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Modelling the effects of climate change on an acidic upland stream

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Abstract. Most modelling studies of soil and surface water recovery from acidification assume a constant influence of climate over the simulation period. Given the likelihood of future climate change, and recent identification of links between climatic fluctuations and surface water trends on decadal time scales, an attempt is made to simulate a number of climate-related effects on the recovery of an acidified stream in mid-Wales. Empirical relationships were derived to model past and future variations in (i) runoff, as a function of rainfall and temperature; (ii) stream chloride concentration and sea-salt deposition, as a function of the North Atlantic Oscillation Index (NAOI); and (iii) stream dissolved organic carbon (DOC) concentration, as a function of summer temperatures and sulphur deposition. Incorporating these relationships in the MAGIC dynamic model reproduced a significant part of the observed variation in streamwater chemistry. Current scenarios of rising UK temperature and NAOI, and falling rainfall and acid deposition, were used to forecast effects of climate change on soil and water recovery from acidification. Results suggest that increasing DOC would have a significant negative impact on soil recovery, with elevated organic acidity lowering soil water pH and severely depleting soil base saturation. The resulting increase in soil base cation export would, however, have a positive impact on streamwater recovery. For increased sea-salt deposition, effects are essentially the opposite; increased base cation inputs enhance the recovery of soil base saturation, but displace acidity to the stream. However, simulated effects of raising DOC considerably outweighed those of increased sea-salt deposition. It is argued that greater consideration of these, and other, climatic effects on biogeochemical cycles needs to be taken when predicting the recovery of soils and surface waters from acidification.

Introduction

Anthropogenic sulphur (S) and nitrogen (N) emissions, primarily from fossil fuel burning and agriculture, have resulted in widespread, well-documented acidification of soils and waters across large areas of Europe and eastern North America (Rodhe et al. 1995). In recent decades, controls on emissions, particularly of S, have led to observed recovery of freshwaters in many areas (Stoddard et al. 1999; Evans et al. 2001a). In Europe, further agreements under the UN Economic Commission for Europe Multi-Pollutant, Multi-Effect, or 'Gothenburg', Protocol should reduce S emissions by 63%, oxidised nitrogen (NO_x) by 41%, and ammonia (NH_3) by 17% in 2010 relative to 1990 levels (UNECE 1999, 2000). This is expected to have widespread benefits for acidified terrestrial and freshwater ecosystems; for the UK, overall exceedance of critical

loads for five sensitive terrestrial ecosystem types is predicted to decrease from 71% of their total area in 1995–1997, to 46% in 2010 (NEGTAP 2001). For a set of 1610 sampled UK lakes and streams, critical load exceedance is predicted to fall from 18% of total catchment area to 9% over the same period.

In support of future re-negotiation of emissions agreements, and to provide time scales of recovery, work is currently under way to apply dynamic models of acidification at national and European scales (UNECE 2002). A number of models are now well developed for simulating change in soil and freshwater systems, including MAGIC (Cosby et al. 2001), SAFE (Warfvinge et al. 1993) and SMART (De Vries et al. 1989). These models appear effective in predicting recovery of soil and surface waters, and have been extensively applied to many acidified regions of Europe (e.g. De Vries et al. 1994; Alveteg et al. 1995; Cosby and Wright 1998; Kurz et al. 1998; Evans et al. 2001b). However, most dynamic model applications operate on the basis that, apart from changes in acid deposition levels, other factors remain constant over both the short and long terms. Recently, however, concerns have been raised regarding the role of 'confounding factors' for recovery (Wright and Jenkins 2001). Confounding factors may be defined as environmental factors that alter the relationship between acid deposition and runoff acidity over time. These factors may operate on relatively short time scales, in which case their main influence will be to mask underlying trends linked to acid deposition, or as long-term changes that either increase or decrease the extent of overall recovery. Of particular interest here are those related to variations in climate, and to long-term climate change.

Numerous climate-related effects on surface water chemistry have been identified. Sommaruga-Wögrath et al. (1997) suggested that the pH of Alpine lakes was influenced by temperature-related weathering rate variations. Nitrate (NO_3) leaching, which is strongly mediated by the biota, has been linked to climatic factors through several mechanisms, including increased concentrations due to increased mineralisation under warmer conditions (Wright 1998), and elevated spring peaks following periods of soil freezing (Mitchell et al. 1996; Monteith et al. 2000). Generation of dissolved organic carbon (DOC) from peaty soils has been found to increase under warmer conditions (Liechty et al. 1995; Tipping et al. 1999; Freeman et al. 2001), and following droughts (Kalbitz et al. 2000). Drought/re-wetting cycles have also been shown to influence recovery trends, as re-oxidation of reduced S stored in waterlogged soils causes sulphate (SO_4) flushes in runoff (Dillon et al. 1997; Harriman et al. 2001).

A recognised indirect impact of climate on water quality occurs through the 'sea-salt effect'. Marine base cations, entrained from sea surfaces during periods of high wind, and deposited on catchments in wet or dry deposition, temporarily alter equilibria between cations in soil solution, and cations adsorbed on soil exchange sites. On an episodic time scale, the displacement of aluminium (Al) and hydrogen (H) ions from exchange sites by marine base cations has been shown to cause transient acidification of surface waters

(Wiklander 1975; Skartveit 1981), with the potential to cause biological damage at sites also subject to anthropogenic acidification (Hindar et al. 1994). In the UK and Scandinavia, sea-salt episodes are associated with periods of strong westerly airflows during winter, which can in turn be related to the North Atlantic Oscillation Index (NAOI), a measure of the difference in sea-surface pressure between the Azores and Iceland (Hurrell 1995). As a result, long-term correlations have been observed in UK acid waters between the winter NAOI and concentrations of both marine ions such as chloride (Cl), and displaced non-marine cations such as Ca, Al and H (Evans et al. 2001c). These relationships suggest that, in addition to episodic effects, varying sea-salt inputs can generate cyclicity in runoff chemistry on a decadal time scale, potentially influencing acidity trends over prolonged periods.

To date, few attempts have been made to incorporate climatic variation in dynamic models of acidification. Wright et al. (1988) demonstrated that MAGIC could successfully model the cation exchange processes associated with the sea-salt effect on an episodic time scale, and Beier et al. (2003) examined the effect of a step increase in future sea-salt deposition. For the current study, an attempt is made to incorporate realistic variations in three climate-related factors with particular relevance to the UK, which may be expected to change under current scenarios of climate warming. The first is variability, and long-term change, in rainfall and runoff. The second is the sea-salt effect, which may have a greater impact in future due to a predicted increase in frequency and severity of winter storms (Hulme et al. 2002). Finally, rising DOC concentrations have been modelled because large, spatially consistent increases have been observed in the UK since the late 1980s (Evans and Monteith 2001), and linked to elevated summer temperatures (Freeman et al. 2001). Climate-related changes in DOC concentration are not thought to have previously been incorporated in acidification models.

This study aims firstly to assess the extent to which observed variations in runoff chemistry can be reproduced using simple climate indices, namely the NAOI, Central England Temperature Record (CET) (Parker et al. 1992) and the England and Wales Rainfall Record (Jones and Conway 1997). These indices have the advantages that, unlike most site-specific meteorological records, they form long-running (>100 year), consistent records on which to base historic model simulations, and that forecasts are available. The NAOI and CET have both previously been linked to changes in surface water chemistry in the UK (Monteith et al. 2000; Evans et al. 2001c; Freeman et al. 2001), and similar approaches have been taken elsewhere, for example linking SO_4 flushes in Canada to the Southern Oscillation Index (Dillon et al. 1997). For the second part of the study, empirical relationships between water chemistry variables and climate indices are used to drive the MAGIC model simulation to present-day, in an attempt to reproduce observed interannual variations in stream acidity. Finally, the potential impact of climate change on future stream and soil chemistry is assessed by comparing model simulations for a mid-range UK climate forecast with a 'no change' scenario.

