COMPARISON OF DYNAMIC ACIDIFICATION MODELS FOR SURFACE WATERS

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Executive Summary

Dynamic models describing the impact of S and N deposition on soil and surface water chemistry have a key role in the future work of the Convention on Long Range Transboundary Air Pollution (CLRTAP). They can provide an estimation of the chemical status to be expected at a site or region at a given time under a specified emission reduction scenario or agreement. In addition, they can be used to estimate the deposition required to achieve a specified chemistry target by a specified year in the future.

Several models have been developed and these differ with regard to their spatial and temporal scale of application. Those models operating on an annual time-step to simulate mean annual chemistry (MAGIC, SMART, SAFE), as recommended in the UN-ECE Dynamic Modelling Manual (Posch *et al*. 2002), have been extensively tested and compared over the last ten years or so. The results of model testing show a high degree of consistency and provide the background for the conclusion that countries may decide upon use of any of the identified models within the framework of the CLRTAP.

In the UK, a further model (CHUM) has been developed which is based on a daily time-step and this has been used to assess potential changes in water chemistry in the Lake District and South Pennines. The CHUM model requires significantly more data than MAGIC for calibration and application, particularly in describing daily deposition fluxes.

A detailed comparison of CHUM and MAGIC shows very similar outputs and suggests that either may be used in a framework for assessing emission reductions. Further work aimed at interfacing the two models and more detailed analysis of the process descriptions of Al dynamics would be worthwhile.

Introduction

The link between emissions of gaseous acidic oxides of sulphur (S) and nitrogen (N) and ecosystem damage through acidic deposition is now well established and understood. On the basis of this understanding, international agreements to limit emissions of S and N have been introduced aimed at limiting the damage to terrestrial and aquatic ecosystems and promoting recovery towards their pre-acidified state. This process has embraced the 'critical load' approach which aims to quantify the level of deposition an ecosystem can tolerate without causing damage to sensitive biological receptors, according to current knowledge.

Critical loads can be estimated for soils and waters using empirical or mass-balance methodologies. Both of these quantify the deposition required to achieve a target chemistry in soil or water at some time in the future when the ecosystem has re-gained an 'equilibrium'. These approaches cannot tell how long it will take to reach this target chemistry. Nor can they provide an estimate of the consequences of not achieving the critical load. Dynamic models, on the other hand, endeavour to simulate the key processes controlling the chemical status of soils and waters and thereby can predict the time scales of future ecosystem response to changing acidic deposition over time. In this respect, dynamic models offer a unique opportunity to predict the future timing and direction of the ecosystem responses to policy decisions undertaken today.

The role of dynamic models as a means of assessing the current international agreements is, therefore, quite clear. It is possible to apply dynamic models to individual sites or to whole regions and determine the likely chemical status at a given time in response to the agreed deposition reductions. These activities are now underway and aim to contribute substantially to the forthcoming review of the Gothenburg Protocol within the UN-ECE CLRTAP.

Dynamic models, however, potentially have an additional role with respect to the development of new international agreements. The models can be used to determine the deposition reduction required within a given timeframe to achieve a target chemistry at a chosen time in the future. In this way it should be possible to provide deposition targets to the Integrated Assessment Models. This role, however, requires further development and, particularly, understanding of the uncertainties in model prediction.

Model Comparisons

The development and application of simulation models is a key component in the analysis of interdisciplinary environmental problems. Models offer a structured and rigorous testing of the internal consistency of chemical and physical databases; of the consistency of data collected from different parts of the ecosystem and often for different immediate objectives (eg soil, surface water and rainfall chemistry); and, of our scientific understanding of the operation and behaviour of the ecosystem. All this is in addition to their role in prediction of effects outlined earlier. As a result of this scientific significance, model comparison is frequently undertaken to confirm the appropriateness of one process over another or to provide confidence that the included processes, by being included in several different model structures, really do capture and represent the observed behaviour.

In addition, because of their relevance to policy regarding long-range air pollution, comparison of the most often used models within this context is necessary to confirm consistency of outputs. This is especially important since different groups of scientists in

different countries tend to favour individual models. Furthermore, different groups of scientists in some countries have developed models for different funding agencies, often with different objectives, but in a policy framework it is important to establish that their outputs are similar or at least to understand the differences between them.

(i) *Comparison of forest bio-geochemical models*

A formal comparison of the performance of 18 forest ecosystem and bio-geochemical models was undertaken in 1993 (van Grinsven *et al*. 1995). The models were independently calibrated by the model originators to a consistent dataset describing the Solling site in the Netherlands. The key conclusions from this exercise were:

- There was a consensus on the representation of processes to simulate forest hydrology and geochemistry.

- In general, mean values and patterns of hydrology and soil water chemical concentrations were reproduced by the models.

- None of the models was able to reproduce the short-term temporal dynamics of N cycling, however, annual export of N was well reproduced.

- No model could correctly predict Al and pH simultaneously. Solid phase Al associated with soil organic matter appeared to play an important role in this process.

- It was not possible to conclude that more complex models were able to reproduce field observations at Solling better than more simple models.

These conclusions are probably still valid today after a further seven years of research.

(ii) *Comparison of dynamic models for critical load assessment*

Critical loads have been determined for soils and surface waters using steady-state and empirical approaches. These calculations underpinned the Gothenburg Protocol. It has been clear from many years, however, that dynamic models can offer a further approach for calculating critical loads and these are termed 'level II' methods (Posch *et al*. 2001). When the dynamic models are run into the future at the critical load for S and N deposition, the target chemistry in the soil and/or water should be simulated once the model has achieved a new equilibrium. In the models, this may take many hundreds of years.

Three models are recommended for use within the UN-ECE Convention, MAGIC (Cosby *et al*. 2001), SAFE (Warfvinge *et al*. 1993) and SMART (Posch *et al*. 1993). A number of studies have set out to compare the consistency of the outputs from these models within the context of critical loads assessment and prediction of the impact of the effects of the Gothenburg Protocol. Additionally, and more recently, a further model has been introduced which is an extension of the simple Mass Balance equation for calculating critical loads for soils, the Very Simple Dynamic model (VSD; Posch and Reinds 2003). This model has been the focus of an extensive calibration, testing and comparison with the MAGIC model as part of the UK Terrestrial Umbrella Programme (Evans and Reynolds 2003). Note that the VSD does not simulate surface water chemistry.

The use of dynamic models to set 'target loads', deposition levels beyond critical loads and with a further time based target, was first assessed by a modelling study in 1992 (Warfvinge *et al*. 1992). They undertook a comparison of the three aforementioned models and one other (MIDAS; Holmberg *et al*. 1989) using consistent input data at three sites in Scandinavia. They concluded that all models simulated similar pre-acidification soil and water chemistry and similar hindcasts over the period 1840 to 1988. The models were in broad agreement regarding the magnitude and timing of the acidification through that period.

A key conclusion was that the weathering rates were very similar between the three models despite the fact that for SAFE these are calculated as inputs based on soil mineralogy, texture and moisture (in effect the PROFILE model) and in MAGIC and SMART these are calibrated to fit observed soil and surface water chemistry. A further key conclusion was that the four models predicted very similar future soil and water chemistry at all sites in response to different deposition scenarios.

These conclusions were further substantiated following a model comparison study, again using MAGIC, SAFE and SMART as part of an ICP-IM initiative (Forsius *et al*. 1997). Here consistent deposition scenarios under various emission reduction strategies were produced by linking the RAINS (country emissions), DAIQUIRI (deposition scenarios to grid cells) and DEPUPT/CALLUNA (site specific deposition and nutrient uptake scenarios) models. These deposition sequences were then used to drive the dynamic models at seven ICP-IM sites across Europe. The results from the models were comparable across all sites.

