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Regional Modelling of Acidification and Predicting Reversibility

by

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Executive summary

Development and application of mathematical simulation models has enabled an assessment of the influence of commercial softwood afforestation on stream chemistry and an assessment of episodic stream chemistry behaviour in response to long term changes in annual mean chemistry.

The forest model incorporates increased dry depositon to the forests as the canopy develops, uptake of ions by the growing forest and increased evapotranspiration as the forest matures. The model has been applied to two upland Scottish sites to compare the relative effects of acid deposition and afforestation on soil and surface water acidification and to assess the likely effects of reductions in future deposition combined with future forestry management practices. The results indicate that afforestation has exacerbated surface water acidification in areas receiving high levels of acidic deposition. This is not predicted in pristine areas even though the nutrient demands of forest growth have caused significant soil acidification.

Two methods have been developed to model short term responses over long time periods. A deterministic statistical approach involves fitting distributions around long term means and a mixing approach utilises the MAGIC model in a two-layer framework. Both methods indicate that the most acute acid episodes will be moderates if atmospheric deposition is reduced by some 60% in the future.

1. Summary of Research

(i) OBJECTIVES

The objectives of the research are many and full details are not given here but can be found in the early project documents. In summary, the objectives of the programme are to develop mathematical models of catchment acidification processes and apply them to several key sites in the UK; to extend the modelling to a regional scale; to link stream chemistry models to an air pollution model; to link models to biological models; and, to investigate the effects of different emission reduction strategies on stream water quality.

More recently, the focus of acidification research has changed towards the concept of defining critical loads for ecosystems. This will enable emission control strategy to be negotiated on a national and international scale. As a consequence, the objectives of this research programme have been extended to address important issues affecting the determination of critical loads for UK freshwater, in particular, the influence of commercial softwood afforestation on stream chemistry and the importance of short term episodic changes associated with shifts in long term mean chemistry.

The application of MAGIC to key sites in Scotland and Wales, together with details of the regional model development and applications in those areas, was detailed in interim report number one. Similarly, extensive development has been undertaken in the linking of biological models to stream chemistry models and this, together with details of validation and sensititivity testing of the MAGIC model, was detailed in interim report number two. This report looks in detail at the way in which commercial afforestation affects stream chemistry in the UK uplands and attempts to quantify the 'acid' contributions from both afforestation and atmospheric deposition. This study has involved considerable refinement and re-structuring of the MAGIC model has been accomplished. Substantial work has also been completed on the link between the long term changes in mean chemistry, as predicted by MAGIC, and the associated changes in episodic chemistry. Two schemes have been developed for linking these time scales.

(ii) FORESTRY EFFECTS

A conceptual model of the combined effects of afforestation and acidic deposition has been applied to two forested sites in central Scotland. Refinements are made to the model inputs specifically to include: increased dry deposition to the forests (in excess of the dry deposition expected for moorland sites) as the forest canopy develops; uptake of ions by the growing forests; and increased evapotranspiration (and thus decreased water yield) as the forests mature. The model is calibrated using a fuzzy optimisation technique which incorporates uncertainty in target variables (stream base cation concentrations and soil exchangeable bases) and uncertainty in selecting values for fixed and adjustable parameters which describe the physiochemical characteristics of the catchments. Simulated present day stream and soil chemistry closely match observed values at both sites. The calibrated models indicate that while the patterns of acidification in the two catchments are broadly similar, some differences do exist between the sites in the responses of the soils to acidic deposition and afforestation. It is concluded that the calibrated models provide a tool for; a) comparison of the relative effects of deposition and afforestation on soil and surface water acidification; and b) assessment of the likely effects of reductions in future deposition combined with future forestry management practices.

The model is further used to perform a series of simulation experiments to assess the relative effects of afforestation and acidic deposition on soil and surface water chemistry. The experiments compare and contrast: a) the simulated historical effects of increased acidic deposition and forest growth, both individually and in combination; and b) the simulated future effects of various levels of reduction of deposition in combination with the forestry strategies of harvesting with and without replanting. Results indicate that historical acidification of surface waters in areas receiving high levels of acidic deposition has been exacerbated by afforestation practices. Afforestation in the absence of acidic deposition, however, has had a lesser effect on surface water acidification even though the nutrient demands of forest growth have caused significant soil acidification. Comparisons of future forest management strategies in conjunction with likely deposition reductions indicate that, in sensitive areas, replanting of a felled forest without treatment of the soil by addition of base cations, should not be undertaken even if significant deposition reductions are realised.

(iii) SHORT TERM RESPONSES

A hybrid deterministic statistical approach has been developed for modelling extremes of water quality in catchments subjected to long-term acidification. The approach is based on the MAGIC model describing long term variations in mean chemistry. Superimposed on these mean projections are distributions providing information on the extremes of water quality. The distributions are fitted to catchment data using maximum likelihood techniques. The approach is general and can be applied to the prediction of other water quality variables where samples can be regarded as belonging to a parametric probability distribution. A simple implementation of the approach using chemical data and a calibrated deterministic model for the Allt a Mharcaidh is used as an illustrative method.

An alternative approach to linking short term behaviour has also been developed using mixing concepts, whereby the flow is assumed to be a mix of water from two distinct sources. Acidic water from the upper soil horizons and well buffered water from deeper 'groundwater' sources are used to represent the two endmembers and a chemical hydrograph separation technique is used to estimate the mean proportions of mix. The MAGIC model is calibrated in its two layer mode to these two endmember chemistries. The model produces a good fit to observed present day stream, soil and baseflow chemistry. Future predictions of changes in endmember chemistry are made so as to enable future episodic response to be modelled. Under a 60% sulphate deposition scenario the model predicts a lowering of hydrogen ion concentrations associated with high flows and even a marginal recovery in baseflow pH.

(iv) REVERSIBILITY OF ACIDIFICATION

In Sections 2 and 3, examples of reversibility in stream chemistry have been detailed. At the afforested Scottish sites the modelling results indicate that combined with deposition reduction of the order of 70%, a second generation forest planted on a recently felled site would not cause significantly greater acidification in the stream. Soil acidification, on the other hand, would continue to deteriorate.

To enable a significant recovery in these areas, which constitute a significant proportion of acid vulnerable sites in the UK, forests should not be replanted without considering the application of soil dressings such as limestone. Better still, second generation planting should not be carried out. In terms of critical load calculation, this work shows how land use change can affect the susceptibility of a site. Felling the forest in conjunction with a decrease in atmospheric deposition significantly improves stream acidity and this must be considered when ciritical loads are calculated for these sites.

The short term models demonstrate the degree to which a 60% decrease in deposition will mitigate highly acid, high flow events. It is encouraging that reductions of this level will decrease the peaks of acid pulses which are especially damaging to young fish. These modelling techniques offer an important step forward towards incorporating short term or episodic reversibility into the critical load concept.

2. Modelling stream acidification in afforested catchments

2.1 LONG TERM RECONSTRUCTIONS AT TWO SITES IN CENTRAL SCOTLAND

INTRODUCTION

Lakes and streams in large areas of eastern North America and northern Europe have become increasingly acidified during the past several decades (e.g., Likens et al., 1979; Wright, 1983; Haines, 1986). The principal cause of this acidification has been attributed to atmospheric deposition of sulphur (Likens, 1976; Wright and Henriksen, 1979; Overrein et al., 1980; Haines, 1986), although land use changes on the acidic soils which may dominate sensitive regions have also been held partly or wholly responsible (Krug and Frink, 1983; Rosenquist, 1980). In the U.K., a determined land management strategy of conifer afforestation, since the 1940s, has also been held responsible for surface water acidification as a result of proton fluxes connected with plant uptake and mineralisation of organic matter (Nilsson, 1985). Indeed, many studies have reported that compared with moorland sites, conifer afforestation enhances the acidity of drainage waters (Harriman and Morrison, 1982; Stoner et al., 1984; Nilsson et al., 1982).

Three mechanisms may increase the acidity of water draining forested catchments; increased water losses through evapotranspiration thereby concentrating dissolved pollutants entering the stream; uptake of base cations by the growing forest; and the increased ability of the forest canopy to scavenge acidic material from the atmosphere (Law, 1956; Calder and Newson, 1979; Miller, 1984; Grennfelt and Hultberg, 1986). Increased scavenging includes contributions from both wet and dry deposition (Fowler, 1984). All of these factors are interactive and, solely on the basis of catchment input-output budgets, it is difficult to discriminate among the effects of the deposition, leaching, interception and vegetation uptake processes.

A modelling approach to examine the relative importance of deposition and afforestation on surface water acidification has, therefore, been adopted. The model used is MAGIC (Model of Acidification of Groundwater in Catchments), an intermediate-complexity process-oriented model for soil and water acidification. To enable the model to be used in a predictive mode for assessing the relative acidifying effects of forest growth and atmospheric acidic deposition, it is first necessary to calibrate the model to forested sites. The model was applied to two catchments, Chon and Kelty, in the Loch Ard Forest area of central Scotland. These catchments have been subjected to similar deposition and land management histories and have similar (but not identical) bedrock geology. Tree species and soil types on the catchments are, however, different. The waters draining both of these catchments are acidified to differing degrees. The historical development of acidification at the two sites, as simulated by the model, is used to interpret the relative effects of deposition and afforestation on present day streamwater chemistry.

Previous applications of MAGIC to assess forest effects identified canopy scavenging and increased dry deposition as important factors causing reductions in the pH of surface water (Neal et al., 1986; Whitehead et al., 1988a,b). Those studies, however, were preliminary applications of the model to afforested sites; they only included increased forest filtering and a simple representation of increased evapotranspiration effects and made no attempt to include uptake of ions from the soil by the vegetation. Here a revised and more thorough application uses a refined version of the model with time varying inputs reflecting the dynamic effects of afforestation and forest growth. It incorporates cation and anion uptake by the vegetation, pre-afforestation dry deposition inputs, enhanced deposition input (both wet and dry) through canopy filtering processes and a continuously variable water yield factor as evapotranspiration increases in response to forest growth.

The structure, calibration procedure and output of the refined model are presented in this paper for the Chon and Kelty catchments. In a companion paper (Jenkins <u>et</u> <u>al.</u>, this volume), the model calibrated for the Chon catchment is used to perform a series of simulation experiments to assess the relative effects of afforestation and acidic deposition on soil and surface water chemistry. Those experiments compare and contrast: a) the simulated historical effects of increased acidic deposition and forest growth both individually and in combination; and b) the simulated future effects of various levels of deposition reduction in combination with the forestry strategies of harvesting with and without replanting.

STUDY AREA

As part of the Surface Water Acidification Programme (Mason and Seip, 1985) integrated monitoring of hydrology, chemistry and biology is being undertaken in two forested catchments, Loch Chon (1.87 km^2) and Kelty Water (1.32 km^2), in the Queen Elizabeth Forest Park, Loch Ard (Figure 1). This area is approximately 40 km north of Glasgow and is subject to high levels of anthropogenic deposition (ca. 20 kg ha^{-1} yr^{-1} sulphate S). Rainfall volume in the area varies from approximately 1.8 to 2.4 m yr^{-1}. The entire area, including that of the two catchments, has undergone extensive conifer afforestation with planting initiated in 1950. The catchment of Kelty Water was planted with Sitka spruce (<u>Picea sitkensis</u>) while the catchment of Loch Chon was planted with Norway Spruce (<u>Picea abies</u>). The geology of both catchments is mainly Dalradian metamorphic-igneous rocks comprised of fine grained slates, phyllites and mica-schists (Anderson, 1947). This is overlain by glacial till deposits derived from local rocks. Sampling at Loch Chon and Kelty Water was initiated in the autumn of 1986 (Miller <u>et al.</u>, in press). We use data for calendar year 1987 in this study.

Field sampling strategies and laboratory analyses of the precipitation and streamwater samples are described by Miller <u>et al.</u> (in press) and Jenkins <u>et al.</u> (1988). Bulk deposition and precipitation volumes were collected bi-weekly at both sites in open, nipher-shielded, funnel guages situated 6 m above the ground in open areas of the forests. The volume weighted mean bulk precipitation chemistries in 1987 are similar for both catchments (Table 1). Streamwater was also collected bi-weekly at both sites using flow-proportional samplers. Despite similar bedrock characteristics and deposition inputs to the two catchments, the volume weighted mean streamwater chemistry for both sites are different in some respects (Table 2). Kelty Water has higher concentrations of aluminum, sulphate, nitrate, and organic ions, and lower pH and calcium concentrations than does Loch Chon. Kelty Water is no longer capable of sustaining a viable fish population but Loch Chon maintains a reduced fish population.

Soil physical and chemical parameters in the two catchments were determined by a detailed sampling and analysis strategy at the outset of the project (Hudson and Hipkin, 1986; Henderson and Campbell, 1986). The soils in both catchments belong to the Strichen association and consist of peaty gleys at Kelty and humus iron podsols at Chon. Soil parameters were measured for individual horizons from a number of soil pits within the catchments. Individual horizon values were weighted using the depth of each horizon to give a vertically aggregated value for each soil type. These vertically aggregated values were then weighted by percentage area of each soil type within the catchment to give weighted mean values of the soil physical and chemical characteristics for use in the model (Table 3).

MODELLING TECHNIQUES

THE MAGIC MODEL

The MAGIC model is a lumped parameter, long-term simulation model of soil and surface water quality (Cosby et al., 1985a, b). It consists of: (i) a soil-soil solution chemical equilibria section in which the concentrations of major ions are assumed governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution and precipitation of aluminium, speciation of organic acids, and dissolution and speciation of carbonic acid; and (ii) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff (Figure 2). At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time due to changes in atmospheric deposition and biological uptake/release, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry.

Sulphate adsorption is treated in the model by a Langmuir isotherm. A detailed investigation of the sulphate subsection of the model is given by Cosby et al. (1986a). Aluminium dissolution and precipitation is assumed to be controlled by equilibrium with a solid phase of $Al(OH)_3$. Speciation of aluminium and inorganic carbon is computed from known equilibrium equations. Cation exchange is treated using equilibrium (Gaines-Thomas) exchange equations. Weathering rates are assumed to be constant with time in the model. Organic acids are modelled as diprotic acids using equilibrium expressions for dissociation based on the pK values of the acid. Given a description of the historical deposition and afforestation effects at a site, the model equations are solved numerically to give long term reconstructions of surface water chemistry.

APPLICATION TO CHON AND KELTY

Until afforestation in 1950 both sites were under moorland vegetation and a water yield of 90% was assumed. This figure is consistent with other model applications to moorland sites in Scotland (Jenkins and Cosby, 1989). Following planting in 1950 a 15 year growth period is assumed before canopy closure, during which time evapotranspiration increases linearly with age of the forest. At the point of canopy closure, evapotranspiration was assumed to be at its maximum and a water yield of 75% was chosen. The net result of this sequence on annual streamflow volumes is shown in Figure 3(a).

Historical loadings to the catchments for use in the simulations were derived in two stages. First, the historical loadings in the absence of growing forests and in the absence of anthropogenic acidic deposition were estimated for both sites for both wet and dry deposition. Second, the moorland wet and dry loadings were modified subsequent to 1950 to reflect the effects of afforestation.

Current (1987) mean annual precipitation input is 2.3 m at both sites; the mean composition of the bulk rainfall is shown in Table 1. These measurements are made in forest clearings with bulk collectors and are taken to be approximately equal to the wet deposition loading the in absence of enhanced scavenging by the forest canopy. These wet loadings can be partitioned into natural (sea salt) and anthropogenic components. Wet loadings for sulphate, nitrate and ammonium in excess of sea salt contributions (anthropogenic components) were assumed to have increased following the sequence of sulphur emissions described by the Warren Springs Laboratory (1983, 1987) up to 1973, with a modification based on sulphur emission data from 1973 to 1987 (Warren Springs Laboratory, unpublished data). The resulting trajectory for wet loading of anthropogenic components in the absence of a forest canopy is shown in figure 3(b). The historical wet loadings of sea salt in the absence of a forest canopy are assumed to be constant.

Particulate or occult (dry) deposition loadings for both sea salt and anthropogenic components were simulated by multiplying the wet loadings by "deposition factors" to obtain total (wet plus dry) loadings: the deposition factors for sea salt are based on occult sea salt deposition calculations for two nearby moorland sites in the region (Jenkins and Cosby, 1989). These factors were derived by calculating the additional sea salt necessary to give a conservative mass balance for chloride, given the measured wet atmospheric deposition and stream export for those moorland sites. The sea-salt deposition factors used in the simulations prior to afforestation in 1950 were 1.10 for Chon and 1.01 for Kelty. A deposition factor of 1.24 for anthropogenic components was used for both sites prior to 1950 to represent dry deposition of particulate and gaseoues sulphur to moorland sites.

This factor was derived by calculating the additional sulphate necessary to give a conservative mass balance for sulphate, given the measured wet atmospheric deposition and stream export for nearby moorland sites (Jenkins and Cosby, 1989; the soils at the sites had low sulphate adsorption capacities as do the soils at Chon and Kelty). Because the deposition factors are multipliers for wet deposition, the effective dry deposition of anthropogenic components increases along the same trajectory as the wet deposition until 1950 (Figure 3a); the effective dry deposition of sea salt components remains constant.

The deposition factors for sea salt and anthropogenic components were increased after 1950, to represent the increases in both wet and dry loadings resulting from the increased scavenging by the forest canopies in Chon and Kelty. For the 15-year tree growth period between planting and canopy closure, the forest filtering effect is assumed to produce a linear increase in total deposition. The assumed pattern of increase in the deposition factors due to forest effects is shown in Figure 3(c). Deposition factors for sea salt components increased to 1.3 for Chon and 1.1 for Kelty. The magnitudes of the increases were calculated to give simulated streamwater chloride concentrations equal to observed chloride concentrations in 1987 with forests present at both sites. Throughfall and stemflow measurements from the two sites indicate that the different tree species in each catchment have different characteristics of pollutant scavenging and canopy leaching, especially with respect to sulphate. Kelty shows consistently higher sulphate concentrations in throughfall and stemflow. The deposition factor for anthropogenic components at Kelty was increased to 1.35 after afforestation while that for Chon was maintained at 1.24. The final deposition factors for the anthropogenic components resulted in good agreement between simulated and observed sulphate for the two sites (Table 2).

The estimation of net nutrient uptake by vegetation is problematic given the difficulties of assessing processes such as crown leaching and below-ground turnover (Miller, 1984). A general pattern of net uptake may, however, be estimated. Miller (1981) showed that, in even-aged forests, the greatest demand for soil nutrients occurs early in the life of the crop, during crown development and the rapid build-up of foliar biomass. The demand for soil nutrients reaches a maximum well before the time of maximum stem growth. As the forest matures, nutrients progressively accumulate on the forest floor as organic litter, at a rate broadly proportional to that of tree growth rate (Miller and Miller, 1976). The nutritional requirements of maturing trees may be much larger than that of younger trees but a larger component is met through recycling of nutrients in litter (Miller, 1981). Older trees recycle a greater proportion of their annual uptake through the litter, and there is an increasing dependence upon nutrient cycling within the organic horizons (Khanna and Ulrich, 1984). The resultant decrease in rates of uptake from the soil, combined with efficient capture of atmospheric nutrients and rapid cycling in the litter, results in a decline in net nutrient demand from the soil as the forest matures. This relative pattern of net nutrient uptake from the soil (Figure 3d) is used in simulations of forest growth. The simulated net uptakes of calcium, magnesium, sodium, potassium and sulphate in the simulations are scaled to the shape in Figure 3d using maximum uptake rates estimated from biomass concentrations of the ions and biomass accumulation rates (Miller and Miller, 1976).

In Scottish forest soils over three quarters of the nitrogen uptake by trees is in the form of ammonium (Williams et al., 1979) and therefore trees accumulate an excess of cations over anions balanced by a reverse flux of hydrogen from the roots to the soil. This nitrogen accumulation thus results in a net acidification of soils by forest growth (Brand et al., 1986) and, although rates of acidification vary with productivity of the stands, the pattern of acidification over time remains the same (Nilsson et al., 1982). In the simulations, uptake of nitrogen species (NO_3^- and NH_4^+) from the soils is modelled as a first order process. The first order rate constant for each catchment is selected such that simulated streamwater concentrations of nitrate and ammonium match observed concentrations.

CALIBRATION OF THE MODEL

The calibrations proceeded in a sequential manner. First, the concentrations of chloride and sulphate were calibrated by adjusting occult and dry deposition of sea salts and gaseous/particulate sulphur compounds under the assumptions outlined in the previous section. Base cation concentrations were then calibrated using an optimization procedure based on the

Rosenbrock (1960) algorithm (described next). Finally, the organic acid concentrations in the streams were calibrated to match the organic anionic charges observed.

The base cation calibration involved fitting the results of long-term model simulations to currently observed water and soil base cation data (surface water concentrations of calcium, magnesium, sodium, and potassium; and soil exchangeable fractions of calcium, magnesium, sodium and potassium). These "target variables" thus comprise a vector of measured values all of which must be reproduced by the model if a calibration is to be successful. The use of multiple, simultaneous targets in an optimization procedure provides robust constraints on model calibration (Cosby et al. 1986b).

Those physico-chemical soil and surface water characteristics measured in the field, are considered "fixed" parameters in the model (Table 4). These measurements are, however, subject to error and so ranges were chosen to represent this error and the spatial heterogeneity within the catchment. A range of uncertainty for each observed, weighted-mean soil parameter was defined using the maximum and minimum vertically-aggregated single-pit values for each parameter. These estimated uncertainties in the observed values (Table 4) were used in the calibration procedure. For those fixed parameters for which no direct measurements were available (i.e., CO_2 partial pressure and organic acid content), single values with no range of uncertainty were assumed.

Base cation weathering rates and base cation exchange selectivity coefficients for the soils are not directly measurable and were used as "adjustable" model parameters to be optimized in the calibration procedure. The calibrations were performed on simulations run from 1847 to 1987. After each historical simulation, the model variables in 1987 were compared with observations in 1987; the adjustable parameters were modified as necessary to improve the fit; the historical simulation was re-run; the procedure was repeated until no further improvement in the fit was achieved.

Because the measurements of the fixed parameters and the target variables are subject to errors, a "fuzzy" optimization procedure was implemented for calibrating the models. The fuzzy optimization procedure consisted of multiple calibrations of each model structure, using perturbations of the values of the fixed parameters and estimated uncertainties of the target variables. The sizes of the perturbations of the fixed parameters were based on known measurement errors or spatial variability of the parameters. The uncertainties in the target variables were estimated as the measurment errors of the variables (5 ueq/L or 10%, whichever was the larger, for concentrations of surface water variables; 0.5% for soil base saturation variables).