Site description

The Afon Gwy (UK Grid Reference SN 842854), part of the Plynlimon group of catchments in mid-Wales, has been studied intensively since the 1970s (Neal 1997). The semi-natural moorland catchment has an area of 3.9 km^2 and an altitude range of 440–730 m. Bedrock geology comprises base-poor Lower Palaeozoic shales, mudstones and grits, overlain in some valley areas by boulder clay. Soils are mainly peaty podzols, with deeper peat on hilltops and in near-stream wetlands. Vegetation is predominantly acid grassland, with heather on hilltop peats, and minor areas of conifer plantation and improved grassland in the lower part of the catchment.

Rainfall and runoff have been gauged at the Gwy since 1975. Water sampling for chemical analysis began in 1979, and apart from a break during 1982 has continued to the present day. Sampling took place weekly prior to 1990, and monthly thereafter. From 1991, the site has formed part of the UK Acid Waters Monitoring Network (UKAWMN). The stream is acidified, with a mean pH of 5.3, and an acid neutralising capacity (ANC) of 9 μeq l^{-1}. Acidification is largely due to elevated levels of non-marine sulphate (xSO$_4$, mean 72 μeq l^{-1}), with a minor contribution from NO$_3$ (mean 10 μeq l^{-1}). Trend analyses (Reynolds et al. 1997; Evans and Monteith 2001) have shown some evidence of recovery in pH or ANC, but trends are partly obscured by inter-annual variability association with climatic factors. A previous application of MAGIC to this site by Jenkins et al. (1997) predicted significant future recovery as S deposition declines.

Methods

Model structure

MAGIC (Cosby et al. 1985) is an intermediate-complexity catchment-scale dynamic model of soil and surface water acidification. The model comprises a set of equations describing equilibrium processes occurring within the soil and streamwater (Table 1), and a set of mass balance equations describing catchment inputs of base cations and strong acid anions in deposition and mineral weathering, vegetation uptake and release, and streamwater outputs. A third set of equations have recently been added to represent nitrogen cycling and saturation as a function of the C/N ratio of soil organic matter. The model requires input of time series describing changes in atmospheric deposition, and other time series describing changes in input fluxes or conditions, for example those related to climatic factors, may also be entered. A detailed, recent description of the model is provided by Cosby et al. (2001).

For this study, MAGIC was applied on an annual time-step and a single catchment soil box, with a number of simplifying assumptions. Firstly, detailed N dynamics were not included; instead, N retention at each time step was

Table 1. Equilibrium reactions represented within the MAGIC model.

Process	Model representation
Soil cation exchange	Partitioning of Ca, Mg, Na, K and Al between solid and aqueous phases in soil (Gaines–Thomas equation).
Soil sulphate adsorption	Partitioning of SO_4 between solid and aqueous phases (Langmuir isotherm).
Aluminium dissolution and dissociation	Equilibrium between soil solution Al and H, and a solid phase of Al trihydroxide (also representative of Al-H cation exchange), and 12 reactions describing formation of aqueous Al complexes with OH, F and SO_4. Equivalent reactions, with the exception of cation exchange, are assumed to occur in streamwater.
Inorganic carbon dissolution and dissociation	Equilibria between gaseous CO_2, dissolved H_2CO_3, HCO_3 and CO_3.
Organic acid dissociation	Triprotic organic acid analogue model (H_3A, H_2A^-, HA^{2-}, A^{3-}). pKa values of 2.5, 4.0 and 5.8 taken from Hruška et al. (2001)

modelled as a fixed proportion of oxidised N deposition, calibrated to present-day stream NO_3. Stream NH_4 concentrations are near-zero, so complete retention of reduced N deposition was assumed. These assumptions essentially represent a 'best case' scenario for N leaching, with no decrease in N retention as soils become more N-enriched. Processes controlling N saturation in moorland catchments remain highly uncertain, and were considered to be outside the scope of this study. A second assumption made was that soil S adsorption at the Gwy is negligible. S adsorption is significant on Fe and Al oxide minerals in strongly weathered soils, but generally minor in younger, glaciated soils. Recent work on UK upland lakes (Cooper and Jenkins 2003) has demonstrated a direct link between S input and output fluxes, confirming that in-catchment processes have a minor impact. Therefore, as in previous MAGIC applications to UK sites (e.g. Jenkins et al. 1997), SO_4 was treated as 'pseudo-conservative', with current stream outputs equal to deposition inputs. Note that, in the model and throughout this paper, ANC is calculated using the charge balance definition, as the sum of base cations minus the sum of acid anions.

Derivation of model input data

Input data were derived from monitoring datasets held by the Centre for Ecology and Hydrology (CEH), previous studies at the site, and national deposition datasets (Table 2). Since Cl and SO_4 were treated as conservative, present-day total deposition was assumed to be equal to the stream output flux (Jenkins et al. 1997); marine base cation deposition was then calculated from Cl according to sea-salt ratios. NO_x, NH_x and non-marine base cation deposition were obtained from 5 km gridded UK deposition estimates for 1998–2000 provided by CEH Edinburgh.

Table 2. Input data used in model calibration.

Input data	Source	Value	
Rainfall	Rainfall for Cefn Brywn, adjacent to catchment, 1970–2000 (CEH)	2.48 m year^{-1}	
Runoff	Calculated from outflow discharge records, 1970–2000 (CEH)	2.11 m year^{-1}	
Soil properties	Local soils data (Jenkins et al. 1997)	Depth: 0.84 m BD: 1122 kg m^{-3} CEC: 78 meq m^{-3}	ECa: 2.32% EMg: 0.51% ENa: 0.99% EK: 0.55%
Reference year streamwater chemistry	Mean of 1999 monthly samples (CEH)	ANC: 32 µeq l^{-1} Ca: 43 µeq l^{-1} Mg: 57 µeq l^{-1} Na: 148 µeq l^{-1} K: 2.4 µeq l^{-1} Al: 2.2 µmol l^{-1}	pH: 5.60 SO$_4$: 55 µeq l^{-1} NO$_3$: 7 µeq l^{-1} Cl: 151 µeq l^{-1} DOC: 3.2 mg l^{-1}
Reference year soil water DOC, pH, Al	10 year mean depth-weighted concentrations for a stagnopodzol in adjacent catchment (CEH)	DOC: 4.2 mg l^{-1} Al: 14.0 µmol l^{-1}	pH: 4.80
Reference year deposition	Calculated from Cl and SO$_4$ runoff, and CEH Edinburgh UK 5 km gridded data (see text)	SO$_4$: 115 meq m^{-2} year^{-1} NO$_x$: 58 meq m^{-2} year^{-1} Cl: 314 meq m^{-2} year^{-1} NH$_x$: 103 meq m^{-2} year^{-1}	Ca: 29 meq m^{-2} year^{-1} Mg: 61 meq m^{-2} year^{-1} Na: 269 meq m^{-2} year^{-1} K: 5.9 meq m^{-2} year^{-1}

Historic sequences of anthropogenic S, NO$_x$ and NH$_x$ deposition were obtained by scaling current deposition to reconstructed emission sequences (Bettelheim and Littler 1979; Warren Spring Laboratory 1987; Simpson et al. 1997). For the period 1980 to present day, deposition records from Eskdalemuir, SW Scotland (Hayman et al. 2001) were used to refine deposition sequences.

S and N deposition forecasts were based on the Gothenburg Protocol. The effects of forecast emission reductions on S and N deposition have been modelled at a 10 km resolution in the UK using the HARM model (Metcalfe and Whyatt 1995). At the Afon Gwy, 2010 levels of S, NO$_x$ and NH$_x$ deposition are predicted to be 28%, 58%, and 66% of 1990 values respectively. Since deposition data were available up to 2000, further reductions required to reach the Gothenburg targets were scaled as a linear ramp from 2000 to 2010. Anthropogenic deposition was assumed constant thereafter.