The general conclusions from these assessments were:

✓ The MAGIC, SAFE and SMART models give consistent predictions in response to future deposition reduction scenarios.

✓ Calibrated and calculated weathering rates match are very similar.

✓ SAFE provides an opportunity for multi-layer soil chemistry simulations at a plot scale.

✓ MAGIC is the most appropriate model for water chemistry simulations which are, necessarily, at a catchment scale.

A comparison of MAGIC, SAFE and SMART in the UK

Although the focus of this report is on comparison of dynamic models for surface waters, the key controls on surface water chemistry are processes occurring in catchment soils. This is reflected in the structure of all three models identified in the UN-ECE process (MAGIC, SAFE and SMART). In all three models, water in the soil is held at elevated partial pressure of CO_2 and at each time step the chemical balance and mass flux equations are solved for the soil water. The soil water is then de-gassed as it is moved to the surface water which adjust the pH, but concentrations of strong acid anions and base cations remain constant between the two compartments. A comparison of the models applied to simulate soil solution chemistry is, therefore, crucial to the assessment of suitability of the models for both soil and surface water application. Comparison of MAGIC with SAFE and SMART at the Afon Cyff, Plynlimon, has been undertaken and is briefly documented below.

(i)   *SMART-MAGIC comparison*

A comparison of the MAGIC and SMART models was undertaken at the soil water measurement site in the grassland Afon Cyff catchment, Plynlimon. SMART models a single soil layer, therefore both models were applied to a single lumped soil box, to simulate soil water draining the base of the C horizon. MAGIC was applied using a standard approach, with weathering rates, soil exchange coefficients, initial soil N content and 'breakthrough' C/N ratio calibrated to reproduce observed soil water base cation concentrations, soil exchangeable base cation fractions, observed NO_3 concentration and soil C/N ratio (Further details are provided by Evans and Reynolds, 2003). To directly compare model outputs, SMART was then parameterised using input data that were, as far as possible, identical to those used for MAGIC. SMART does not incorporate a calibration routine, therefore values of parameters optimised in MAGIC were used as inputs to SMART.

Although the MAGIC and SMART models are fundamentally very similar, small differences exist between the models. These include their treatment of cation exchange (MAGIC models base cations individually, SMART lumps divalent base cations together, and assumes that monovalent base cations are not exchanged) and organic acid dissociation. SMART also includes more complex N cycling through its integration with the SUMO vegetation succession model. SUMO simulates growth and competition between five vegetation functional types (herbs, dwarf shrubs, shrubs, pioneer trees and climax trees) as a function of site type, grazing, light, moisture and N availability (Wamelink *et al.*, submitted). SUMO therefore takes values of available N from SMART, utilises this for vegetation uptake, and returns any remaining N to SMART for immobilisaiton or leaching. The application of SUMO to the UK is currently under development, therefore the model simulation presented here, particularly for NO_3, should be considered preliminary.

Results (Figure 1) show that ANC, pH and Al simulations all correspond well between the two models. SMART predicts slightly higher initial base saturation, and a greater desorption of Ca and Mg, leading to transiently higher soil water concentrations during the hindcast period. These discrepancies reflect the different treatments of base cation exchange by the two models, but overall these differences appear to have a fairly minor impact, particularly for future predictions. The disparity between NO_3 simulations is greater, and results from the inclusion of the SUMO vegetation model within SMART. Without SUMO, SMART and MAGIC have very similar methods for modelling N processes, and far closer NO_3 predictions would be expected. Overall, the degree of comparability between the two models is encouraging.

(ii)   *SAFE-MAGIC comparison*

SAFE and MAGIC were compared at the same site but, since SAFE can model multiple soil horizons, a three-box application was undertaken to model soil and soil solution chemistry within the O, B and C horizons . This approach is relatively simple in SAFE, with base saturation calibrated sequentially in each horizon during a single model run. As noted earlier, SAFE weathering rates are pre-determined as a function of soil mineralogy and texture using PROFILE. The methods used here are adapted from a previous SAFE application to this site using an older version of the model (Reynolds 1997). MAGIC has not previously been applied to three soil horizons, but recent model developments now make this possible. In this application, weathering rates and cation exchange coefficients were calibrated individually for each soil horizon, with soilwater outputs from upper horizons forming inputs to the lower

horizons. The calibrated horizons were then combined into a single, three-layer model simulation. Details of this model application are described by Evans and Reynolds (in prep.)

Model simulations for the O horizon and C horizon are shown in Figure 2. These show a good degree of similarity, although several differences are apparent. In the O (peat) horizon, a key difference between models is that SAFE nitrifies all incoming NH_4 to NO_3, whereas in MAGIC nitrification can be adjusted to fit observed data. Since the O horizon contains high NH_4 concentrations, this leads to an error in SAFE predictions of pH and ANC. Recent alterations to nitrogen component of SAFE should however overcome this problem (M. Alveteg, pers. comm.) In the mineral C horizon, differences between simulations result from significantly higher weathering estimates obtained from PROFILE than from the MAGIC calibration. This leads to higher simulated base cation concentration, ANC and pH by SAFE. Weathering rates calculated by PROFILE are based on relationships between soil properties and weathering rate for Scandinavian soils. They are strongly dependent on the estimate of mineral surface area, derived from soil texture data. Further work would be beneficial in determining whether the relationships used in PROFILE to estimate weathering rate are widely applicable to UK soils.

(iii)   *Conclusions*

The comparison of MAGIC, SAFE and SMART at the UK site yields modified conclusions to those from the earlier published work at European sites as documented earlier (page 4). These are:

-       MAGIC, SAFE and SMART give <u>reasonably</u> consistent historical simulations and future predictions of soil water chemistry. For a single site, MAGIC-calibrated and SAFE-predicted weathering rates were significantly different. Until additional sites have been modelled, it is uncertain whether this indicates a consistent discrepancy between models;

-       SAFE provides the opportunity for multi-layer soil chemistry simulation at a plot scale.

-       SMART is suitable for single-box modelling at the soil plot scale. Incorporation of the SUMO succession model should in future make this model appropriate for simulation of linked soil and vegetation responses.
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-       MAGIC is the most appropriate model for surface waters. It is also suitable for one- to three-layer application at the soil plot scale.

A comparison of MAGIC and CHUM models

Development of dynamic models to predict the responses of surface waters to changing land-use and acid deposition requires a detailed knowledge and understanding of the soil processes that lead to loss of soil base status and the acidification of surface waters. Such models require simplification of the complex physico-chemical processes that determine ion concentrations throughout the soil column without affecting the model's ability to predict the catchment scale responses. This 'averaging' or 'lumped parameter approach' allows the models to be easily applied on a catchment and regional basis with limited input data required to calibrate and drive the model. Different models make different levels of process

aggregation largely depending on the spatial and temporal scale of their application and depending on their intended use.

Two models aimed at assessing future surface water chemistry change in response to changes in S deposition are MAGIC and CHUM. MAGIC is a lumped model aimed at simulating mean annual chemistry whereas CHUM is less aggregated, especially in its hydrological routing, and simulates daily chemistry. The MAGIC model (Cosby *et al*. 1985a) has been widely applied and tested in Europe and North America and is one of the models recommended in the UN-ECE handbook on Mapping Critical Loads (Posch *et al*. 2001). A full model description is given in Jenkins *et al*. (1997). The CHUM model has been extensively tested at sites in the UK (Tipping *et al*. 1998).