Each of the multiple calibrations began with: i) a random selection of perturbed values of the fixed parameters; ii) a random selection of the starting values of the adjustable parameters; and iii) specification of uncertainty in the target variables. The adjustable parameters were then optimized using the Rosenbrock algorithm to achieve a minimum error fit to the target variables. The optimization algorithm was stopped and the calibration considered complete when the simulated values of all target variables were within the pre-specified uncertainty limits for the observations. This procedure was undertaken ten times for each site. The final calibrated model for each site consists of the mean parameter and variable values of at least 8 successful calibrations.

Using the fuzzy optimization based on multiple calibrations, uncertainty bands for the model simulations can be presented as maximum and minimum values for output variables in any year derived from the group of successful calibrations. These uncertainty bands encompass the range of variable values which were simulated, given the specified uncertainty in the fixed parameter values and measured target variables. When examining simulation results, the maximum and minimum values are both plotted through time. The "true" model calibration is taken to fall between these lines. When comparing simulation results from two model structures, the overlap of the uncertainty bands provides a measure of the degree to which the structures behave similarly.

ORGANIC ANIONS IN THE MODEL

Organic anions in MAGIC are simulated by specifying the total amount of a diprotic organic acid (in mmoles L^{-1} of carboxyl groups) and the two pK values (for dissociation of the carboxyl groups). Thus, a total organic acid content of 10 mmol

L^{-1} (as H_2A) would produce 10 ueq L^{-1} of organic charge when the first proton was totally dissociated (all acid as HA^-) and 20 ueq L^{-1} of organic charge when the second proton was also totally dissociated (all acid as A^{2-}). By selecting appropriate values for the total organic acid content and the pK values, the total organic charge ($[HA^-] + [A^{2-}]$) can be adjusted for any pH. The ratio of total organic charge to the total dissolved organic carbon concentration (DOC, on a weight per volume basis) is referred to as the effective charge density of the organic acid. In calibrating the model, therefore, either the total organic acid content or the effective charge density and DOC of the organic must be specified along with the pK values. These values are needed for both the soil and surface water compartments of the model.

As seen from the measured ionic concentrations in the streams of the two catchments (Table 2), organic anions comprise a significant proportion of the total ionic charge at each site. No direct measurement of the dissolved organic charge was available for either soil or stream water. The DOC was available for the streams (Chon = 6 mg L^{-1}; Kelty = 16 mg L^{-1}). These measurements were used, with the assumption of an effective charge density of approximately 10 for the organic acids, and that the organic acids in the soils were equivalent to those in the stream, to derive the total organic acid content for the soil water at the two sites given in Table 4. The pK values for the first dissociation in the two soils are also given in the table. The pK values for the second dissociation were set to 10.5

(thus effectively producing a monoprotic acid for the low pH of these soils). The models were calibrated to the observed base cation concentrations observed in the streams (as described above) with these values of parameters for the organic acids in the soils and stream.

Subsequent to the calibration of the soils, the parameters of the organic acids simulated in the stream were modified (calibrated) to give an effective organic charge concentration approximately equal to that calculated from the observations (Table 2). The calibrated stream organic acid parameters (Table 4) corresponded to an effective charge density of 3.3 for the 6 mg L^{-1} DOC measured in Chon, and 12.5 for the 16 mg L^{-1} DOC measured in Kelty.

RESULTS

Simulated stream chemistry (Table 2) matches observed chemistry closely at both Chon and Kelty. The model also succesfully simulates present day soil chemistry (Table 6) as soil base exchange fractions at the two sites are well matched with measured data. The final values of the optimized parameters (weathering rates and soil exchange selectivity coefficients) resulting in these fits to the data are given in Table 5. Values of weathering of calcium and magnesium are higher at Chon and this accords well with field observation of a doleritic dyke within the catchment which affects the outflow concentrations of these ions.

Stream pH, hydrogen, alkalinity (expressed as sum of base cations plus ammonium minus sum of acid anions), calcium and sulphate hindcast reconstructions for the two sites from 1847 to 1987 are shown in Figure 4. Chon shows a very low background hydrogen concentration with an increasing trend which accelerates in the period 1950 to 1960 to give a rapid increase in hydrogen concentration (Figure 4). Kelty shows a similar accelerated increase during that period but has a very high background hydrogen concentration. This is due to the high levels of organics in the catchment, which are assumed to be at a constant level throughout the simulation. The period of rapidly increasing hydrogen corresponds to the planting and growth of the forest. At the time of canopy closure, 1965, both catchments are subject to the most severe acidifying processes; (i) total load of anthropogenic wet and dry deposition is at a high level as the assumed deposition curve peaks at this time; (ii) input from canopy filtering is also at a maximum because canopy closure (and thus, maximum filtering by the trees) and maximum deposition coincide; (iii) maximum cation uptake coincides with canopy closure: and, (iv) the concentrating effect of increased evapotranspiration is also at a maximum. Around 1970 stream concentrations level off and by 1980 have started to decrease. This is in response to the falling deposition levels in recent years (Figure 3b) and to the decrease in uptake of base cations as the forest matures.

The base saturation reconstruction (Figure 5) indicates a progressive soil acidification through time as base cations are leached in response to the incoming acidity. High weathering rates at Chon produce a high initial base saturation although this falls steadily until 1950 and then accelerates downwards at the onset of afforestation. At Kelty, although the apparent initial base saturation is not as high as at Chon, the model indicates that cation losses from the soil will result in slightly higher percent base saturation. No recovery of base saturation is seen at either site in response to decreased emissions since 1970, although the rate of decrease slows, and this accords well with the expected slower recovery of soils as they continue to desorb sulphate (Wright et al., 1988).

DISCUSSION

The application of the MAGIC model to these two sites demonstrates the effect of soil properties and forest growth on the historical acidification pattern in this area. It also demonstrates that the two sites, in relatively close proximity, show broadly similar responses but are quite different in detailed comparison. Clearly, the organics in the Kelty system have a major influence on historical pH, although sulphate is the dominant mobile anion affecting the historical decline in alkalinity at both sites. A discussion of the sulphate budget and dynamics as simulated by the model, therefore, can aid understanding of the acidification history of these two sites and offers an explanation for the observed differences between them.

Observed wet sulphate loading is similar at both sites (Table 1); under the deposition assumptions used, the total sulphate (wet plus dry) was historically similar until afforestation in 1950 (Figure 6a). Thereafter, differences in the effects of tree species (altering dry deposition and interception) have enhanced the differences in total sulphate loading between the two sites (Figure 6a). The decrease after 1970 at both sites is due to decreased emissions. The relative difference between the two diminishes because the dry deposition factors for the sites are applied as a constant proportion of wet deposition. Simulated stream sulphate concentrations closely follow the deposition curve (Figure 6b), Kelty being consistently higher because of its higher input and the greater soil adsorption at Chon (Figure 6c).

The cumulative loss of total exchangeable base cations at the two sites demonstrates that more base cations are lost from the exchange sites at Chon compared to Kelty and that the relative difference in loss rates intensifies as anthropogenic sulphate input increases over time (Figure 7). At the period of forest planting and growth the two curves converge as loss from soil exchange sites is dominated by plant uptake which exceeds losses of base cations associated with mobile sulphate anions. At canopy closure, uptake rates decrease and the differences between the two sites become apparent again.

Forest growth at the two sites accelerates acidification of the surface water from the steady pre-afforestation decline caused by the gradual increase of anthropogenic deposition. The model clearly demonstrates that evapotranspiration and cation uptake cause a significant acidification of the soil on top of the effect of canopy interception. This can at times cause enhanced surface water acidification, the degree depending on the dynamics of the mobile-anion and the base cation status of the soil. At Kelty the increased soil acidification appears to lead to water acidification because hydrogen is leached from the soil, whereas at Chon, the exchange of base cations affords some buffer to the stream acidity.

If uptake is an important process affecting the surface water and soil responses at these sites, the mechanisms and processes of uptake need adequate representation in the model. Uptake has been treated relatively simply, and no account is taken of organic matter build-up in the litter layer. It is, however, impossible to separate true vegetational uptake from immobilisation in the organic matter accumulation. Due to the role of the latter in nutrient cycling during growth, it is assumed to be an inseparable component of vegetatal uptake within the context of the model. Also, at no time in the lifespan of the forest did nutrient requirements exceed supply from the soil, i.e. no stand fertilization was required for major elements and no trace element deficiencies developed. Finally, it is assumed that deposition levels of anthropogenic pollutants, in this area of Scotland, do not have a direct effect upon tree physiology either through direct physical damage, mineral nutrition, metal toxicity, or increased susceptibility to biological attack.

CONCLUSIONS

1. The use of a relatively simple model of soil/water chemistry with inputs reflecting the effects of forest growth can provide a conceptual basis for comparing the relative effects of afforestation and acid deposition on surface water acidification.

2. When applied to two forested sites in Scotland, the model successfully simulates present day chemistry at both sites and can be used to examine current and historical differences in the responses to acidification between the sites.

3. These succesful applications suggest that the coupled model can be used in speculative simulation experiments to assess the relative effects of land use changes and/or deposition reductions on soil and surface water acidification. The results of these experiments are presented in the companion paper by Jenkins _et al._ (this volume).

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Table 1. Volume weighted mean bulk precipitation concentrations at Chon and Kelty for 1987. Mean annual precipitation volume was 2.3 m at both sites.

Concentrations are given in µeq L^{-1}.

	CHON	KELTY
Ca^{2+}	19.1	16.8
Mg^{2+}	19.4	26.9
Na^{+}	112.4	135.5
K^{+}	7.5	5.5
NH_4^{+}	16.3	25.0
SO_4^{2-}	56.2	60.4
Cl^{-}	130.5	148.3
NO_3^{-}	11.4	11.0
H^{+}	22.4	31.0
pH	4.6	4.5

Table 2. Volume weighted annual stream concentrations observed and simulated at Chon and Kelty for 1987.

Concentrations are given in $\mu eq\ L^{-1}$

(Sum base cations = sum of calcium + magnesium + sodium + potassium concentrations; sum acid anions = sum of chloride + sulphate + nitrate concentrations; calculated alkalinity = sum base cations plus ammonium minus sum acid anions).

	CHON		KELTY	
	Observed	Simulated	Observed	Simulated
Ca^{2+}	43.3	45.4	19.0	20.1
Mg^{2+}	48.3	46.0	36.9	35.5
Na^{+}	181.3	184.1	200.9	199.9
K^{+}	7.1	8.2	7.8	8.1
NH_4^{+}	7.2	6.9	13.2	12.9
SO_4^{2-}	93.3	102.8	100.0	106.1
Cl^{-}	224.5	217.7	216.5	214.7
NO_3^{-}	3.0	2.9	10.2	10.1
Al^{3+}	24.4	20.0	48.8	48.2
H^{+}	24.5	24.4	95.5	95.2
pH	4.6	4.6	4.0	4.0
Organic Anion	15.3 *	14.2	95.4 *	95.2
Sum Base Cations	280.0	283.7	264.6	263.6
Sum Acid Anions	320.8	323.4	326.7	330.9
Calculated Alkalinity	-33.6	-32.8	-48.9	-54.4

* Observed organic anion concentrations calculated as difference between the sum of concentrations of positively and negatively charged ions.

Table 3. Observed soil characteristics at Chon and Kelty. Weighted mean values for the aggregated soils in each catchment (see text).

	CHON	KELTY
Depth (m)	1.0	1.0
Cation Exchange Capacity (meq kg^{-1})	204	410
Sulphate Adsorption Maximum Capacity (meq kg^{-1})	7.0	3.5
Sulphate Adsorption Half Saturation (meq m^{-3})	1200	1200
Bulk Density (kg m^{-3})	964	844
Base Saturation (%)	3.0	3.5
Exchangeable Ca^{2+} (%)	1.2	1.9
Exchangeable Mg^{2+} (%)	0.6	0.7
Exchangeable Na^{+} (%)	0.5	0.6
Exchangeable K^{+} (%)	0.7	0.3

Table 4. The ranges and mean values of fixed parameters used in the optimisation procedure.

	CHON		KELTY	
SOIL	Range	Mean	Range	Mean
Depth (m)	0.9-1.1	1.02	0.9-1.1	1.00
Bulk density (kg m^{-3})	864-1064	962	744-944	842
Cation Exchange Capacity (meq kg^{-1})	154-254	202	360-460	410
Sulphate Adsorption Maximum Capacity (meq kg^{-1})	5.0-9.0	7.0	2.0-5.0	3.4
Sulphate Adsorption Half Saturation (meq m^{-3})	1100-1300	1211	1100-1300	1190
Al solubility coefficient ($\log_{10}$)	8.7-9.4	9.1	8.7-9.4	9.1
CO_2 partial pressure (atm)	------	0.033	------	0.033
Organic matter content (mmol m^{-3})	------	60	------	150
Organic matter pK_1 ($\log_{10}$)	------	4.25	------	4.50
WATER				
Runoff (m yr^{-1})	1.56-1.90	1.78	1.56-1.90	1.74
Al solubility coefficient ($\log_{10}$)	------	8.6	------	7.2
CO_2 partial pressure (atm)	------	0.0033	------	0.0033
Organic matter content (mmol m^{-3})	------	20	------	300
Organic matter pK_1 ($\log_{10}$)	------	4.25	------	4.40

Table 5. Optimised weathering rates and soil exchange selectivity coefficients for the Chon and Kelty models.

	CHON	KELTY
Weathering rates		
Calcium (meq m^{-2} yr^{-1})	53.3	0.6
Magnesium (meq m^{-2} yr^{-1})	58.3	16.8
Sodium (meq m^{-2} yr^{-1})	7.7	26.8
Potassium (meq m^{-2} yr^{-1})	10.2	14.1

	CHON	KELTY
Selectivity Coefficients		
Calcium ($\log_{10}$)	1.16	-0.82
Magnesium ($\log_{10}$)	2.22	0.77
Sodium ($\log_{10}$)	0.28	0.07
Potassium ($\log_{10}$)	-3.42	-3.62

Table 6. Observed and simulated soil chemistry variables.

	CHON		KELTY	
	Observed	Simulated	Observed	Simulated
Exchangeable Ca^{2+} (%)	1.2	1.2	1.9	1.7
Exchangeable Mg^{2+} (%)	0.6	0.6	0.7	0.9
Exchangeable Na^{+} (%)	0.5	0.5	0.6	0.6
Exchangeable K^{+} (%)	0.7	0.4	0.3	0.4
Base Saturation (%)	3.0	2.7	3.5	3.6

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Figure 2 Schematic representation of the MAGIC model

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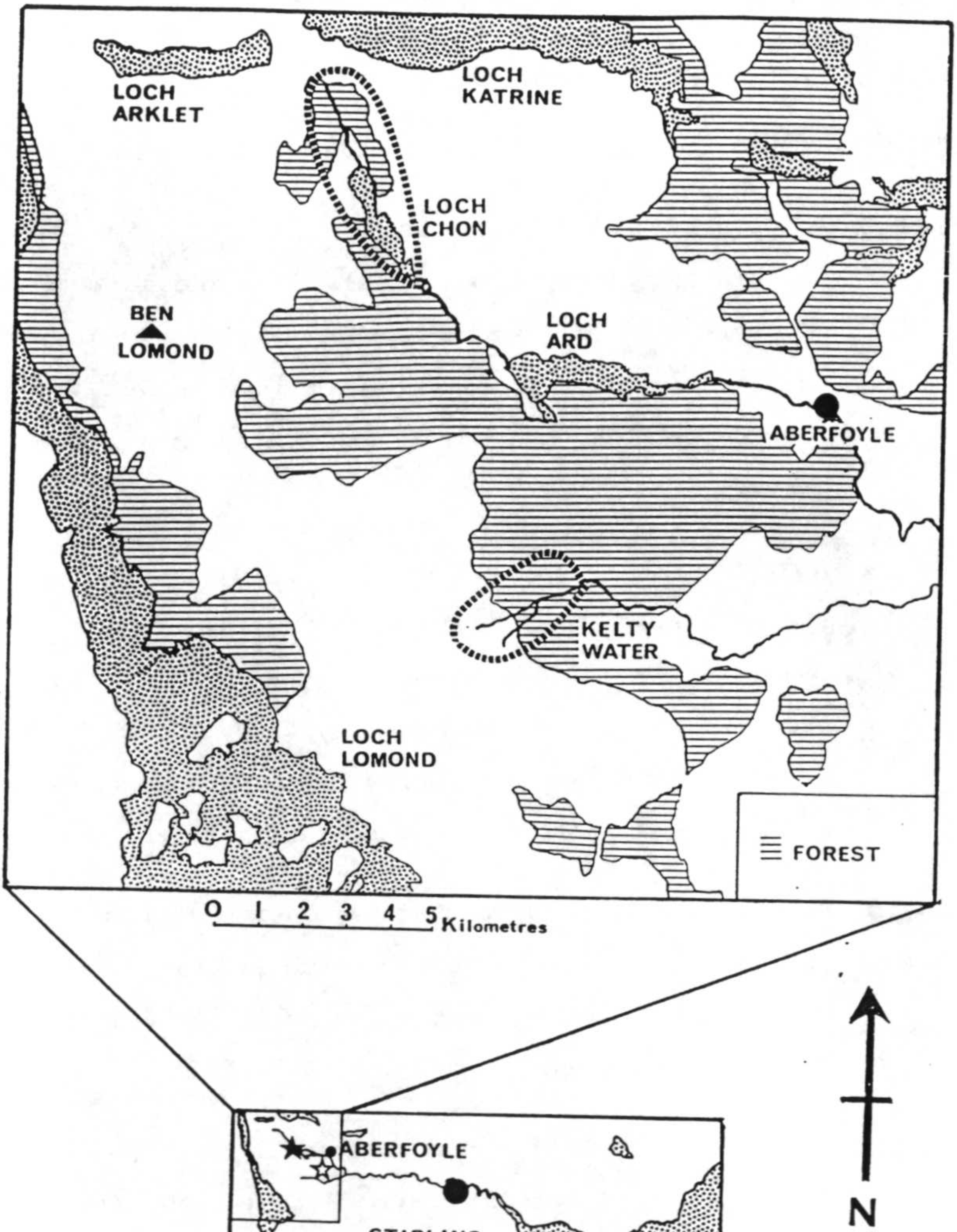
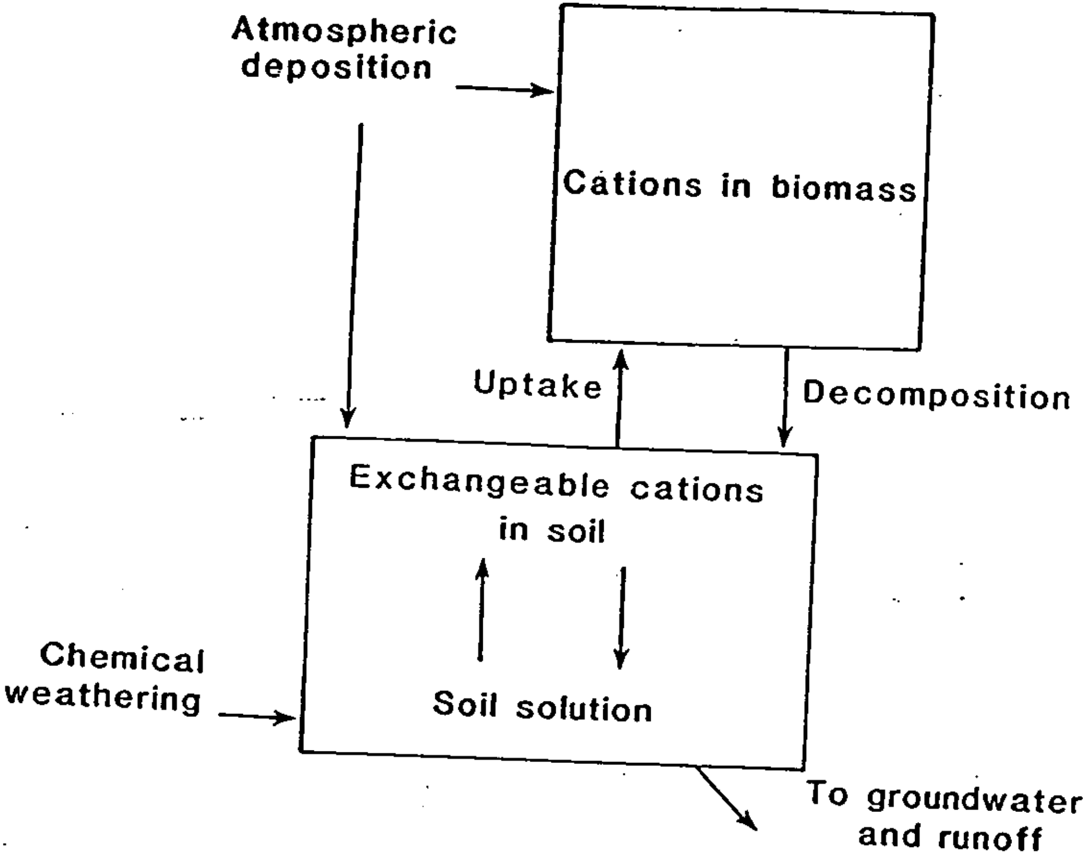
Figure 4 Simulated values at Chon (——) and Kelty (---) of: (a) stream sulphate concentration; (b) alkalinity concentration; (c) hydrogen ion concentration; (d) pH; and (e) calcium concentration. The two curves for each site represent the confidence limits of the simulation as derived from the fuzzy optimisation.

