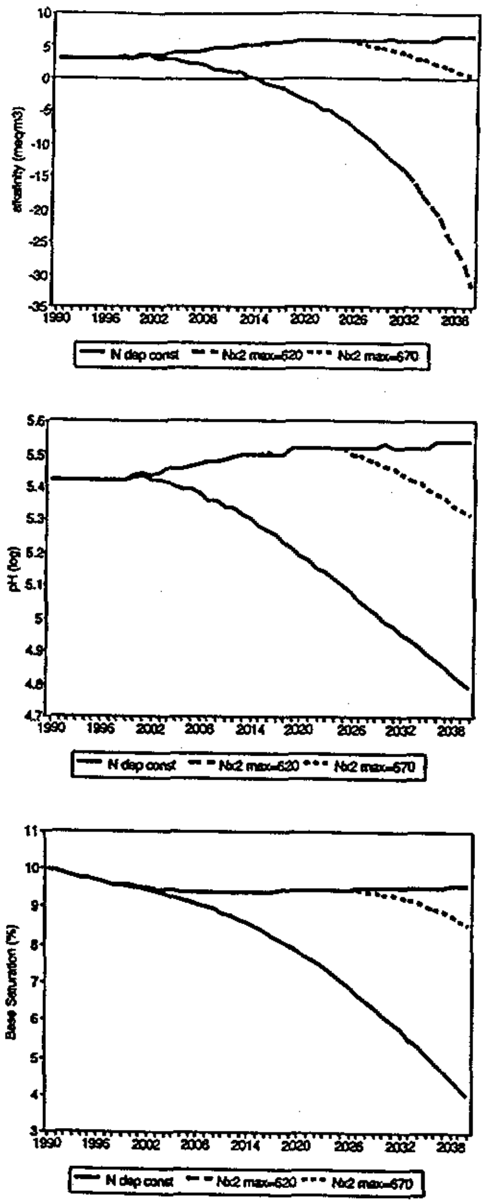

Figure 4.2. The effect of N breakthrough in response to different plant uptake functions on stream water and soil chemistry; (a) stream water alkalinity; (b) stream water pH; (c) soil base saturation.

(iii) a 70% decrease in sulphur deposition by 2010, no increase in nitrogen deposition and a decrease in K_{max} over a 20 year period such that the internal nitrogen cycle is "closed" i.e. mineralisation equals uptake.

(iv) a 70% decrease in sulphur deposition by 2010, a doubling of nitrogen deposition and a decrease in Kmax over a 20 year period such that the internal nitrogen cycle is "closed" i.e. mineralisation equals uptake (worst case).

These scenarios were run for a combination of acid sensitive and non-acid sensitive sites and high (1.6 g m^{-2}) and low (0.3 g m^{-2}) nitrogen deposition. The resulting model predictions emphasise the importance of nitrogen dynamics for the future acidification status at a wide range of sites (Figure 4.4). At the sensitive site, a decrease in sulphur deposition combined with no change in nitrogen dynamics (scenario 1) leads to little change in future alkalinity. Changes in nitrogen deposition fluxes and internal nitrogen dynamics (scenarios 2,3 and 4) are similarly predicted to have little effect at low deposition sites. Under high nitrogen loads, however, alkalinity is predicted to be severely decreased. It should also be noted that scenario 4, which combines scenarios 2 and 3, is not simply the additive effect of the two due to the dynamics of ion exchange in the model. This is well illustrated for the non-sensitive site where under scenario 4 an extreme surface water acidification is predicted.

These "games" using hypothetical catchments serve to illustrate some of the capabilities of the model structure and the ways in which the model can, and should, be used to assess a range of future scenarios.

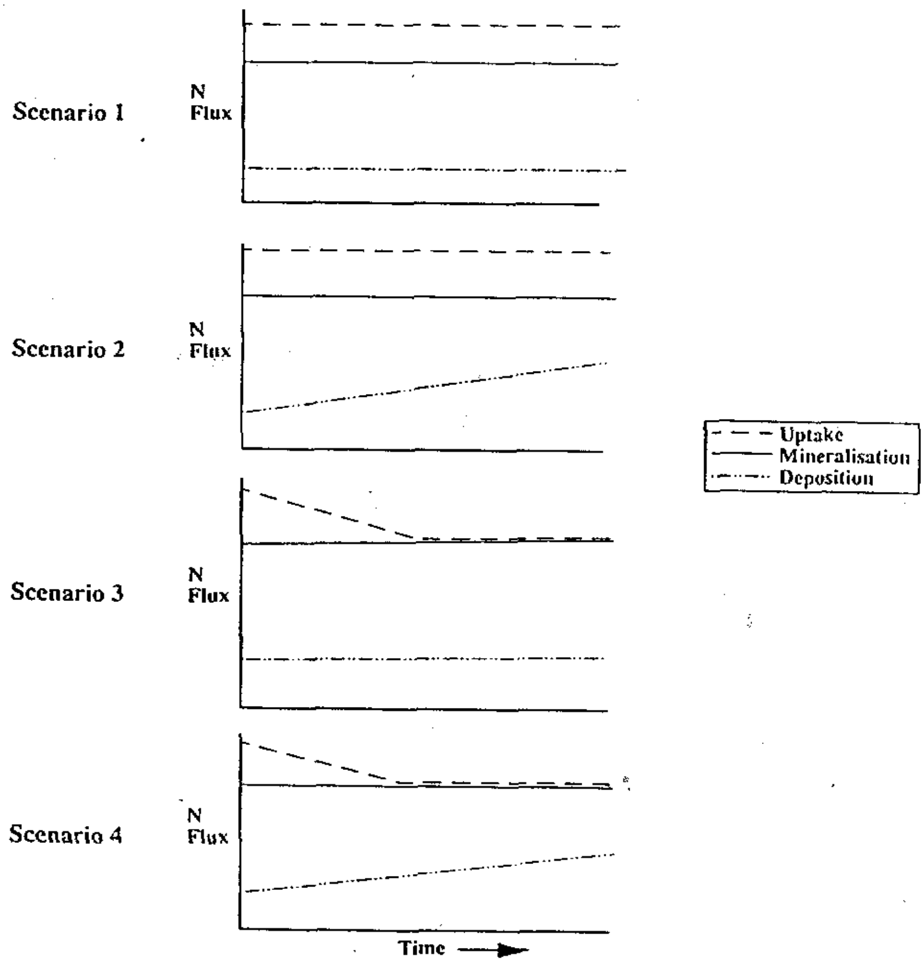

Figure 4.3. Four generalised scenarios representing changes in catchment internal nitrogen cycling. See text for explanation.