A detailed comparison of the MAGIC (Model of Acidification In Groundwaters; Cosby *et al*. 1985a,1985b, 2001) and the CHUM (Chemistry of the Uplands Model; Tipping 1996) has been undertaken. The models are calibrated using consistent data. Hypothetical future deposition scenarios are used to compare predictions from the models.

(i)   *The Study Site*

The study site for model application and comparison is Mosedale Beck located in the upper catchment of the River Duddon in the English Lake District. The catchment is underlain by rocks of the Borrowdale Volcanic Series. Soils consist of peats and stagnopodsols but there are appreciable areas of bare rock. Vegetation consists mainly of grasses, bracken and *Sphagnum* moss. The catchment is used as rough pasture for the low-density grazing of sheep and there is no evidence of lime or fertiliser application.

(ii)   *The CHUM Model*

The original CHUM model (Tipping 1996) was based on a soil column consisting of three horizons: the top two of which were assumed to be dominated, in terms of solid-solution interactions, by natural organic matter. Horizon 3 was the zone in which weathering occurred to provide inputs of Na, Mg and Ca to the percolating water. Precipitation of $Al(OH)_3$ also took place in this horizon. The soil column was assumed to contain two types of water: immobile water in contact with the soil solids could exchange solutes with more mobile water in larger pores and moving under the influence of gravity. The immobile water was assumed to be in chemical equilibrium and the distribution of chemical species was calculated using WHAM (Tipping 1994). Water could move from one column to another downhill with the possibility of return flow. Using several soil columns, therefore, the model could represent hillslope variations in soil properties, slope, rainfall, vegetation, etc. Implementation of the model in this way, however, requires considerable input data. As a consequence, the model used in this analysis is a simplified version, CHUM-LDl (Tipping *et al*. 1998).

For CHUM-LD1, a simple soil column is used comprising a thin organic top horizon above two thicker mineral horizons. Soil properties are derived from observations made at a range of sites in the area of the Lake District underlain by rocks of the Borrowdale Volcanic Series. The catchment is assumed to be hydrologically sealed. Flow routing through the soil column, incorporating evaporation loss as a function of air temperature and water availability is calculated on a daily basis. In Horizons 1 and 2, cation exchange and SO_4 retention occurs. In Horizon 3, weathering of base cation occurs and Al is precipitated from solution. This reaction assumes that the Al removal is due to adsorption to an oxide phase.

For nitrogen, it is assumed that all deposited N is available for plant uptake and above a specified threshold temperature all available N is removed. Any NH_4 not taken up by plants is converted to NO_3.

(iii)   Calibration of CHUM to Mosedale Beck

Soil chemical and physical data were derived from a variety of sources including observation, assumption and calibration (Table 1). The aim of the modelling was to simulate surface water chemistry from the 1970s to present and then into the future. The model runs on a daily time step and requires considerable input data. These were not fully available and the approximations and estimates used are documented below.

Daily rainfall volumes were estimated from a site at Ambleside. For future predictions, 1999 to 2020, the pattern of the four years 1995-1998 was repeated. Daily air temperature was also taken from the Ambleside site and the same assumptions used for the future predictions.

CHUM requires daily wet deposition chemistry which was derived from a mixture of data sources and under a number of assumptions which vary according to time period:

> 1950-1974: Rainfall composition in non-leap years assumed to be the same as observed in 1975 and those in leap years to be the same as 1976.

> 1975-1976: Observed bulk depositions at Wraymires were apportioned into 12 two-monthly periods on the basis of seasonal variations in wet deposition observed for the period 1983-1995. This accounts for the tendency for sea-salts to be greatest in winter and for wet deposition of N compounds to be greatest in spring.

> 1977-1980: Assumed to have the same annual volume-weighted compositions as 1975-1976.

> 1981-1982: Assumed a linear change in annual volume-weighted concentrations of all solutes over these two years.

> 1983-1998: Composition determined for collectors at Esthwaite Water, Ennerdale and Cockley Beck were averaged.

> 1999-2020 (1): Assuming no change from the period 1995-1998 and the annual variation over the four years was repeated sequentially.

> 1999-2020 (2): As above, except NO_3 and SO_4 concentrations were decreased by 50% over the period 2000-2010 and constant thereafter.

Dry deposition was estimated from UKRGAR (1997) data. Future scenarios utilised a constant dry deposition of SO_4 and NO_3 and a 50% reduction between 2000 and 2010, as above.

The net effect of these assumptions on the pattern of deposition are reflected in the MAGIC simulated SO_4 concentration (Figure 3) since MAGIC assumes no SO_4 adsorption the input and output flux at each time step are in balance.

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The details of the model fit to observed data are given in Tipping *et al.* (1998). In general, the model captures the observed inter-annual variation in solute concentrations during the periods 1971-1972, 1986 and 1997-1998. The major conclusion from this study was that the CHUM-LD1 model provides a quantitative explanation of stream chemistry on a daily timescale.

(iv)   *The MAGIC Model*

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

The soil-soil solution equilibria equations describe cation exchange using a Gaines-Thomas expression for monovalent and divalent cations. Dissolution and precipitation of inorganic Al is represented as an equilibrium with a solid phase of aluminium hydroxide. Dissolution of carbon dioxide (CO_2) followed by dissociation to bicarbonate (HCO_3) and carbonate (CO_3) is also included. Dynamic mass balance equations are derived for the base cations and strong acid anions because these ions have discrete and measurable sources in the catchment. These are used to calculate the Acid Neutralising Capacity (ANC) as the sum of base cations minus the sum of the strong acid anions ($Ca+Mg+Na+K-SO_4-NO_3-Cl$). ANC in the model is conserved as the soil water moves into the stream and is used as an objective, uncalibrated parameter for comparison with observed data. Ions such as H, Al and HCO_3 have diffuse sources and sinks and so concentrations of these are determined at any time by the model inputs, the total amounts of the strong acid anions and base cations and the equilibrium equations.

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

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

The strong acid anions Cl, NO_3 and fluoride (F) have no adsorbed phase in the model. The relationship of dissolved and adsorbed SO_4 is assumed to follow a Langmuir isotherm and is concentration dependent. SO_4 is not strongly adsorbed on to the exchange complex in most upland UK soils, which are relatively young and not deeply weathered. MAGIC comprises an extremely simplified representation of N involving a net catchment retention at each time step (zero order uptake) to calibrate the simulated against observed NO_3 concentrations in streamwater.

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

The calibration for each site is carried out sequentially. First, the concentrations of the stream Cl and SO_4 are calibrated by adjusting filter and dry deposition of sea-salts and gaseous/particulate sulphur compounds, under the assumption that these ions are in approximate steady state without respect to atmospheric inputs. Next the NO_3 and NH_4 concentrations are calibrated by adjusting first-order uptake functions to match observed surface water concentrations. Finally, the base cation concentrations are calibrated using an optimisation procedure.

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

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

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

(v)   *Calibration of MAGIC to Mosedale Beck*

Soil physical data were taken from those derived for an earlier application of the model to Scoat Tarn (Jenkins *et al*. 1997), also located on the Borrowdale Volcanic Series. The data were obtained from soil series maps and from representative profile descriptions in soil memoires. An appropriate depth and space weighing (Helliwell *et al*. 1998) scheme was adopted to lump the distributed variation in soils into one representative soil 'box' for the catchment (Table 2).

Surface water chemistry targets for the model calibration procedure were calculated as the mean annual observed data for 1998. Calibrated weathering rates and ion-exchange coefficients are given in Table 2.