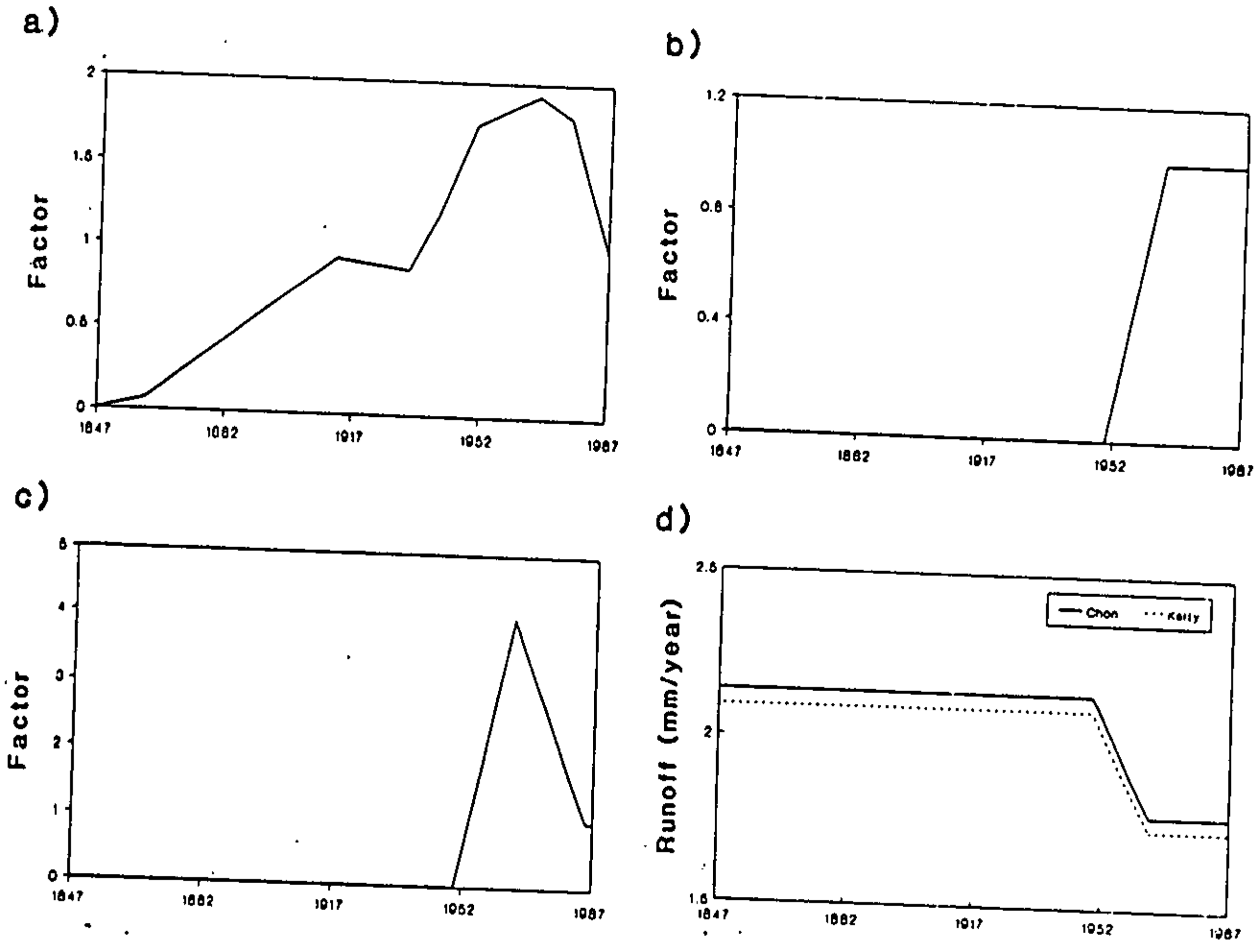
Figure 5 Simulated soil percent base saturation at Chon (——) and Kelty. The two curves for each site represent the confidence limits of the simulation as derived from the fuzzy optimisation.

Figure 6 Components of the sulphate budget at Chon (——) and Kelty (----): (a) total deposition loading; (b) total stream output; and (c) soil adsorbed sulphate.

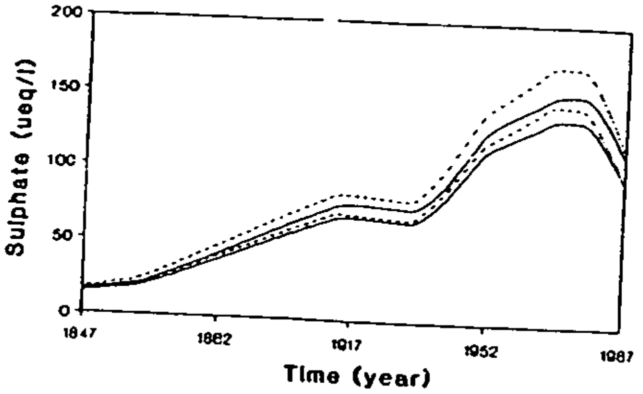
Figure 7 Cumulative loss of total exchangeable base cations from the soils at Chon (——) and Kelty (---).


LOCH ARKLET
LOCH KATRINE
LOCH CHON
BEN LOMOND
LOCH ARD
ABERFOYLE
KELTY WATER
LOCH LOMOND
FOREST
0 1 2 3 4 5 Kilometres
N
ABERFOYLE
STIRLING
EDINBURGH
GLASGOW


Atmospheric deposition
Cations in biomass
Uptake
Decomposition
Exchangeable cations in soil
Chemical weathering
Soil solution
To groundwater and runoff

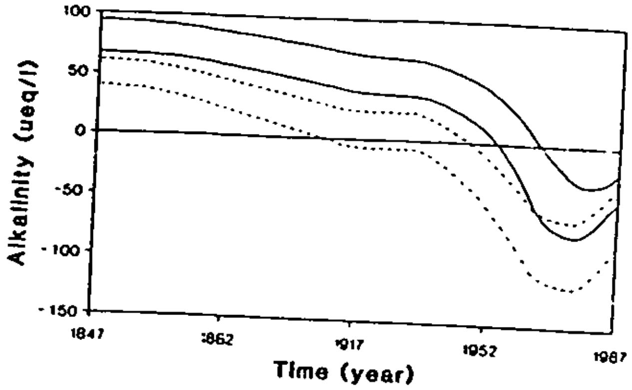

a)
Factor
2
1.5
1
0.5
0
1847
1882
1917
1952
1987
b)
Factor
1.2
0.8
0.4
0
1847
1882
1917
1952
1987
c)
Factor
5
4
3
2
1
0
1847
1882
1917
1952
1987
d)
Runoff (mm/year)
2.5
2
1.5
1847
1882
1917
1952
1987
Chon
Kelly

a)



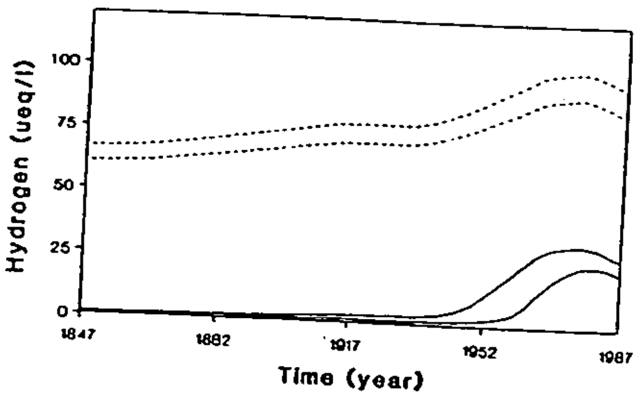
Sulphate (ueq/l)
200
150
100
50
0
1847
1882
1917
1952
1987
Time (year)

b)



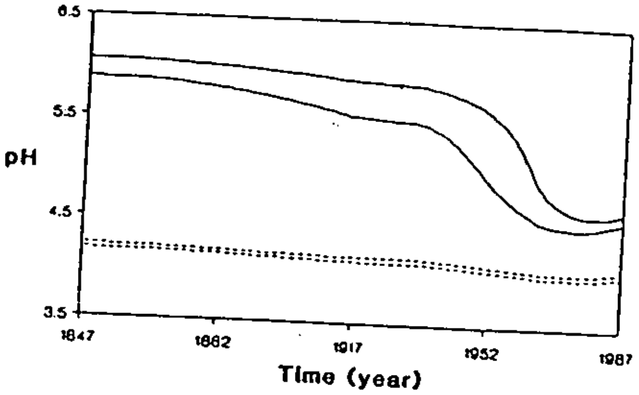
Alkalinity (ueq/l)
100
50
0
-50
-100
-150
1847
1882
1917
1952
1987
Time (year)

c)



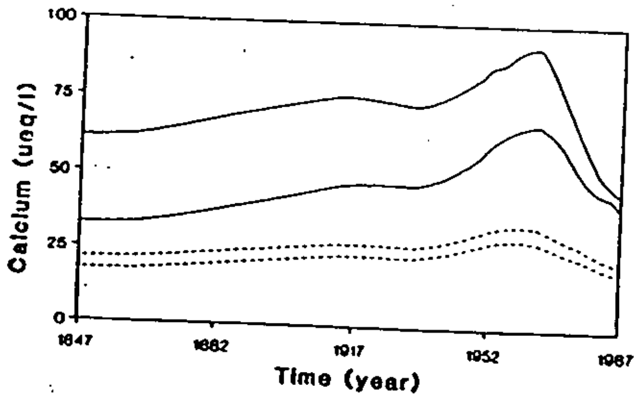
Hydrogen (ueq/l)
100
75
50
25
0
1847
1882
1917
1952
1987
Time (year)

d)

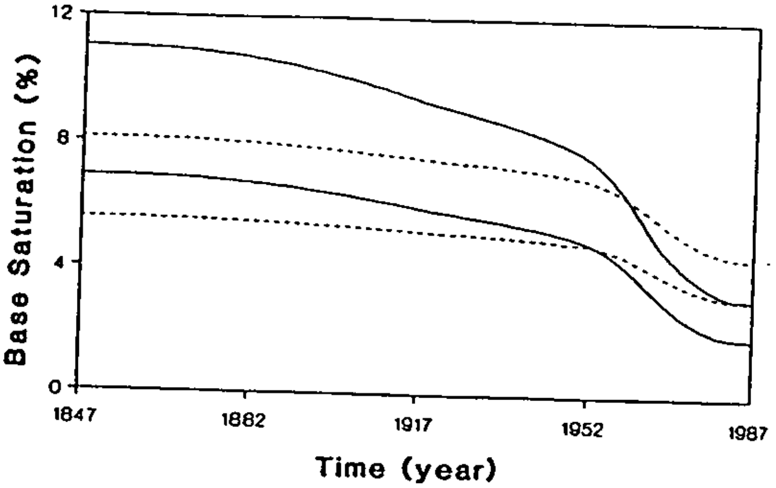


pH
6.5
5.5
4.5
3.5
1847
1882
1917
1952
1987
Time (year)

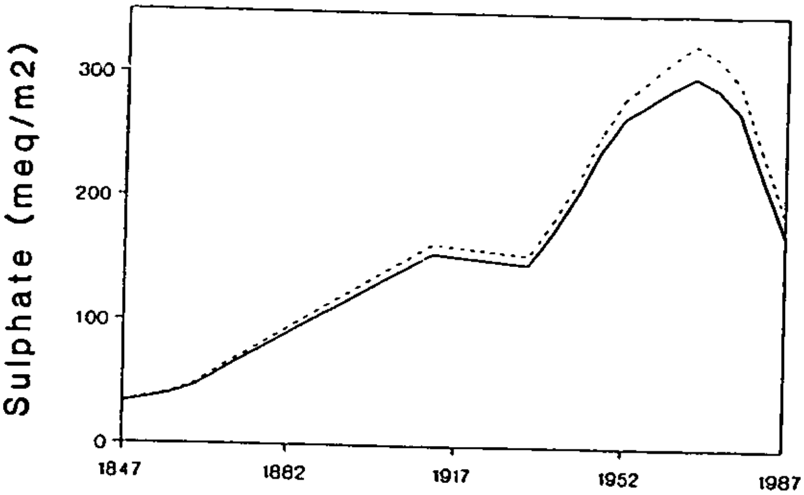
e)



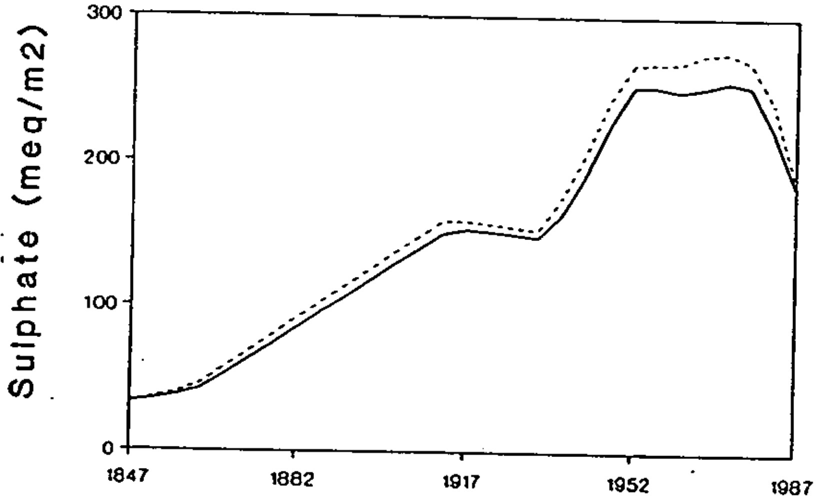
Calcium (ueq/l)
100
75
50
25
0
1847
1882
1917
1952
1987
Time (year)


12
8
4
0
Base Saturation (%)
1847
1882
1917
1952
1987
Time (year)

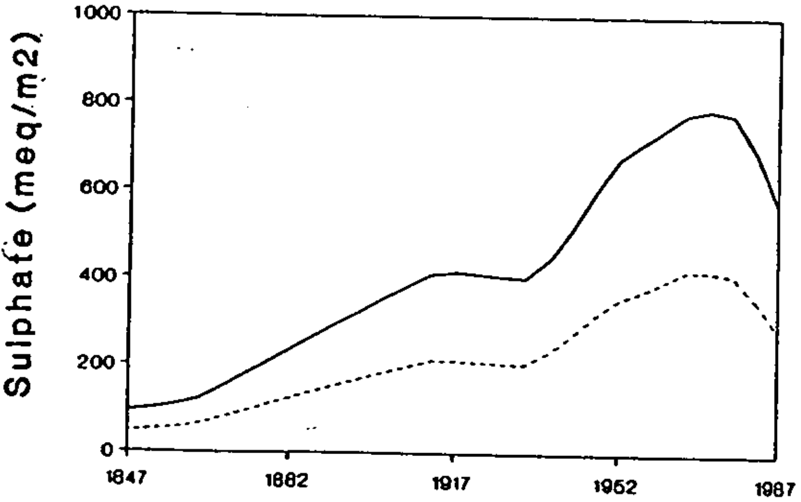
a)

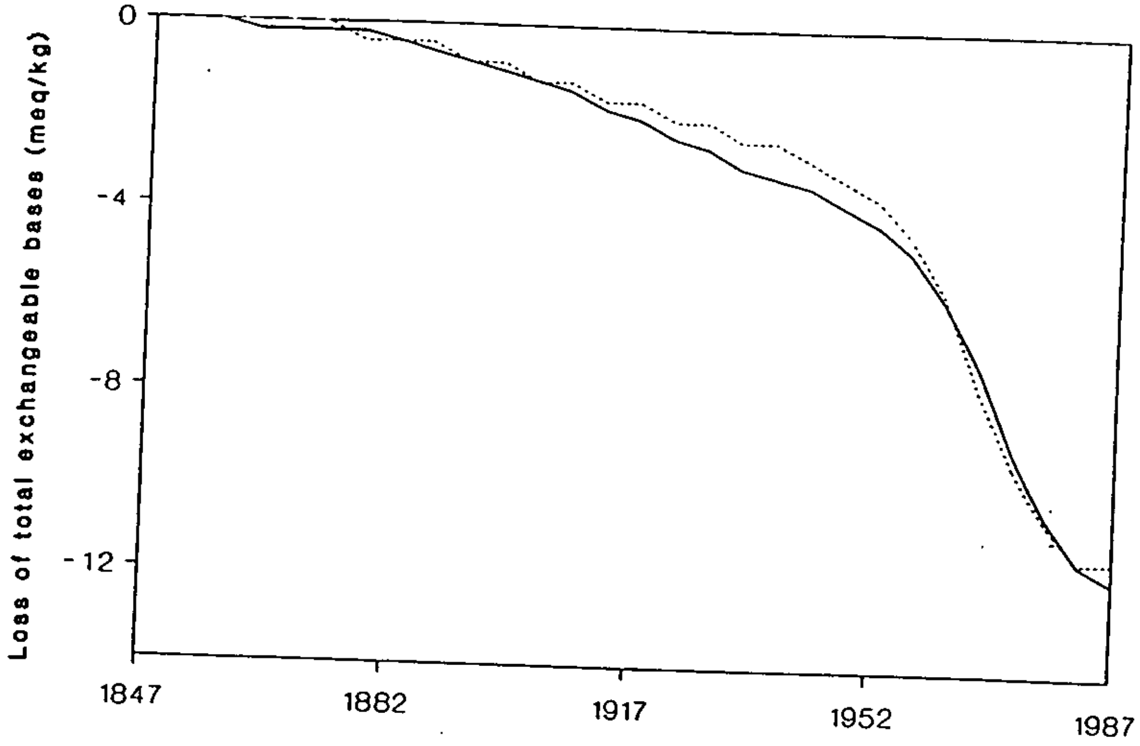

Sulphate (meq/m2)
300
200
100
0
1847
1882
1917
1952
1987

b)


Sulphate (meq/m2)
300
200
100
0
1847
1882
1917
1952
1987

c)


Sulphate (meq/m2)
1000
800
600
400
200
0
1847
1882
1917
1952
1987


Loss of total exchangeable bases (meq/kg)
0
-4
-8
-12
1847
1882
1917
1952
1987

2.2 AN ASSESSMENT OF THE RELATIVE EFFECTS OF ACID DEPOSITION AND AFFORESTATION

INTRODUCTION

In large areas of eastern North America and Europe a recent trend toward increased acidification has been observed in lakes and streams (e.g., Likens et al., 1979; Wright, 1983; Haines, 1986). This has occured in surface waters draining both moorland and afforested catchments although paired catchment studies have concluded that runoff from forested catchments is more acidic than from moorland catchments (Harriman and Morrison, 1982; Stoner et al., 1984). Many studies of soils in forested areas have demonstrated that enhanced soil acidification has occurred and that the effect of coniferous trees themselves is stronger than that resulting from atmospheric deposition (Troedsson, 1980). On the other hand, in moorland areas, no clear evidence exists as to whether acidic precipitation has enhanced the podsolisation process (Linzon and Temple, 1980); yet many studies in moorland areas demonstrate increased surface water acidity in response to acidic deposition (Battarbee, 1988).

Empirical evidence from catchment monitoring experiments is difficult to interpret because of the synergistic nature of afforestation and of acid deposition in causing acidification. Recent modelling studies have indicated that forests promote acidification by a combination of increased deposition, increased evapotranspiration and increased uptake of base cations to support tree growth (Neal et al., 1986; Whitehead et al., 1988a, b; Cosby et al., this volume). These findings lend support to the results of the paired catchment studies. Whether the trees themselves, in the absence of acidic deposition, would decrease surface water alkalinity to the same extent remains an enigma.

Considerable debate has arisen in the UK as to whether afforestation in the uplands should continue without due recourse to the sensitivity of drainage waters to acidification (Department of Environment, 1989). Nisbet (1989) and Bancroft (1988), argue that evidence for the acidifying effect of forests from paired catchment studies is not conclusive because of physical and chemical differences between the study catchments and suggest that only long-term studies can provide acceptable data. Historical data from upland areas, however, are insufficient to show changes following afforestation and the gathering of suitable data will require considerable time (Department of Environment, 1989).

This contribution to the debate uses the MAGIC model for long term soil and water chemistry reconstructions. The model has previously been applied succesfully to afforested catchments in central Scotland and performs well in capturing the major processes thought to be operating. These applications are fully described in a companion paper (Cosby et al., this volume). Here the calibrated model for one of the sites is subjected to a series of hypothetical land use and deposition scenarios to assess the relative contribution of forests and acid deposition to soil and water acidification. The model is also run in predictive mode to explore the recovery of soils and surface water in response to planting/harvesting and to decreased atmospheric emission strategies.

MODELLING PROCEDURE

The MAGIC model is a lumped parameter, long-term simulation model of soil and surface water quality (Cosby, et al., 1985a, b, c). The application of a modified version of MAGIC to two forested catchments in the Loch Ard area of central Scotland describes in detail the calibration and parameterisation of the model to these sites (Cosby et al., this volume). The modified model incorporates cation and anion uptake by the growing forest, pre-afforestation dry deposition inputs, enhanced deposition input through canopy filtering processes and a continuosly variable water yield as evapotranspiration changes in response to the water demand of the forest. For this study the calibrated model for the Loch Chon site is chosen to manipulate input and land use scenarios.

The Chon site was afforested in 1950. The area currently receives an acidic deposition loading of approximately 20 kg ha^{-1} yr^{-1} sulphate-S. Surface water is acidic but relatively high concentrations of calcium and magnesium, possibly due to the existence of a doleritic dyke within the catchment area, facilitate the maintainance of a fish population. Cosby et al. (this volume) suggest that both soils and surface water have undergone severe acidification since pre-industrial times and that the rate of acidification increased markedly following the period of afforestation. In the simulation experiments which follow, the values for all fixed parameters (hydrological and soil physical parameters) and chemical variables (weathering rates and initial base saturations) were taken from the previously calibrated model (Cosby et al., this volume).

Relative effects of historical acid deposition and afforestation

Three simulation scenarios were implemented to assess the relative effects of afforestation and acid deposition on historical changes in soil and surface water chemistry. The base line scenario (i) consists of the model as calibrated by Cosby et al. (this volume) with both acid deposition and afforestation present. By modifying wet and dry deposition, runoff yield and vegetation uptake sequences two further hindcast simulations are undertaken here. These describe the historical build-up of soil and water acidification through time for an area with identical chemical and physical characteristics to the Chon site but with (ii) acid deposition with no forest growth and (iii) no acid deposition with forest growth.

(i) Acid deposition with afforestation

This represents the historical and prevailing deposition and land use scenario at the site. Present day observed deposition are increased by dry deposition of sea salts and dry deposition of sulphate (Cosby et al., this volume). Deposition of all ions is assumed to be constant throughout the hindcast period except for sulphate, nitrate and ammonium which increase as a result of anthropogenic sources. The trajectory for those ions which increase follows that described by the Warren Springs Laboratory (1983, 1987) for anthropogenic emmissions with a modification based on sulphate deposition data from 1973 (Warren Springs Laboratory, unpublished data). Background sulphate concentration is assumed to be equal to seasalt concentration. Background concentrations of nitrate and ammonium are assumed to be zero.

Prior to afforestation in 1950 the Chon catchment was under moorland vegetation and so a runoff yield factor of 90% was assumed which is consistent with previous model calibrations to moorland sites in Scotland (Jenkins and Cosby, 1989). After afforestation the trees are assumed to decrease runoff yield, through increased evapotranspiration, at a linear rate until the canopy closed in 1965 when a yield of 75% is assumed. The increased ability of the growing forest to scavenge atmospheric pollutants is achieved by incorporating an explicit, time-varying dry deposition factor. This increased deposition is assumed to begin when the forest is planted and increases linearly until a maximum is reached at canopy closure; thereafter, this maximum level of enhanced input continues for the life of the forest. Uptake of base cations and sulphate ions from the soil in response to the nutritional requirements of the growing forest are pre-specified in the model (Cosby et al., this volume).

