Regional modelling of acidification in Wales; calibration of a spatially distributed model incorporating land use change

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Abstract

The model of acidification of groundwater in catchments (MAGIC) has been calibrated to 94 catchments in Wales, enabling the quantification of regional response to reduced emissions under the second sulphur protocol and incorporating the potential impact of future changes in afforestation. To calibrate the model the methodology utilises, for each site, the best available data derived from databases which are consistent across the whole region but which vary in spatial resolution. The calibrated model closely matches observed stream water chemistry across the region. The predicted future response is a reduction in acidity of surface waters in the region. The recovery is less marked at forested catchments, and some forested sites undergo a further decrease in acid neutralising capacity (ANC). The predictions from the multiple-site method are statistically consistent with those produced by an alternative regional modelling method which is based upon Monte-Carlo procedures. The multiple-site method, however, has the advantage of providing future predictions which are also spatially distributed across the region.

Introduction

The link between atmospheric deposition of acidic oxides and acidification of soils and surface waters is now well-established and has led to the negotiation of international agreements to curb emissions, most recently based upon the critical load or source-receptor concept (Murlis, 1995; Grennfelt et al., 1995). In support of these negotiations, dynamic models have played a key role in assessing the potential for ecosystem recovery from acidification (Jenkins et al., 1997; Werner and Spranger, 1996). To date, the focus of these studies has been model applications to individual headwater lakes and streams over a large gradient of atmospheric deposition and encompassing a broad range of biogeochemical environments (e.g., Forsius et al., 1997). Such applications have enabled model sensitivity analyses (Jenkins and Cosby, 1989), validation against both palaeoecological pH reconstructions (Jenkins et al., 1990), and ecosystem manipulation experiments involving both increased and decreased acidic deposition fluxes (Cosby et al., 1995), links with biological status (Ormerod et al., 1989) and assessment of land use impacts, particularly the impact of plantation forestry (Cosby et al., 1990; Jenkins et al., 1997).

With the increasing recognition of the importance of dynamic models in assessing the time-dependence of critical loads and the potential damage to areas where critical loads remain exceeded in the future, has come the desire to extrapolate model applications from small catchments to whole regions. Such a development in modelling strategy will potentially provide policy makers with a spatial resolution capable of representing the impacts of emission reduction strategies and providing a statistical basis on which to formulate economic assessments.

In the UK, the MAGIC model (Cosby et al., 1985a,b) has been extensively applied to individual sites across the UK (Jenkins et al., 1997). Two procedures for regionalisation of MAGIC in the UK have also been developed; these are Monte-Carlo and multiple-site calibrations. The Monte-Carlo procedure uses frequency distributions derived from observations of the soil and surface water chemistry and physical characteristics within a region to calibrate the model; thus, specific soil and water data for each catchment are not essential. This approach (Sefton and Jenkins, 1998) simulates the response of the whole population of lakes and streams over time, but cannot distribute predicted changes in space. The multiple site technique uses best available information for the chemical and physical characteristics of soil and water at many sites in a region and makes regional assumptions where data are missing. This has the benefit of enabling prediction in time and space, but may be limited by availability of data at a sufficient level of resolution either to calibrate the model

adequately at each site or at enough sites to enable statistically relevant predictions relating to the region as a whole. This paper describes an application of the multiple-site approach to Wales to determine the adequacy of available data, to assess the performance of the modelling techniques, and to predict regional hydrochemical response under currently-agreed future reductions in S emission. The assumptions, calibration and predictions from the multiple-site method are also compared with a Monte-Carlo model application to Wales described by Sefton and Jenkins (1998). The basic data for this modelling analysis were collected and compiled as part of the Welsh Acid Waters Survey (WAWS) undertaken to assess the current status of acidity in surface waters in Wales and to determine changes since a previous survey 10 years earlier (Stevens et al., 1997).

The MAGIC model

MAGIC is a process-oriented dynamic model for the long term reconstruction and future prediction of soil and surface water acidification at the catchment scale (Cosby et al., 1985a,b). The model consists of: (i) soil-soil solution equilibrium equations in which the chemical composition of the soil solution is assumed to be governed by simultaneous reactions involving sulphate (SO4) adsorption, cation exchange, dissolution and speciation of inorganic and organic carbon; and (ii) mass balance equations in which fluxes of major ions to and from the soil and surface water are assumed to be governed by atmospheric inputs, mineral weathering, net uptake by biomass and loss to streamwater.