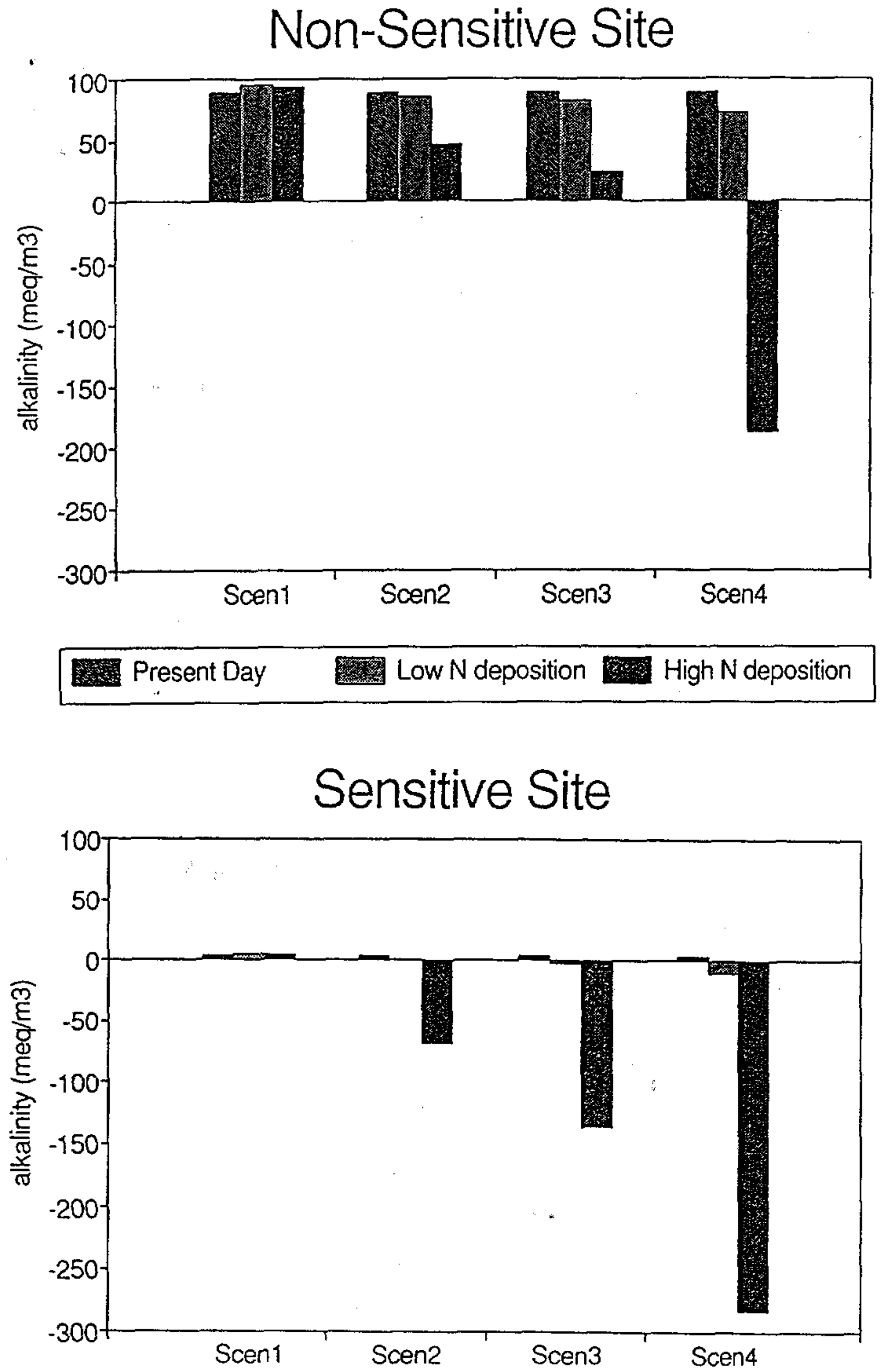

Figure 4.4. Model predictions stream alkalinity 50 years from present at a non-sensitive (a) and sensitive (b) site under the four generalised N cycling scenarios.

5. Site Applications

MAGIC-WAND has been calibrated to a forested and a moorland site in Scotland. Present day observed water chemistry is derived from the UK Acid Waters Monitoring Network database. Present day deposition fluxes are estimated using data collected under the DoE Acid Deposition Network. Soil chemical and physical data is supplied by the Macaulay Land Use Research Institute (MLURI). Values of nitrogen fluxes and uptake parameters are derived from literature. The calibrated model is used to predict future behaviour under decreasing and constant nitrogen deposition.

Three nitrogen deposition scenarios; (i) Total nitrogen deposition held constant at present day level throughout the forecast; (ii) Total nitrogen deposition increased linearly to a level 50% higher than present in 2010. The relative proportions of NO_x and NH_x are maintained throughout; (iii) Total nitrogen deposition decreased linearly to a level 50% lower than present in 2010. The relative proportions of NO_x and NH_x are maintained throughout.

The impact of NO_3 leaching at a site on soil and surface water acidification status and recovery will be dependant upon the magnitude and timing of leaching, the future sulphur deposition and the chemical characteristics of the soils and bedrock in terms of ion-exchange coefficients and base cation weathering. It is not appropriate, therefore, to interpret the simulated chemical changes at Loch Grannoch or Round Loch on a more general basis or to extrapolate these results to other sites.

5.1. Moorland Site

The model has been calibrated for the Round Loch of Glenhead, an unimproved heather and grass moorland catchment in the Galloway region of SW Scotland. The estimated nitrogen deposition for the area is 183.5 meq nitrogen m^{-2} yr^{-1} and this is dominated by NH_x (63%). Observed stream chemistry over a 5 year period (ENSIS in press) shows mean NO_3 concentration of 5 meq m_{-3} with a distinct seasonal pattern, concentrations peaking in the autumn and winter. NH_4 concentrations are below detection limits. Nitrogen deposition history at the site is assumed to follow the estimated curve for nitrogen emissions (Figure 5.1) derived by the Warren Springs Laboratory (DOE 1983, DOE 1990). Future sulphur deposition at these sites is based upon the currently agreed emissions reduction strategy for the UK to 30% of 1980 levels by 2005 and to 20% by 2010 (University of Hull, unpublished).

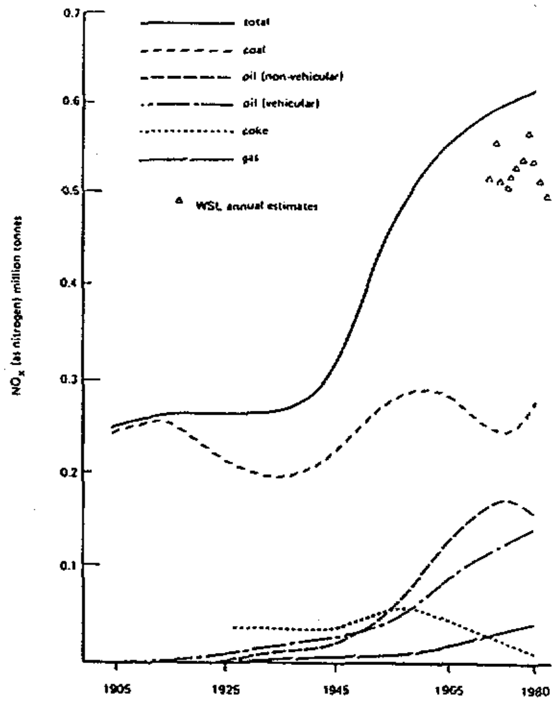

Figure 5.1. Estimated NO_x emissions in the UK (DOE 1983, DOE 1990) from which N deposition sequences were scaled.

5.1.1. Calibration of Nitrogen Dynamics

Three combinations of parameters are used to describe the hyperbolic uptake function (Figure 5.2) with mineralisation constant at 300 meq m^{-2} yr^{-1} and nitrification rate, expressed as the number of times the pool turns over per year, of 365 $year^{-1}$. The mineralisation flux represents the maximum of the range of values reported in Tables 3.1 but this high value is closest to the values reported and used for forest vegetation. The three combinations of uptake parameters are;

Model (i), $K_{max} = 464$ and $K_{1/2} = 15$ (Figure 5.2). In this case K_{max} is equal to mineralisation plus total nitrogen deposition at present day and represents the minimum level of uptake necessary to achieve the low and seasonally evident NO_3 leaching at the site. The low value for $K_{1/2}$ effectively precludes any non-linearity in uptake except at very low external nitrogen concentrations and assumes that the plants are always attempting to take nitrogen at the rate of K_{max}.

Model (ii), $K_{max} = 500$ and $K_{1/2} = 15$ (Figure 5.2). In this case K_{max} is arbitrarily set to allow the vegetation to continue to take all available nitrogen at higher external concentrations. In reality, K_{max} for a moorland vegetation is likely to increase as the vegetation species change in

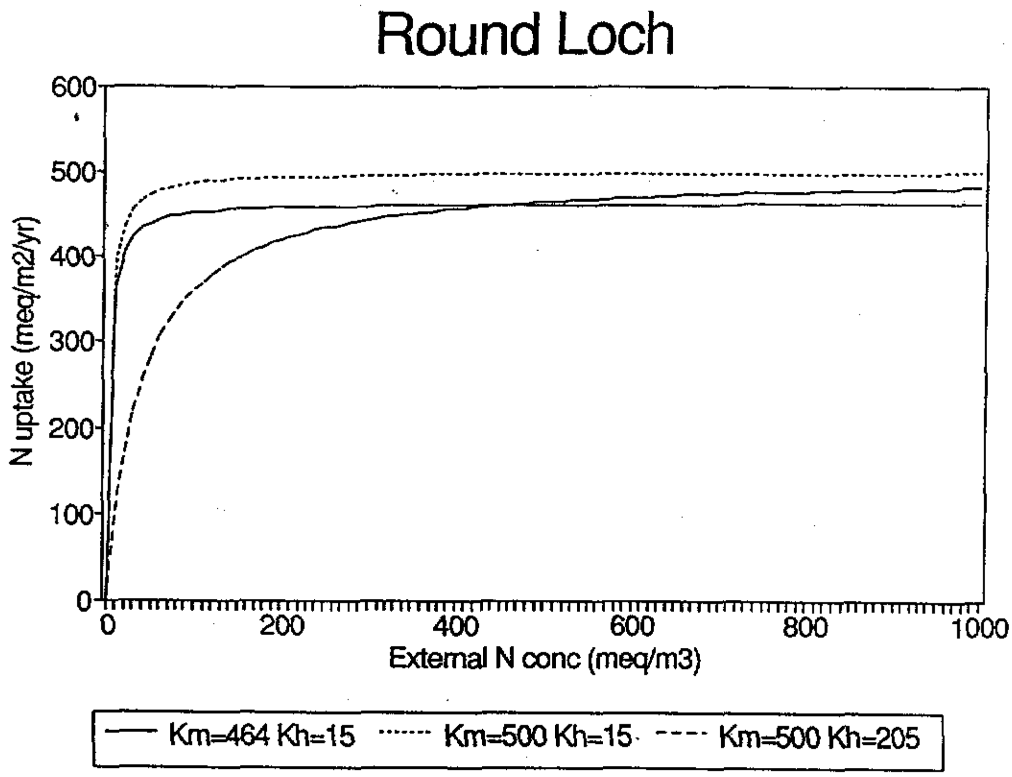

Figure 5.2. The plant uptake functions used corresponding to models (i) - (iii).