(ii) Acid deposition with no forest growth.

Deposition of base cations, ammonium, and acid anions follow the same assumptions as (i). There is no forest growth and so the runoff yield factor remains constant at 90%. Dry deposition is constant at the level calculated for moorland conditions (see Cosby et al., this volume) and there is no increased deposition from canopy scavenging. Vegetation uptake is not included except for the first order functions for nitrate and ammonium.

(iii) No acid deposition with forest growth.

There is no change in atmospheric deposition of any ion throughout the hindcast simulation. That is, the deposition of anthropogenically derived sulphate, nitrate and ammonium remain at the background levels, while deposition of base cations and chloride are assumed to be at present day observed concentrations adjusted to account for sea-salt contributions. Sulphate is assigned the relevant sea-salt fraction whilst nitrate and ammonium are assumed to be zero to maintain consistency with (i) and (ii) where background concentrations of these ions in rainfall are assumed to be zero. The forest uptake and runoff yield sequence described in (i) is followed and increased scavenging by the forest canopy is assumed to be in ratio only to seasalt concentrations.

Relative effects of future deposition reductions and forestry strategies

Fifty year forecast simulations were carried out to investigate the future course of acidification for the three historical situations under consideration: (i) the current "true" situation of afforestation with acid deposition; (ii) the simulated situation of acid deposition with no afforestation; and (iii) the simulated situation of afforestation with no acid deposition. The forecasts examine a combination of future emission scenarios and forest management options (Figure 1a).

Three future deposition strategies were simulated; (1) constant deposition at 1987 levels until the year 2037; (2) a linear decrease to 50% of 1987 levels by the year 2000 with deposition held constant at the reduced level thereafter until the year 2037; and, (3) a linear decrease to background seasalt levels (i.e., no acid deposition) by the year 2000 with deposition held constant at background level thereafter until the year 2037. For the deposition reduction scenarios, only the anthropogenically derived components of current deposition were reduced (Sulphate, Nitrate and ammonium).

Three future forest management options were also simulated: (1) leave the existing forest in place for the 50 year simulation; (2) harvest the forest assuming clear felling in 1990, leaving the site as moorland after the harvest; and, (3) harvest the forest assuming clear felling in 1990, followed by replanting the forest in 1992. For the cases of clear felling, the simulated runoff yield, canopy enhanced dry deposition, and uptake all revert to the pre-afforestation values described above for the historical simulations. For the case of re-planting in 1992, these model inputs follow the same temporal patterns described above for the historical afforestation (see also Cosby et al., this volume).

These future land management and deposition scenarios represent extreme options in some cases (i.e., leaving a 50 year old forest in place for a further 50 years, or complete reduction of anthropogenic deposition) and in reality are unlikely to be employed. However, these assumptions were made to examine the maximum degree of reversibility, or further deterioration, which may be expected in the future.

Most probable forestry and emissions reduction strategies

Further 50 year forecast simulations were used to examine the response of the hypothetical systems to deposition and land management scenarios considered most likely in the light of currently proposed reduction strategies and forestry options (Figure 1b). Land management practices most pertinent to upland forestry in the UK currently consist of planting or not planting a moorland site (future land use for historical situation (ii), above), and felling a forested site and planting or not planting a second generation crop on the same site (future land use for historical situation (i), above). The most probable deposition reduction strategies are the accepted UK policy to reduce emmissions by 30% and the recently proposed reduction to 70% of present day levels by 2003.

RESULTS AND DISCUSSION

The effects of the various combinations of historical/future forestry practices and deposition on stream chemistry were examined by considering two important chemical characteristics of surface waters: hydrogen ion concentration (H^+, μeq L^{-1}) and alkalinity concentration (ALK, μeq L^{-1}, defined here as the sum of base cation concentrations plus ammonium concentration minus the sum of acid anion concentrations). These stream variables are measures of the acid nuetralizing capacity or acidity of stream waters. The effects on soils were examined by considering two soil chemical characteristics: the soil base saturation (BS, %)

and the total exchangeable bases in the soil (TEB, eq m^{-2}, defined here as the product of base saturation times cation exchange capacity times bulk density of the soil times depth of the soil). These soil variables are measures of the buffering capacity of soils.

Relative effects of historical acid deposition and afforestation

For the case of afforestation with no acid deposition (case iii) stream chemistry remains constant (Figure 2) until it is perturbed by afforestation. The growth of the forest is associated with a decrease in alkalinity from a pre-afforestation value of 76.5 μeq L^{-1} to 59.5 μeq L^{-1} at the end of the simulation. This decrease in alkalinity is accompanied by only a slight increase in hydrogen ion concentration from 1.1 to 1.6 μeq L^{-1}. The net effect of afforestation on the streamwater is a loss of alkalinity, but no significant increase in mineral acidity. The effect of forest growth on the soils, however, is more pronounced. Soil base saturation responds to the varying nutritional requirement of the growing trees for base cations. This requirement is assumed to be at a maximum at the time of canopy closure whereafter it falls slowly to a constant level 20 years after canopy closure (see Cosby _et al._, this volume). In response to this uptake sequence, the rate of decline of percent base saturation is initially large, then decreases and begins to level off by 1980 (Figure 3).

The interaction between increased dry deposition of sea salts and uptake by the forest explains these observed changes in soil and streamwater chemistry. Both the sum of acid anions (SAA, sum of nitrate plus chloride plus sulfate concentrations) and the sum of base cations (SBC, sum of calcium plus magnesium plus sodium plus potassium concentrations) in the stream increase after the forest is planted (Figure 4). This effect occurs largely through increases in chloride and sodium scavenged by the canopy and passed through the soil to the stream. The base cations other than sodium tend to decrease in concentration as uptake requirements of the growing forest exceed increases in input and the base saturation of the soil declines. The net effect is a slower increase in SBC than SAA and a subsequent decline in alkalinity. The model supports the hypothesis that in the absence of acidic deposition afforestation will not lead to increases in mineral acidity of the stream but will tend to lower the stream alkalinity and the base status of the soil. Such declines in soil base status under afforestation have been documented by Hallbacken and Tamm (1986) and Falkengren-Grerup (1987).

The moorland site under acid deposition (case ii) shows a progressive streamwater acidification as sulphate emissions increase (Figure 2). Alkalinity drops from 76.5 to 18.6 μeq L^{-1} and hydrogen increases from 1.1 to 7.2 μeq L^{-1} (Table 1). These changes in stream water chemistry are greater than those produced by afforestation in the absence of acid deposition. Some recovery in alkalinity is simulated, however, after 1976 as sulphur emissions have decreased. Soil percent base saturation declines gradually to 4.8% at present from a background value of 8.7% (Figure 3, Table 1), as base cations are leached in response to increased input of mobile sulphate ions. This decrease represents a loss of approximately 50% of the total exchangeable bases held on the soil (Table 1). As for the stream variables, the simulated changes in soil variables produced by acid deposition are greater than those produced by afforestation alone (acid deposition results in almost twice the loss of soil base cations, Table 1). This pattern of acidification is characteristic of previous model applications to moorland sites in Scotland and compares well with palaeoecological reconstructions at those sites (Jenkins et al., in press).

Growing a forest on a site receiving acid deposition (case i) produces the most severe acidification response in both soils and streamwater (Figures 2 and 3). The net result is not simply the sum of the two previously discussed situations. The combined system perturbations produce enhanced ionic input, and the model responds by producing very different chemical dynamics. Streamwater alkalinity decreases from 76.5 to -32.5 μeq L^{-1} and hydrogen increases from 1.1 to 24.2 μeq L^{-1} (Table 1). Soil base saturation is depleted from a background level of 8.7% to 2.7% at present day, a loss of approximately 60% of total exchangeable cations held on the soil (Table 1). Stream and soil acidification intensifies as the increased sulphate input from canopy filtering far exceeds the forest uptake requirement. At the same time occult inputs of base cations are far lower than uptake requirement and so the soil must contribute an increasing amount of base cations to support tree growth, thereby, enhancing soil acidification. This is reflected in the sharp decrease in percent base saturation following planting (Figure 3). This simulation corresponds to the currently observed conditions at the site.

Relative effects of future deposition reductions and forestry strategies

For the situation of historical afforestation with no acid deposition (case iii), recovery was assessed for three future forestry strategies: leave the forest, cut the forest, and cut and re-plant the forest. Fifty year forecasts with the forest left in place indicate that there will be essentially no recovery in hydrogen ion or alkalinity concentrations of the stream, and that total exchangeable bases in the soil will continue to decline (Table 2). If the forest is felled and not replanted, significant recovery is simulated for stream alkalinity and total exchangeable bases over the fifty year forecast period (Table 2), although hydrogen ion concentration changes little. Replanting a forest on a clear felled site, however, produces a further deterioration in all variables over the fifty year future simulation (Table 2), largely due to the uptake requirements of the second forest exceeding input loadings. It must be noted, however, that the simulated changes in all of the forecast scenarios are small (in the absence of acid deposition) and even under the replant scenario the stream retains a high positive alkalinity and low hydrogen ion concentration.

For the situation of moorland site subjected to historical acid deposition (case ii) recovery was assessed under three deposition reduction scenarios: 0%, 50% and 100% reduction. The major effect of the fifty year simulations with no reduction of acid deposition is a further loss of soil base cations (Table 2). In general, little improvement in stream chemistry is found for this scenario. A significant recovery in streamwater chemistry is achieved by a 50% reduction in deposition although recovery of the soil base status is markedly slow (Table 2). Total reduction of emissions, produces the largest simulated changes in both stream and soil variables (Table 2). Comparing simulated historical changes (Table 1) with forecast changes for the fifty year simulation (Table 2), indicates that the stream has recovered 67% of its lost alkalinity, lost 89% of the increased hydrogen concentration and yet the soils recovered only 24% of their lost exchangeable bases for this extreme deposition reduction.

For the situation of historical afforestation with historical acid deposition (case i), recovery was assessed for six future scenarios representing extreme combinations of the various forestry and deposition reduction strategies (Figure 1a). Effects of three deposition reductions (0%, 50% and 100% reduction) were assessed for the forestry strategy of leaving the forest in place. Because the major interaction of forest and deposition is the increased scavenging of pollutants, leaving the forest in place while assessing deposition reductions should produce the greatest effect of those reductions. Effects of three forestry strategies (leave the forest, cut the forest, and cut and replant the forest) were assessed for no decrease in deposition.

If the forest is left in place for the fifty year forecast and no deposition reductions are implemented, a slight recovery of alkalinity and hydrogen ion is achieved with no appreciable change in soil exchangeable base cations (Table 2). On the other hand if the forest is felled and no deposition reductions are implemented, significant improvements in alkalinity, hydrogen ion and total exchangeable bases are achieved (Table 2). Replanting on the same site with no deposition reduction causes a further serious increase in both soil and water acidity (Table 2).

If the forest is left in place and deposition reductions are implemented, improvements in both stream and soil variables are realized (Table 2). As might be expected, the improvements for 100% reduction are greater than for 50% reduction, but the recoveries are not all linear with deposition reduction. Stream alkalinity and hydrogen ion improve by approximately a factor of two for the doubling in reductions implemented, but the recovery of the soil base cations is much slower (Table 2).

The reafforestation scenarios make no attempt to account for soil treatment prior to replanting. Clearly, if soil fertilisation is undertaken the effect of the second generation forest growth on soil and water chemistry may be ameliorated. However, fertilisation of these systems generally consists of an application of nitrogen, phosphorous and potassium at establishment of the stand with additions as prescribed until canopy closure and depending on soil type and tree species

(Miller and Miller, 1987). Addition of base cations in the form of lime is not a standard treatment and so the effect of the fertilisation is unlikely to influence the acid status of the soils and surface water.

Most probable forestry and emissions reduction strategies.

Given that much of northern England, Scotland and Wales currently receives (and historically have received) high levels of acidic deposition and that large areas of these uplands are under pressure from commercial forestry land management options, the most likely future scenarios have been simulated (Figure 1b).

The time sequences of hydrogen ion, alkalinity and soil base saturation under the two probable deposition reduction strategies at a forested site that is clear cut and not replanted all show marked improvement (Figure 5). The relative improvement in stream variables for the larger deposition reduction is roughly in proportion to the relative increase in deposition reduction (Table 3). The effects of the clear cutting are immediately apparent in the stream variables for both levels of deposition reduction (Figure 5). These immediate effects are produced by the decreased scavenging of pollutants as the forest canopy is removed, and the increased runoff as the site reverts to a moorland.

Changes in the soil base saturation are much slower, not showing an immediate response to clear cutting, but indicating slower long-term improvement for both deposition reductions if the forest is not replanted. Soil acidification has a much longer recovery period than does stream acidification.

The time sequence of hydrogen ion, alkalinity and soil base saturation under the two probable deposition reduction strategies at a forested site that is clear cut and then replanted differ markedly from the case where no replanting is undertaken (Figure 5). The initial responses of the stream variables to the clear felling is similar, but the effects of the second forest growth produce much lower alkalinity and higher hydrogen ion concentrations (Figure 5, Table 3). Even with a 70% reduction in deposition, replanting a forest following clear felling results in acidic stream conditions during the growth of the second forest. The acidic conditions persist even after the forest growth is complete (Figure 5).

As with the case of no re-planting, there is little difference in the future soil base saturation between the two probable deposition reduction scenarios when a second forest is planted. Compared to the case of no replanting, however, large differences in base saturation occur. With replanting, the soils show further deterioration following replanting and recover only slowly following forest maturation in either deposition case. Regardless of the deposition reduction, the largest differences in the future soil base saturation depend on whether or not the decision to re-plant the forest is taken (Figure 5, Table 3).

Moorland sites, as previously discussed, are subject to lower deposition loading than afforested areas and so decreases in deposition produce a rapid recovery in stream alkalinity if no forest is planted (Figure 6, Table 3). Comparison of simulated historical changes (Table 1) with forecast changes for the fifty year simulation (Table 3), indicates that a 70% reduction in deposition recovers 71% of stream alkalinity, allows hydrogen to decrease by 91%, and allows the soil to recover 23% of its lost base cations. Recoveries of this order would allow fish populations to return to many acidified moorland areas.

On the other hand, planting a forest on these moorland areas, despite large reductions in deposition, will lead to rapid and severe acidification (Figure 6, Table 3); this will be particularly severe in the soil, the base saturation of which has been steadily depleted through acidic deposition for many years prior to future afforestation (Figures 3 and 6, Tables 1 and 3).

CONCLUSIONS

This simulation analysis demonstrates that, in areas receiving high levels of acidic deposition such as upland Scotland, afforestation exacerbates the acidification problem in both soils and surface waters. Afforestation per se does not greatly acidfy surface waters in the absence of acidic deposition (although there is a small salt - effect). Afforestation does, however, lead to a significant decrease in the base status of the soil, mainly due to the uptake requirements of the growing forest. This decrease in the base status of the soils can render the soils (and surface waters) more sensitive to acid deposition. Acid deposition, on the other, can directly cause acidification of surface waters, either in the presence or absence of afforestation because of the high input of acidic, mobile anions.

Clear-felling a forested site will cause a significant reversal in stream acidification; it will also allow the soils to begin recovering. Deposition reductions produce a similar reversal of soil and surface water acidification. The interactions of forestry practices and deposition reductions are not strictly additive. In general, however, the greater emissions reductions that can be achieved, the greater the degree of soil and surface water recovery. Re-planting a forest on the same site will lead to further soil and stream acidification but, provided a reduction in acidic deposition can be simaltaneously achieved, the stream will not deteriorate to a greater level than under the first generation forest. Because of the slower response of soils to decreased deposition, however, the second generation forest will cause an enhanced soil acidification effect. This analysis indicates that in sensitive areas replanting in the absence of soil amendments (addition of bases) should not be undertaken even in the light of large reductions in deposition levels.

It should also be noted that the site chosen for this analysis has relatively high calcium and magnesium input from weathering due to the presence of a doleritic dyke within the catchment area. In areas where soils are of a lower base status, the effects demonstrated here would be enhanced and so the absolute levels of acidity are not necessarily representative on a wider regional scale. The relative pattern of changes will, however, be similar across the region if the same assumptions regarding deposition and afforestation effects are applied.

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Table 1. Simulated background (1847) and present day (1987) stream hydrogen ion (H) and alkalinity (ALK) concentrations, soil percent base saturation (BS) and total exchangeable base cations (TEB). The magnitude of the change from 1847 to 1987 is shown in brackets.

(ALK, H = μeq L^{-1}, BS = %, TEB = eq m^{-2})

Hindcast Scenario	1847				1987			
	ALK	H	BS	TEB	ALK	H	BS	TEB
Forest/ No Acid Deposition	76.5	1.1	8.7	17.3	59.5	1.6	6.3	12.5
					(-17)	(+0.5)	(-2.4)	(-4.8)
No Forest/ Acid Deposition	76.5	1.1	8.7	17.3	18.6	7.2	4.8	9.5
					(-57.9)	(+6.1)	(-3.9)	(-7.8)
Forest/ Acid Deposition	76.5	1.1	8.7	17.3	-32.5	24.2	2.7	5.4
					(-109)	(+23.1)	(-6.0)	(-11.9)

Table 2. Simulated future (2037) stream hydrogen ion (H) and alkalinity (ALK) concentration, soil percent base saturation (BS) and total exchangeable base cations (TEB). The magnitude of the change from 1987 to 2037 is shown in brackets. 1987 values in Table 1.
(ALK, H = μeq L^{-1}, BS = %, TEB = eq m^{-2})

Hindcast Scenario	Deposition Reduction	Forestry Option	2037			
			ALK	H	BS	TEB
Forest/ No Acid Deposition	0%	Leave forest	58.5	1.6	6.0	11.9
			(-1.0)	(0.0)	(-0.3)	(-0.6)
	0%	Cut forest	66.9	1.3	6.7	13.4
			(+7.4)	(-0.3)	(+0.4)	(+0.9)
	0%	Replant forest	44.2	2.4	4.4	8.6
			(-15.3)	(+0.8)	(-1.9)	(-3.9)
No Forest/ Acid Deposition	0%	Moorland	21.7	6.2	4.5	9.0
			(+3.1)	(-1.0)	(-1.8)	(-0.5)
	50%	Moorland	41.1	2.6	5.1	10.2
			(+22.5)	(-4.6)	(+0.3)	(+0.7)
	100%	Moorland	58.8	1.6	5.7	11.4
			(+40.2)	(-5.6)	(+0.9)	(+1.9)
Forest/ Acid Deposition	0%	Leave forest	-19.2	20.7	2.7	5.4
			(+13.3)	(-3.5)	(0.0)	(0.0)
	50%	Leave Forest	10.7	9.5	3.2	6.3
			(+43.2)	(-14.7)	(+0.5)	(+0.9)
	100%	Leave Forest	35.4	3.3	3.7	7.3
			(+67.9)	(-20.9)	(+1.0)	(+1.9)
	0%	Cut forest	8.2	11.2	3.5	6.9
			(+40.7)	(-13.0)	(+0.8)	(+1.5)
	0%	Replant forest	-46.1	27.2	1.7	3.4
			(-13.6)	(+4.1)	(-1.0)	(-2.0)

Table 3. Simulated future (2037) variables for most probable future scenarios. Stream hydrogen ion (H) and alkalinity (ALK) concentration, soil percent base saturation (BS) and total exchangeable base cations (TEB). The magnitude of the change from 1987 to 2037 is shown in brackets. 1987 values in Table 1.

(ALK, H = μeq L^{-1}, BS = %, TEB = eq m^{-2})

Hindcast Scenario	Deposition Reduction	Forestry Option	2037			
			ALK	H	BS	TEB
No Forest/ Acid Deposition	30%	Plant	-7.2	17.0	2.8	5.5
			(-25.8)	(+9.8)	(-2.0)	(-4.0)
	70%	Plant	16.5	8.0	3.1	6.2
			(-2.1)	(+0.8)	(-1.7)	(-3.3)
	30%	No plant	34.0	3.5	4.9	9.6
			(+15.4)	(-3.7)	(+0.1)	(+0.1)
	70%	No plant	48.5	2.1	5.3	10.6
			(+29.9)	(-5.1)	(+0.5)	(+1.1)
Forest/ Acid Deposition	30%	Cut forest	21.6	6.2	3.7	7.4
			(+54.1)	(-18.0)	(+1.0)	(+2.0)
	70%	Cut forest	37.2	3.0	4.1	8.2
			(+69.7)	(-21.2)	(+1.4)	(+2.8)
	30%	Replant forest	-26.3	22.7	1.8	3.6
			(+6.2)	(-1.5)	(-0.9)	(-1.8)
	70%	Replant forest	-1.1	14.9	2.1	4.1
			(+31.4)	(-9.3)	(-0.6)	(-1.3)

LIST OF FIGURES.

Figure 1. The combination of land use and deposition reduction scenarios adopted to assess (a) the degree of reversibility and (b) the implications of currently proposed emissions reduction and land management strategies on stream water and soil acidification.

Figure 2. Simulated streamwater alkalinity (a) and hydrogen ion concentration (b) for the three historical scenarios. Forest with acid deposition i.e. past and prevailing situation (━━), no forest with acid deposition (——) and forest with no acid deposition (---).

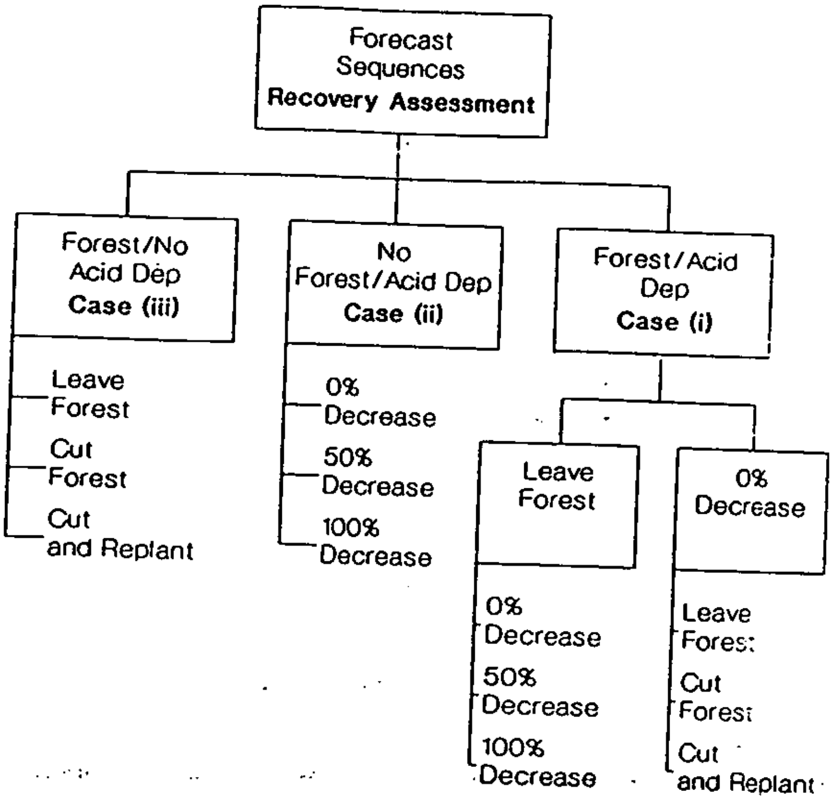
Figure 3. Simulated soil percent base saturation for the three historical scenarios. Forest with acid deposition i.e. past and prevailing situation (━━), no forest with acid deposition (——) and forest with no acid deposition (---).