Simulation of rainfall and runoff

Discharge records from 1975 to 2001 for the catchment outflow, and rainfall collected over the same period from the Cefn Brwyn rain gauge, 2 km from the outflow, were provided by CEH Wallingford. Annual rainfall (in mm) was then simulated for 1850–1974 based on regression against the England and Wales Record (EWR):

$$\text{Site rainfall} = -432 + 3.11\text{EWR} \qquad R^2 = 0.61, \ p < 0.001, \ n = 27 \qquad (1)$$

Future rainfall was simulated for two climate scenarios. Scenario 1-0 assumes no future rainfall trend, and 1970–1999 variations were simply repeated through to 2080 in order to provide a realistic inter-annual pattern (Figure 1a). Scenario 1-1 incorporates available climate change predictions based on the 'medium-high' emissions scenario of the UK Climate Impacts Programme (UKCIP) (Hulme et al. 2002). For this location, a small decrease in annual rainfall of 8.5% is predicted by 2080 (note that the annual resolution of this analysis did not permit the incorporation of predicted increases in the seasonality of this rainfall). The decreasing rainfall trend was superimposed on the inter-annual variations included in Scenario 1-0 (Figure 1a).
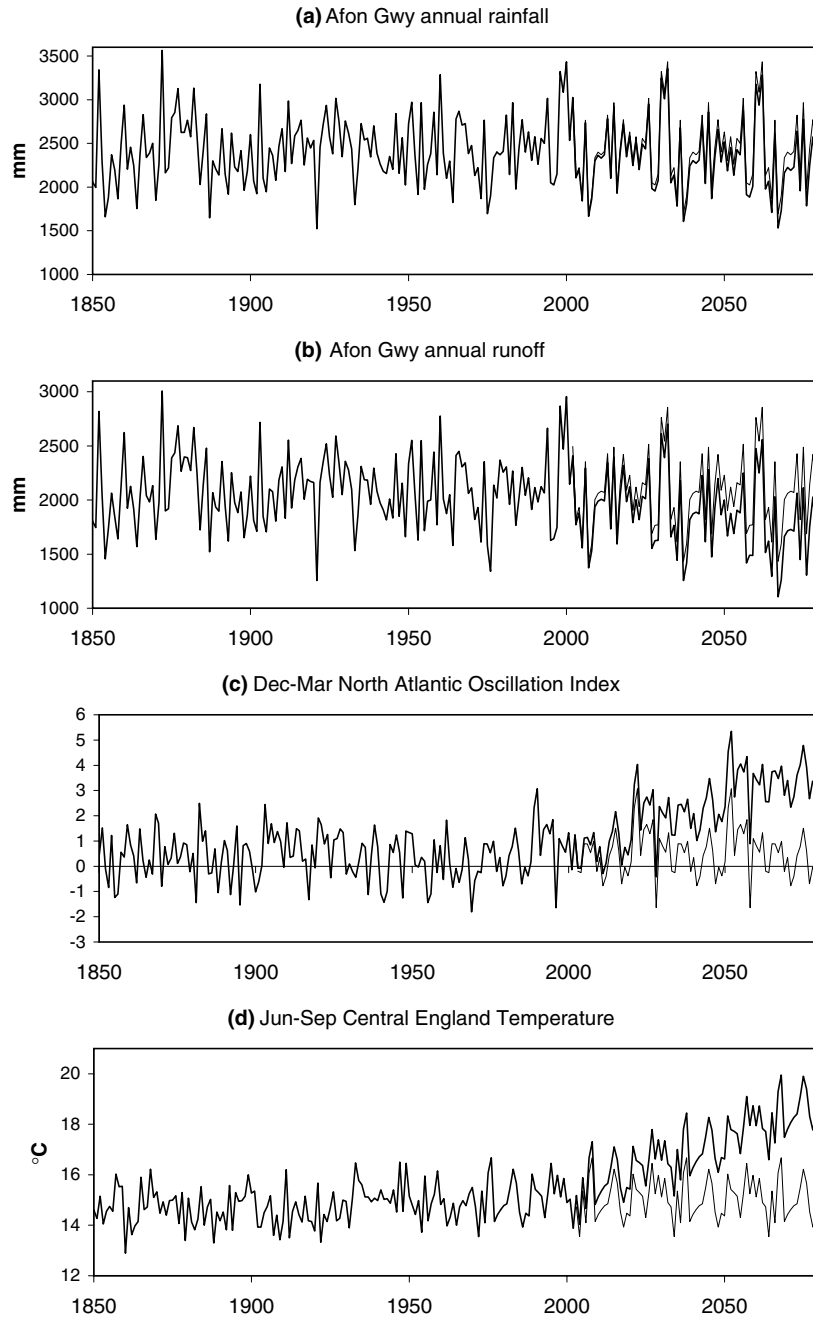
Historic runoff variations were simulated based on a regression of observed 1975–2001 runoff against measured rainfall and annual mean Central England Temperature (CET_{annual}):

$$\text{Runoff} = 761 + 0.833\text{Rainfall} - 74.0\text{CET}_{annual} \qquad R^2 = 0.87,$$
$$p < 0.001, \ n = 27 \qquad (2)$$

where runoff and rainfall are expressed as mm, and CET_{annual} as °C. Predicted vs. observed runoff values are shown in Figure 2a. Equation (2) was used to simulate future runoff for scenarios 1-0 and 1-1 based on the rainfall simulations described above, and similar simulations of CET_{annual}: For Scenario 1-0, 1970–1999 values of CET_{annual} were repeated in future, and for the climate change Scenario 1-1 a rising temperature sequence was added, based on UKCIP predictions of a 1.8 °C temperature rise by 2050, and 3.2 °C by 2080. The combined impact of rainfall decreases and temperature increases is a fall in runoff of around 18% by 2080 (Figure 1b).

Simulation of sea-salt deposition

Sea-salt deposition occurs primarily during winter frontal storms, and was therefore expected to show a relationship to winter values of the NAOI. Since Cl moves conservatively through the catchment, a similar relationship was expected between winter NAIO and stream Cl outputs. Annual Cl flux estimates, calculated from regular sampling and continuous discharge data, were analysed relative to a range of climatic variables including annual and seasonal

(a) Afon Gwy annual rainfall

(b) Afon Gwy annual runoff

(c) Dec-Mar North Atlantic Oscillation Index

(d) Jun-Sep Central England Temperature

Figure 1. Observed and simulated future variations in the climatic indices used for modelling. Thick line shows past variations, and simulated future climate changes based on UKCIP medium-high emissions scenario. Thin line shows forecasts with no long-term climate change.
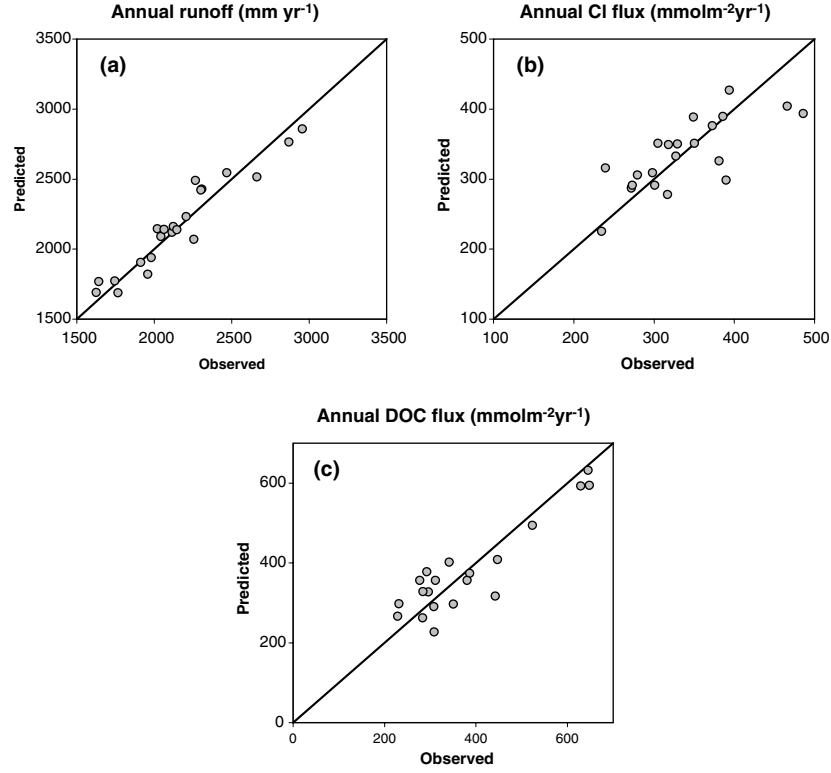
Figure 2. Predicted vs. observed values for runoff, chloride and DOC fluxes over the monitoring period (based on Equations (2)–(4)).

rainfall, NAOI and CET values. Based on a stepwise variable selection (significance threshold $p = 0.15$) the best regression equation to predict Cl flux was:

$$\text{Cl flux} = 84.2 + 0.090\text{Rainfall} + 25.2\text{NAOI}_{\text{Dec–Mar}} \quad R^2 = 0.52,$$
$$p = 0.001, \ n = 21 \tag{3}$$

where Cl flux is expressed as mmol m^{-2} year^{-1}, rainfall as mm and the NAO Index is calculated as the difference between normalised sea-level pressures over Gibraltar and Southwest Iceland. Predicted vs. observed fluxes are shown in Figure 2b. Equation (3) is consistent with the expected influence of the NAO on sea-salt deposition, and of rainfall on water flux. Given the low temporal resolution, and the indirect nature of the NAOI as a predictor variable, this appears a reasonable relationship on which to reconstruct past variations in Cl deposition and, based on sea-salt ratios, of marine-derived inputs of other ions.