response to increased availability of N. That is, nitrogen poor species decline as those species thriving on luxury nitrogen uptake increase e.g. heather declines quickly to be replaced by grass. For this exercise, this represents a best case scenario but arbitrarily imposes the timing of nitrogen breakthrough.

Model (iii), $K_{max} = 500$ and $K_{1/2} = 205$ (Figure 5.2). Here $K_{1/2}$ is selected as the highest possible value (and hence the lowest slope), given K_{max}, under the constraint of no historical NO_3 breakthrough. The non-linearity introduced in this case allows uptake to increase or decrease in proportion to a change in external concentration.

The effects of the three nitrogen deposition scenarios and the three model structures on nitrogen uptake dynamics are shown in Figure 5.3. If nitrogen deposition is held constant over the simulation period, uptake remains constant under each model structure and the nitrogen system remains in steady state for the length of the simulation and no breakthrough occurs. If nitrogen deposition increases, uptake in model (i) remains effectively unchanged at K_{max} and no breakthrough occurs, model (ii) allows uptake to increase with increasing nitrogen deposition until nitrogen deposition exceeds K_{max} causing breakthrough at that point in time and in model (iii), uptake increases only slowly allowing breakthrough immediately although

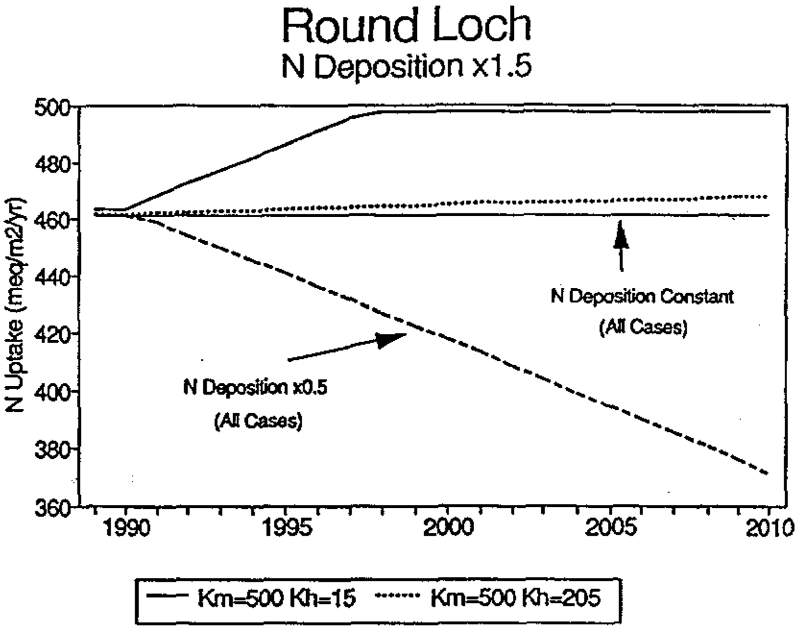

Figure 5.3. The effect of the three uptake functions used in models (i) - (iii) on plant uptake flux.

only in proportion to incoming N. If nitrogen deposition decreases, uptake in all models simply decreases in response to the decrease in external nitrogen concentration since K_{max} is always greater than external N.

5.1.2. Predicted Soil and Water Chemistry Response

Surface water alkalinity predictions (Figure 5.4) under constant nitrogen deposition show a steady improvement as a result of the decline in sulphur deposition alone since the nitrogen system remains in steady state in all cases. If nitrogen deposition is increased, this recovery is slowed, the degree of which is determined by the timing and amount of nitrogen breakthrough (Figure 5.4b). Conversely, if nitrogen deposition is decreased the recovery is slightly greater as a result of the lower flux of mobile anions through the catchment (Figure 5.4a).

Soil base saturation and Al^{3+} concentration shows a narrow band of response to nitrogen deposition scenarios and different model structures (Figure 5.5). The best case, model (i) under decreased nitrogen deposition, is a slight increase in base saturation and a decline in Al^{3+} to almost zero. The worst case is predicted by model (i) under increased nitrogen deposition as a very small decline in base saturation, c. 0.5% and 2 meq/m^{-3} for base saturation and Al^{3+}, respectively, over the simulation period.

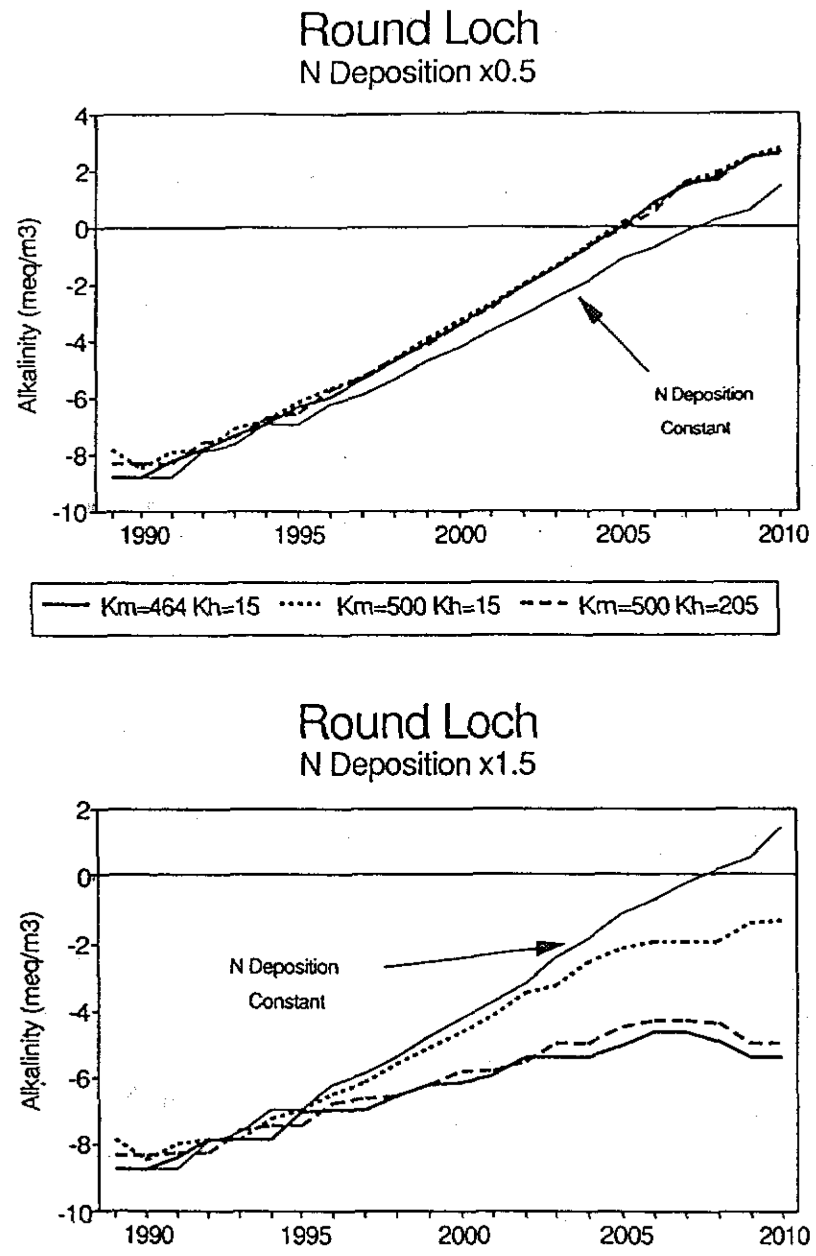

Figure 5.4. Surface water alkalinity predictions under (a) decreased and constant and (b) increased and constant nitrogen deposition scenarios.