MAGIC uses a lumped parameter approach to; (i) aggregate the complex chemical and biological processes active at the catchment scale into a few readily described processes; and (ii) lumped catchment characteristics to represent the spatial heterogeneity of soil properties throughout the catchment. Dynamic simulation of soil and stream water chemistry is achieved by coupling the equilibrium equations with the dynamic mass balance equations for each of the major cations.

Data sources and assumptions

The application of the multiple site approach to Wales involved calibration of MAGIC at each of 102 sites included in the WAWS in 1995 using consistent databases to derive model parameter values and driving variables. The study region covers most of Wales (Fig. 1) but is focussed in the upland areas in the west. The region is underlain by Cambrian, Ordovician and Silurian rocks which are generally resistant to chemical weathering and regarded as acid-sensitive (Hornung et al., 1990). Rainfall, runoff, stream and soil chemistry, land use and atmospheric deposition data for each site were derived from a variety of sources and at different spatial and temporal resolutions.
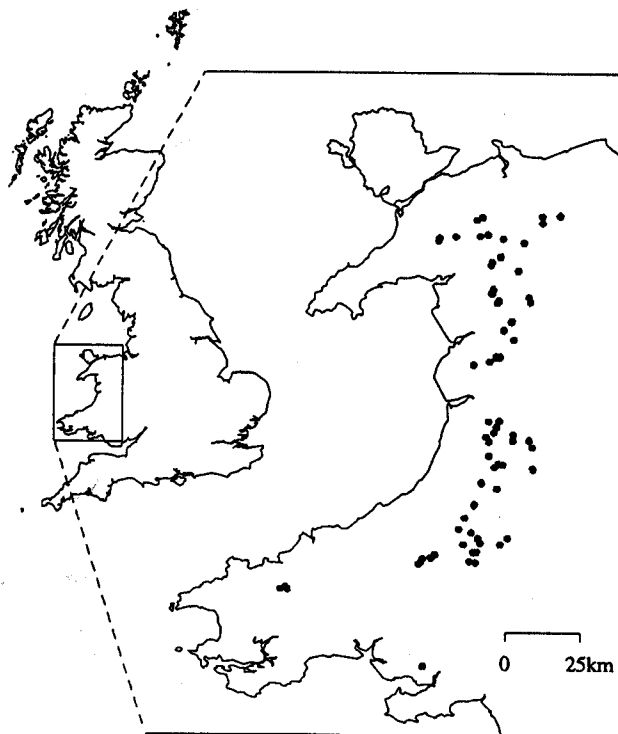

Fig. 1. *The study region and location of the 102 sites in the Welsh Acid Waters Survey.*

DEPOSITION FLUXES

Bulk deposition samples were collected during 1995 from 19 sites across the region, and these data were interpolated to provide estimates of wet deposition on a 20-km grid (Stevens et al., 1997). These values were then modified, using the mean altitude of each grid cell, to account for the variation of rainfall and ion concentrations in rainfall with altitude due to orographic enhancement mechanisms (Fowler et al., 1989). Within MAGIC, chloride (Cl) is treated as conservative and is assumed to be in steady state with respect to input-output flux at each time step. Consequently, at moorland catchments the wet-deposited Cl input flux, derived from the 20-km deposition grid, was compared to the stream output flux at each site and inputs were modified as necessary; the difference was assumed to represent dry and occult deposition. All Cl enhancement was assumed to derive from a marine source, and is added as neutral salt, thereby not affecting the pH of the rainfall.

Sulphate is not strongly adsorbed onto the exchange complex in most upland UK soils which are relatively young and not deeply weathered. Consequently, it was assumed that SO4 is in steady-state at present, with no sulphur (S) adsorption within the catchment systems. If S adsorption has occurred historically in soils within the region, recovery times are likely to be greater than those predicted by the model. No detailed geochemical evidence is available on a regional basis to make any site-specific

assumptions regarding S inputs from weathering, so this source has been disregarded. Some sites, however, may have an internal geological source of S which contributes to natural acidification. The deposition flux is enhanced to represent dry deposition of anthropogenic S to the catchment as SO_2.