No-change (Scenario 2-0) and climate change (Scenario 2-1) forecasts of Cl flux were undertaken from Equation (2), using similar methods to those used

for rainfall and runoff. For Scenario 2-0, 1970–1999 $NAOI_{winter}$ and rainfall variations were repeated through to 2080. Scenario 2-1 is based on UKCIP predictions that winters will become more 'westerly' in nature, with mean $NAOI_{winter}$ increasing under the medium-high emissions scenario from 1.0 during the 1990s to approximately 3.5 in the 2070s. This increase was added to the variations in Scenario 2-0 as a linear ramp (Figure 1c). This sequence, together with the climate-change rainfall forecast described above, was then used to predict future Cl fluxes.

Simulation of organic acidity

Long-term simulation of changes in DOC concentration required an empirical relationship between observed DOC flux and one or more predictors. The cause of recently observed DOC increases in many European and American freshwaters is subject to ongoing debate, with proposed mechanisms including increased temperature (e.g. Freeman et al. 2001; Evans et al. 2002), hydrological changes (e.g. Tranvik and Jansson 2002) and decreased soil acidity as sulphur (S) deposition decreases (e.g. Stoddard et al. 2003). Given this uncertainty, both climate variables and S deposition were included in the stepwise regression. Annual mean xSO_4 concentrations in precipitation were obtained from a long-running record at Eskdalemuir, SW Scotland (Hayman et al. 2001). This was adjusted to a shorter local record using a simple adjustment factor (0.74, $R^2 = 0.82$), and converted to a flux by multiplying by local rainfall. The best equation obtained for DOC flux by stepwise regression was:

$$DOC\ flux = -1283 + 0.274 Rainfall + 45.8 CET_{Jun-Sep}$$
$$- 2.11 xSO_4 Deposition \qquad R^2 = 0.82,\ p < 0.001,\ n = 19$$

$$(4)$$

where DOC flux and xSO_4 deposition are expressed in mmol m^{-2} year^{-1}, rainfall in mm, and $CET_{Jun-Sep}$ in °C. This correlation suggests that higher temperatures and reduced S deposition both have a positive influence on DOC flux. Summer temperatures appear to be most important, as most organic matter decomposition occurs during this period; this is reflected in stream DOC peaks which occur generally during summer and early autumn. The good agreement between predicted and observed fluxes (Figure 2c) and correspondingly high R^2 value are encouraging, suggesting that the main driving variables may have been identified.

For the constant climate Scenario 3-0, DOC fluxes were simulated by repeating 1970–1999 annual rainfall and $CET_{Jun-Sep}$ into the future. Stream DOC concentrations were then calculated by dividing by runoff for the corresponding year. For the climate change Scenario 3-1, the changes in rainfall and runoff described in Scenario 1-1, and UKCIP predictions of June–Sep-

tember temperature increases of 2.3 °C by 2050, and 4.0 °C by 2080, were superimposed on these patterns. Gothenburg protocol reductions in S deposition, as described above, were used for both scenarios, whilst predicted sea-salt deposition fluxes for Scenarios 2-0 and 2-1 were incorporated in Scenarios 3-0 and 3-1 respectively.

Finally, MAGIC considers organic acids rather than DOC *per se*, modelled using a triprotic acid analogue (Table 1) in which carboxylic acid groups within soil and stream water DOC dissociate as a function of pH. The 'site density' of carboxylic acid groups was estimated from measurements made at Svartberget, Sweden, by Hruška et al. (2001) as 8 meq (mg $DOC)^{-1}$. This was converted to 4 mmol (mg $DOC)^{-1}$ based on the assumption of Hruška et al. (2001) that site density is distributed equally between the three acid functional groups of the triprotic model; their results also suggest that site density is approximately constant over time. Soil-water organic acid concentrations, which are also required by MAGIC, were estimated from stream concentrations based on the ratio of present-day measured stream and soil-water DOC concentrations at the site; in effect, this assumes that a fixed proportion of soil-water DOC reaches the stream at each time step.

Model calibration

MAGIC was calibrated to a 1999 reference year. Base cation (Ca, Mg, Na and K) weathering rates and initial soil exchangeable concentrations, and reference year soil organic acids, were calibrated to reproduce reference year observed stream and soil exchangeable base cation concentrations, and soil water pH. In the initial calibration, all climate variables were held constant over time (Simulation 0). The calibrated model was then re-run with (i) variable rainfall and runoff (Simulation 1), and (ii) additional variation in sea-salt deposition (Simulation 2). Both of these simulations accurately reproduced present-day conditions. However, the additional inclusion of variable organic acid concentrations (Simulation 3) required re-calibration of the model in order to

Table 3. (a) R^2 values for modelled vs. observed annual mean chemistry, 1980–2001. (b) Nash–Sutcliffe model efficiencies for each model simulation, relative to Simulation 0 'base case'.