5.2. Forested Site Application

The model has been calibrated for Loch Grannoch, a forested catchment in the Galloway region of SW Scotland. The estimated nitrogen deposition for the area is 165 meq nitrogen m^{-2} yr^{-1} and this is dominated by NH_x (63%). Observed stream chemistry over a 5 year period (ENSIS in press) shows mean NO_3 concentration of 14 meq m^{-3} with a distinct seasonal pattern, concentrations peaking in the autumn and winter. NH_4 concentrations are below detection limits.

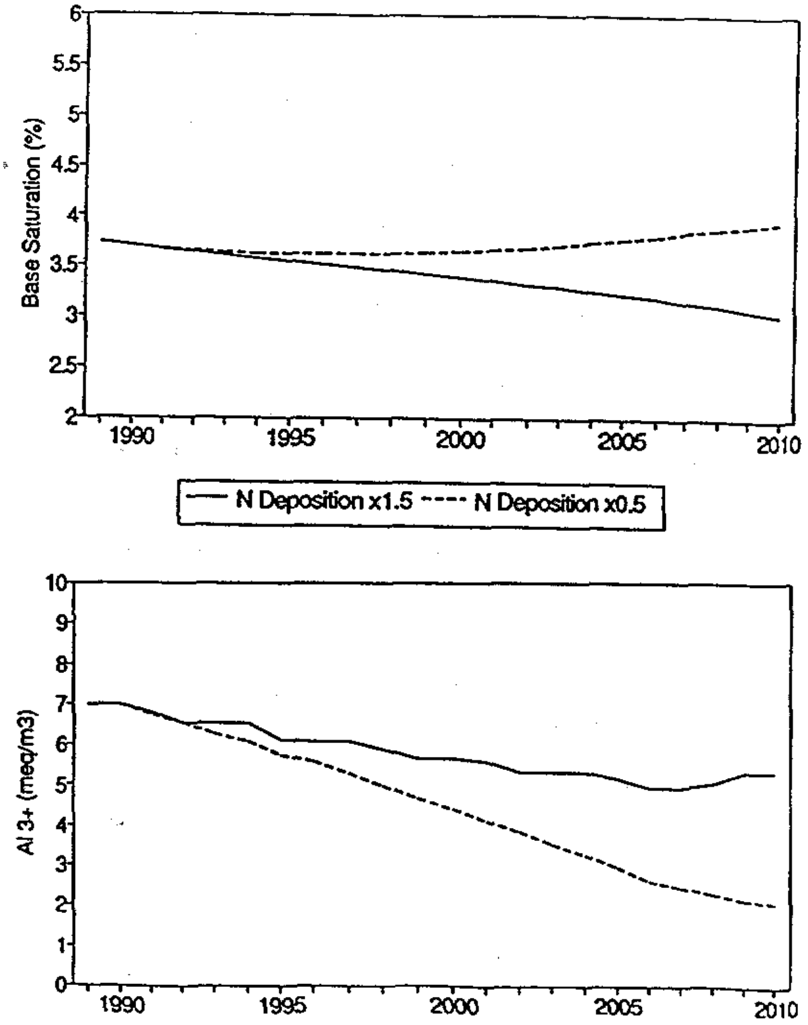

Figure 5.5. The range of predicted soil base saturation (a) and surface water Al^{3+} concentration (b) under the different nitrogen deposition scenarios and model structures.

Nitrogen deposition history at the site is assumed to follow the estimated curve for nitrogen emissions (Figure 5.1) derived by the Warren Springs Laboratory (DOE 1983, DOE 1990). Future sulphur deposition at the site is based upon the currently agreed emissions reduction strategy for the UK to 30% of 1980 levels by 2005 and to 20% by 2010 (University of Hull, unpublished). Forest dynamics are simulated in the model by specifying time sequences for uptake of ions by the growing forest, enhanced deposition through canopy scavenging processes and discharge as affected by the changing water use of the forest (Cosby et al. 1990).

5.2.1. Calibration of Nitrogen Dynamics

Three combinations of parameters are used to describe the hyperbolic uptake function (Figure 5.6) with mineralisation constant at 400 meq m^{-2} yr^{-1} and nitrification rate, expressed as the number of times the pool turns over per year, of 365 year^{-1}. The three combinations of uptake parameters, are;

Model (i), K_{max} = 565 and $K_{1/2}$ = 15 (Figure 5.6a). In this case K_{max} is just greater than mineralisation plus total nitrogen deposition at present day and represents the minimum level of uptake necessary to achieve the low and seasonally evident NO_3 leaching at the site. The low value for $K_{1/2}$ effectively precludes any non-linearity in uptake except at very low external nitrogen concentrations and assumes that the plants are always attempting to take nitrogen at the rate of K_{max}. K_{max} is then linearly decreased to 500 meq m^{-2} yr^{-1} in line with measured nutritional requirements for 50 year old Sitka spruce of yield class 16 and excluding internal translocation (MLURI unpublished data).

Model (ii), K_{max} = 900 and $K_{1/2}$ = 15 (Figure 5.6b). In this case K_{max} is set to the highest reported plant uptake (Table 4.2). This represents a best case scenario. K_{max} is then linearly decreased to 500 mg m^{-2} yr^{-1} in line with model(i).

Model (iii), K_{max} = 900 and $K_{1/2}$ = 1285 (Figure 5.6c). Here $K_{1/2}$ is selected as the highest possible value (and hence the lowest slope), given K_{max}, under the constraint of no historical NO_3 breakthrough. The non-linearity introduced in this case allows uptake to increase or decrease in proportion to a change in external concentration. K_{max} is then linearly decreased to 500 mg m^{-2} yr^{-1} in line with model(i).

The effects of the three nitrogen deposition scenarios and the three model structures on nitrogen uptake dynamics are shown in Figure 5.7. If nitrogen deposition is held constant over the simulation period (Figure 5.7a); uptake decreases linearly in response to the linear decrease in K_{max} (model i); remains constant until K_{max} falls below external nitrogen concentration at some point in the future (model ii); or, decreases dramatically (model iii). Models (i) and (ii) reach the same level of uptake at the end of the simulation since they are forced have identical parameters at this time.

If nitrogen deposition increases (Figure 5.7b), model (i) gives an identical uptake response to that under constant nitrogen deposition since uptake is always at its maximum rate which is always less than the external concentration. Model (iii) also behaves in the same way as for constant nitrogen deposition. On the other hand, model (ii) allows nitrogen uptake to increase with increasing nitrogen deposition until the declining K_{max} falls below the external nitrogen concentration whereupon uptake declines.