The increased deposition flux attributable to the ability of the tree canopy to filter pollutants from the atmosphere results in higher stream output fluxes (Stevens *et al.*, 1997). At forested sites, therefore, the extra deposition required to balance the output fluxes of Cl and SO_4 must represent both the dry deposition assumed for moorland sites as well as the extra flux from the forest filtering effect. For each forested site, therefore, it was assumed that the present-day deposition enhancement at the nearest moorland site would also occur at the forested site irrespective of the existence of the tree canopy, and the canopy filtering effect only provides deposition in excess of that received at the moorland site.

The mass balance method for estimating the dry and occult deposition of Cl and SO_4 is not applicable to nitrogen (N) species due to their strong retention in most terrestrial ecosystems and, as a consequence, steady-state with respect to stream outputs cannot be assumed. Instead, dry deposition of NO_x and NH_x, as monitored during the WAWS and interpolated to provide a 20-km grid for Wales, was used. The values were enhanced to account for forest filter deposition based upon the amount of forestry in each grid cell. N deposition to a moorland catchment that is located in a predominantly forested cell is, therefore, likely to be overestimated and at some forested sites the converse is likely to be true. The values obtained from the dry deposition grid were added to those of the orographically-enhanced wet deposition grid to provide total N deposition.

Non-marine base cation concentrations in bulk deposition are very small and changes through time are not important relative to cation exchange and weathering fluxes in this region.

The cumulative effect of atmospheric deposition since pre-industrial times was modelled on an annual time step and driven by changes in anthropogenic S and N emission over time. The historical trend in wet deposited non-marine SO_4 was assumed to follow the sequence described by the Warren Spring Laboratory (DOE, 1983; 1990). The sequence reflects the pattern of increased industrial growth from the onset of industrialisation in the mid-to-late 1800s. As increases in energy consumption accelerated, emissions of acidic oxides increased. The peak in emissions in the 1970s was followed by international agreements to curtail the emission of non-marine SO_4 in the early 1980s. NO_3 and NH_4 deposition were assumed to have increased since industrialisation in accordance with the estimated NO_x emissions in the UK (DOE, 1983; 1990). All other ions in bulk deposition were assumed to remain constant throughout the historical reconstruction and for future forecasts.

LAND USE

Three processes in MAGIC simulate the impact of afforestation on acidification of soils and surface water: (i) enhanced dry and occult deposition (Mayer and Ulrich, 1977), (ii) ion uptake by growing forests (Miller, 1981), and (iii) decreased water yield concentrating pollutants in surface waters (Neal *et al.*, 1986). Uptake, enhanced deposition and stream discharge were all specified at each time step and were calculated with respect to forest age and the percentage of catchment covered. Of the 102 WAWS study sites, 57 are forested, and the planting year and spatial coverage of each stand at each site were provided by the Forestry Enterprise (pers. comm.). These data include clearfelling and rotation and provide a detailed forest history from implementation of the conifer afforestation strategy in the UK during the 1940s to the present day.

The time sequence of increased deposition due to forest filtering was represented as a linear increase from moorland (zero canopy filtering) to forest at canopy closure (maximum canopy filtering). This general pattern was then modified at each site as a function of the age and cover of each stand at each time step (Jenkins *et al.*, 1997).

Base cation uptake by the trees was specified at each time-step and followed a sequence through time which described the net effect of the growth of the forest (Cosby *et al.*, 1990). Nitrate (NO_3) uptake was described as a catchment net retention calculated simply as the difference between input and output flux at the present day. This percentage was assumed to be constant throughout the model simulation. At forested sites, the input flux included the estimated filter deposition of N. As stream concentrations of ammonium (NH_4) were consistently low in all stream samples, net retention of NH_4 was set to 100%. This extremely simplified representation of N is likely to introduce significant uncertainty into the prediction of future catchment responses in areas with large N deposition. Alternative models incorporate a detailed representation of nitrogen dynamics, e.g. NUCSAM (Groenberg *et al.*, 1995) and SMART 2 (Kros *et al.*, 1995); however, these fail to account for the link, established by a number of empirical studies (eg. Tietema and Beier, 1995) between N leaching and the carbon:nitrogen (C:N) ratio of forest soils. This research suggests that future increases in N deposition will decrease soil C:N, promoting increased net mineralisation. Recent new developments of MAGIC have focussed upon nitrogen dynamics and on the inclusion of C:N as a key factor controlling N leaching (Wright *et al.*, 1998).