Rainfall totals for each year were calculated from the sum of the daily rainfalls derived for the CHUM-LD1 application. Annual inputs of wet and dry deposition were calculated from the daily fluxes derived for CHUM-LD1. An additional input of Cl and SO_4 was required each year to match the observed runoff chemistry. This results from a mismatch between annual input and output flux of these 'conservative' ions and the extra deposition required to match the output flux is assumed to represent an underestimation of dry deposited sea-salt and SO_2. Additional base cations were added in proportion to sea-salt ratios.

The model calibration successfully matches the observed runoff chemistry and soil base saturation in 1998 (Figure 3 to 6). The simulation suggests that Mosedale Beck was historically well buffered with a pre-acidification pH of above 6.0. Calcium concentrations in runoff are predicted to have increased slightly through time in response to the increased deposition (and runoff concentration) of SO_4 but the increase in strong acid anions is considerably larger than base cations. As a result, stream pH has declined to a minium of about 5.0 in 1978 which coincides which the peak in S deposition. Since then the decline in deposition, reflected in the SO_4 concentration, has led to a slight improvement in the pH to c.5.4 in 1998.

(vi)   *Comparison of Model Simulations*

The key problem in comparing the outputs of MAGIC and CHUM lies in the different model timesteps. By converting the daily simulated pH from CHUM to H^+ ion a mean annual pH has been calculated from 1970 to 2020. This is used for a direct comparison with the mean annual pH simulation from MAGIC and with observed pH for various years calculated in the same way. Both models show a very close match with observed historical pH in the early 1970s and mid 1980s (Figure 7). The CHUM simulated pH is more variable but this reflects the nature of the lumping of catchment soils in MAGIC compared to CHUM and the greater influence of wet *v*. dry years given the more distributed hydrology in CHUM.

Yet more encouraging is that both models provide very similar predictions under the two future deposition scenarios (Figure 7), in terms of the rate of recovery of pH and the predicted end pH under the 50% reduction scenario. Both models predict a stabilisation of current pH under the constant deposition scenario. The models clearly agree that a rapid and significant increase in pH is likely at this currently acidic site if large reductions in S inputs are achieved. The consequences of this recovery in terms of ANC as simulated by MAGIC are that the 50% reduction leads to an increase of c.30 µeq l^{-1} from the present day ANC of c.-5 µeq l^{-1} (Figure 8).

A less satisfactory comparison is achieved with the simulated Al concentrations (Figure 9). During the period 1970 to 2000 MAGIC consistently over-predicts Al relative to CHUM. Beyond 2000, the reverse is true although both models simulate very low concentrations in response to the 50% reduction scenario (< 10 µmol l^{-1}). This is clearly a function of the Al dynamics which differ between the two models and requires further assessment.

Conclusions and Recommendations

1.   The MAGIC, SAFE and SMART models produce reasonably consistent simulations of soil waters at a plot scale.

2.   The CHUM model has significantly higher data requirement for calibration than MAGIC, due mainly to the daily time step which requires detailed hydrological routing. The advantage of CHUM in this respect is the possibility that the daily time-step provides for analysis of high-flow chemistry and how this changes under future deposition scenarios.

3.   The MAGIC and CHUM models produce similar simulations of streamwater pH when driven with consistent deposition inputs implying that either model can be used in a policy framework or to assist in deriving information relating to the time to surface water recovery from acidification.

4.   Both models suggest that streamwater pH recovery will be rapid and significant over the next 20 years if significant reduction in S deposition can be achieved (50% reduction or more) by 2010.

5.   Both models predict that pH will stabilise at the current level over the next 20 years if there are no further reductions in S deposition.

6.   Further work is required to rationalise the differences in Al simulations between the two models and to determine the best modelling approach in this respect.

7.   Further work to explore the possibility of interfacing MAGIC and CHUM with a view to assessing the future changes in episode chemistry would be useful.

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Description	How determined
Depth of Horizon 1	Estimated at 0.15 m from field data
Depth of Horizon 2	Estimated at 0.5 m from field data
Depth of Horizon 3	Fixed at 1 m
Macropore porosity	Fixed at 10% of total soil volume in Horizons 1, 2 and 3
Micropore porosity – Horizon 1	Estimated to be 63% of total soil volume
Micropore porosity – Horizon 2	Estimated to be 26% of total soil volume
K_{pond} rate constant for drainage of ponded water from Horizon 1	Fixed at 0.5 day^{-1}
V_{max} maximum volume of water in large pores, ie total large pore space	Computed from soil depth and porosity
$K_{hyd,min}$ minimum rate constant for drainage of water from soil	Adjusted *to match observed discharges*
$K_{hyr,max}$ maximum rate constant for drainage of water from soil	*Adjusted* to match observed discharges
N_{hyd} exponent describing the transition of the effective drainage rate constant from $K_{hyd,min}$ to $K_{hyr,max}$	*Adjusted* to match observed discharges
F_{H2} fraction of drainage water not entering Horizon 3	*Adjusted* to account for observed stream water chemistry
K_e rate constant for evaporation	Adjusted to *achieve 500 mm evaporation*
T_E threshold temperature for evaporation	*Adjusted* to match observations for Welsh moorlands (Calder 1990)
$V_{mic,min}$ minimum volume of water in Horizon 1 micropores – limits evaporative loss	Fixed at 50% of maximum (total) volume
T_N threshold temperature above which all available n is removed by plants	*Adjusted* to fit observed stream water NO_3
F_N fraction of wet deposited N available for plant uptake	*Adjusted* to maintain stream NO_3 above zero in summer
Partial pressure of CO_2 in Horizon 1 micropores	Fixed at 0.0l atm
Partial pressure of CO_2 in Horizon 2 micropores	Fixed at 0.01 atm
Partial pressure of CO_2 in Horizon 3 micropores	*Adjusted* to fit chemical data
Partial pressure of CO_2 in streamwater	Fixed at 0.0007 atm
Production rate of fulvic acid in Horizon 1	*Adjusted* to fit chemical data
Content of AOX (SO_4 adsorbent) in Horizon 2 (mol sites g^{-1})	Estimated from SO_4 adsorption results
Equilibrium constant for HSO_4^- adsorption by AOX	Estimated from experimental data
Content of MOX in Horizon 3 (mol sites g^{-1})	*Adjusted* to fit chemical data
K_{MOXAl} decay constant for Al adsorbed to MOX	Fixed at 0.05 per day
K_{MOXAl} constant relating MOXAl decay to pH	Fixed at 3×10^{-6} mol dm^{-3}
Equilibrium constant for H^+/MOX adsorption	Fixed at 10^2
Equilibrium constant for MG/MOX adsorption	Fixed at 0.0l
Equilibrium constant for Al/MOX adsorption	Fixed at 10
Equilibrium constant for AlOH/MOX adsorption	Fixed at 10^{10}
Equilibrium constant for Ca/MOX adsorption	Fixed at 0.01
K_M weathering rate constants for metals – Na, Mg, Al, K, Ca	*Adjusted* to match chemical data
m weathering exponent	Determined from experimental data

Table 1 Summary of parameters in CHUM-LD1. Those that are *adjusted* to fit observations are included.