Figure 4. Simulated streamwater sum of acid anion concentrations, SAA (a) and sum of base cation concentrations, SBC (b) for the three historical scenarios. Forest with acid deposition i.e. past and prevailing situation (━━), no forest with acid deposition (——) and forest with no acid deposition (---).

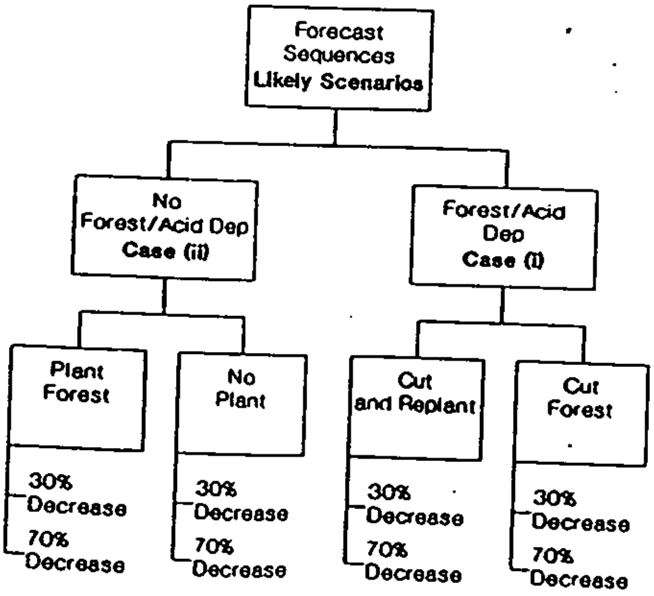
Figure 5. Simulated stream alkalinity (a), hydrogen ion concentration (b) and soil percent base saturation (c) for a presently forested catchment under likely future land management and emissions reductions scenarios. Replanting under 30% reduction (——), replanting under 70% reduction (━━), felling under 30% reduction (......) and felling under 70% reduction (---).

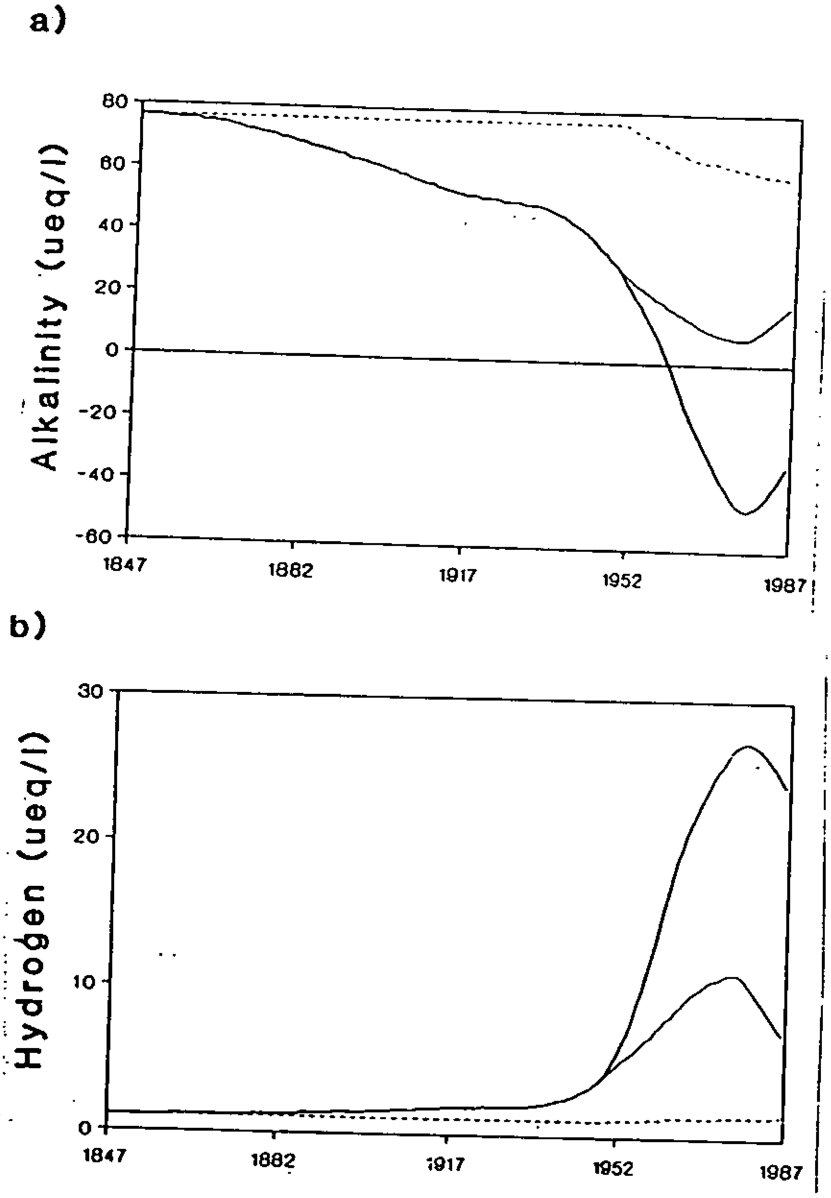
Figure 6. Simulated stream hydrogen ion concentration (a), alkalinity (b) and soil percent base saturation (c) for a presently moorland catchment under likely future land management and emissions reductions scenarios. Planting under 30% reduction (——), planting under 70% reduction (━━), no planting under 30% reduction (.......) and no planting under 70% reduction (---).

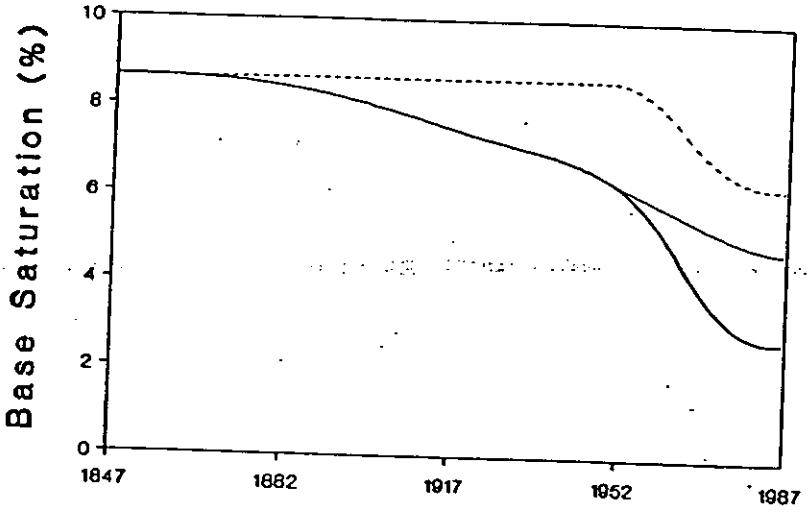
a)


Forecast Sequences
Recovery Assessment
Forest/No Acid Dep
Case (iii)
Leave Forest
Cut Forest
Cut and Replant
No Forest/Acid Dep
Case (ii)
0% Decrease
50% Decrease
100% Decrease
Forest/Acid Dep
Case (i)
Leave Forest
0% Decrease
50% Decrease
100% Decrease
0% Decrease
Leave Forest
Cut Forest
Cut and Replant

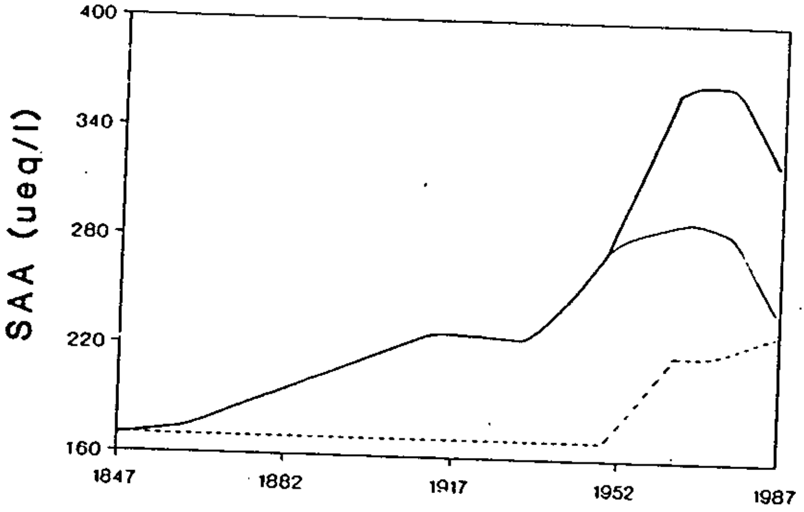
b)


Forecast Sequences
Likely Scenarios
No Forest/Acid Dep
Case (ii)
Plant Forest
30% Decrease
70% Decrease
No Plant
30% Decrease
70% Decrease
Forest/Acid Dep
Case (i)
Cut and Replant
30% Decrease
70% Decrease
Cut Forest
30% Decrease
70% Decrease

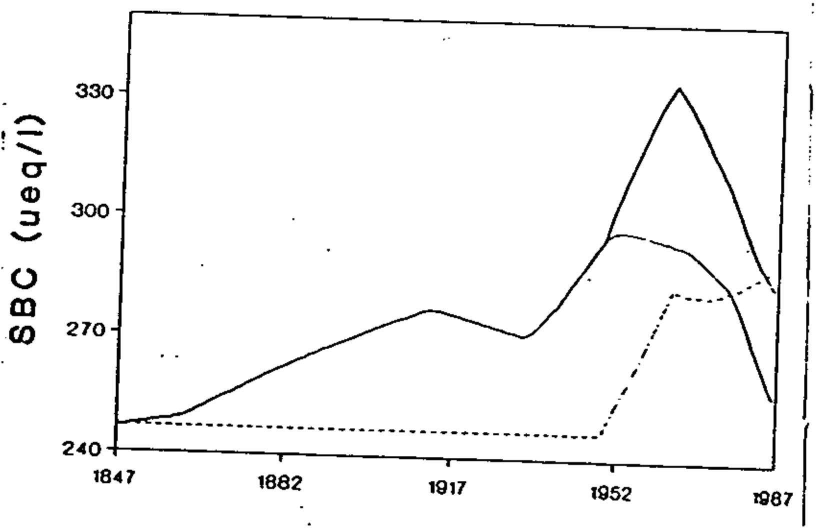

a)
Alkalinity (ueq/l)
80
60
40
20
0
-20
-40
-60
1847
1882
1917
1952
1987
b)
Hydrogen (ueq/l)
30
20
10
0
1847
1882
1917
1952
1987


Base Saturation (%)
10
8
6
4
2
0
1847
1882
1917
1952
1987

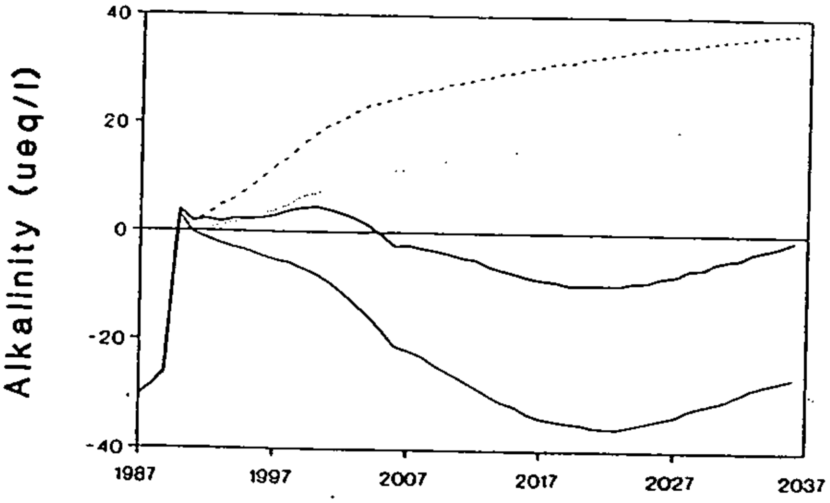
a)


SAA (ueq/l)
400
340
280
220
160
1847
1882
1917
1952
1987

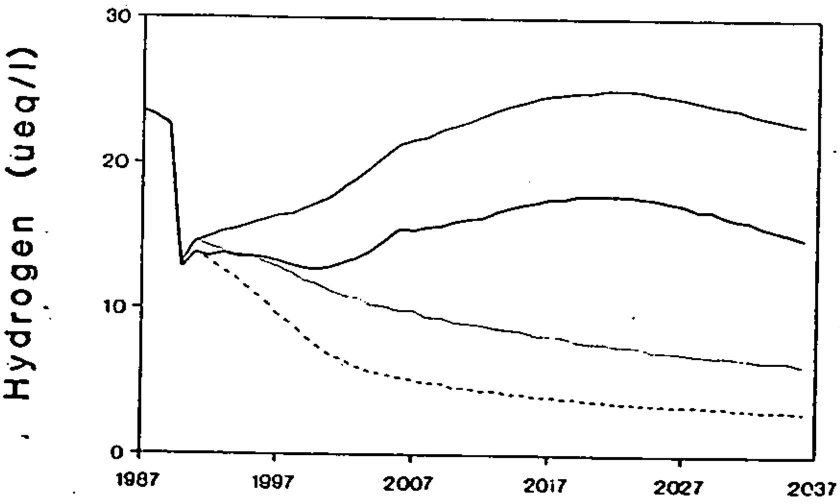
b)


SBC (ueq/l)
330
300
270
240
1847
1882
1917
1952
1987

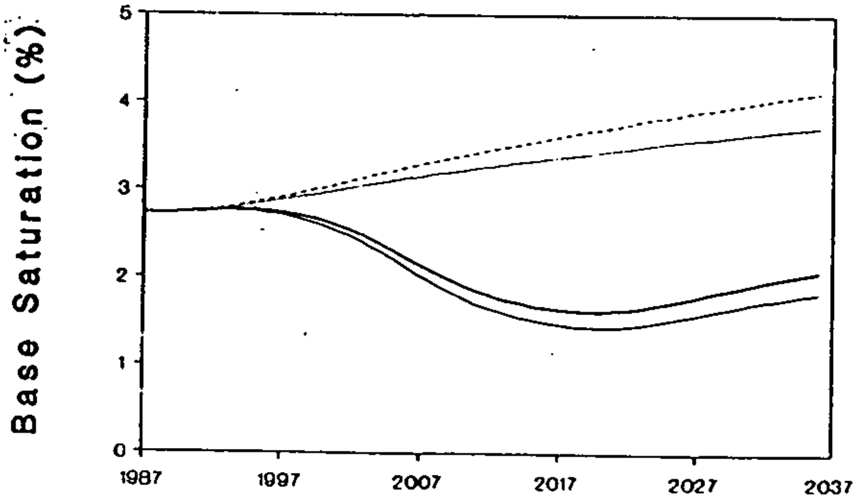
a)


Alkalinity (ueq/l)
40
20
0
-20
-40
1987
1997
2007
2017
2027
2037

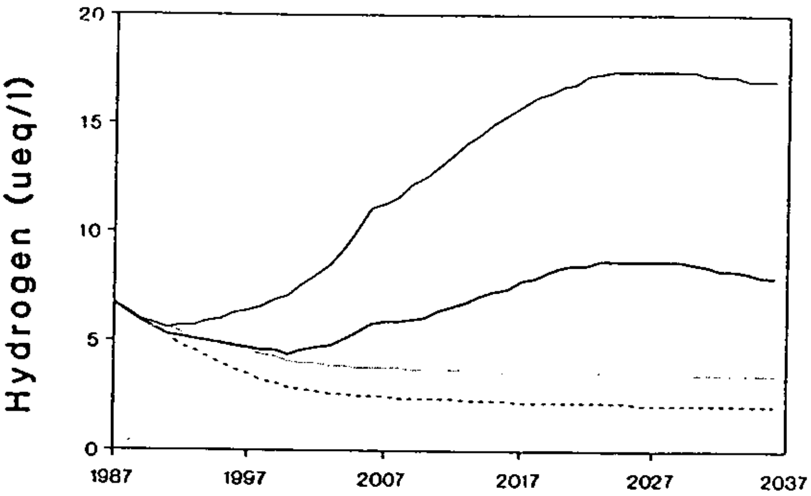
b)


Hydrogen (ueq/l)
30
20
10
0
1987
1997
2007
2017
2027
2037

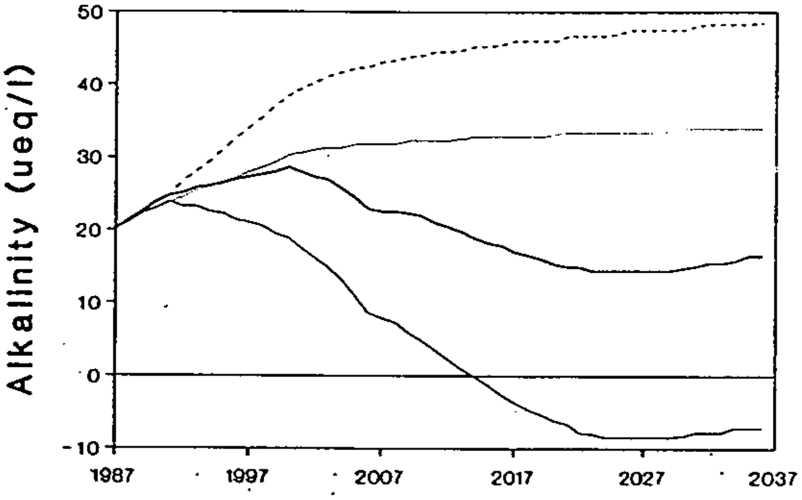
c)


Base Saturation (%)
5
4
3
2
1
0
1987
1997
2007
2017
2027
2037

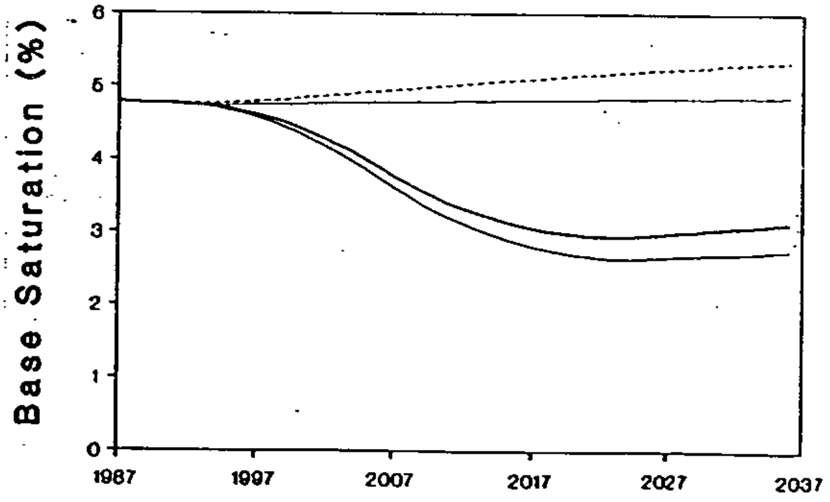
a)


Hydrogen (ueq/l)
20
15
10
5
0
1987
1997
2007
2017
2027
2037

b)


Alkalinity (ueq/l)
50
40
30
20
10
0
-10
1987
1997
2007
2017
2027
2037

c)


Base Saturation (%)
6
5
4
3
2
1
0
1987
1997
2007
2017
2027
2037

3. Modelling future episodic changes in stream chemistry

3.1 A METHOD FOR PREDICTING THE EXTREMES OF STREAM ACIDITY AND OTHER WATER QUALITY VARIABLES

INTRODUCTION

Mathematical models of complex environmental processes are often only capable of reasonable prediction of long term mean values of some quantity of interest. In the area of acidification modelling, long term models such as MAGIC (Model of Acidification of Groundwater In Catchments) have been developed to simulate long term trends and have been applied to a wide range of catchments (Cosby et al, 1985a,b, 1986; Wright et al, 1986; Jenkins et al, 1988, 1989; Whitehead et al, 1987, 1988). Whilst MAGIC may produce acceptable historical and future trends based on average annual chemistry, there are difficulties in modelling acidification at time scales of the order of hours and days (Neal et al, 1988). On this short time scale severe acid pulses are associated with hydrograph events.

Predictions of the extremes of behaviour during storm periods are difficult to obtain. Yet knowledge of the extremes is required in order to assess the likely biological effects of increased acidification in certain catchments or, alternatively, the biological recovery given reductions in acid deposition (Ormerod et al, 1988).

Process knowledge gaps, spatial heterogeneity and the cost of data acquisition contribute substantially to the difficulties besetting the prediction of extremes solely from process models. Nevertheless there are strategies at our disposal to provide information on extremes even when the environmental processes are very complex.

Much prior information may be obtained from statistical analysis of the characteristics of data already accrued. There are many examples where modellers analyse historical data to find a prescriptive solution to their problem. Simple parameterisations of probability density functions are fitted to outputs of processes for river flow management (Chow, 1964) air quality management (Jakeman and Taylor, 1989) and industrial manufacturing (Bain, 1978). In these cases, analysis should be undertaken to guarantee that the data being fitted are sufficiently independent and identically distributed (i.i.d.) so that the models can be used to synthesise more random samples or to extrapolate extreme values with acceptable confidence. Another example where modellers ignore physically based process knowledge is the use of purely stochastic models. A great deal of attention has been paid to the construction of autoregressive moving average models for forecasting (El-Shaarawi and Esterby, 1982) and, in application, the analysis depends on the stationarity (or absence of trend) of the data being fitted.

In the case of stream acidification the associated time series often contain long term trends. We cannot solely appeal to stationarity properties over the longer term to make predictions. Furthermore, if we wish to improve understanding of the processes associated with acidification and if we wish to assess control strategies, then we do need a process based description which is sensitive to, or largely determined by, the major forcing factors.