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

STREAM OUTPUT FLUXES

Stream samples were collected monthly during the WAWS through 1995 and analysed for all major ions. With the exception of pH, the determinands were log normally distributed at each site; annual geometric means were used for the model calibration procedure (Table 1). Acid neutralising capacity (ANC) was defined as the difference in equivalent sum of base cations less the equivalent sum of strong acid anions. At only 2 sites does observed mean pH fall below 5.0. This reflects the fact that stream sampling was predominantly undertaken during periods of relatively low flow and that low pH (<5.0) is not common in headwater streams in Wales. At 15 sites, 12 forested and 3 moorland, however, acid neutralising capacity (ANC) was <0, indicating that many streams are likely to suffer adverse biological impacts in response to present-day chemistry.

Table 1. Annual geometric stream chemistry for the 102 streams of the 1995 WAWS. All units, except pH, are in μeq l^{-1}.

	Mean	Standard Deviation	Minimum	Maximum
pH	6.18	0.45	4.92	6.90
Ca	116	64	37	321
Mg	98	37	43	227
Na	216	55	146	379
K	6	5	2	38
SO$_4$	113	47	51	294
Cl	240	65	151	427
TON	17	18	2	86

Discharge was not recorded at each site, and was derived from estimates of ET and rainfall. It was assumed that ET ranges from 10% of rainfall for a moorland catchment to 20% for a fully-forested catchment. Runoff was therefore calculated at each site by linearly interpolating ET from 10–20% as a function of the percentage mature forestry cover. Rainfall was derived from a 1-km gridded database compiled by the UK Meteorological Office.

SOILS

Soil depth, cation exchange capacity (CEC), bulk density and exchangeable base cation fractions were determined for each site from a database for England and Wales compiled by the Soil Survey and Land-Use Research Centre. This provides physical and chemical characteristics of typical horizon sequences for soil series in England and Wales. The database was developed from a variety of published and unpublished data sources including the SEISMIC database, (Hallett *et al.*, 1993), maps at various spatial scales, profile descriptions and chemical analyses. Single profile values for each chemical attribute within a series were derived by weighting according to horizon thickness. The spatial component to the data was derived from a 1-km resolution raster version of the National Soil Map that identifies the series composition of each pixel. As the catchments are generally small (mean area is 7 km^2), data for each site were obtained from the pixel in which the stream sampling point was located. Each physical and chemical characteristic was then weighted to account for the spatial contribution of different series to a pixel. In the absence of data describing the relative contribution to streamflow of soil water at different depths and hence of different chemistries, soils were represented in the model in the simplest form, as a single box and all rainfall was assumed to drain through the soil before entering the stream. Peats, stagnopodsols, brown podsols, gleys and rankers provide the dominant soil types of the region. These show a general trend with topography; the peats and stagnopodsols are commonly found at higher altitudes with brown podsols and gleys on the lower slopes and valley bottoms. Rankers were found on the steeper slopes particularly in the Snowdonia area. Minimum, maximum and mean CEC of the soils of the region are 68, 604 and 292 meq kg^{-1}, respectively.

Model calibration procedure

The model calibration at each site was carried out sequentially. First, the concentrations of the stream Cl and SO$_4$ were calibrated by estimating occult and dry deposition of sea salts and gaseous and particulate S compounds under the assumption that these ions are in approximately steady state with respect to atmospheric inputs. Next, the NO$_3$ and NH$_4$ concentrations were calibrated by adjusting first-order uptake functions to match observed surface water concentrations. Finally, the base cation weathering rates and soil cation exchange coefficients were calibrated to observed soil and streamwater base cation data (target variables) using an optimisation procedure (Jenkins and Cosby, 1989). The target variables consist of surface water concentrations of calcium (Ca), magnesium (Mg), sodium (Na), potassium (K) and soil exchangeable fractions of Ca, Mg, Na and K, and comprise a vector of measured values which must all be reproduced by the model if a calibration is to be considered successful.

Soil and surface water physico-chemical characteristics measured in the field (for example soil depth, bulk density, porosity, CEC, etc.) are considered 'fixed' in the model, and the measurements are used directly during the calibration procedure. Base cation weathering rates and selectivity coefficients for the soils are adjustable model parameters to be optimised in the calibration procedure. The calibrations are performed on simulations run from 1855 to 1995. After each historical simulation, the present day model variables are compared to present day observations, the adjustable parameters 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.