Fixed parameters	
Discharge, annual	1.62
Precipitation, annual	2.14
Soil depth	0.88
Bulk density	1133
CEC	70
SO_4 adsorption half saturation	100
SO_4 maximum adsorption capacity	0.1
pCO_2, soil	0.66
pCO_2, stream	0.066
Temperature, soil	7
Temperature, stream	7
pK_1 of organic acids, soil	2.5
pK_1 of organic acids, stream	2.5
pK_2 of organic acids, soil	4.0
pK_2 of organic acids, stream	4.0
pK_3 of organic acids, soil	5.8
pK_3 of organic acids, stream	5.8
Organic acids, soil	63
Organic acids, stream	10
Ca saturation	2.9
Mg saturation	0.5
Na saturation	1.2
K saturation	0.6
Total base saturation	5.2
Vegetation uptake Ca	15.2
Vegetation uptake Mg	4.7
Vegetation uptake Na	1.2
Vegetation uptake K	5.8
Optimised parameters	
$Al(OH)_3$ solubility constant, soil	9.01
$Al(OH)_3$ solubility constant, stream	10.0
Weathering Ca	50
Weathering Mg	26
Weathering Na	6
Weathering K	30
Weathering of (Ca+Mg+K+Na)	112
Weathering F	0
Selectivity coefficient Al-Ca	-0.09
Selectivity coefficient Al-Mg	2.51
Selectivity coefficient Al-Na	-0.77
Selectivity coefficient Al-K	-4.27
Ca saturation (pre-industrial)	7.4
Mg saturation (pre-industrial)	1.7
Na saturation (pre-industrial)	1.8
K saturation (pre-industrial)	1.5
Total base saturation (pre-industrial)	12.4