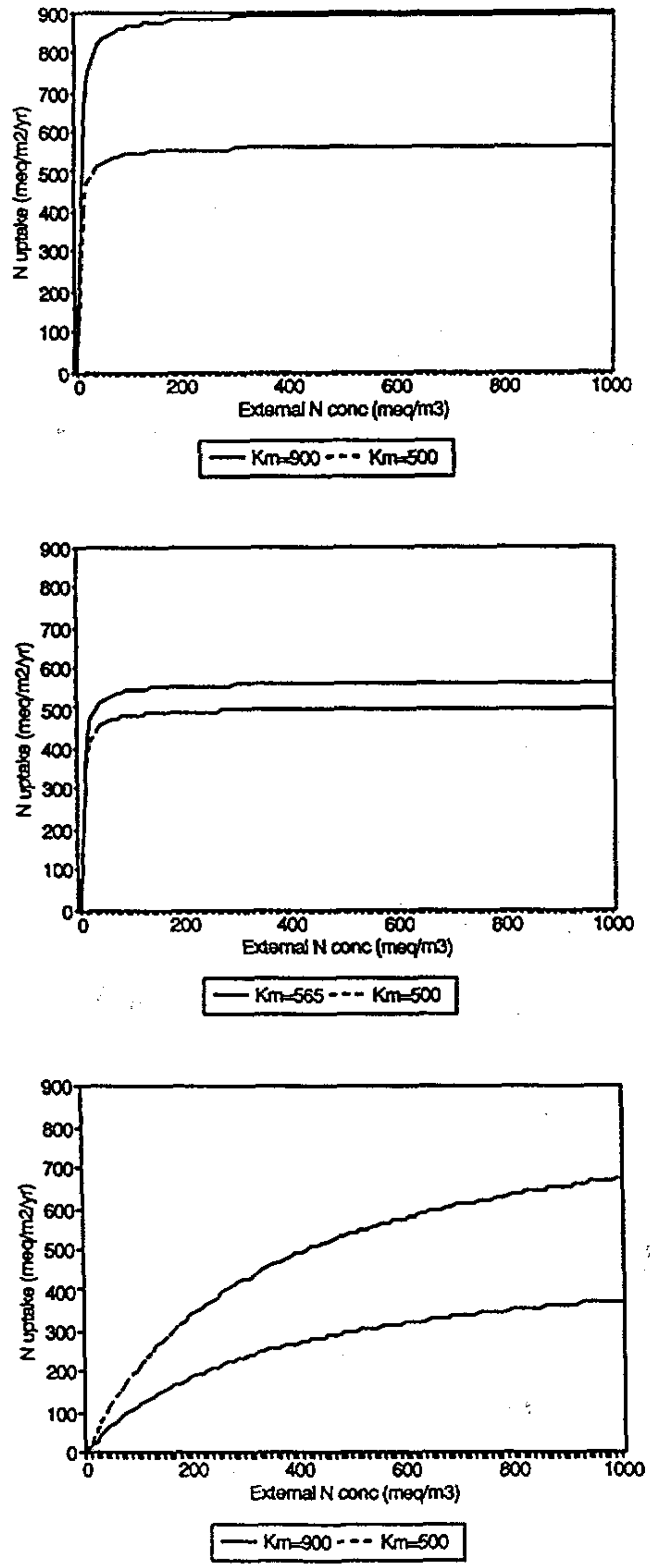

Figure 5.6. The three combinations of uptake functions used at Loch Grannoch; (a), (b) and (c) correspond to models (i) - (iii), respectively.

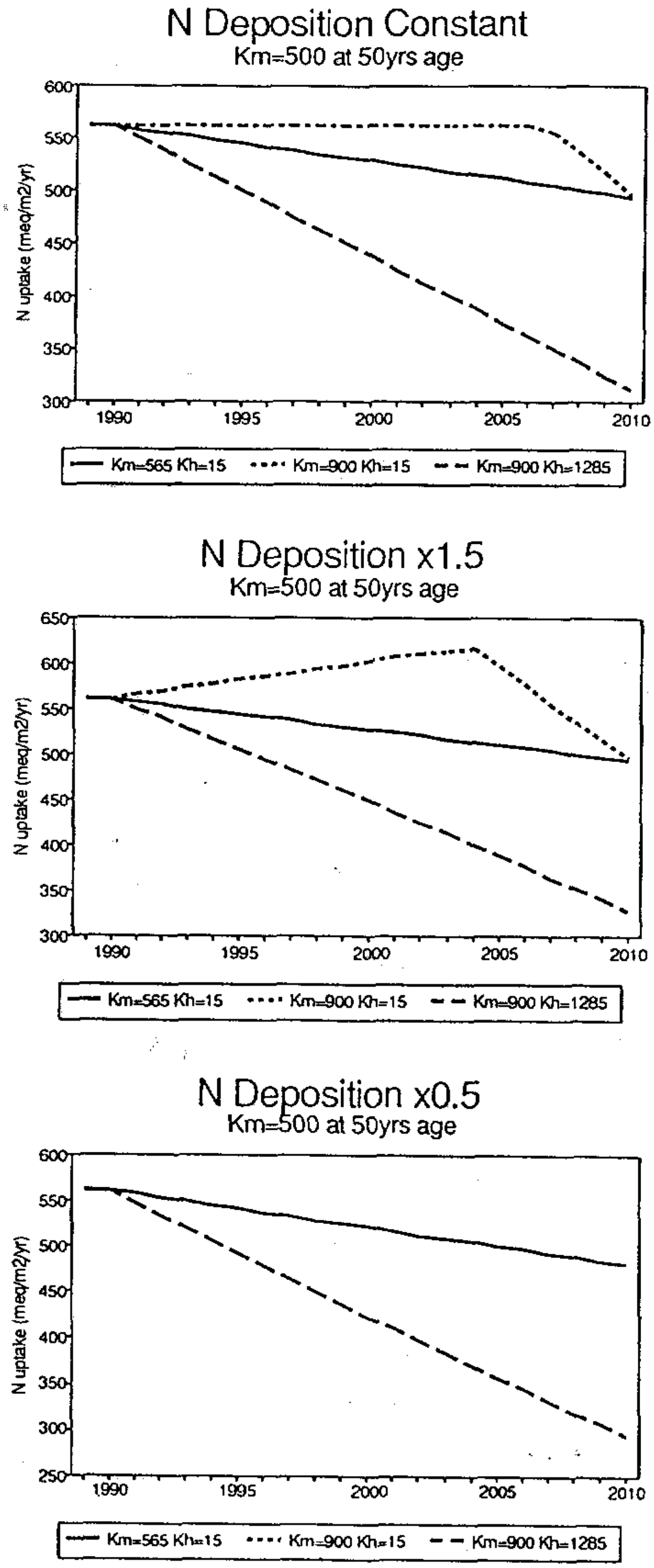

Figure 5.7. The effects of constant (a), increased (b) and decreased (c) nitrogen deposition scenarios and three model structures on nitrogen uptake fluxes.

If nitrogen deposition decreases (Figure 5.7c), uptake in models (i) and (ii) simply decreases in line with the prescribed decrease in K_{max} through time. In both cases, the external nitrogen concentration declines more rapidly than K_{max} and so the plants are always able to remove all N. For model (iii) the decrease in external nitrogen concentration causes uptake to fall lower than under constant or increasing deposition. This is counter intuitive and indicates that the high $K_{1/2}$ used in model (iii) is inappropriate although serves to provide a worst case behaviour.

5.2.2. Predicted Soil and Water Chemistry Response

In terms of surface water alkalinity (Figure 5.8) and under the constant nitrogen deposition scenario (Figure 5.8a), no recovery occurs under model (ii) despite a complete uptake of nitrogen until the latter 5 years of the simulation where alkalinity declines in response to nitrogen leaching. The decrease in sulphur deposition is matched by a decrease in the base cation concentrations (inputs of base cations are high at this site as a consequence of forest scavenging processes) and alkalinity remains stable. Under model (i), the decrease in sulphur compensates to some extent for the increase in NO_3 leaching but a slight decrease in alkalinity is predicted. Model (iii) predicts an extreme acidification effect in response to leaching of high levels of NO_3 in response to the marked decline in plant uptake. If nitrogen deposition is increased, these effects are enhanced (Figure 5.8b). If nitrogen deposition is reduced (Figure 5.8c), again the expected improvement in alkalinity in response to sulphur deposition reduction alone, despite plant uptake removing all nitrogen from the soil pool, is not marked due to the relationship between the mobile anion and base cations. The extreme acidification shown by model (iii) is an unlikely behaviour but represents an extreme possibility. The sensitivity of the site to nitrogen deposition is very much dependant upon the value of K_{max} (Figure 6.9) and further work is required to identify ranges of values appropriate to given forest species, site conditions and climatic conditions.

Soil base saturation under all deposition scenarios and models shows a gradual decline within a relatively narrow sensitivity band (Figure 5.10). This is because the projected decrease in sulphur deposition at the site is still too high to prevent depletion of the soil exchange pool, especially given the base cation requirements of the growing forest. The best cases are models (i) and (ii) under decreased nitrogen deposition and the worst case is model (iii) under increased nitrogen deposition.

The impact of the deposition scenarios and model structures on lake Al^{3+} concentrations is marked (Figure 5.11). The predicted changes are entirely consistent with the predicted changes in nitrogen leaching and alkalinity.