| Simulation	Cl	DOC	SO$_4$	Ca	Mg	Na	pH	ANC
Panel a								
0: No climate variation	0	0	0.77	0.02	0.05	0	0.36	0.33
1: Variable rainfall/runoff	0	0	0.76	0.04	0.23	0.09	0.24	0.19
2: + Variable sea-salts	0.34	0	0.76	0.13	0.19	0.32	0.25	0.23
3: + Variable organic acids	0.34	0.59	0.76	0.22	0.12	0.29	0.27	0.40
Panel b								
1: Variable rainfall/runoff	0.05	0.00	0.02	−0.30	0.24	0.12	−0.10	−0.15
2: + Variable sea-salts	0.39	0.00	−0.05	−0.26	0.22	0.42	−0.38	−0.08
3: + Variable organic acids	0.39	0.61	−0.06	0.33	−0.04	0.40	−0.77	0.13
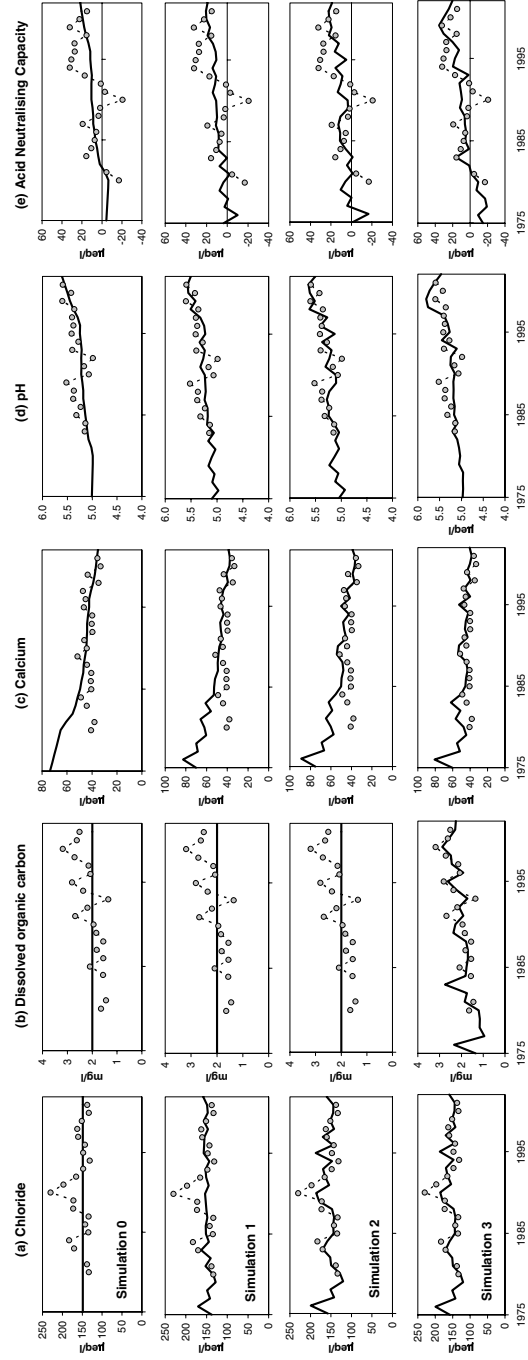
Figure 3. Modelled (solid line) and observed (circles and dashed line) annual mean streamwater chemistry for each simulation (Simulation 0: no climate change; Simulation 1: variable rainfall/runoff; Simulation 2: plus variable sea-salt deposition; Simulation 3: plus variable organic acids).
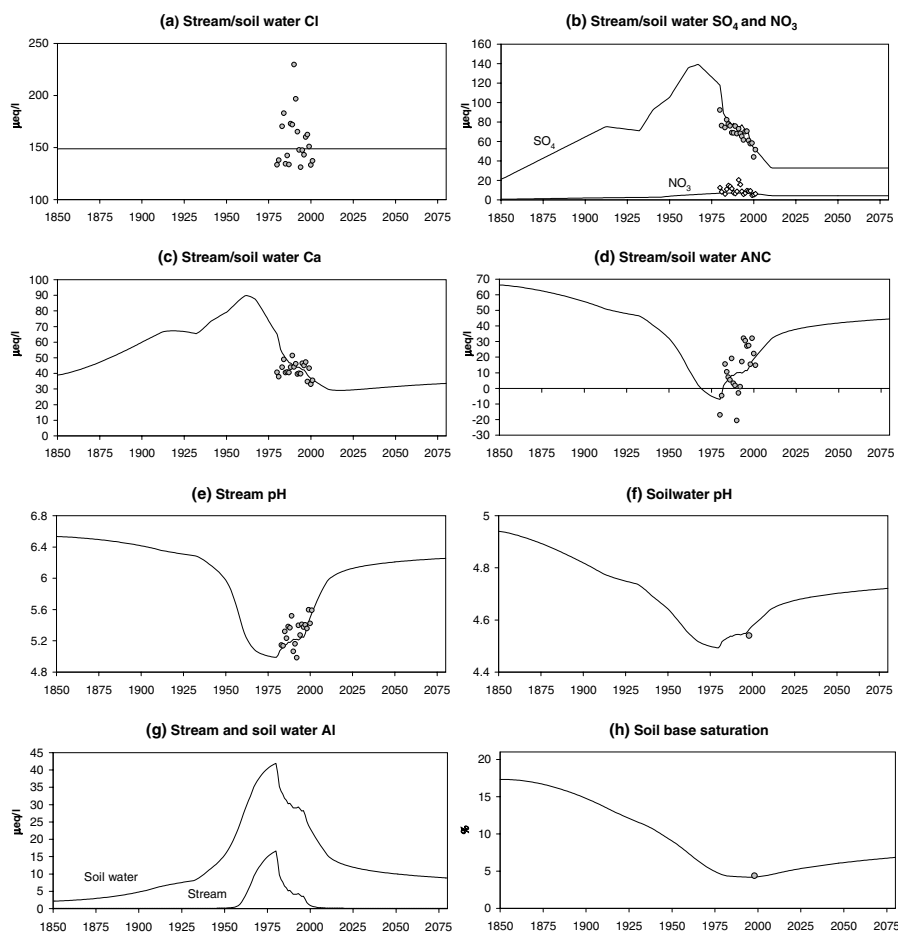
Figure 4. Modelled stream and soil chemistry for Simulation 0: constant climate (variable acid deposition).

correctly simulate present-day conditions. This was due to the dependence of organic acidity on S deposition in Equation (4), which led to differences in modelled soil base cation depletion, and hence in the trajectory of hindcast acidification.

Results

Comparison with observed data

Comparisons of predicted and observed concentrations of key chemical variables for each model simulation are presented in Figure 3, and correlations for

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a wider range of variables in Table 3a. The relative performance of each model simulation was also assessed using Nash–Sutcliffe model efficiencies (Nash and Sutcliffe 1970; Table 3b), which indicate the proportion of residual variance accounted for by the addition of each climatic factor to the model, relative to the 'base case' Simulation 0. A positive model efficiency for a given variable indicates that the inclusion of climatic variation has improved the fit to observed values, relative to Simulation 0.

Results show that Simulation 0, which includes only S and N deposition as driving variables, reproduces the underlying trends in pH and ANC reasonably
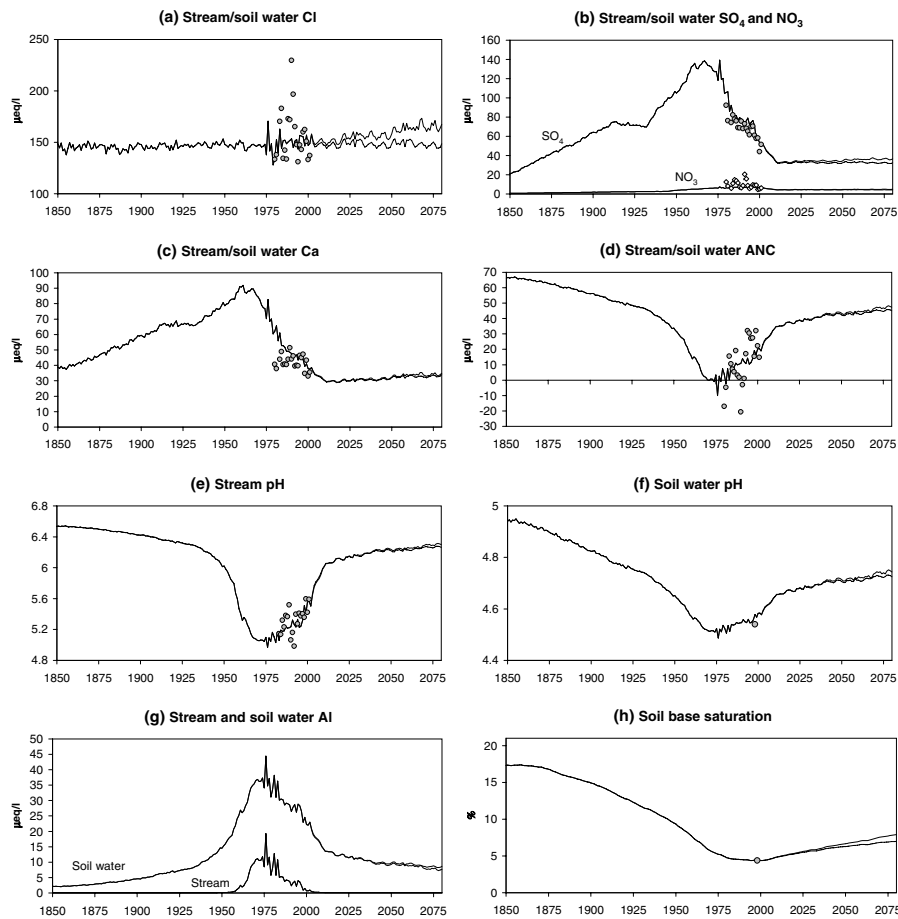
Figure 5. Modelled stream and soil chemistry for Simulation 1: variable rainfall and runoff. Thick line shows reconstructed historic chemistry, and forecasts incorporating effects of climate change (Scenario 1-1). Thin line shows forecasts without climate change (Scenario 1-0). Circles and dashed line show observed chemistry.

well, giving acceptable correlations between predicted and observed values of these variables. The strong correlation between modelled and observed stream SO_4 supports the earlier assumption that this ion is approximately conservative within the catchment, and consequently that stream outputs are largely a function of deposition inputs in that year. Since short-term deposition and climatic variability are not incorporated within this simulation, inter-annual variations in water chemistry are not reproduced, and this is reflected in low or zero R^2 values for base cations, Cl and DOC.