Table 2   Selected parameter values for the MAGIC model calibration at the catchments
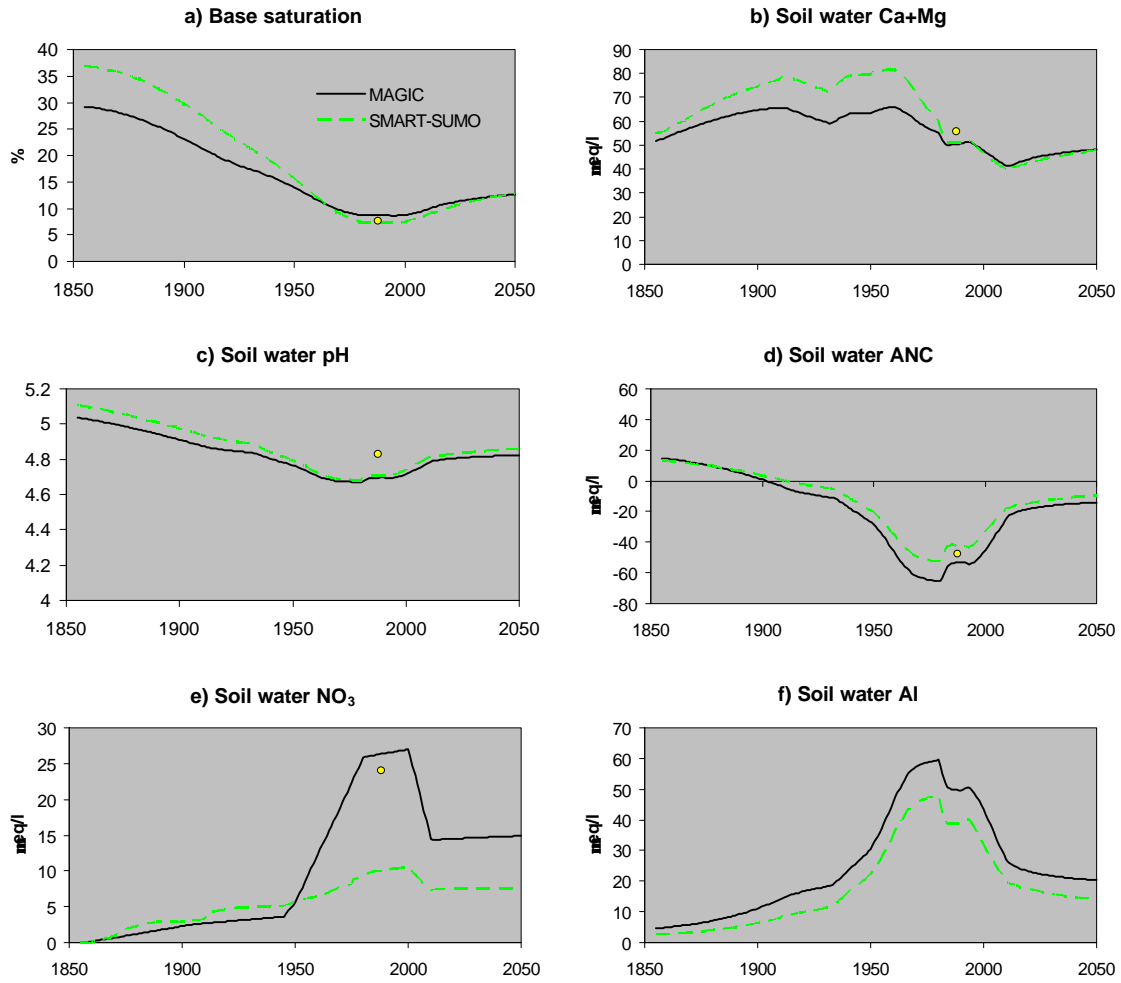
Figure 1   MAGIC and SMART-SUMO simulations for a single soil box, Plynlimon grassland site. Black line shows MAGIC simulations, dashed green line shows SMART simulation. Dots indicate mean observed chemistry, 1985-1991.
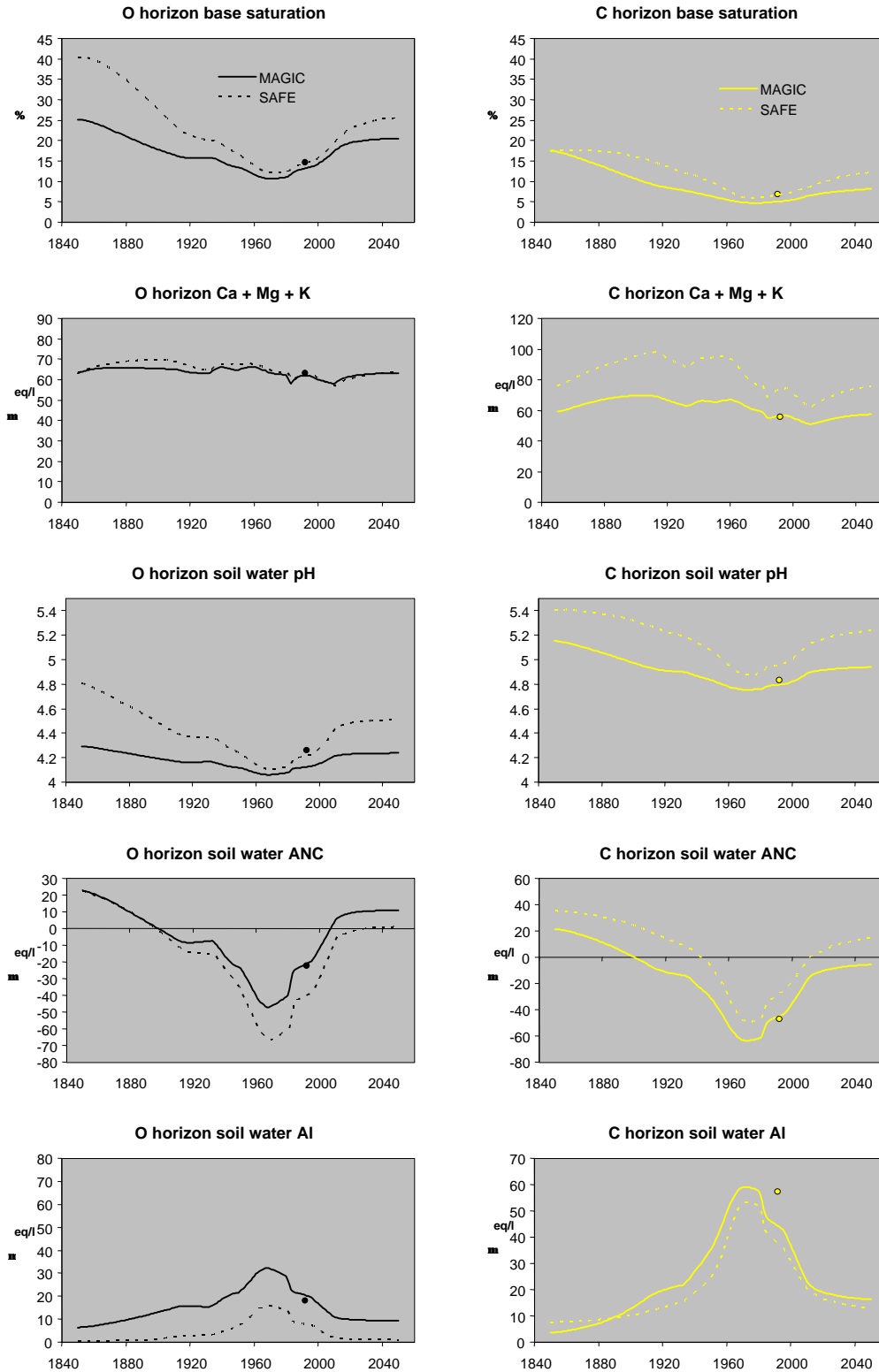
Figure 2   MAGIC and SAFE simulations for O and C horizons, Plynlimon grassland site. Solid lines shows MAGIC simulations, dashed line shows SAFE simulation. Dots indicate mean observed chemistry, 1985-1991
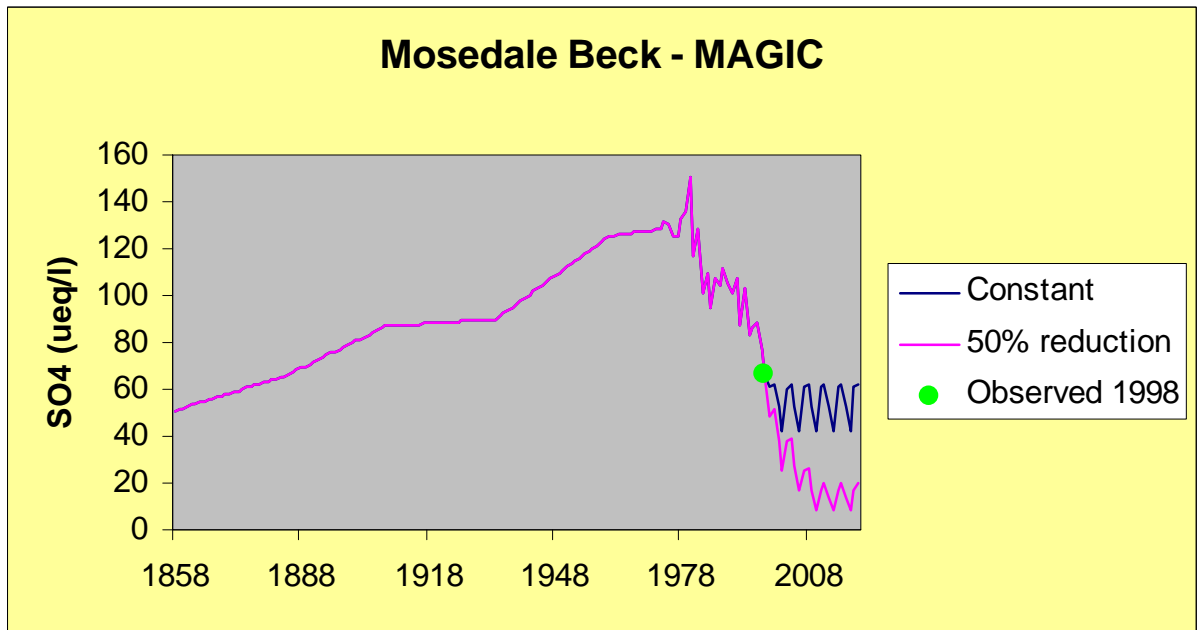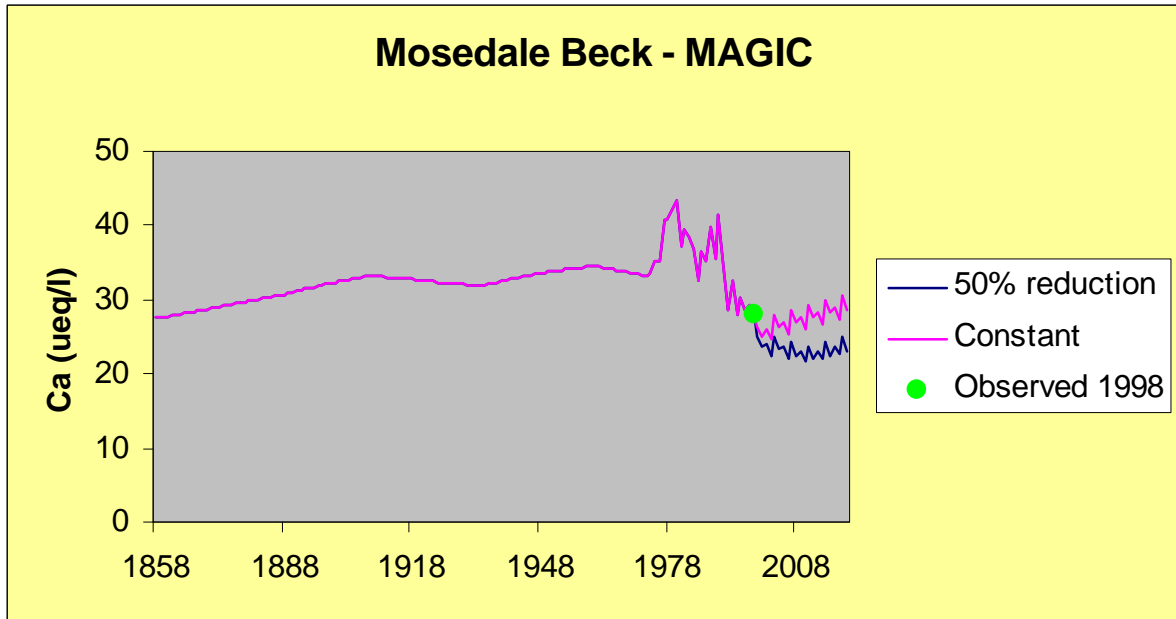
Figure 3 The MAGIC simulated surface water SO$_4$ concentration. The historical pattern from 1858 to 1998 is driven by the assumptions and data sources detailed in the text. The two forecasts 1998 to 2020 show the assumption of four year cycles of deposition (1995-1998) and the constant and 50% reduction scenarios.
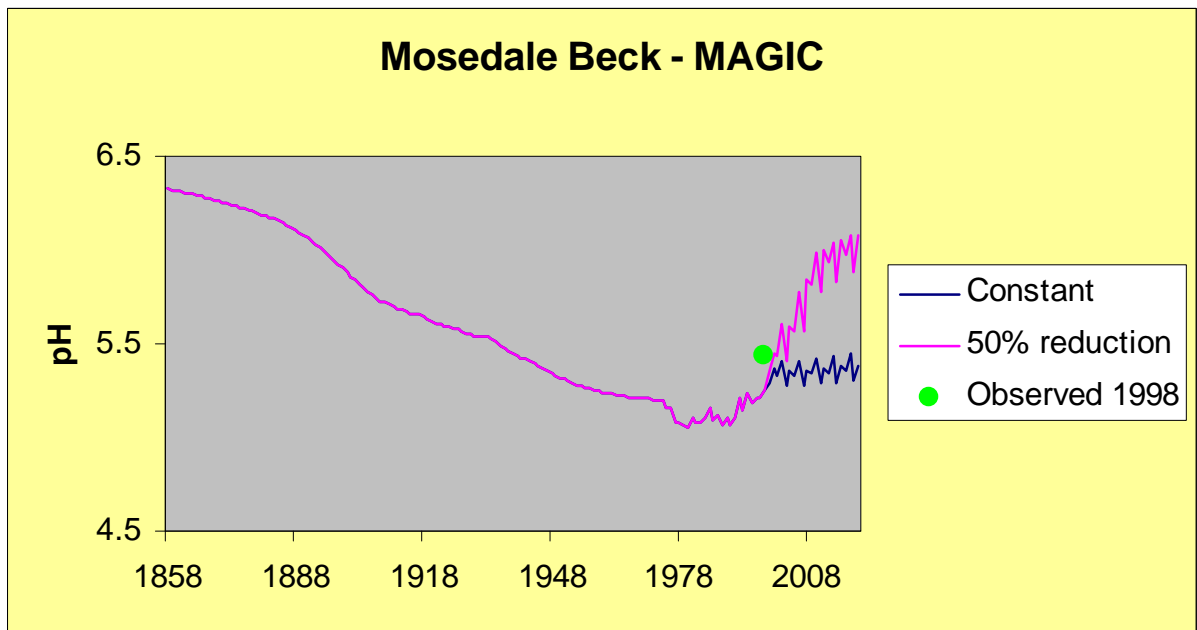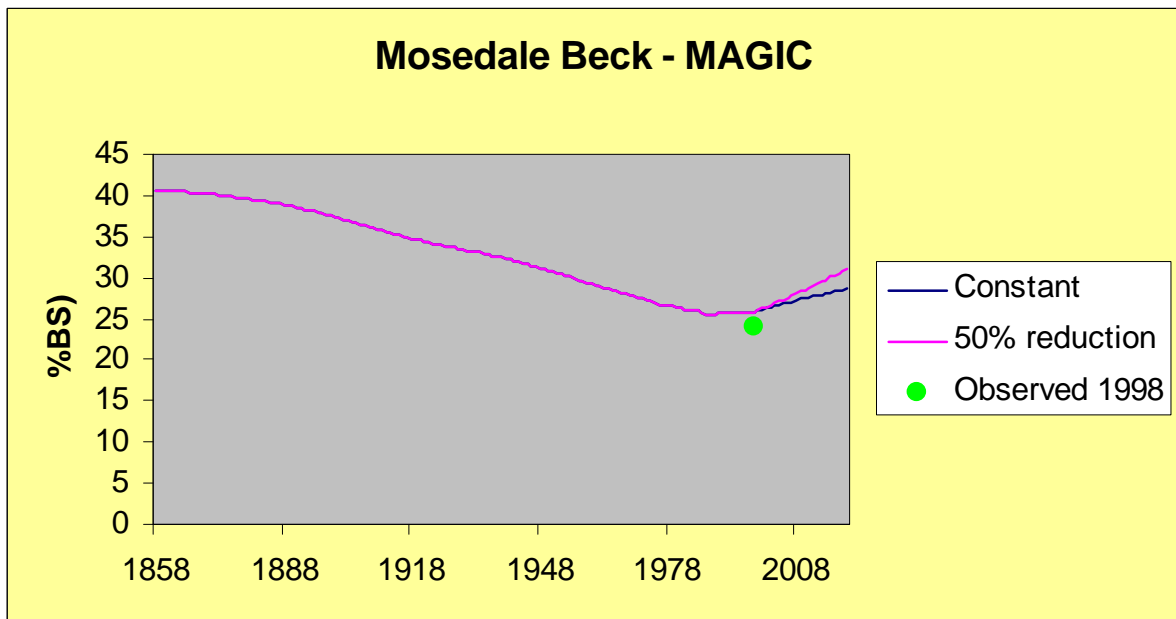