Fortunately, it is possible to combine the advantages of deterministic and statistically based-approaches into one that is hybrid. This has been constructed by Jakeman et al. (1988) for predicting extremes of air pollutant concentrations but the approach is a generic solution to many modelling problems.

In this paper we show a deterministic model, MAGIC, that predicts the long term trend of stream acidity variables in combination with probability distribution models that characterise the variability of the trend. These probability distributions must belong to some parametric family, our choice here being among two and three parameter Weibull, gamma and lognormal forms (see Jakeman and Taylor, 1989, for their mathematical definition). We develop and apply this hybrid model using data from the Allt a Mharcaidh catchment purely to illustrate the approach. It is stressed that insufficient years of data were available to confirm the validity of all the assumptions underlying the hybrid approach.

The paper is organised as follows. The general hybrid approach is stated in the next section. This is followed by a brief description of MAGIC used to predict the mean annual stream concentrations. Another section is devoted to analysis of the characteristics of stream concentration data. The statistical results allow us to subsequently devise a particular implementation of the hybrid approach. Predictions of the hybrid model are given and some analysis is reported of the sensitivity of the method to its underlying assumptions. We illustrate the practical use of the model by applying it to output from the MAGIC model. The conclusions suggest how the approach could be further explored and developed.

THE HYBRID APPROACH

The hybrid deterministic - statistical distribution approach of Jakeman et al (1988) can be stated in four steps as:

(1) Select a deterministic or physically-based process model of the phenomenon of interest to make predictions at the desired intervals (eg annually as in MAGIC).

(2) Identify, from a range of alternatives, the parametric form of the probability distribution (ie 2 or 3 parameter Weibull, gamma or lognormal) of historical observations within individual intervals (eg weekly) and assess its consistency over all intervals;

(3) For each prediction interval, fit the predictions of the model output in (1) to the parametric form identified in (2) so that its parameters can be estimated;

(4) Calculate the extremes of the probability distribution function (pdf) for each interval from a knowledge of the estimated parameter values.

The major assumptions of the approach are:

(A1) Within an interval, the probability distribution can be characterised by a simple parametric form;

(A2) The parametric form (but not the parameter values) of the pdf at a fixed site remains consistent from one interval to another;

(A3) The deterministic model yields sufficiently accurate properties of the pdf, such as the mean, to determine the parameter values.

In the case of stream acidification MAGIC is not presently capable of predicting any properties of the pdf other than the mean. Therefore, additional assumptions related to the values of some of the pdf parameters must be made.

The analytical tools required for the statistical component of the hybrid approach are:

(a) parameter estimation or fitting methods for probability density functions;

(b) identification criteria for discriminating among pdf alternatives.

THE DETERMINISTIC MODEL MAGIC

MAGIC (Model of Acidification of Groundwater In Catchments) is explicitly designed to perform long term simulations of change in soilwater and streamwater chemistry in response to changes in acidic deposition (Cosby et al, 1985a, b). The processes on which the model is based are:

- anion retention by catchment soils (eg sulphate adsorption);

- adsorption and exchange of base cations and aluminium by soils;
- alkalinity generation by dissociation of carbonic acid (at high CO_2 partial pressures in the soil) with subsequent exchange of hydrogen ions for base cations;
- weathering of minerals in the soil to provide a source of base cations;
- control of Al^{3+} concentrations by an assumed equilibrium with a solid phase of $Al(OH)_3$.

A sequence of atmospheric deposition and mineral weathering is assumed for MAGIC. Current deposition levels of base cations, sulphate, nitrate and chloride are needed along with some estimate of how these levels have varied historically. Historical deposition variations may be scaled to emissions records (Cosby et al, 1986) or may be taken from other modelling studies of atmospheric transport into a region (Derwent, 1987). Weathering estimates for base cations are extremely difficult to obtain. Nonetheless, it is the weathering process that controls the long term response and recovery of catchments to acidic deposition, and some estimate is required. An optimization scheme is used to determine key parameters (Jenkins and Cosby, 1989).

The MAGIC programme has been applied extensively to a range of catchments as mentioned previously and details of the model and its application are presented elsewhere (see Cosby et al, 1985a,b, 1986)

The approach suggested in this paper, to investigate the extremes of water quality behaviour, is to analyse the observed chemistry data from a catchment and quantify the inherent variability in such data. The data used here are taken from the Allt a Mharcaidh catchment in the Cairngorm region of Scotland and represent a site which is not at present chronically acidified but is subject to severe acid pulses during high flow events.

DATA, DESCRIPTION AND PRIOR ANALYSIS

The Allt-a-Mharcaidh catchment lies on the western flank of the Cairngorm Mountains draining an area of approximately $10km^2$. Vegetation is mainly a mixture of heather and fescue grassland. The soils are essentially of three main types with c60% alpine and peaty podsols and 40% blanket peat. The site was selected as a transitional site, that is, a catchment which is not acidified but is thought to be at risk as regards future acidification problems.

Two years of approximately biweekly chemistry data are available from the catchment. For each year, two and three parameter versions of the Weibull, gamma and lognormal distributions were fitted and compared. These distributions are skewed shape-scale location distributions which were felt to cover a large range of possible shapes from which the historical data could be assumed to be derived. The normal distribution was not fitted to the data because it will predict negative (and hence physically meaningless) values of concentration for its lowest extremes. Furthermore, the three selected distributions are capable of fitting a symmetric bell-shaped density ie near enough normal.

Table 1 lists the chemical species studied together with basic statistics (mean, standard deviation etc). Figures 1 and 2 are time series plots of Alkalinity and Calcium over the two year period of 1986 and 1987. For some of the measurements such as alkalinity, pH and sulphate there appears to be a reasonably constant trend over the two years. For most of the remaining, there are higher levels on average in the first half of 1986 while the trend is reasonably constant but lower for the remaining one and a half years. This category includes conductivity, sodium, calcium, potassium, magnesium and nitrate.

TABLE 1 The Allt a Mharcaidh Catchment Chemistry Data for 1986 and 1987

	N	Mean	Standard Deviation	Min.	Max.
1986					
Alkalinity	120	46.0	21.8	3	97
Ph	90	6.0	0.4	4.7	6.5
Conductivity	97	27.3	5.2	18	45
Na	117	129.5	21.5	81	196
Ca	117	43.3	10.3	25	70
K	117	7.4	2.0	5	13
Mg	117	31.0	8.1	19	66
SO4	114	53.8	8.7	34	83
NO3	114	1.6	2.7	0	16
1987					
Alkalinity	99	51.0	14.0	17	76
Ph	97	6.0	0.3	4.8	6.4
Conductivity	95	24.5	2.5	17	29
Na	102	124.8	12.6	92	145
Ca	102	40.5	5.5	25	57
K	102	6.5	2.5	3	20
Mg	102	26.4	3.8	14	37
SO4	102	53.6	7.4	32	79
NO3	102	1.0	1.4	0	6

In terms of the assumptions required to fit probability distributions to these data, two points should be made. First, the data sets generally appear generally stationary (ie of constant trend) in 1987, and for some of the sets, this property also applies in 1986. Second there appears to be only a modest level of autocorrelation in all the data. Although application of probability distribution models to the data assumes independent random samples, Jakeman et al (1988) point out that quite high levels of autocorrelation can be tolerated and provide some quantification of the errors to be expected for varying degrees of autocorrelation. Jakeman et al (1989) also demonstrate that non-stationarity in time series of data does not represent a problem provided the samples can be regarded as belonging to a well-identified probability distribution.

Table 2 shows some of the likelihood values obtained from fitting our range of pdf models to the chemical species available for the Allt a Mharcaidh. Various criteria which trade off model fit against model complexity are available for using the likelihood to discriminate among model (parametric) alternatives. The criteria chosen should reflect the intended use of the model. A well known criterion which is biased towards overfitting is the Akaike Information Criterion (Akaike, 1972). The AIC is defined as

$$AIC(m) = -2 \log(\text{likelihood}) + 2m$$

where m is the number of independent parameters. This criterion therefore only accepts a three parameter model if its log likelihood is more than one unit higher than a two parameter model. We have used this criterion to indicate our preliminary choice of superior model for each chemical species and each year in Table 2. The results for only two years are expectedly mixed, there not being enough years to determine if there is a consistently superior parametric model for any particular pollutant. The same distribution type is identified in each year for alkalinity, Na, Ca and NO_3. For SO_4 the two parameter gamma is the superior one for 1987, for 1986 this distribution is almost as good an assumption as the two parameter lognormal. For the other

TABLE 2 Log-likelihood values obtained from fitting different distributions to some of the chemical species measured in 1986 and 1987

Distribution	Alkalinity	pH	Conductivity	Na	Ca	K	Mg	SO_4	NO_3
Weibull-3 1986	*	**	-292.2	-524.1	-433.6(/)	-178.3	-389.4	-406.8	289.4
1987	*	-20.70	-218.4	-417.8	-319.3(/)	-210.8	-281.2(/)	-350.7	23.6
Weibull-2 1986	-537.6(/)	-44.40(/)	-304.0	-529.7	-441.1	-248.7	-417.6	-417.3	-139.8
1987	-399.3(/)	-562.4	-218.5(/)	-829.8	-321.4	-236.0	-282.5	-357.1	-69.6
Lognormal-3 1986	*	*	-292.2	*	*	*	-382.3(/)	-403.3	*
1987	*	*	*	*	*	-187.9(/)	*	*	*
Lognormal-2 1986	-555.0	-55.32	-293.1(/)	-524.9	-435.1	-236.2	-391.3	-403.4(/)	-124.3
1987	-413.7	-19.35	-224.4	-407.2	-321.6	-192.6	-283.7	-347.3	-66.9
Gamma-3 1986	*	*	-292.1	*	-434.8	-155.8(/)	-385.1	-403.6	295.1(/)
1987	*	*	*	*	*	-197.3	*	*	35.9(/)
Gamma-2 1986	-543.0	-54.15	-294.2	-524.2(/)	-435.2	-238.6	-396.7	-404.2	-137.6
1987	-408.0	-17.65(/)	-223.2	-405.5(/)	-320.3(/)	-205.3	-282.2(/)	-346.9(/)	-67.7

* denotes negative parameter value(s) obtained, usually location
(/) denotes superior model(s)
** denotes lack of convergence

chemical species, pH, conductivity, K and Mg, the distribution identified depends upon the year. Finally for 6 of the 9 species, a two parameter assumption is preferable to a three parameter in both years, the exceptions being K, Mg and NO_3. As will be seen, this is an advantage in constructing a hybrid model because a two parameter model requires less information for calibration.

Figure 3 shows the fit of the two parameter Weibull distribution to the empirical cumulative distribution function of the alkalinity data for the years 1986 and 1987. The agreement between the observed and fitted distribution functions is good in both cases.

A HYBRID METHOD AND PREDICTIONS

We demonstrate one possible implementation of the hybrid approach using the alkalinity data set only. The intention is to illustrate the method as simply as possible rather than draw conclusions about the extremes of acidification in the Allt'a Mharcaidh catchment. Alkalinity is the obvious species to select for this purpose since both the 1986 and 1987 data sets visually conform to the i.i.d. assumption and a two-parameter Weibull distribution is preferred for both years. However, it is stressed that independence and stationarity of the time series of a variable are not necessary conditions to obtain good parametric fits and hence hybrid model results.

In choosing a method it must first be appreciated that the deterministic model MAGIC at present predicts only mean annual values (see Jenkins et al, 1988). No variability of this mean is yet reliably available as the model output. Because the distribution identified for alkalinity is a 2-parameter version, two pieces of information are needed to describe it. An obvious strategy is to use the deterministic model to provide the mean of the identified distribution (Weibull for alkalinity) assume a range of values for the shape parameter of the distribution, compute the scale parameter from the mean and shape and look at the sensitivity of the result to values within the shape range.

Table 3 contains the parameter values for the model fit to the 1986 and 1987 Weibull alkalinity data sets. These were two extremely different years, in terms of snowfall. In other years we might therefore expect the shape parameter to lie between or nearby the 1986 and 1987 estimates. On this basis, we select a shape parameter range of 1.5 up to 6 in an attempt to cover most possibilities.

TABLE 3 Parameter values for Weibull model fit to alkalinity data set

Year	Shape parameter	Scale parameter
1986	2.230	51.81
1987	4.341	56.17

The mean of the Weibull distribution is given by

$$\text{mean} = \text{scale} \times \text{Gamma}\left(1 + \frac{1}{\text{shape}}\right)$$

so that knowledge of scale straightforwardly ensues from a fixed shape. Figure 4 shows the result of calibrating the scale parameter for a range of assumed shape parameter values, using the known mean alkalinities from 1986 and 1987 (ie we do not bother to use our deterministic model to predict the mean, accepting that this can be done to an acceptable accuracy). It demonstrates the nature of the above relationship that the scale parameter has a low sensitivity to changes in the value of the shape parameter and is largely determined by the mean, especially if the mean is large compared to the shape.

Figure 5 shows the sensitivity of percentile predictions to errors in knowledge of the shape parameter. The observed percentiles are indicated as are the predicted results if the best shape parameter value was that underlying the Weibull description of the 1986 or 1987 alkalinity data sets. Figure 6 shows the errors in the estimated 67% and 95% percentiles. The error is expressed as a percentage of the observed percentile values (assumed to be correct).

The results were obtained from the Weibull cumulative distribution function for a range of shape parameter values and the known mean. The 67% and 95% upper percentiles were arbitrarily chosen (5% and 33% percentiles, which in the case of alkalinity would correspond to harmful extremes, could equally well be considered). For both 1986 and 1987 the estimated 67% upper percentile was not sensitive to the choice of shape parameter value. However the 95% upper percentile expectedly showed more sensitivity particularly when the shape values were low (as was the case in 1986). With additional years of data it should be possible to determine a realistic range for the shape parameter and hence a range for each percentile. Even more desirable would be an extension of the deterministic model so as to calculate not only the mean but also accurate predictions of percentiles close to the mean which would enable improved estimation of the shape parameter. In any case the percentile value for a very low shape parameter choice serves as an upper bound on the extreme value.

In its simplest form the hybrid approach, as outlined in this paper, may be implemented using the mean value, M, the percentile, p, where 0<p<100 and the shape parameter, c, to estimate the percentile of interest, Lp, as follows:

$$Lp = M \frac{\left| \ln\left(\frac{100-p}{100}\right) \right|^{1/c}}{\text{Gamma}\ (1 + c^{-1})} \qquad (1)$$

or $$Lp = M \times F(c,p) \qquad (2)$$

where F(c,p) is a shape factor

Table 4 lists values of the factor F(c,p) for varying values of the percentile and the shape parameter. In order to implement the hybrid approach using Table 4 all that is required is an estimate, derived from the deterministic model, of M and an estimate of the shape parameter. If no estimate of the shape parameter is available then a middle range of c=2.5 could be assumed. Then, based on the percentile for which a prediction is required and the value of the shape parameter a value for F(c,p) may be selected from Table 4. The estimate of the percentile follows simply according to equation (2).

It should be noted that a bound of uncertainty could be approximated by estimating Lp at the highly skewed c=1 and nearly unskewed c=6 shape parameter values.

APPLICATION TO THE MAGIC MODEL

MAGIC has been used to predict past and future mean alkalinity values. The hybrid approach has been applied to these predictions and estimates of the 95% and 5% percentiles have been derived. The predicted means and estimated percentiles are plotted in Figure 7. Two estimates of each percentile are plotted - these are based on shape parameter values for the years 1986 and 1987. The wide spread of behaviour reflects the variability associated with catchment chemistry especially those subject to snow melt and extreme hydrological events. Nevertheless the ranges provide valuable information to biologists to assess fishery survival in acid streams (Ormerod et

Table 4: The factor F(c,p) for the two parameter Weibull distribution calculated over a range of percentiles and shape parameter values.

	Percentile (p)							
	67	75	80	85	90	95	97	99
SHAPE PARAMETER (C)								
1	1.11	1.39	1.61	1.90	2.30	3.00	3.51	4.61
1.25	1.17	1.39	1.57	1.79	2.09	2.58	2.93	3.64
1.5	1.19	1.38	1.52	1.70	1.93	2.30	2.56	3.07
1.75	1.19	1.35	1.47	1.62	1.81	2.10	2.30	2.69
2	1.19	1.33	1.43	1.55	1.71	1.95	2.11	2.42
2.25	1.18	1.31	1.39	1.50	1.64	1.84	1.97	2.23
2.5	1.17	1.28	1.36	1.46	1.57	1.75	1.86	2.08
2.75	1.17	1.27	1.34	1.42	1.52	1.67	1.77	1.96
3	1.16	1.25	1.31	1.39	1.48	1.61	1.70	1.86
3.25	1.15	1.23	1.29	1.36	1.44	1.56	1.64	1.78
3.5	1.14	1.22	1.27	1.33	1.41	1.52	1.59	1.72
3.75	1.14	1.21	1.26	1.31	1.38	1.48	1.55	1.66
4	1.13	1.20	1.24	1.29	1.36	1.45	1.51	1.62
4.25	1.13	1.19	1.23	1.28	1.34	1.42	1.48	1.57
4.5	1.12	1.18	1.22	1.26	1.32	1.40	1.45	1.54
4.75	1.12	1.17	1.21	1.25	1.30	1.38	1.42	1.51
5	1.11	1.16	1.20	1.24	1.29	1.36	1.40	1.48
5.25	1.11	1.16	1.19	1.23	1.27	1.34	1.38	1.45
5.5	1.10	1.15	1.18	1.22	1.26	1.32	1.36	1.43
5.75	1.10	1.14	1.17	1.21	1.25	1.31	1.34	1.41
6	1.10	1.14	1.17	1.20	1.24	1.29	1.33	1.39

al, 1988)

Further years of data can be used to assess the general adequacy of assumption (A2) in the hybrid approach as well as the most likely range of shape values for the identified parametric form. Whenever sufficient years are available, the method then can be used to investigate important biological questions for a catchment of interest from more comprehensive analysis than is illustrated here.

CONCLUSIONS

In this paper we have seen how the hybrid approach can be used to supplement the predictions from process models such as MAGIC. Data from an existing catchment have been analysed and a preliminary form for the distribution has been chosen. The mean values produced by the MAGIC model have then been combined with this knowledge of the distribution and estimates of the extremes derived. The approach is general and can be applied to the prediction of other water quality variables where samples can be regarded as belonging to a parametric probability distribution.

Further work is required to examine the validity of our assumption that, for a given catchment, the selected form of distribution does not change substantially over time. Data from long term catchment sites such as that of Birkenes in Norway could profitably be studied (Christophersen et al, 1989). The approach also has potential use in the study of catchments where strong artificial perturbations have occurred such as at Llyn Brianne where liming has taken place (Whitehead et al, 1988). Finally, estimation of the extremes could be substantially improved if the process model were to yield accurate predictions not just of the mean but also the variance or a range of percentiles about the mean, however narrow that range. This type of additional information would aid calibration of the shape parameter value for the pdf that is assumed or statistically identified from historic data sets.

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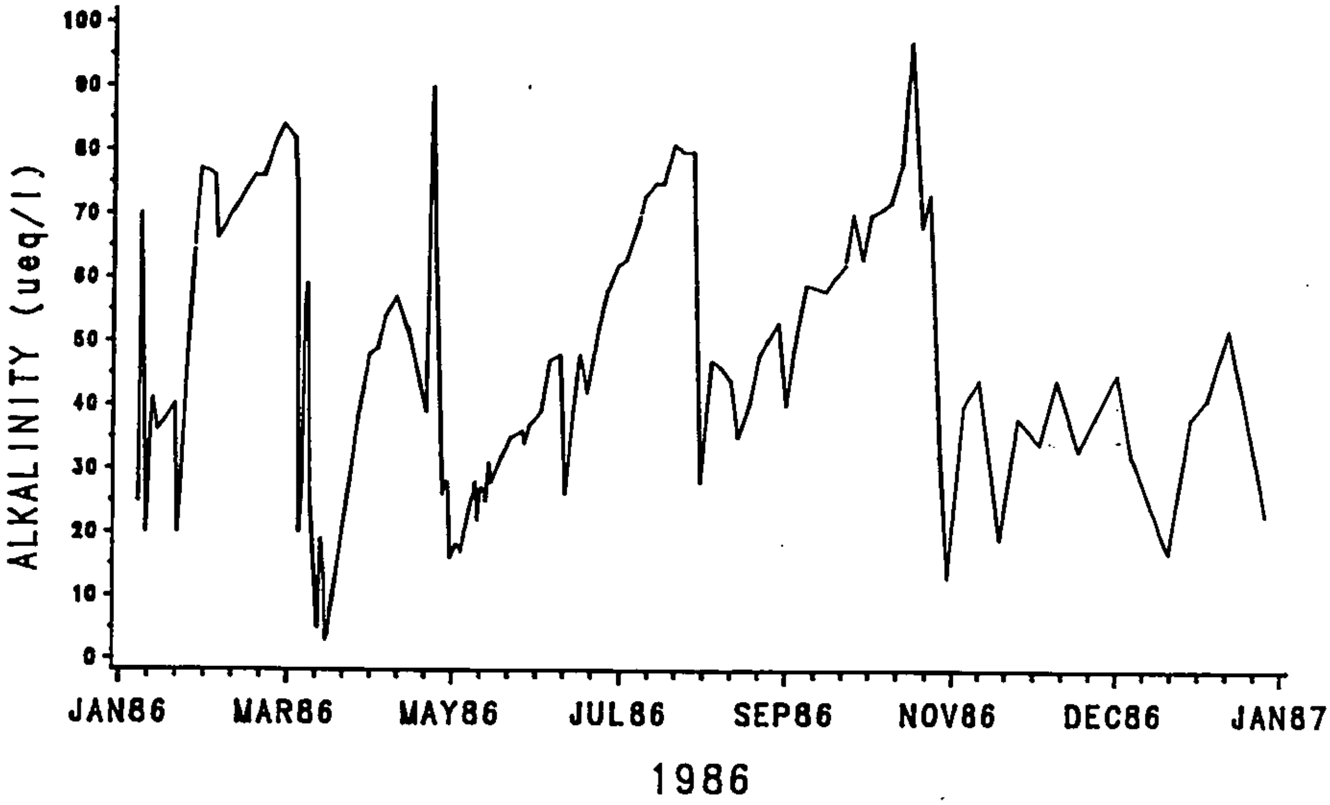
Figure 1.