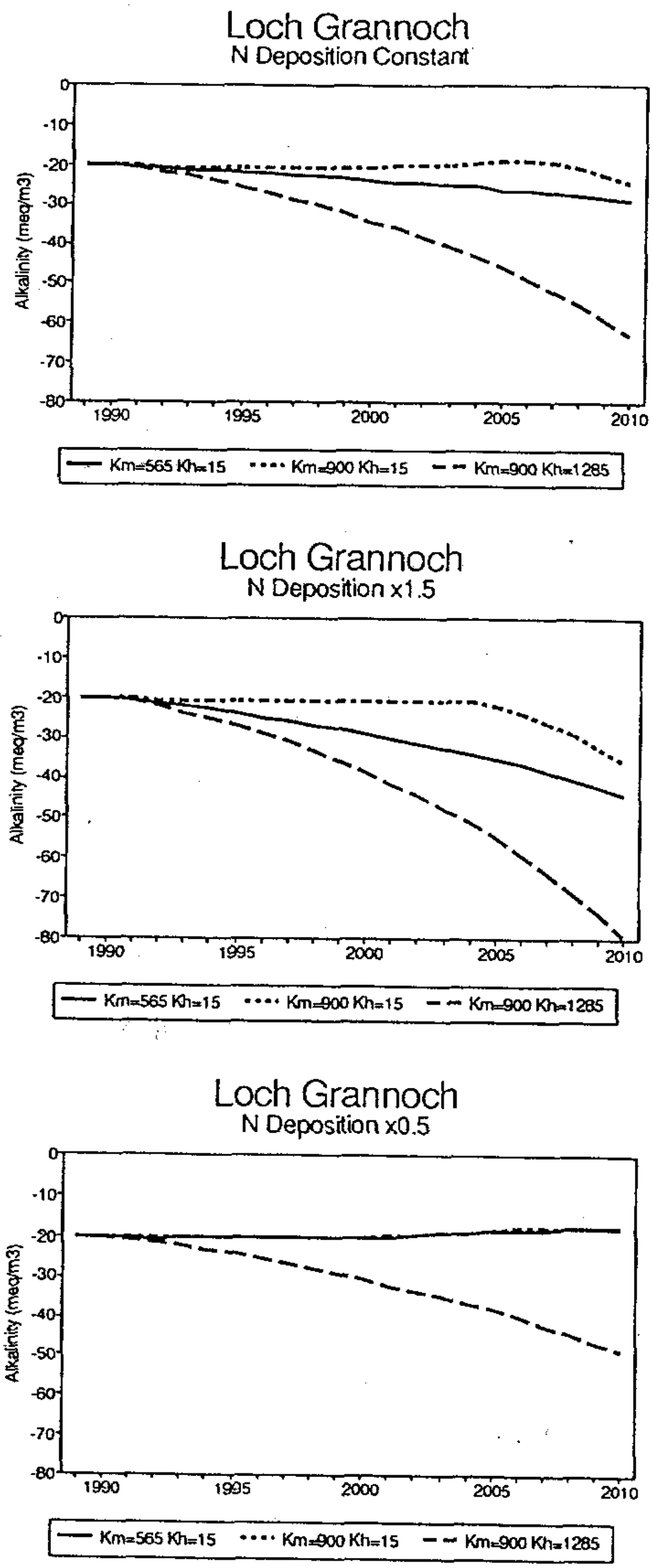

Figure 5.8. Predicted response of surface water alkalinity under constant (a), increased (b) and decreased (c) nitrogen deposition scenarios for the three model structures.

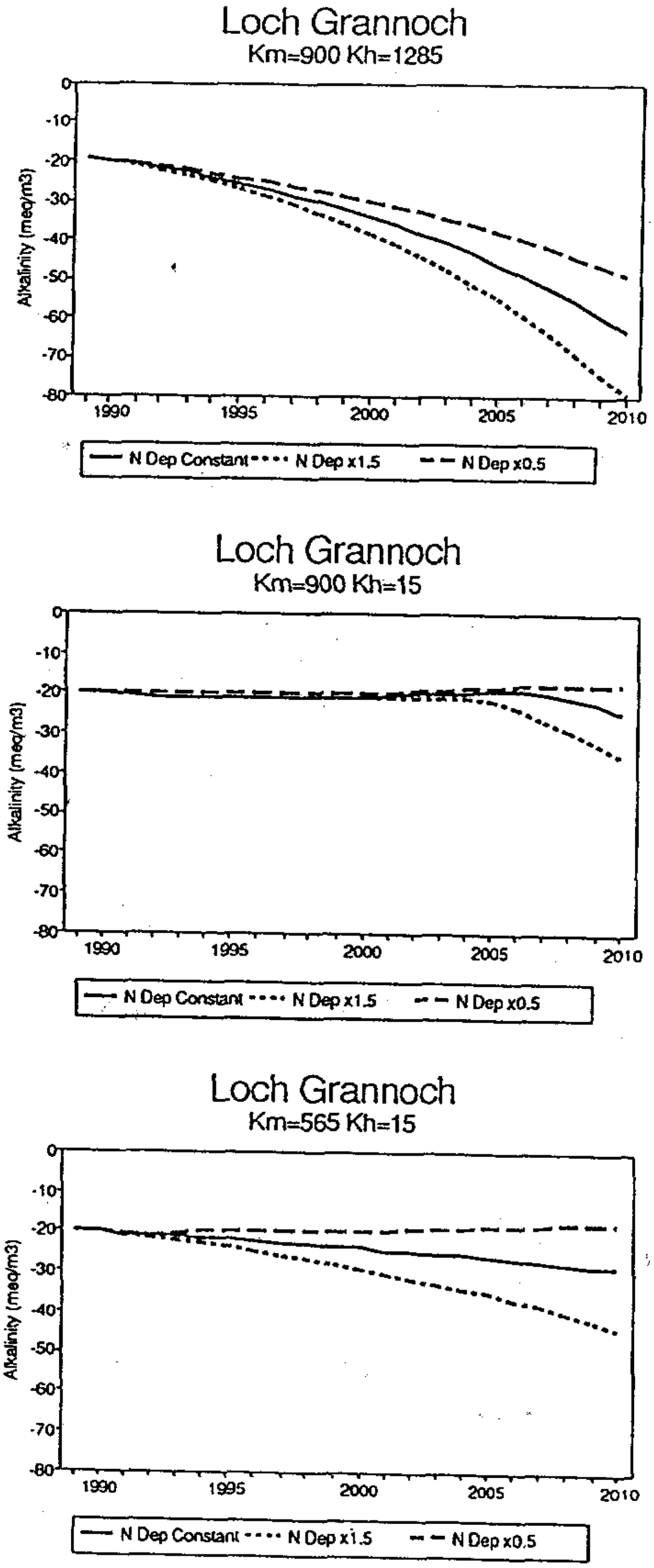

Figure 5.9. Predicted response of surface water alkalinity for (a) model (i), (b) model (ii) and (c) model (iii) assuming constant, increased and decreased nitrogen deposition. The sensitivity of the site to nitrogen deposition is most dependant on the value of K_{max}.

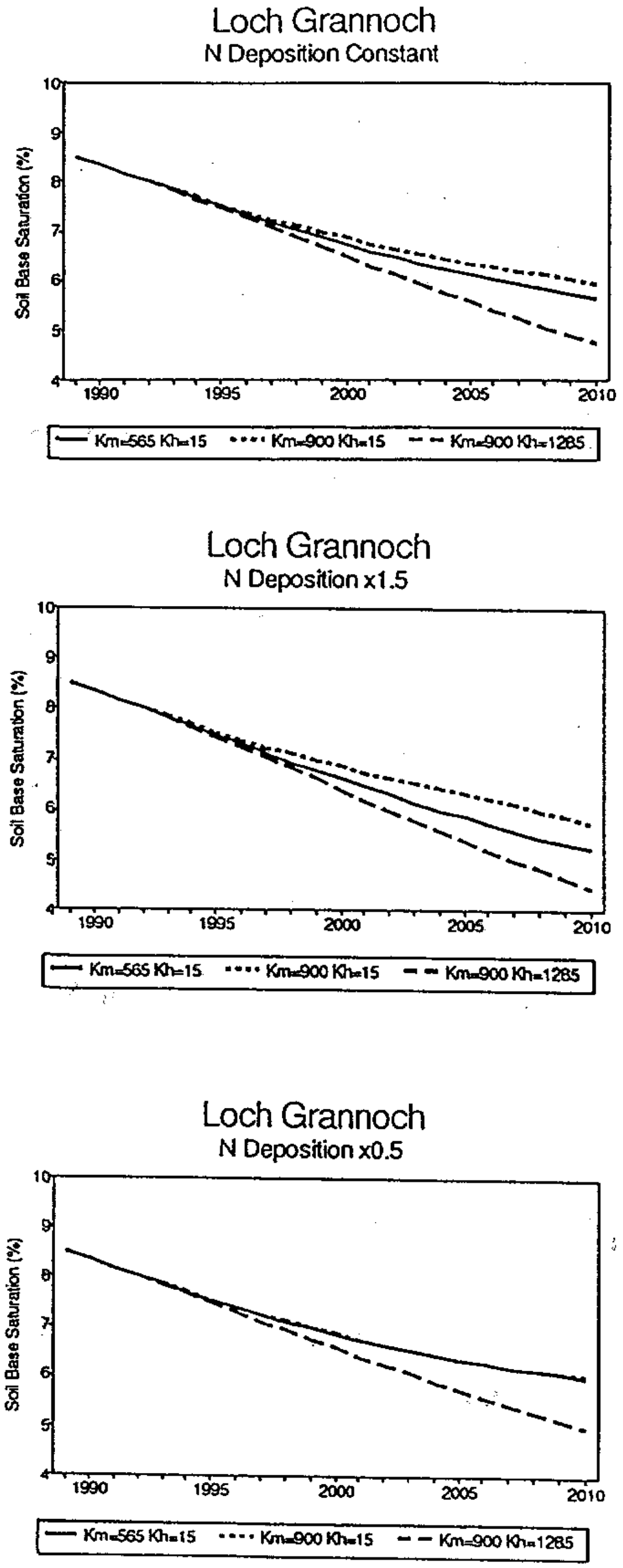

Figure 5.10. Predicted response of soil base saturation under constant (a), increased (b) and decreased (c) nitrogen deposition scenarios for the three model structures.