Results

COMPARISON OF OBSERVED AND SIMULATED DATA

A close match between observed and simulated stream chemistry for 1995 indicates an acceptable model calibration (Fig. 2). Eight of the 102 sites failed to calibrate and were ultimately discarded from the analysis. Two factors accounted for these calibration failures. At 4 sites, the deposition flux of base cations was too high relative to the observed stream flux and despite zero weathering, stream base cation concentrations could not be matched. If bulk deposition samples provide an accurate record of deposition flux, this imbalance may reflect uncertainty associated with stream chemistry samples taken at monthly frequency and used to quantify the annual flux. The remaining 4 sites that failed to calibrate were forested and characterised by significantly lower stream concentrations of Cl and/or SO_4 than for nearby moorlands. Given the regional assumptions used in the model calibration procedure, a match between input and output fluxes could be achieved only by incorporating anion retention into the model, and there is no consistent basis on which to do this across the entire region.

PREDICTED FUTURE RESPONSE

The suite of 94 calibrated sites comprising the regional model for Wales was used to make predictions to the year 2045 under the most recent international agreement to reduce emissions, the Second S Protocol. Under this protocol, relative to the year 1980, the UK will reduce national S emissions by about 70% by the year 2005 and about 80% by the year 2010. The emission reductions under this agreement were converted to a regional deposition scenario at 20-km grid scale for the UK using the Hull Acid Rain Model (HARM; Metcalfe and Whyatt, 1995). Given the observed link between forestry and surface water acidification, a future forest management scenario has been derived for each forested site, bearing in mind that future atmospheric deposition reductions will be superimposed on land-use changes—in particular deforestation and potentially, second rotation planting. Each stand is felled at 50 years age and replanted immediately such that the forest area remains constant and net uptake, water yield and filter deposition assumptions are repeated. No changes in land use are assumed at the moorland sites.

The predicted response within 50 years, relative to the present day, is generally a small recovery in surface water ANC across the whole region (Fig. 3). The more acidified, low ANC sites are generally located in the central and northern parts of the region (Fig. 3). That no marked spa-
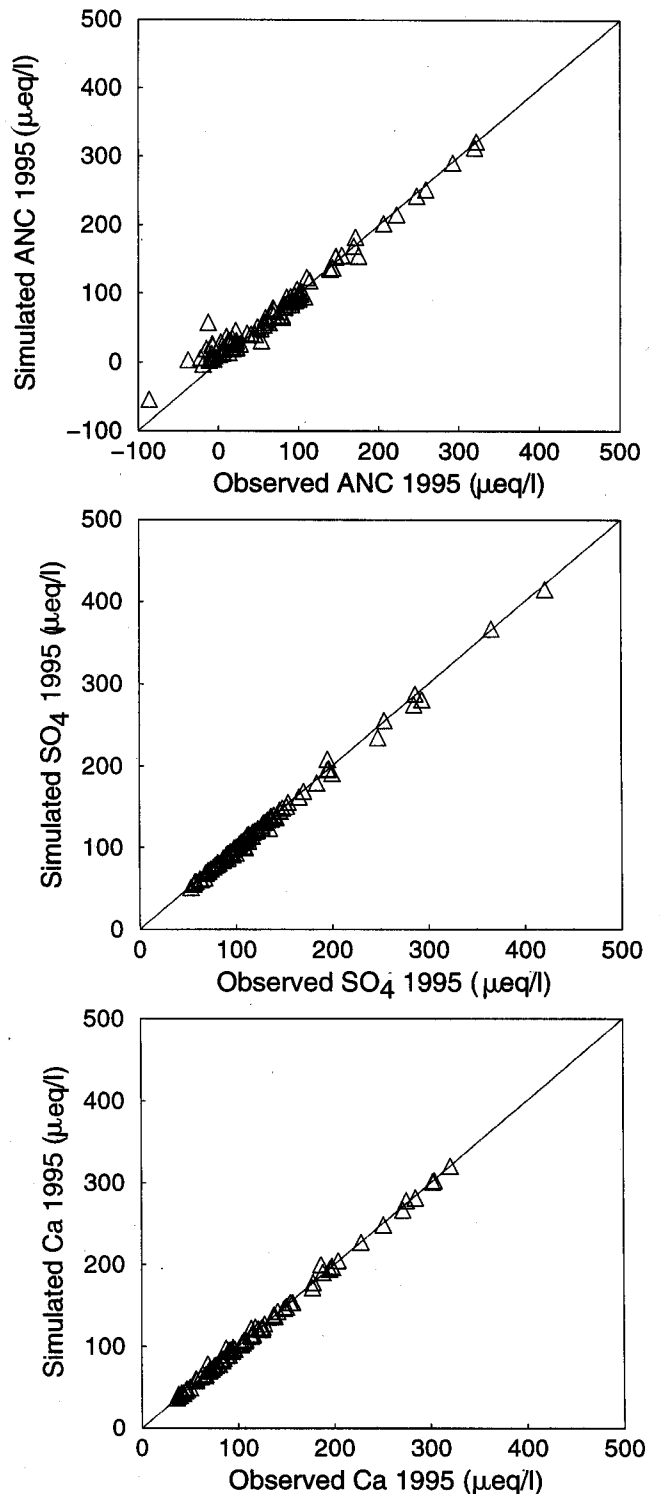