Time series plot of Alkalinity (1986)



Time series plot of Alkalinity (1987)

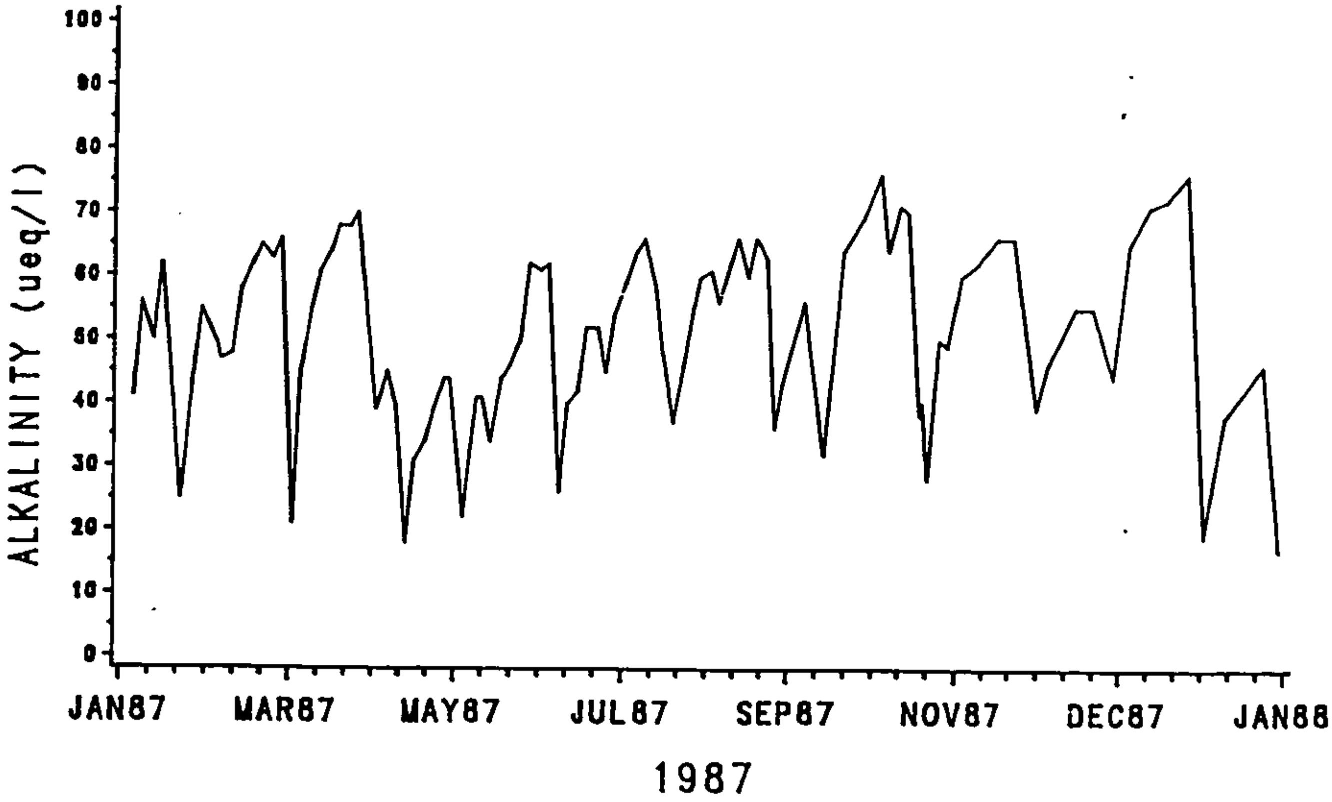
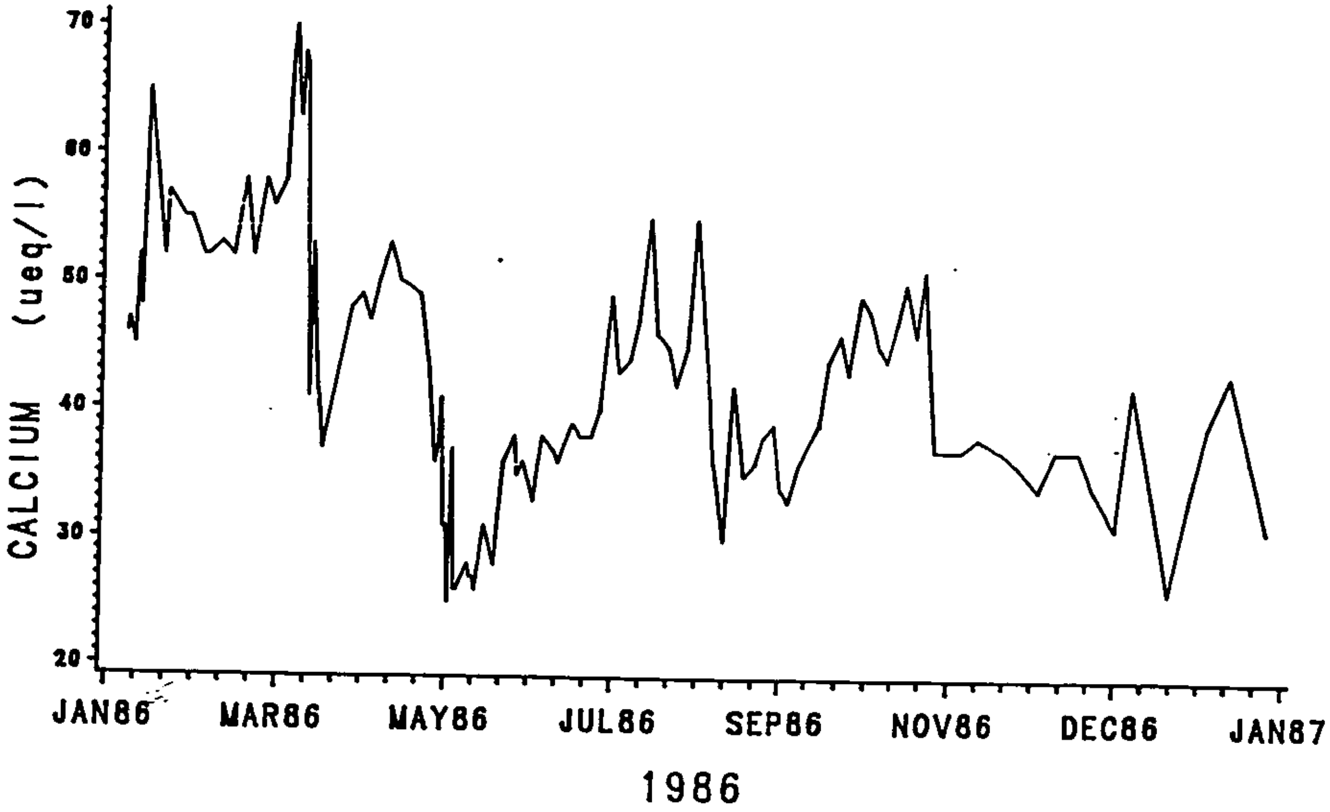


Figure 2.

Time series plot of Calcium (1986)



Time series plot of Calcium (1987)

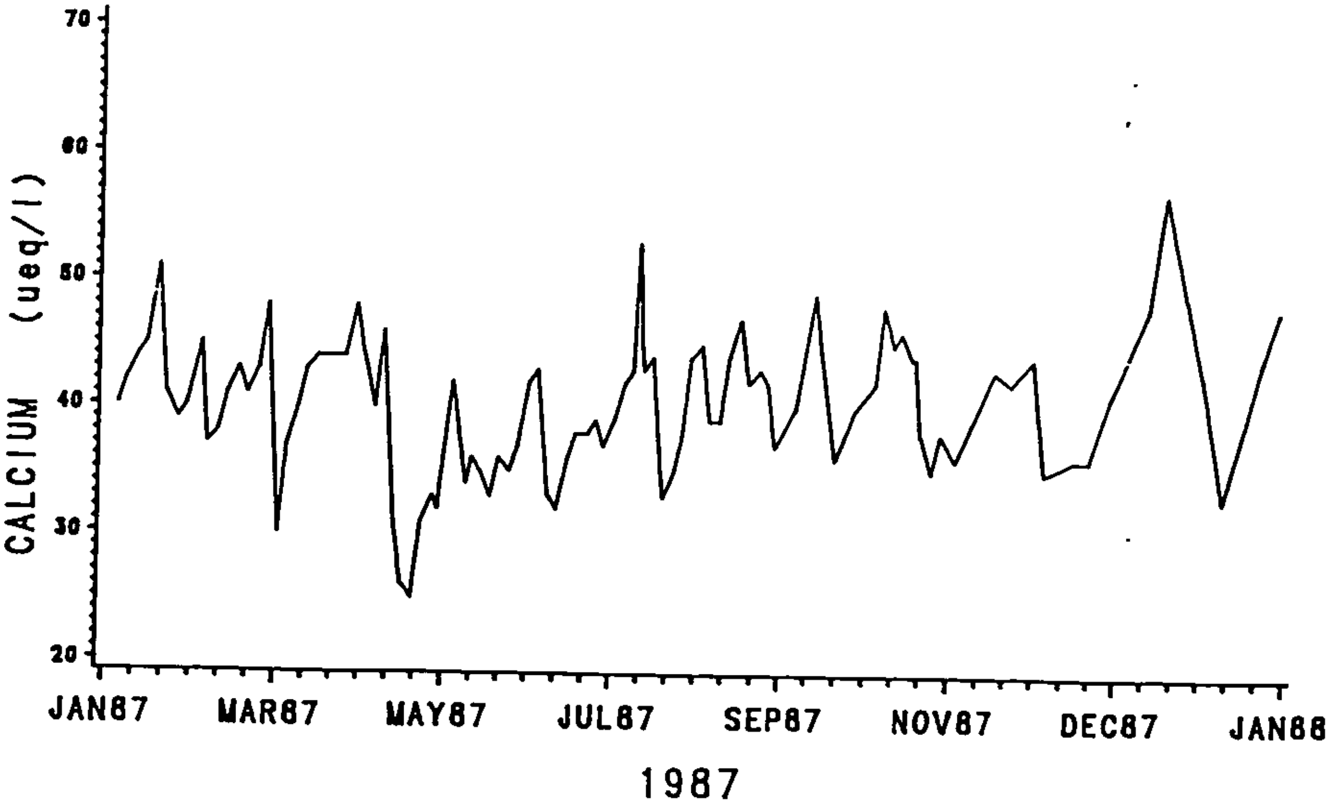


Figure 3.

Fit of the two parameter Weibull distribution
to the empirical cumulative distribution function

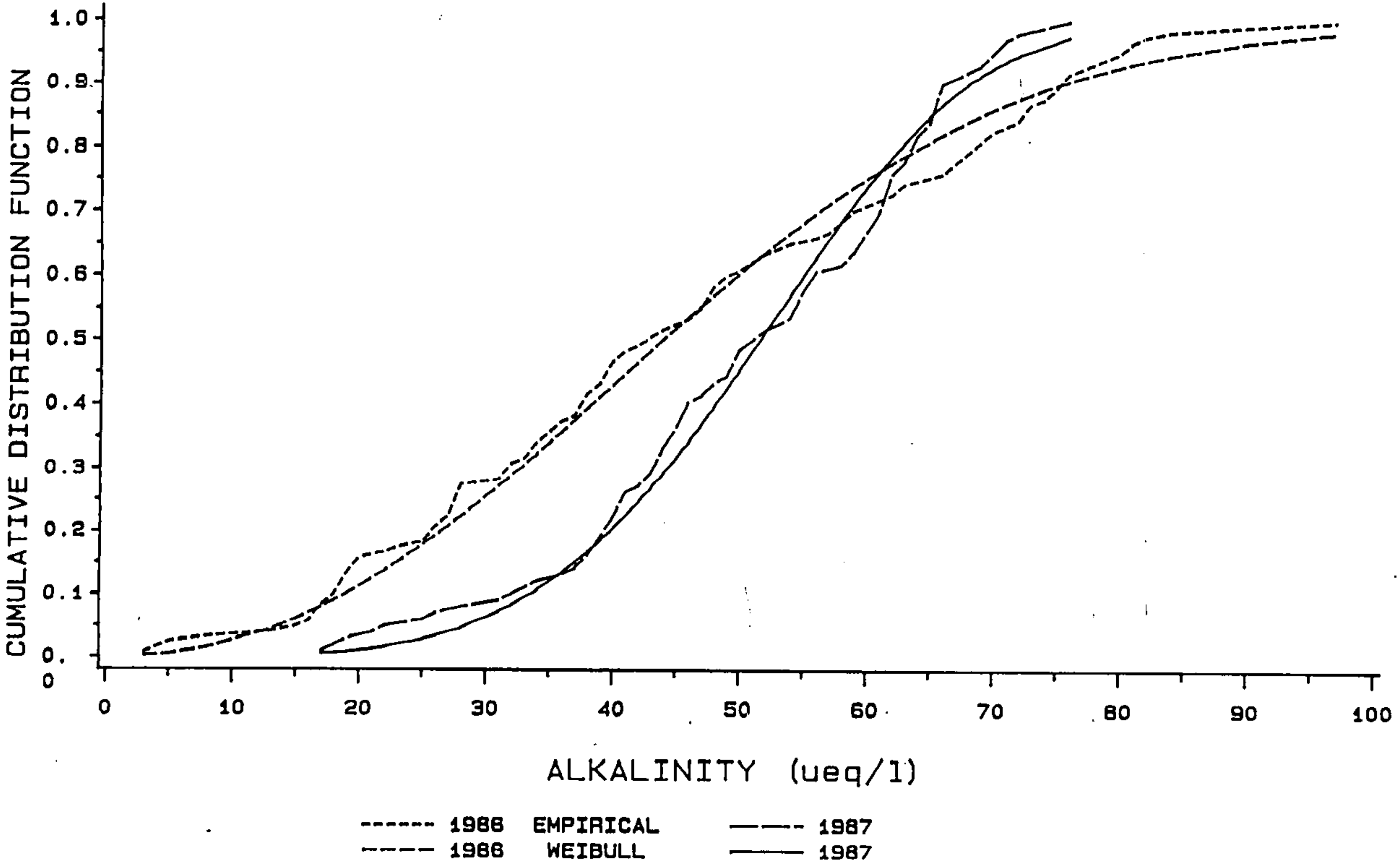


Figure 4.

Plot showing dependency of the scale parameter on the shape parameter using mean values from 1986 and 1987

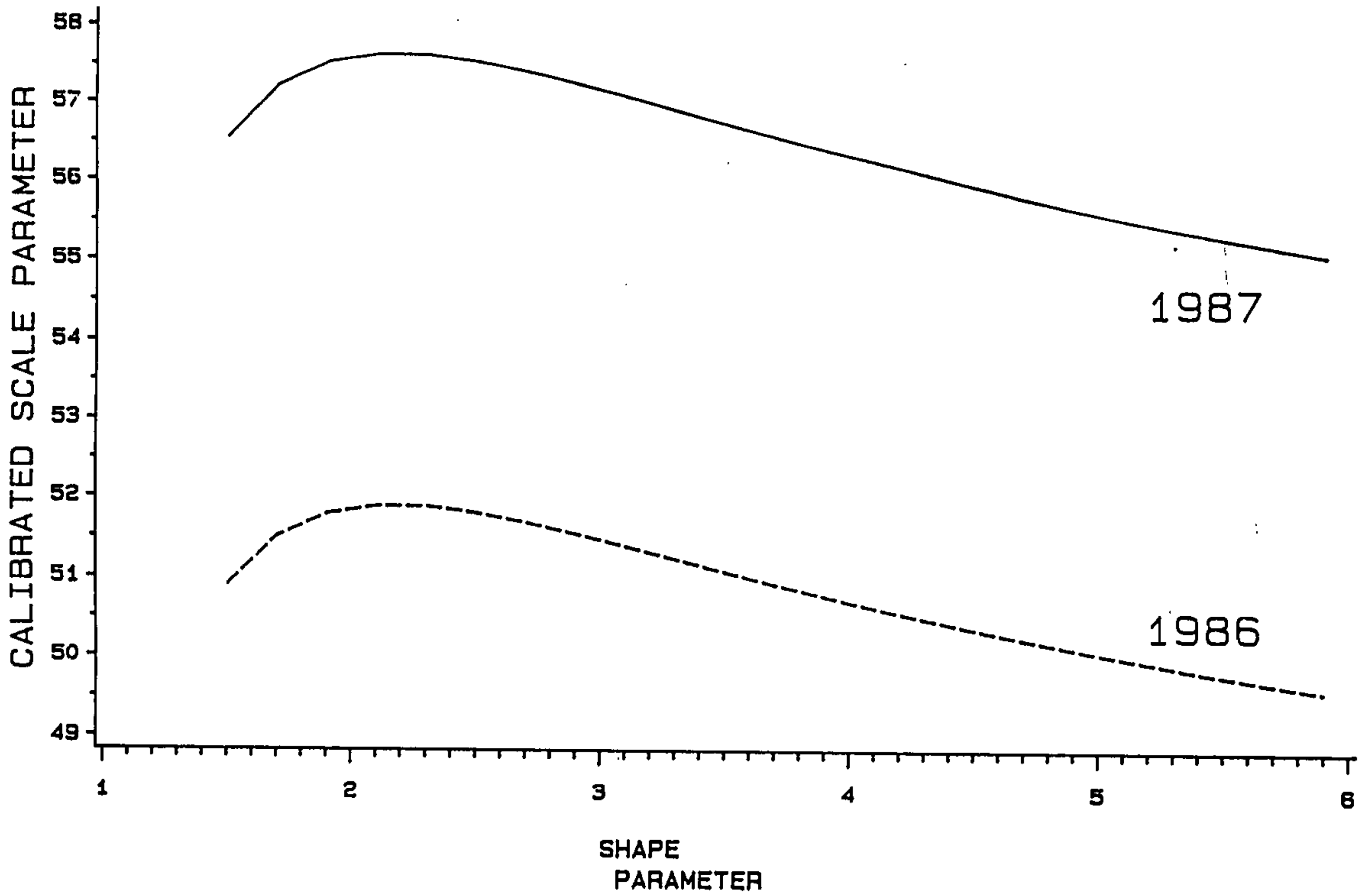
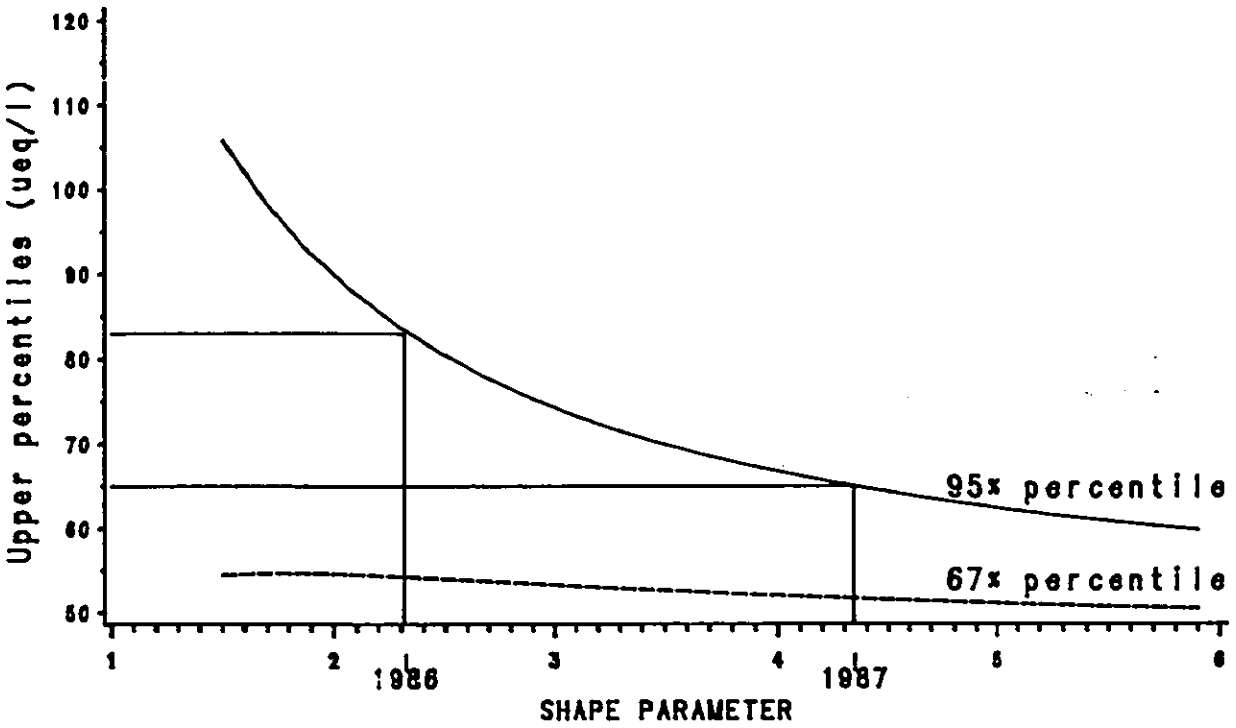


Figure 5.