Figure 4 The MAGIC simulated surface water pH concentration. The historical pattern from 1858 to 1998 is driven by the assumptions and data sources detailed in the text. The two forecasts 1998 to 2020 show the assumption of four year cycles of deposition (1995-1998) and the constant and 50% reduction scenarios.

Figure 5 The MAGIC simulated surface water Ca concentration. The historical pattern from 1858 to 1998 is driven by the assumptions and data sources detailed in the text. The two forecasts 1998 to 2020 show the assumption of four year cycles of deposition (1995-1998) and the constant and 50% reduction scenarios.
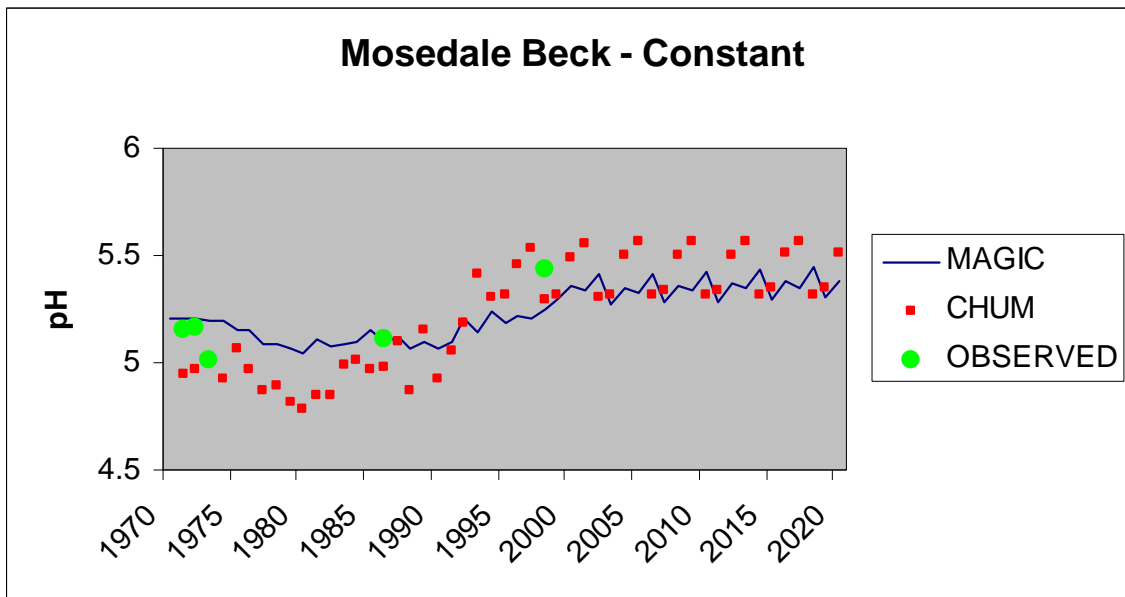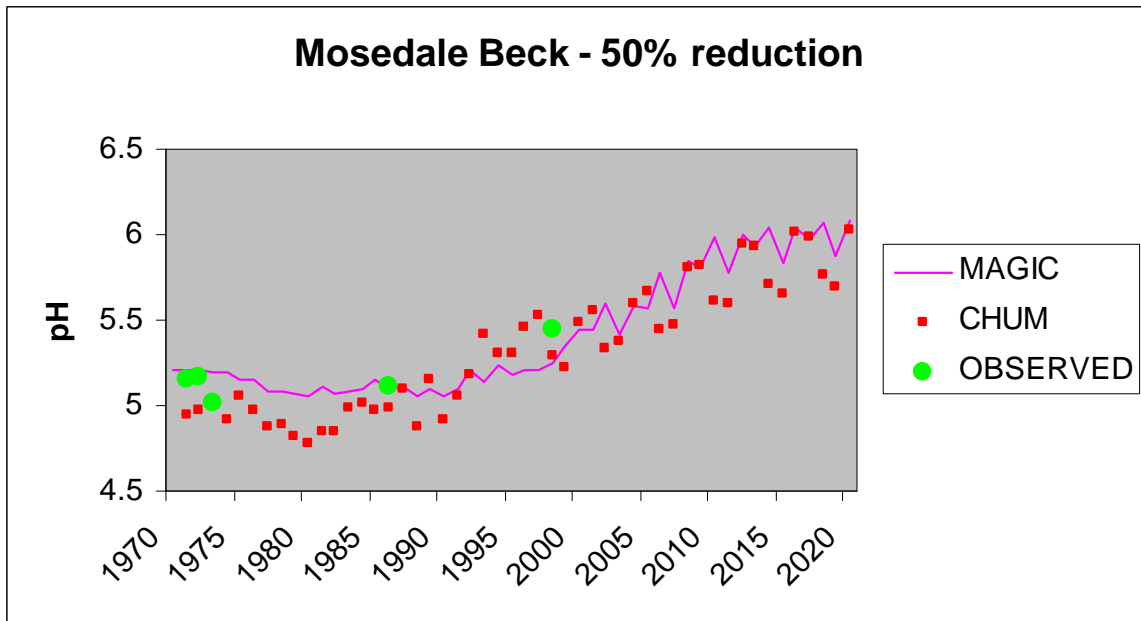