Fig. 2. *Observed and simulated present-day streamwater ANC (a), SO₄ (b) and Ca (c) for the 96 sites comprising the multiple-site regional model.*

tial pattern can be detected in predicted ANC probably reflects the generally similarly predicted decrease in deposition across the region. Indeed, no correlation is apparent for the region as a whole between the magnitude of ANC recovery and present-day acidification status.

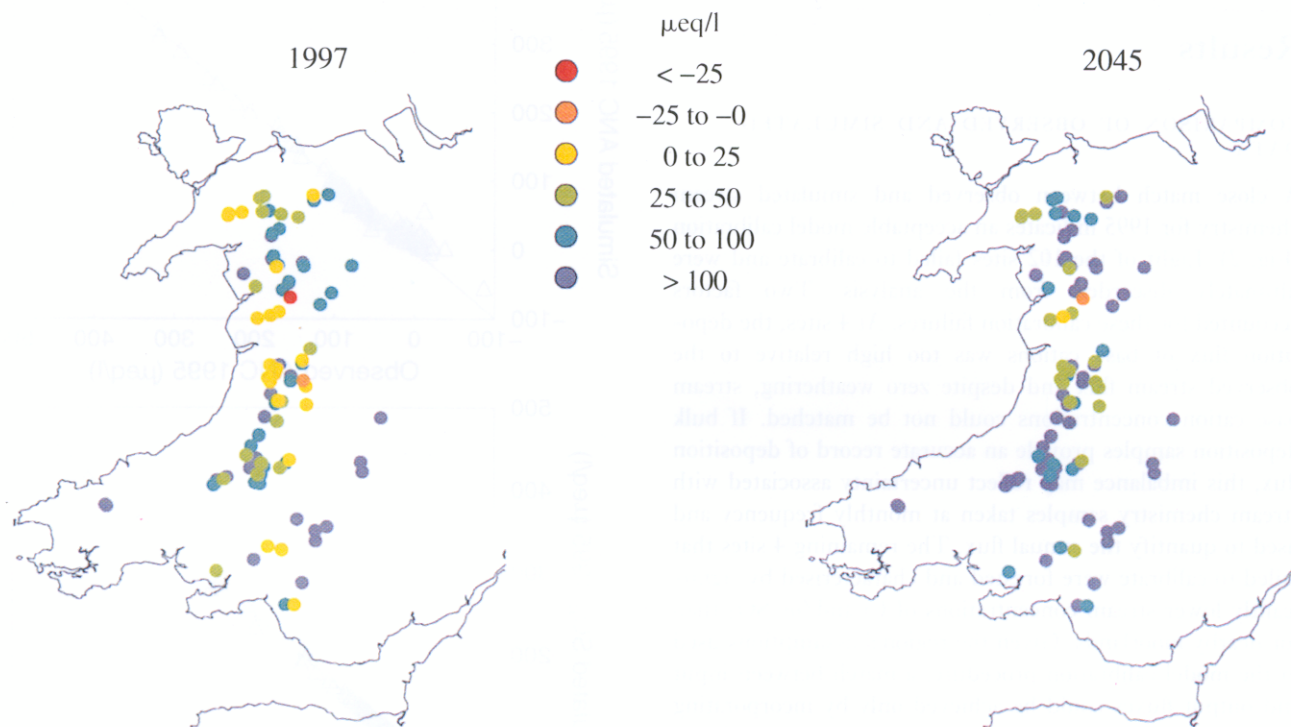## ANC Recovery: Assessment of Second Sulphur Protocol

Fig. 3. *Simulated 1997 ANC and predicted 2045 streamwater ANC in response to the emission reductions agreed under the Second S Protocol.*