Incorporation of variable rainfall and runoff in Simulation 1 results in some inter-annual chemical variability, but this is much smaller than observed
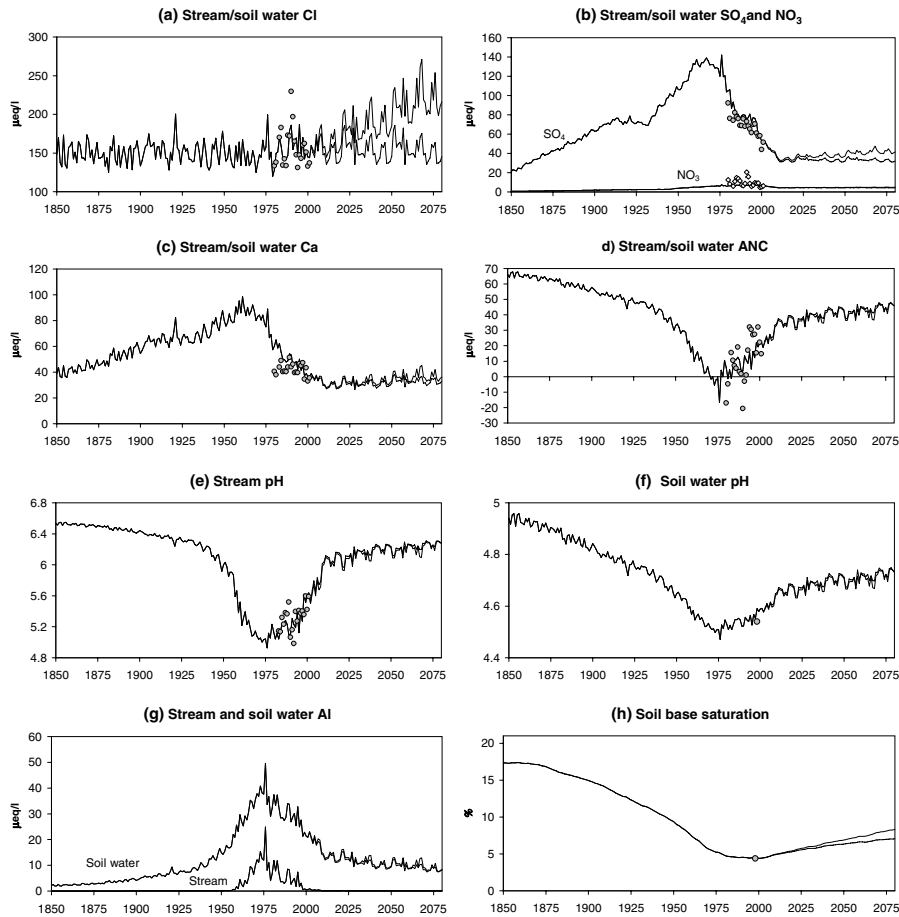
Figure 6. Modelled stream and soil chemistry for Simulation 2: variable sea-salt deposition. Thick line shows reconstructed historic chemistry, and forecasts incorporating effects of climate change (Scenario 2-1). Thin line shows forecasts without climate change (Scenario 2-0). Circles and dashed line show observed chemistry.

variations, and does not improve correlations or model efficiencies relative to Simulation 0. While this appears to suggest a limited influence of hydrological variations on water quality, a more complex hydrological model might be expected to show larger effects (discussed later).

Simulation 2, incorporating variations in sea-salt deposition, adds further short-term variation to modelled concentrations, and significantly improves the fit between predicted and observed Cl. Model performance is also improved with regard to the predominantly marine-derived base cations, Na and Mg. However, as a consequence of the relatively low R^2 obtained by regression (Equation (3)) the success of Cl predictions is limited, particularly in reproducing extreme values such as the peak in 1990. Sea-salt inputs typically occur during a small number of discrete deposition events, and it appears that the occurrence of these events can only crudely be predicted from the NAO index. The failure to fully capture the high 1990 sea-salt input results in a significant over-prediction of ANC for that year. In general, it appears that the modelled variations in sea-salt deposition are insufficient to explain the range of observed variation in ANC, and to a lesser extent pH, although this may reflect the limitations of the deposition simulation, rather than implying that variable sea-salt deposition does not impact on runoff chemistry.

The prediction of DOC in Simulation 3 is good, as a consequence of the high R^2 value for Equation (4). The inclusion of variable organic acidity has a significant impact on modelled chemistry, notably in giving the best simulation of ANC. The long-term trend in Ca also appears to be substantially better reproduced by this model run. Although the inclusion of organic acidity does not improve the simulation of stream pH, overall this simulation appears to give the best fit to observed stream chemistry.

Simulation 0: variable acid deposition, constant climate

Applying the model with variable S and N deposition but constant climate (Figure 4) provides a base case from which to assess the effects of climatic changes on runoff chemistry. The main driver of change at this catchment is S deposition, since most N deposition is retained (and, in this application, this is assumed to continue in future). S deposition has been falling since the 1970s, and is predicted to continue doing so until 2010 in response to current emissions reduction agreements. Stream chemical recovery is predicted to be relatively rapid, and large, at this moderately buffered catchment. By 2080, stream ANC and pH are predicted to increase to around 1930s levels, and stream Al to fall close to zero, with much of the recovery occurring by 2010. As in previous modelling studies, however (e.g. Skeffington and Brown 1992; Reynolds 1997), soil base saturation recovery is much slower; at a modelled pH of 6.2 in 1940, base saturation was 10.5%, but in 2050, at the same modelled pH, base saturation is only 6.1%.
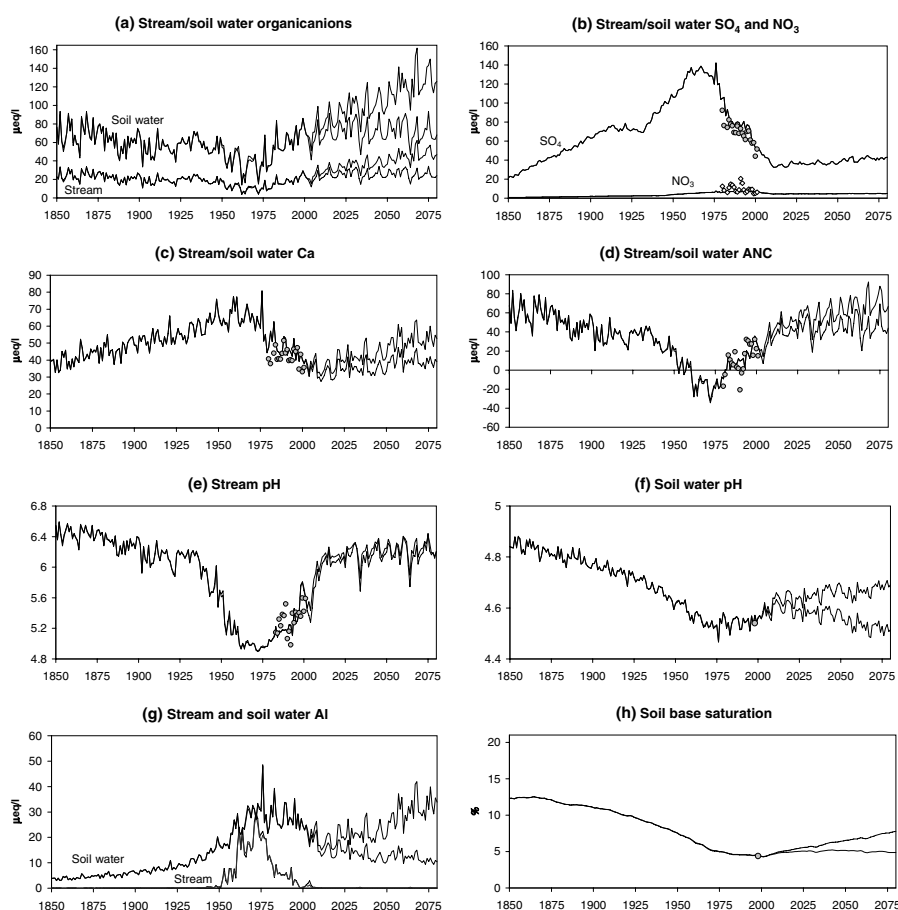
Figure 7. Modelled stream and soil chemistry for Simulation 3: variable sea-salt deposition. Thick line shows reconstructed historic chemistry, and forecasts incorporating effects of climate change (Scenario 3-1). Thin line shows forecasts without climate change (Scenario 3-0). Circles and dashed line show observed chemistry.