Figure 6 The MAGIC simulated soil % base saturation. The historical pattern from 1858 to 1998 is driven by the assumptions and data sources detailed in the text. The two forecasts 1998 to 2020 show the assumption of four year cycles of deposition (1995-1998) and the constant and 50% reduction scenarios.

Figure 7 Comparison of CHUM-LD1 and MAGIC simulated and observed surface water pH under the two deposition scenarios; 50% reduction (top) and constant at current level (bottom).
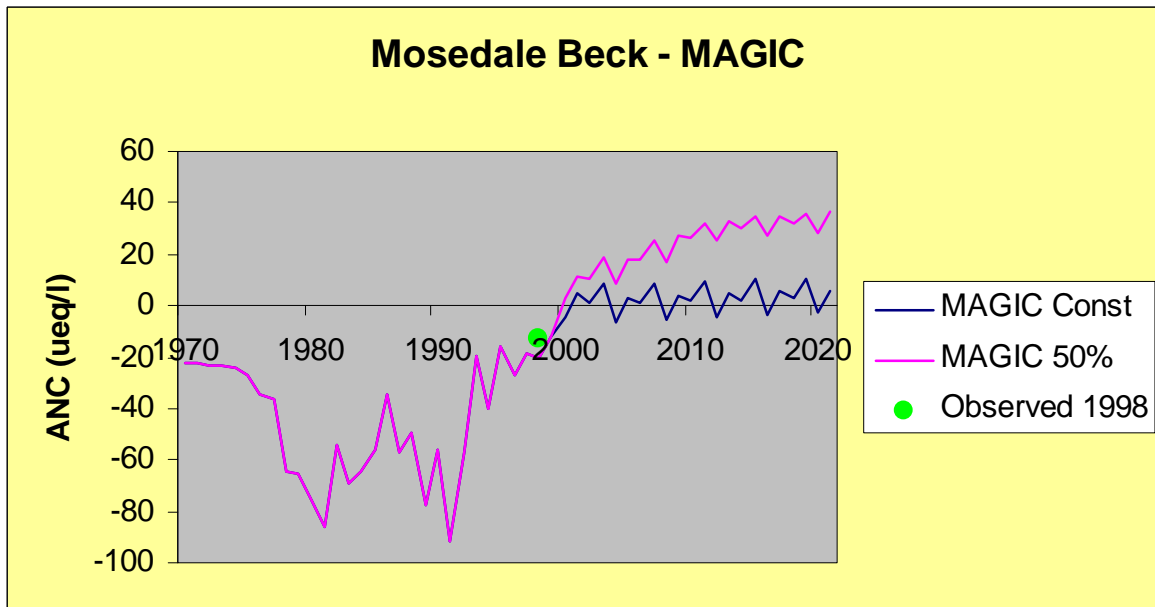
Figure 8 The MAGIC simulated surface water ANC concentration. The historical pattern from 1858 to 1998 is driven by the assumptions and data sources detailed in the text. The two forecasts 1998 to 2020 show the assumption of four year cycles of deposition (1995-1998) and the constant and 50% reduction scenarios.
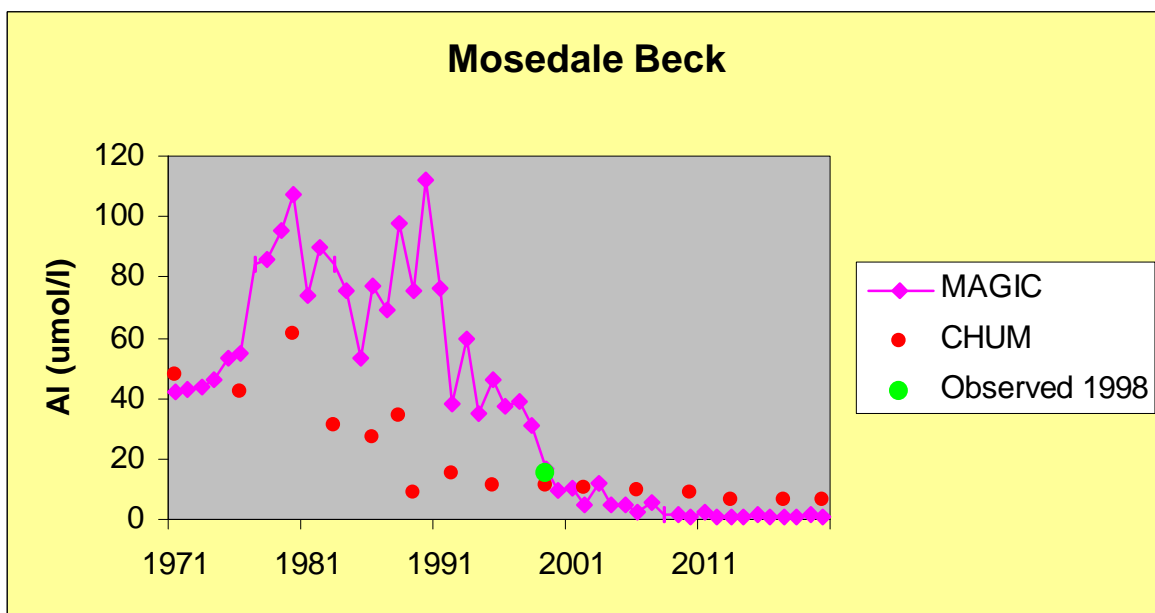

Figure 9 Comparison of CHUM-LD1 and MAGIC simulated surface water Al concentration from 1970 to 2020. The simulation from 1998 assumes a 50% reduction in S deposition by 2010.