Variation in the extent and age of forestry across the region may mask a stronger spatial pattern. A clear difference is predicted between recovery at moorland and forested sites. Mean ANC recovery by 2045 at moorland sites is 20.9 μeq l^{-1} in comparison with 10.6 μeq l^{-1} at forested sites. In addition, all moorland sites predict an increase in ANC, whereas, despite the emission reductions, 11 of the forested sites undergo a further drop in ANC. These ANC decreases are, however, less than 8 μeq l^{-1}. At 4 of the forested sites ANC is predicted to remain below zero. During the forecast period, forested sites will undergo cycles of transient recovery as trees are felled, followed by acidification as stands grow and uptake and deposition increase. Furthermore, this pattern is superimposed upon a number of stands of different ages within the same catchment. The predicted response at forested sites is therefore complex and needs to be interpreted at the individual site scale. Despite the predicted recovery in surface water ANC, soil base saturation will generally decrease slightly over the next 50 years with a mean decrease for the region of –0.9 percentage points.

COMPARISON WITH THE MONTE CARLO APPROACH

An alternative regional modelling approach utilising the same basic data from the WAWS, but invoking Monte-Carlo techniques and using frequency distributions to describe the physical and chemical characteristics of the region, is detailed by Sefton and Jenkins (1998). Briefly, this approach selects model input parameters randomly from the defined regional frequency distributions and retains those combinations of parameters which produce simulations that fall within observed streamwater chemistry ranges for the region. The model is run many thousands of times to accumulate a sufficient number of acceptable parameter sets to match the frequency distribution of the present-day observed streamwater chemistry. This approach does not require spatially-distributed data, but instead relies upon the available data adequately to describe the whole range of physico-chemical environments which occur in the region. The resulting model cannot provide spatially-distributed predictions of hydro-chemical changes in response to changes in acidic deposition and cannot incorporate land-use change explicitly, but has the advantage of providing statistically-relevant out-

puts which are potentially useful in terms of economic assessment of emission reduction policies.

Predictions for future recovery of the region as a whole from both regional modelling approaches are very similar (Fig. 4). Predicted ANC, SO_4 and Ca for 2030, expressed as cumulative frequencies, reveal a close fit between the multiple-site and Monte-Carlo procedures. Both approaches predict that ANC will not recover above zero across the whole region. The slightly more irregular nature of the multiple-site cumulative frequency curves relative to the Monte-Carlo reflects the variation in predicted response due to the explicit incorporation of forest dynamics and change scenarios.

Despite the broad similarities in predictions, however, some discrepancies are apparent. For example, the Monte-Carlo results predict a higher percentage of the region with ANC <0 in 2030. Also, in contrast to the Monte-Carlo application in which ANC recovery was predicted to be greatest at the most acidic sites, no such correlation was apparent with the multiple-site approach. These differences may be partially explained by the use of a mean value of predicted reduction in S deposition, derived from the HARM model for the region as a whole, in the Monte-Carlo approach. In comparison, the multiple-site application utilised the 20-km HARM deposition grid and, therefore, incorporated spatial variability in future deposition reductions. In addition, the Monte-Carlo approach excluded forestry dynamics and land-use scenarios which introduce large variations in response between sites. Finally, the two methods used different sources of soils
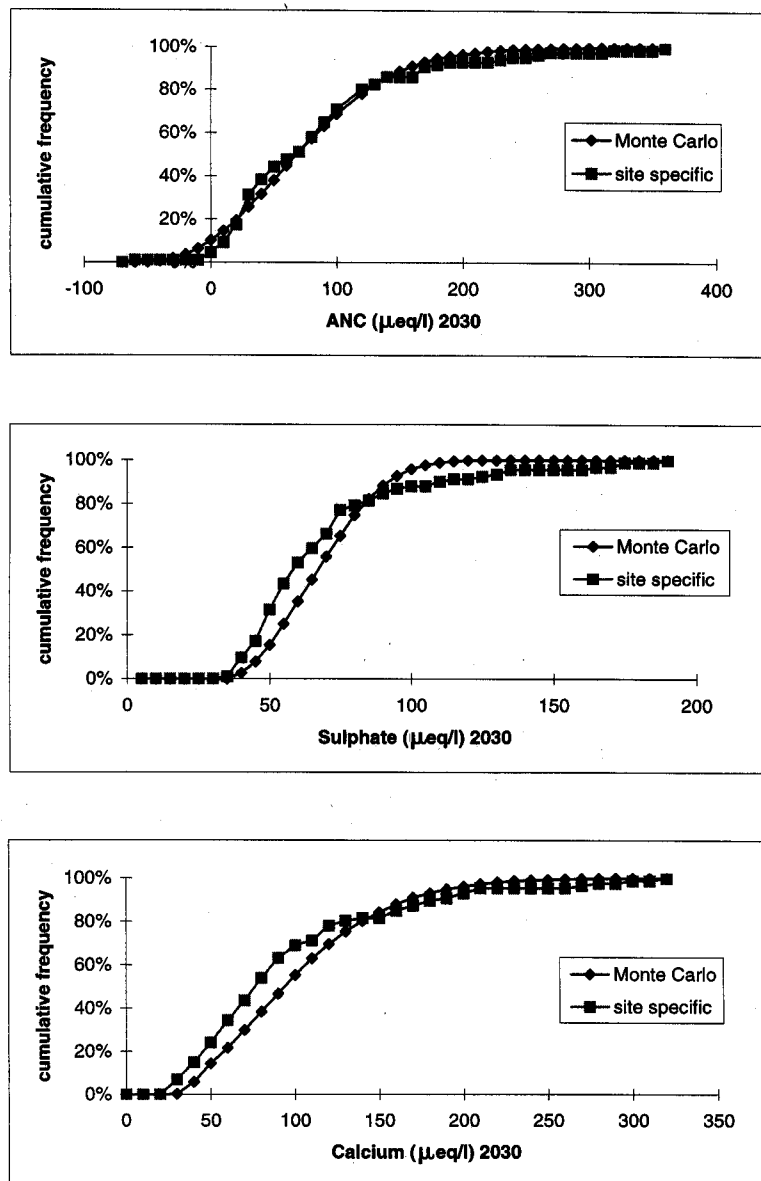