Simulation 1: variable rainfall and runoff

Hindcast simulations incorporating variable rainfall and runoff (Figure 5) follow an identical trajectory to those of Simulation 0, with small inter-annual fluctuations in solute concentrations the result of variations in evapotranspiration. The absence of any long-term divergence between the two simulations reflects the lack of significant systematic trends in rainfall or runoff over the hindcast period. Applying the climate change forecast Scenario 1-1 does however result in some small changes relative to the constant-hydrology Scenario 1-0, due to predicted decreases in runoff as a proportion of rainfall, and

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consequent increases in solute concentrations. Since this evaporative concentration affects both cations and anions, the overall impact on acidity is minor. The slightly accelerated recovery in soil base saturation is a consequence of increased cation concentrations in soil water, which favours adsorption of mono- and divalent base cations relative to trivalent Al.

Simulation 2: variable sea-salt deposition

Long-term simulations incorporating variable sea-salt deposition (Figure 6) show stream Cl largely tracking winter NAO, with large inter-annual variability, and slight long-term cyclicity with peaks around 1900, and during the 1990s. Associated variations in marine base cation (mainly Na and Mg) input should,
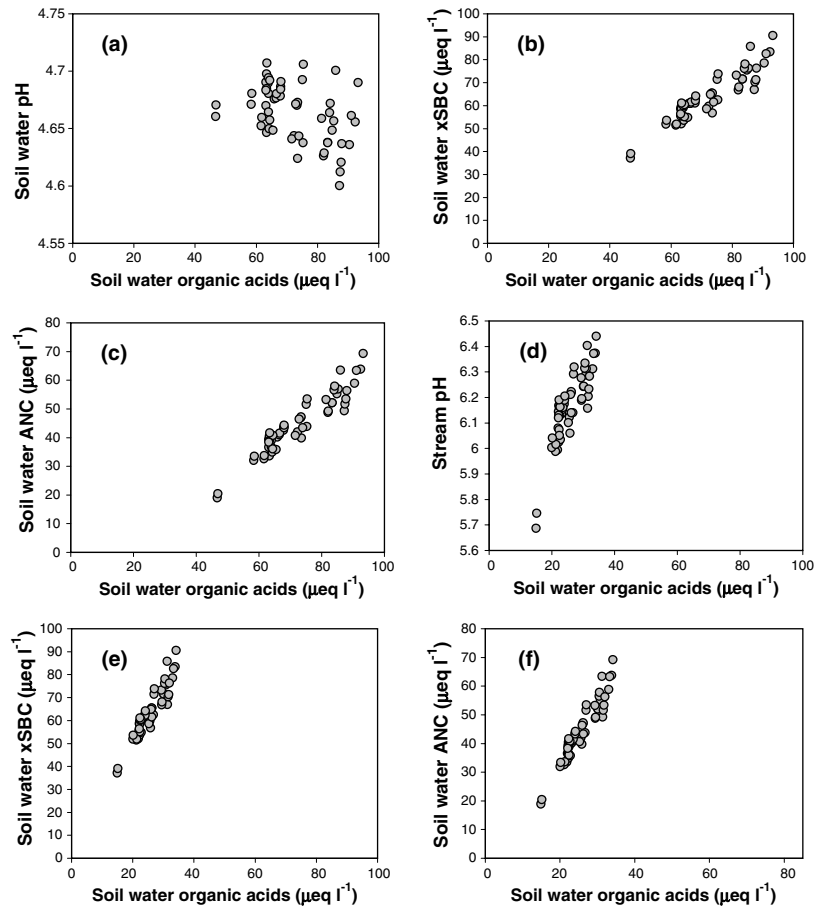

Figure 8. Modelled stream and soil water pH, non-marine base cations and ANC vs. organic acidity, for Simulation 3-0 (2025–2080).

via cation exchange, cause fluctuations in cations with predominantly non-marine sources, namely Ca, H and Al. Prior to 1950, the main cation displaced is Ca, which shows year-to-year fluctuations of over 10 μeq l^{-1} during this period, whereas simulated pH and soil Al are largely stable. However as base saturation is depleted (Figure 6h) reduced availability of Ca leads to increasing displacement of Al and H. This is evident both in the long-term trend from 1950 to 1975, with pH falling from over 6.0 to 5.0, and stream Al rising from 0 to 18 μeq l^{-1}, and also in the year-to-year variation, which exceeds 0.2 pH units and 5 μeq l^{-1} Al between 1950 and the present day. This, in effect, is the 'sea-salt' effect widely recognised on an episodic time scale, but shown here also to operate an inter-annual basis. This simulation supports the suggestion that such a damaging release of acidity does not occur under pre-acidification conditions (Harriman et al. 1995), where the main displaced cation is likely to be Ca, and that 'sea-salt episodes' are thus an effective consequence of anthropogenic acidification, rather than solely a natural process.

Under both future climate scenarios, the slow recovery of soil base saturation relative to stream chemistry noted earlier has the consequence that marine base cations continue to exchange primarily with H and Al, rather than Ca. Therefore, despite recovery in mean pH and ANC, the stream will remain somewhat susceptible to sea-salt episodes. This is evident in the model forecasts, which show continued depressions in annual mean stream pH of over 0.2 units during high sea-salt years (the pattern is similar for Scenarios 2-0 and 2-1, as the sequence of year-to-year deposition variation is the same for both).

The climate change Scenario 2-1 incorporates large Cl increases in response to rising winter NAOI, accentuated by decreasing runoff; by 2080, average concentrations are predicted to be 71 μeq l^{-1} higher than under Scenario 2-0 Figure 6a). The effects of increased sea-salt deposition are apparent in other ions with a marine component, such as SO_4 and Ca, which show slight relative increases. In addition, increased marine cation deposition results in an increase in soil base saturation (mainly exchangeable Na and Mg), beyond that observed due solely to declining acid deposition under Scenario 1-0 (Figure 5h). This increase in soil base saturation, by displacing H and Al, would be expected to result in more acidic conditions in both soil and stream waters under Scenario 2-1. This response is indeed observed, in soil and stream water ANC and pH, and soil water Al, but is very small. The effects of a long-term increase in sea-salt deposition are thus equivalent to those from an episodic increase, raising soil base saturation but acidifying soil and stream waters; however, the long-term impact appears minor.

Simulation 3: variable organic acidity

Model runs incorporating variable DOC (as well as variable hydrology and sea-salt deposition) are shown in Figure 7. Simulated stream organic anions show high short-term temporal variability, in the order of 10–20 μeq l^{-1}. The

long-term trend is approximately the inverse of that in SO_4, reflecting the negative correlation identified between DOC and S deposition (Equation (4)). A small additional reduction in organic anions under acid conditions is caused by the increased protonation of organic acid functional groups, according to the triprotic model. One implication of these modelled relationships is that part of the increase in mineral acid anions due to acid deposition is offset by simultaneous decreases in organic acid anions. This is consistent with the suggestion by Krug and Frink (1983) that mineral acidity variations are buffered by opposing changes in organic acidity. However, this organic acid buffering is clearly only partial, since the magnitude of soil and stream acidification is similar to that in the preceding simulations.

The modelled effects of varying organic acids on soil and stream water chemistry are large, and somewhat counter-intuitive. They may be illustrated by examining Scenario 3-0 (no climate change) for the relatively stable period 2025–2080. Plots of soil and stream water variables vs. organic acid concentrations Figure 8) show some tendency for years with high organic anion concentrations to have lower soil solution pH. However, most of the protons associated with the organic acids are exchanged with soil base cations, so there is a much stronger positive correlation with the sum of non-marine base cations (xSBC). Additionally, using the charge balance definition, base cations contribute positively to ANC, whereas organic anions have no effect, so soil water ANC is raised by this process.