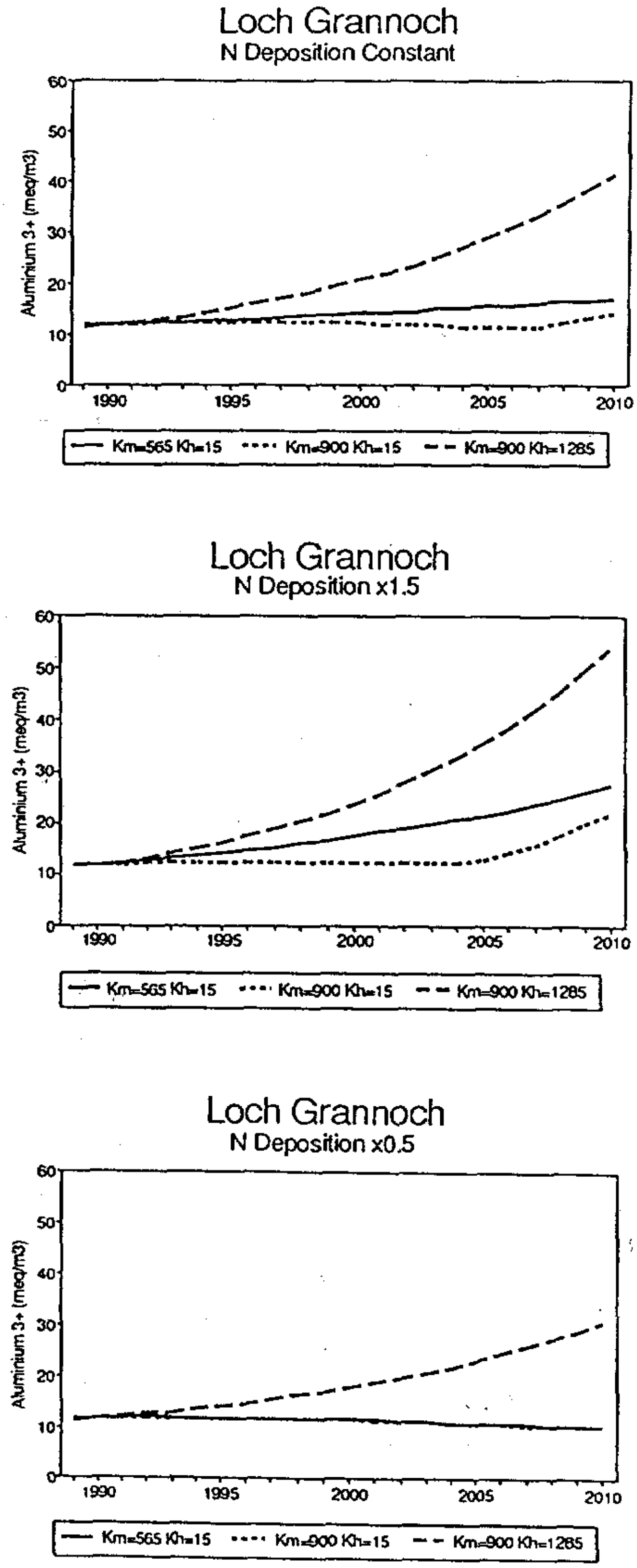

Figure 5.11. Predicted response of surface water Al^{3+} concentrations under constant (a), increased (b) and decreased (c) nitrogen deposition scenarios for the three model structures.

6. Deposition of Reduced and Oxidised Nitrogen

Reduced and oxidised forms of nitrogen have different emissions sources and, although closely linked, have different dynamics in catchment systems. With regard to deposition of nitrogen the associated counter ions are also important in driving the soil and surface water response. Ammonium emissions have been identified as being associated primarily with agricultural practices, while nitrate has been identified as resulting from the combustion of fossil fuels and especially vehicular emissions.

Deposition of ammonium can be directly as ammonia gas or; in solution with neutral salts such as ammonium chloride; acidic salts such as sulphate; or in a basic form as ammonium hydroxide. Similarly nitrogen deposition as nitrate can be balanced with a proton counter ion (HNO_3), or as a neutral salt such as calcium nitrate. The specific form of the deposition, in particular the counter ion associated with the nitrogen species is particularly important in terms of soil and surface water acidification. A key role for dynamic modelling studies, therefore, is to incorporate these potential interactions when predicting the response of terrestrial and aquatic systems to any potential net increase in nitrogen deposition.

The importance of the form of the deposited nitrogen and the associated counter ions has been examined using MAGIC-WAND at the Round Loch of Glenhead. A series of counter ions were coupled with a future deposition scenario based on a linear increase in nitrogen deposition flux of 40 meq m^{-2} yr^{-1} by 2010 from present day to 2010 and combined with a reduction in sulphur deposition in line with agreed reductions to 80% of 1980 levels by 2010. The net effect of different counter ions and nitrogen species on the pH of the incident precipitation is shown in Figure 6.1. Currently, rain pH is approximately 5.9 and there would be little or no change in this value if the additional nitrogen deposition was as calcium nitrate or ammonium chloride. This is to be expected as both these are neutral salts. However, there is a dramatic increase in pH associated with ammonium deposition alone (an increase in ammonium deposition in MAGIC-WAND results in the production of ammonium hydroxide in order to maintain electro-neutrality). Similarly there is a concomitant decrease in rain pH associated with ammonium sulphate and nitric acid deposition.

The effects of enhanced nitrogen deposition on the catchment soil base saturation is presented in Figure 6.2. The greatest reduction in base saturation is associated with enhanced nitrogen deposition in the form of ammonium sulphate. This is because the deposition of strong acid anions increases the loss of base cations from the soil exchange complex. This response is also observed with the addition of ammonium chloride, because the uptake of the weak acid

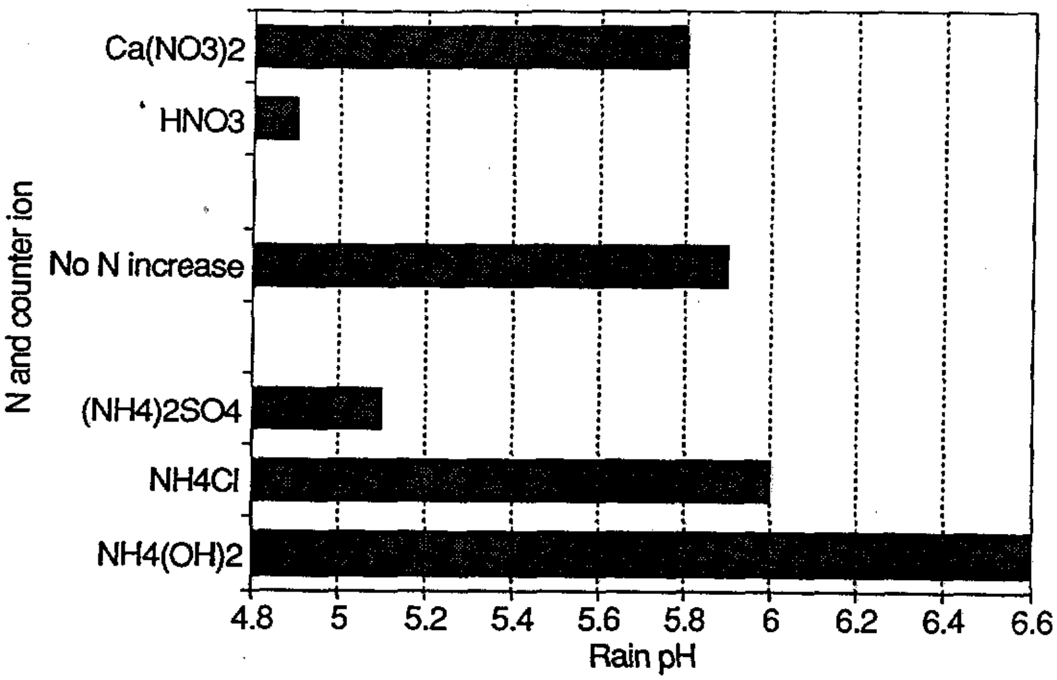

Figure 6.1. The net effect of different counter ions and nitrogen species on precipitation pH.