Fig. 4. *Comparison of predicted 2030 streamwater ANC (a), SO4 (b) and Ca (c) regional frequency distributions from multiple-site and Monte-Carlo procedures.*

data and the range of values for soil parameters chosen in the Monte-Carlo approach did not match the distribution of values used in the multiple-site application.

Conclusions

The MAGIC model has been applied to 96 catchments in Wales using consistent data and calibration procedures to produce a regional representation which closely matches present-day observed water chemistry.

Prediction of future chemistry response under the most recently agreed reduction in S emissions, the Second S Protocol, indicates a general rise in ANC throughout the region. The emission reductions, however, are insufficient to promote recovery of ANC >0 at all sites. In particular, the decreased deposition would not reverse acidification at forested sites significantly; indeed at 11 sites a further drop in ANC by 2045 is predicted.

Interpretation of these results must account for potential bias in the base data, particularly the WAWS surface water chemistry. Two uncertainties are important. Firstly, of the 96 sites calibrated, only 15 have a mean observed ANC <0, and this may not be representative of the region as a whole. More detailed spatial sampling would determine the true extent of acidified waters in the region. Secondly, it is likely that present-day observed mean stream ANC is overestimated because the monthly sampling regime may not capture the acidic pulses observed during high winter flows. These pulses may cause significant effects on freshwater biota, whilst the mean annual ANC derived from monthly samples indicates no significant acidification. Again, higher temporal resolution data would elucidate the true flow-weighted mean chemistry.

Prediction of future recovery throughout the region using both multiple-site and Monte-Carlo approaches is similar. This is perhaps not surprising given that the same surface water chemistry data were used for the model calibrations. The Monte-Carlo methodology enables impacts at streams not encompassed by the survey to be inferred by including model parameter sets which may not have been encountered at the individual sites. The consistency in the two approaches, therefore, indicates the robustness of the model and the available databases and implies that the multiple-site methodology captures the regional characteristics. This enables statistics relating to the future chemical behaviour to be drawn for the region as a whole using both methods.

Conversely, the Monte-Carlo approach does not account for the interrelationships between site characteristics and may derive combinations that are unlikely to be observed. In addition, impacts cannot be quantified for a given location within the region, and the dynamics associated with plantation forestry cannot be incorporated explicitly. The key strengths of the multiple-site approach is that impacts are assessed on a site-specific basis and so enable forest growth to be included thereby enabling the spatial pattern of recovery in response to the combined impacts of reduction in acidic deposition and land-use change to be assessed for the whole region.

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