In MAGIC, base cations and mineral acid anions, and hence xSBC and ANC, transfer conservatively from soil to stream water. Organic acids are not conservative, with lower concentrations in streamwater due to retention of DOC in mineral soils. The reduction in organic acidity consumes H^+ (and Al), and pH is therefore significantly raised. Although organic acids in streamwater continue to exert a negative direct impact on stream pH, this appears to be outweighed by the positive effect of soil water organic acids causing increased base cation export to the stream. The surprising result, therefore, is a positive correlation between modelled stream pH and organic acidity from year to year (Figure 8c).

The climate-change forecast (Scenario 3-1) shows a dramatic increase in organic concentrations, with 2080 stream organic anion concentrations almost double those for the no-change Scenario 3-0. Prior to 2010, the increase is driven partly by decreasing S deposition, but in large part it can be attributed to the large forecast increases in summer temperature, amplified slightly by the decrease in runoff. The long-term effects of the rising trend in DOC under Scenario 3-1 reflect the same processes identified over the short-term: the increased organic acidity lowers soil water pH by around 0.2 units relative to Scenario 3-0 in 2080, displacing base cations from soil exchange sites into the stream, and thereby generating a long-term relative increase in both base cation concentrations and ANC. The negative aspect of this sustained increase in export of base cations to the stream, however, is a depletion of soil base saturation; predicted 2080 levels are 4.9% for Scenario 3-1, compared to 7.8% for Scenario 3-0. In effect, the projected increase in soil water DOC would

completely offset modelled recovery in soil base status due to reduced acid deposition under the Gothenburg Protocol, returning base saturation to present-day levels by 2080. The effect on soil water pH is even similarly severe. Interestingly however, the overall long-term impact on stream pH is relatively small, with similar values predicted for the two scenarios.

Discussion

Most previous dynamic acidification model applications have assumed smooth sequences of deposition inputs, and generally invariant climatic conditions. The empirical relationships used in this study to simulate seasalt deposition and dissolved organic matter production lead both to more accurate simulations of streamwater Cl and DOC, and to improved model performance in reproducing observed base cation and ANC variations. Together with previous research indicating that both processes may be significantly affected by climate change, these results suggest that the modelling approach used provides a useful first step towards assessing the potential impacts of climatic variability, and long-term climate change, on soil and water quality in acid-sensitive systems. Nevertheless, it is emphasised that this is an exploratory study, and the predictions made remain speculative; in particular, there is uncertainty regarding the respective roles of temperature and acid deposition on DOC generation. The relationships used here, although empirically based, essentially form an independent model input. Since the causes of recent observed DOC increases in the UK are not yet fully understood, different predictions might be obtained with different assumptions, or by incorporating other drivers. This study should therefore be considered an assessment of the effects on water quality *were* these two drivers jointly responsible for observed DOC increases, rather than a prediction of future changes *per se*. At the simplest level, it illustrates the significant extent to which recovery would be affected by a future continuation of recent observed DOC increases. This effect has not previously been incorporated in the MAGIC model.

Variable sea-salt deposition has, as noted earlier, been incorporated in a small number of previous modelling studies. Jenkins and Cullen (2001) applied MAGIC to 12 UKAWMN sites using measured annual deposition to drive the model from 1988 to 1999. Some inter-annual ANC variation was predicted, primarily due to changes in sea-salt deposition but, as in the present study, the ANC range simulated due to this mechanism alone was smaller than that observed. Beier et al. (2003) applied MAGIC to three 'clean rain' experimental sites in Scandinavia with 15–20 year sequences of measured sea-salt deposition repeated through the simulation. For an 'increased storm intensity' scenario, sea-salt deposition was increased by 50% as a step change superimposed on this cycle. Modelled catchment responses were fundamentally the same as those of this study; increased marine cation deposition was predicted to displace H and Al to the streams, and to accelerate recovery in base saturation.

However, the magnitude of predicted change was far greater; long-term ANC decreases of around 100 μeq l^{-1} were predicted for two of the sites relative to a 'no climate change' scenario, compared to just a few μeq l^{-1} for the Gwy. Relative base saturation increases of 2.5–5.0% were predicted, compared to 1.3% for the Gwy. To some extent, this may reflect differences between catchments, two of which receive much greater sea-salt inputs than the Gwy, but differences between the scenarios also appear important. The 50% increase in sea-salt deposition exceeds that predicted for the Gwy from Equation (3) (21% by 2080), and the step change has a much greater impact than a steady increase, effectively generating a large, immediate dislocation of runoff chemistry and soil base saturation, followed by a gradual return to baseline conditions. In effect, the study by Beier et al. more clearly demonstrates catchment response to increased sea-salt deposition, but the present study may provide a more realistic prediction of the magnitude of such a response under current climate scenarios, at least for UK sites.

In practice, other water quality responses to climate change may also prove to be significant. As noted earlier, climate effects on N leaching are likely to be large and varied. Monteith et al. (2000) previously linked NO$_3$ variations to climate at a number of sites, including the Afon Gwy, but this effect was not modelled here due to the relatively small contribution of NO$_3$ to stream acidity. In areas of higher N leaching, further consideration of climatic effects on N cycling will be needed. It is also uncertain whether current high levels of N retention in many catchments, including the Gwy, will be sustained under an altered climate regime.

The hydrological variations incorporated in this model application were relatively simple, limited to variability in the balance of rainfall and runoff a single soil box, annual time-step model. A more complex model application incorporating seasonal and episodic hydrological variation, and vertical/horizontal catchment heterogeneity, would probably demonstrate a more substantial hydrological impact on runoff chemistry, both directly via changes in water flowpath, and indirectly via impacts on biogeochemical processes. As one example, changes in rainfall seasonality might be expected to alter the frequency of drought-induced S flushes. Changes in the frequency and severity of individual storm events will impact on chemical extremes occurring within the stream, and therefore potentially on the biota. In this context, it is also worth noting that the range of variation modelled in this study only represents variation in annual means; seasonal and episodic variations will be superimposed on these patterns, leading to a considerably wider overall range of conditions.

Conclusions

(1) Correlations identified between stream Cl and winter NAO Index, and between DOC and summer temperature, are consistent with the mecha-

nisms proposed in previous studies. An inverse correlation between DOC and S deposition suggests that decreasing acid deposition may also make a partial contribution to recently observed DOC increases.

(2) Results suggest that variations in both sea-salt deposition and organic acidity contribute to observed inter-annual changes in streamwater chemistry. Incorporating these variations will improve simulation of biologically important 'extreme' years, rather than simply the average conditions for a given acid deposition scenario. It is also important that these processes be understood when interpreting long-term trend data in relation to changes in acid deposition.

(3) 'Sea-salt acidification' is not a natural process. Model results show that, under pristine conditions, elevated marine base cation inputs only displace Ca from soil exchange sites, and consequently do not effect stream acidity. Only after soil base saturation has become depleted by acid deposition are H and Al displaced to the stream. Since model simulations generally show very slow recovery of soil base saturation at poorly buffered catchments, transient periods of sea-salt acidification can be expected to continue in future, despite decreases in acid deposition.

(4) Forecast simulations, based on current climate predictions, show a dominant effect of temperature-linked DOC increases, particularly in soilwater, on recovery of both soils and streamwaters. Modelled increases in organic acidity lead to re-acidification of soil waters, and consequently to a complete reversal of the recovery in base saturation and soil water pH resulting from reduced acid deposition. By displacing soil base cations into solution, however, this process leads to a concurrent increase in the ANC of runoff. Compared to increased DOC, the simulated rise in sea-salt deposition has an opposing effect, raising base saturation and acidifying the stream, but the magnitude of this effect appears considerably smaller for the climate scenario used.

(5) This study suggests that climate change may profoundly affect soil and surface water quality, and have a significant influence on the recovery of acidified soils and waters. The processes modelled here remain uncertain, and relate to just a limited set of climatic variables; further work will be required to provide a more accurate, and complete, indication of climate change impacts on these systems. Studies of ecosystem recovery from acidification, and of soil and water quality in general, may in future need to consider the concurrent impacts of anthropogenic climate change in order to provide accurate predictions of future conditions.

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