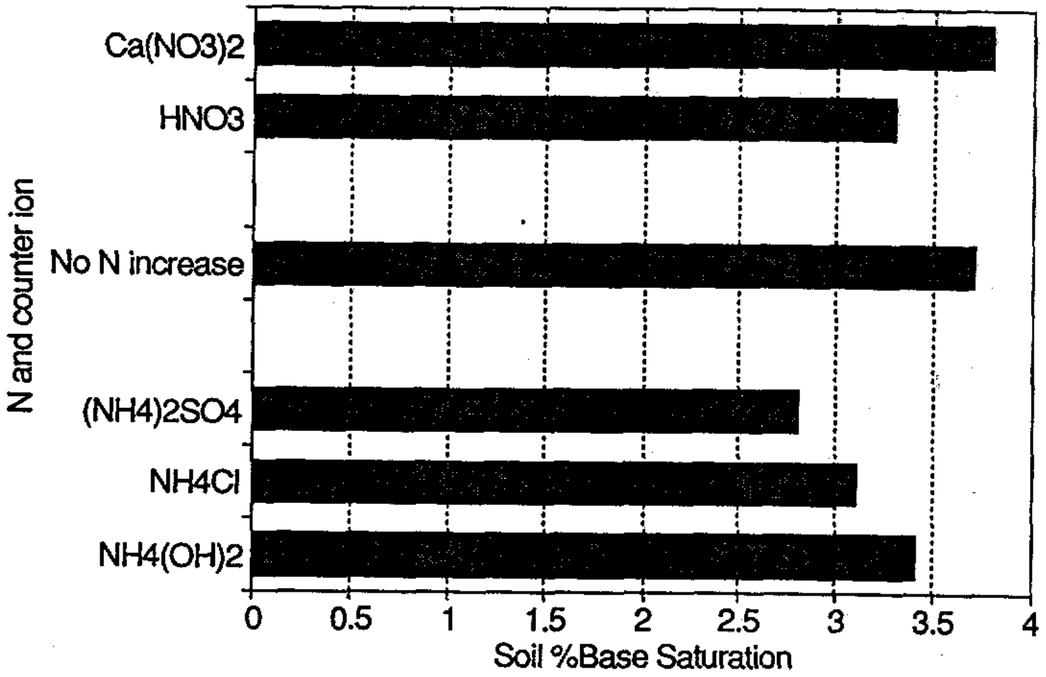

Figure 6.2. The effects of enhanced nitrogen deposition associated with different counter-ions on soil base saturation.

ammonium component by the plant is balanced with an efflux of protons. This forms hydrochloric acid and so leads to a net soil acidification. The uptake of ammonium from ammonium hydroxide is also balanced by the efflux of a proton, however this results in no net change in base saturation.

Nitrate shows a different response. When associated with a proton, the assimilation of nitrate is balanced by an efflux of hydroxyl and no net acidification takes place in a non nitrogen saturated system. However, in this example the calibrated value of K_{max} has been exceeded and nitrate leaching occurs causing a reduction in soil base saturation. If nitrate is associated with a base cation such as calcium, there is a net recovery in base saturation.

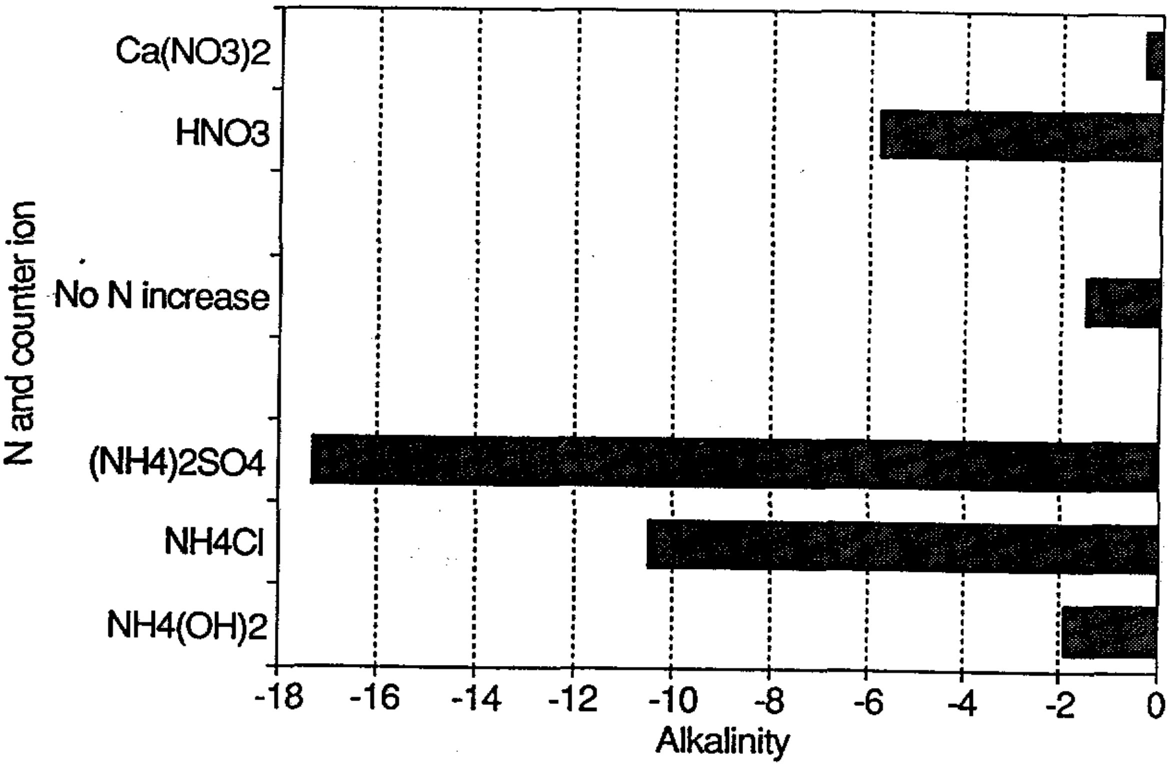

Figure 6.3. The effects of enhanced nitrogen deposition associated with different counter-ions on surface water alkalinity.

The deposition of different nitrogen species also has a dramatic effect on catchment water quality (Figure 6.3). Ammonium sulphate and ammonium chloride cause a decrease in alkalinity due to the presence of strong acid anions. Also, because of the exceedance of K_{max} and the leaching of nitrate from the catchment soils, there is a reduction in alkalinity following enhanced deposition of nitric acid. Only if the deposition increase occurs in the form of ammonium hydroxide or calcium nitrate would there be no change, or a slight improvement, in water quality, respectively.

7. Summary and Conclusions

There exists a clear need for the development and application of dynamic models capable of predicting the response of soils and surface waters to coupled nitrogen and sulphur deposition scenarios. The MAGIC-WAND model provides one such tool and offers wide application within the UNECE Convention on Long Range Transboundary Air Pollution and in particular, within the critical loads programme. The model describes the major dynamics and transformations of nitrogen within catchment soils and surface waters and couples this to the existing sulphur based model. Ammonium exchange within soils is not yet included in the model. The relatively simple structure of the model and ease of calibration provide the scope for regional application at large spatial scales.

Calibration and application of the model emphasises the sensitivity of the soil and water chemistry to those parameters describing the nitrogen dynamics, particularly uptake and mineralisation. There exists a clear need for further observational and experimental work on nitrogen fluxes, and dynamics, from different ecosystems to facilitate the site specific and regional model calibrations.

The model is sensitive to the form of the nitrogen deposition, reduced or oxidised, and in particular the counter ions associated with the nitrogen. Since reduced and oxidised nitrogen have essentially distinct emissions sources, the model provides an important tool in the development of nitrogen deposition reduction protocols.

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