Sensitivity of upper percentile
to the shape parameter value - 1986
YEAR=1986



Sensitivity of upper percentile
to the shape parameter value - 1987
YEAR=1987

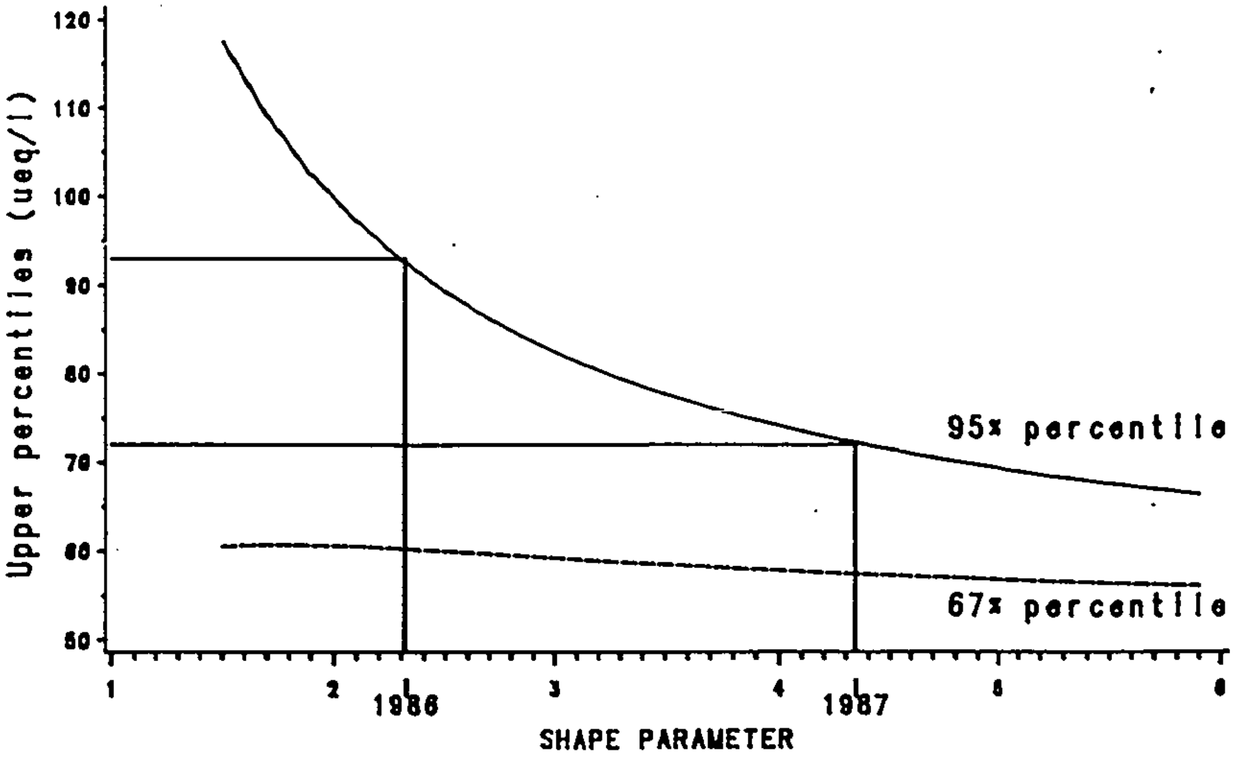
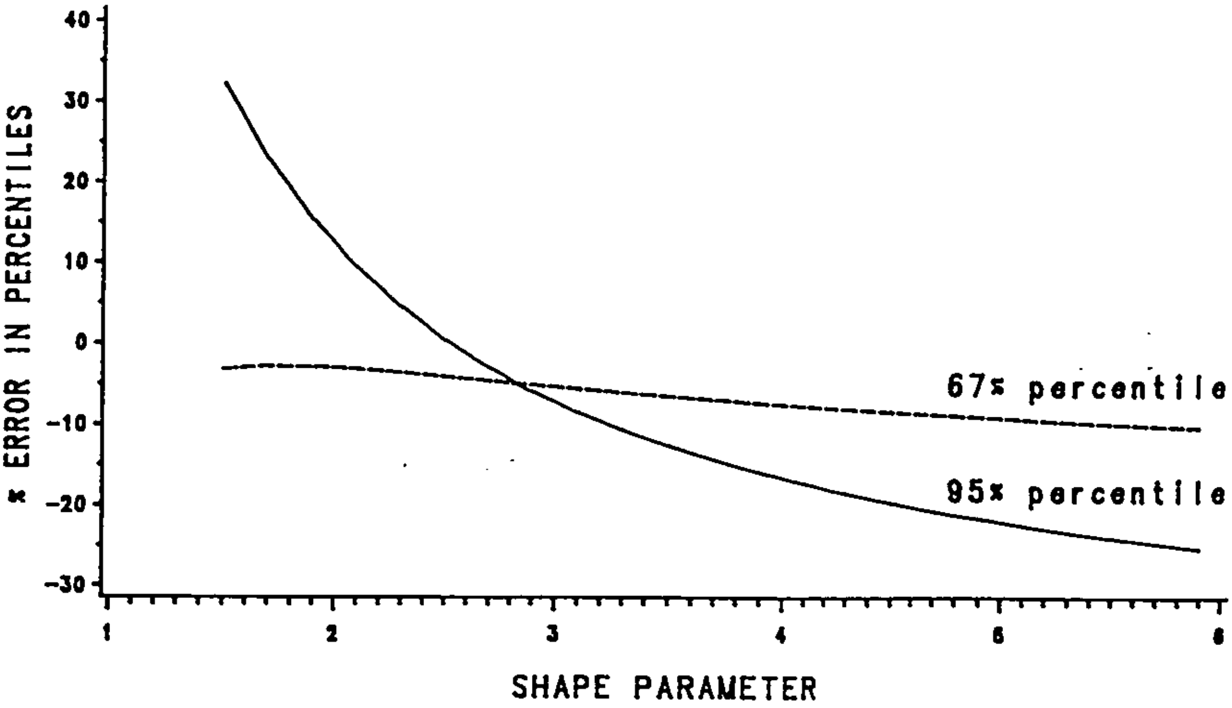


Figure 6.

Plot showing effect of shape on errors in the percentiles for 1986, assuming that the observed percentiles are correct
YEAR=1986



Plot showing effect of shape on errors in the percentiles for 1987, assuming that the observed percentiles are correct
YEAR=1987

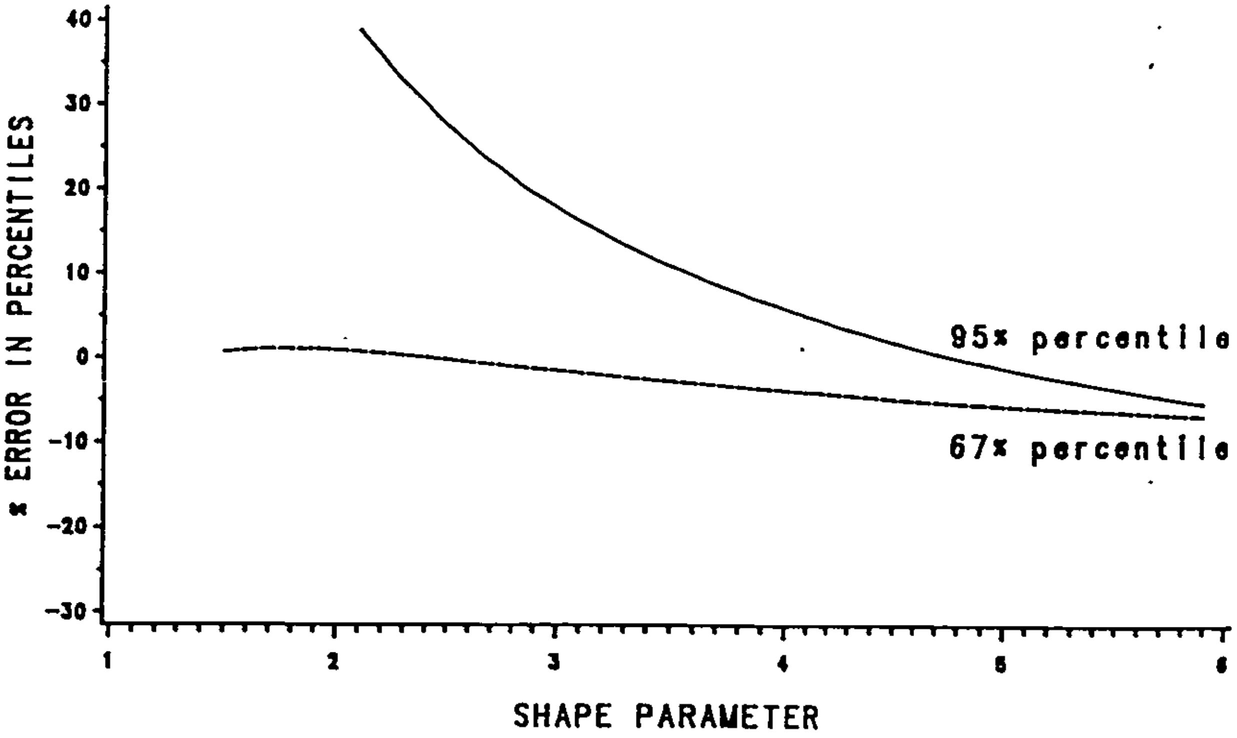
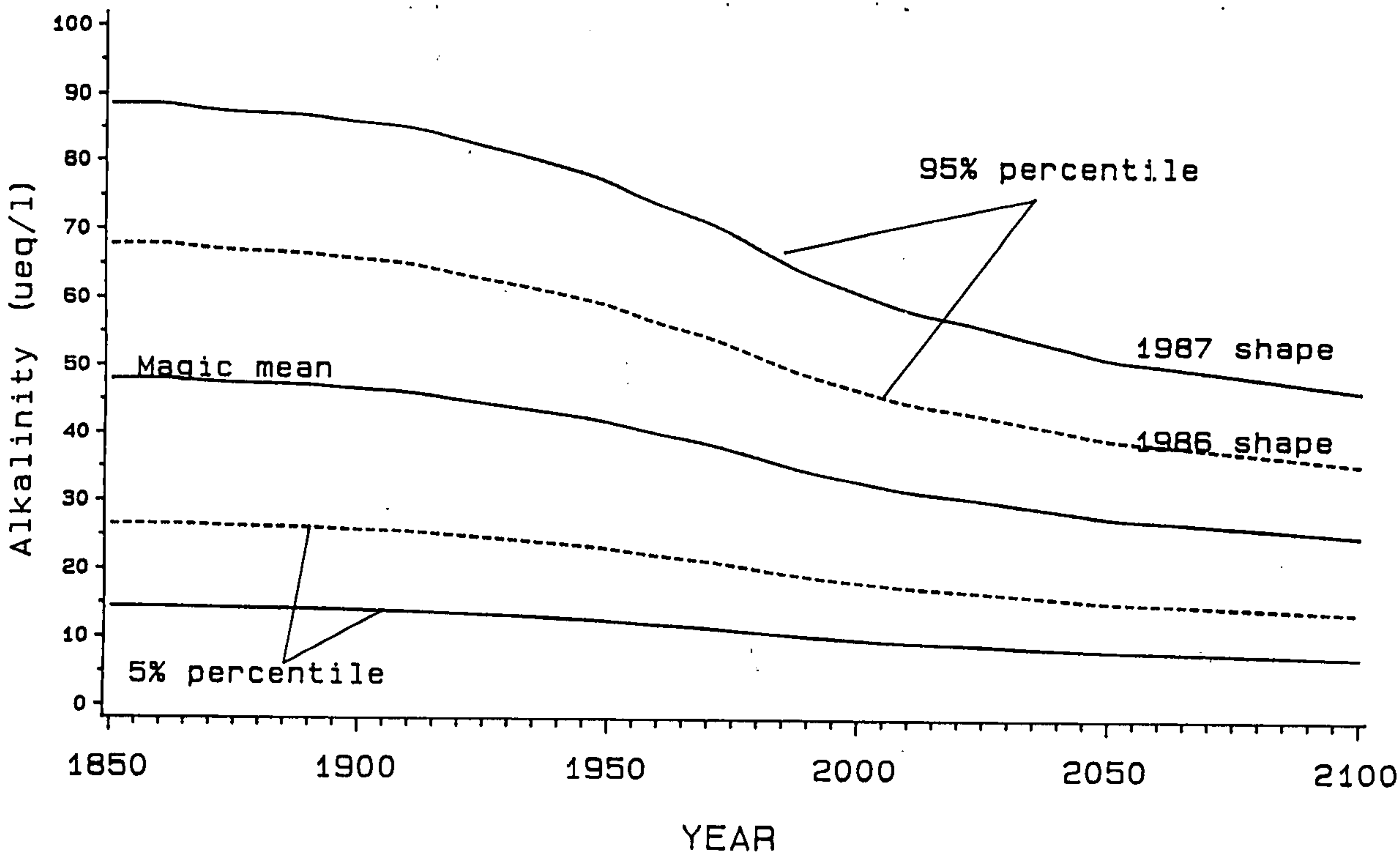


Figure 7.

Predicted means from MAGIC with estimated
95% and 5% percentiles



3.2 PREDICTING FUTURE EPISODIC CHANGES IN STREAM CHEMISTRY

INTRODUCTION

An assessment of the impact of surface water acidification on ecosystems requires an understanding of changes in stream chemistry over two timescales. That is, the long term build up of chronic acidity over periods of years and the short term acute changes associated with storm events. These short term acidic pulses are superimposed on long term trends and reconciliation of the two timescales is difficult. Hydrochemical models have been developed to simulate either long term changes in mean concentrations of water quality variables (MAGIC;Cosby et al. 1985a: RAINS;Kamari et al. 1984), or have focused on short term hydrologically driven responses (ILWAS;Chen et al. 1984: TRICKLEDOWN;Schnoor et al. 1984: BIRKENES;Christophersen et al. 1982). None of these models have proved sufficiently robust to work across the two timescales.

The link between long term build up of acidity and the extinction of fish populations in many surface water ecosystems is now well documented (Haines, 1986). It is also established that the survival of fish in upland streams is dependant not just on mean stream pH but the duration and severity of acid episodes (Turnpenny et al. 1987). Little is known, on the other hand, about the link between mean acidity and extreme values during episodes. A long term decrease in mean pH could theoretically be accompanied by two alternative episodic responses; both baseflow and peakflow waters show a corresponding drop in pH or, baseflow waters remain well buffered but the severity of the acid pulses at peak flow increases. To distinguish between these possibilities it is necessary to identify the mechanisms of flow generation and the source areas of the flow components comprising the flows at all discharge levels.

In this paper the link between long term and episodic response is examined through the development of a technique for modelling the changes important to short term stream water quality variations under continued acid deposition. This involves, (1) a mixing model approach to identify simple flow pathways and components of stream flow (endmembers), (2) a two layer version of MAGIC calibrated to present day endmember chemistry and used to predict the changes which will occur in the endmembers under acid deposition, and, (3) an assessment of future short term water quality variations using the predicted endmembers. The technique is applied to the Afon Gwy a small, moorland catchment at Plynlimon in mid-Wales.

THE STUDY SITE

The Afon Gwy catchment forms part of the headwaters of the river Wye. The geology consists of lower Palaeozoic mudstones, shales and grits with locally derived glacial and postglacial drift. Soil types include peats, brown earths, stagnogleys and stagnopodzols. The vegetation is acid grassland dominated by Nardus, Festuca and Agrostis species. Mean annual rainfall and runoff for 1983 - 1984, 1984 -1985 was 2385 and 2111 mm/year, respectively. Average rainfall, stream water and soil water chemistry is shown in Table 1 together with the stream water composition at baseflow, that is, from samples taken during very low flow periods when the water is assumed to originate from deeper, 'groundwater' sources and so is characterised by low acidity and high alkalinity.

THE MIXING APPROACH

The essence of the mixing approach is the concept that stream waters are generated by the mixing of chemically distinct water types (Christophersen et al., 1990; Hooper et al., 1990; Neal et al., 1990). The mean composition of each of these components (endmembers) is assumed to change only slowly and at most from year to year. The rapid chemical changes seen in the stream, in response to rainfall, are assumed to be the result of mixing varying proportions of the endmembers. The quantity or proportion of each endmember contributing to the stream is determined by changing catchment flowpaths as the storm intensifies and recedes.

The choice of characterisic endmembers for the catchment is based on the ion-flow relationships in the stream. Chemical response of the Gwy is typical of many British upland streams in that during high flow the pH falls, aluminium levels rise and base cation concentrations decrease (UKAWRG, 1988). At times of low flow the stream waters are well-buffered, of high pH and relatively rich in base cations. A simple interpretation of this can be made. During peak flows, when the water table is high, waters move through the acidic upper soil layers to the stream. During low flow, waters originate from deeper sources where weathering reactions with the bedrock occur (Neal et al., 1985). Only two components of flow are identified at this stage but this helps to limit the complexity of the modelling work and fits with observed variations (Neal et al., 1990; Robson and Neal, 1990; Kleissen et al., 1990). The natural choice is to take soil water as one endmember and a well buffered deep water (ground water) as the other. The rationale for the choice of these two components is discussed further in Neal et al. (1990). The soil water endmember chemistry is derived from L, O, E and B horizon soil water chemistry . The deep water component, however, has not yet been sampled directly and the composition of these waters is inferred from the chemistry of the baseflow waters seen in the stream.

To calibrate the MAGIC model, a mean annual proportion of mix between the two endmembers is required to fix the flow pathways in the model. This proportion of mix can be calculated by using a conservative chemical characteristic as a tracer such as the acid neutralising capacity (ANC). ANC is defined by:-

ANC = Sum "strong" base cations - Sum "strong acid anions"

and is determined from the chemical composition of the water, all terms being expressed in μEq/l. The ANC distinguishes well betwen the two chosen endmember water types and it is unaffected by CO_2 degassing. Extensive details of the use of ANC in hydrograph separation are given in Neal et al., (1990) and Robson and Neal, (1990). Calculated ANC for stream water, soil water and baseflow water is given in Table 2.

Since ANC is conserved during mixing the average proportion of soil water can be derived;

$$\text{Average proportion soil water} = \frac{\text{ANC deep water} - \text{ANC stream}}{\text{ANC deep water} - \text{ANC soil water}}$$

Using this relationship, the calculated mean flow-weighted proportion of soil water for the Gwy was approximately 0.48.

Clearly, a number of limitations exist in the use of this mixing approach and it is necessary to assume that, (1) streamflow is generated by water from two sources, (2) the direct contribution of rain to the stream is negligible, (3) a single soil endmember is representative of the upper soils even though the soils show heterogeneity both spatially and with depth, (4) the deep water component has uniform composition, and, (5) the chemistry of the endmembers remains constant during a storm.

Given the limitations of these assumptions and analytical error in the chemical measurements, a perfect match between the modelled and the observed chemical species in the stream is unlikely. The ANC gives a good indication of the overall composition of a water sample and whereas some deviations in individual determinands are acceptable, it is important that the modelled ANC is accurate.

THE MAGIC MODEL AND APPLICATION TO THE GWY

The MAGIC model uses equilibrium equations to describe soil processes and mass balance equations to describe catchment input-output relationships. Detailed descriptions of the conceptual basis of tha model and the equations on which it is based are documented elsewhere (Cosby et al.,1985 a,b). In this application a two layer version of MAGIC is used (Jenkins and Cosby, 1989) enabling the simulation of two chemically distinct waters. Here, the waters are chosen to correspond with the flow components identified from the mixing considerations outlined earlier. That is, the top layer represents the lumped L, O, E and B soil horizons while the bottom layer represents the C- horizon and deeper till layers. Similarly, the flow proportions included in the model are those suggested by the mixing approach. That is, all rain passes through the upper soils (top layer) and 42% of that percolate contributes directly into the stream whilst the remainder is routed via the deeper zones (bottom layer) to the stream (Figure 1.).

Concentrations of chloride and sulphate in the rainfall and stream were adjusted for occult and dry deposition of sea-salts and anthropogenic sulphur compounds. Between 1844 and 1984 the modelled rainfall inputs were varied according to the deposition sequence outlined by the Warren Springs laboratory (1983).

The two layers in the model were conceptualised such that different reaction mechanisms dominate each layer since they generate waters with distinct chemistries. The water from the upper soils is acidic and aluminium rich suggesting that ionic exchange mechanisms are the most important influence on soil water chemistry. Water from the deeper sources is rich in base cations indicating that it comes from a high weathering zone. In this application, therefore, it is assumed that ion-exchange occurs in only the top layer and that the ion exchange capacity of the lower soils and till layers is small enough to be neglected. On the other hand, weathering is assumed to take place predominantly in the deeper layers. A source of base cations was found to be essential in the upper soils, however, in order to fit the observed ANC. This may be attributed to biological activity or cycling. Only weathering inputs for calcium and magnesium were necessary in the top layer. Observations of throughfall chemistry support this: concentrations of calcium and magnesium are 15 and 18 µmol/l, respectively in throughfall compared with 4 and 10 µmol/l, respectively, in rainfall, allowing for evaporation: for sodium the throughfall concentration (94 µmol/l) is little different from rainfall (85 µmol/l) and so no extra input to the top layer is necessary.

The soil characteristics used in the model are given in Table 3. The depth of the upper soil (0.4m) corresponds to the average combined depth of the L, O, E and B horizons. An average depth of 1m is assumed for the remainder. The bottom layer is denser and of lower porosity. The partial pressure of carbon dioxide is assumed to be 30 times atmospheric for both layers (Neal and Whitehead, 1988). For the stream the pCO_2 was set to 3 times atmospheric pressure (Neal, 1988 a,b). The organic acid concentration in the two layers was calculated from the average observed DOC concentration assuming 9 carbon atoms per molecule. Dissociation constants were specified according to previously used values for similar sites in Scotland and are the same for each layer.

MODEL CALIBRATION

The model was calibrated to the chemistry of the stream water, the soil water and the deeper groundwater by adjusting weathering rates, uptake rates and the initial soil base saturation. The optimised values for the adjustable parameters are given in Table 4. Sulphate adsorption in the model is described by a Langmuir isotherm which has two parameters (Hornberger, 1986). These are calibrated on the assumption of a present day steady state condition with respect to sulphate input and output. Unique isotherms were calibrated for each layer under the assumption that the bottom layer has a greater capacity to adsorb sulphate than the top layer.

Nitrate and ammonia were modelled by calibrating catchment uptake to match the difference between inputs and outputs. Nitrate input was further increased to account for the high nitrate levels in the top layer resulting from a combination of dry deposition and biologically activated nitrogen mineralization.

RESULTS

The results from the calibrated model, shown in table 5, demonstrate a good agreement with stream chemistry although soil and groundwater chemistry are less well simulated. Given the variability of soil water chemistry with depth and aerially across the catchment, however, it is encouraging that each of the determinands falls within the measured range of soil water chemistry. The chloride concentration in the bottom layer is lower than observed in stream baseflow and is a consequence of the assumption of chloride conservativity in the model: this forces the chloride concentration in all of the model compartments to be constant. As a result of the low chloride level, simulated base cation concentrations are also lower than observed in the bottom soil layer.

Simulated stream ANC lies within 1 ueq/l of the value calculated from observed stream chemistry and the simulated ANC in the top soil layer is well within the observed range for soil waters. The simulated ANC for the lower box, however, is slightly higher than for stream baseflow water, probably because at baseflow the stream water includes a small soil water component. In this case the "true" groundwater endmember may be characterised by a higher ANC than that of stream baseflow.

The time trends of reconstructed soil, ground and stream water chemistry from 140 years ago, that is pre-acidification, up to the present day, are shown in figure 2. The pH (Figure 2a) of the stream falls rapidly as deposition increases in the 1950's and levels out in the 1980's in response to decreases in atmospheric deposition in recent years. The pH of the two endmembers changes similarly, but to a lesser degree, through the same period as a result of the higher partial pressure of carbon dioxide in the two layers. As a consequence of CO_2 degassing, the pH of the stream is not always bounded by the two endmember pH values, espescially at higher pH levels.

Sulphate concentrations in all three model compartments increase through time (Figure 2b) in line with the assumed increase in sulphate deposition. The variation in response between the endmembers reflects the sulphate adsorption constants chosen in the calibration whilst the stream concentration represents a direct mix of the two components. Calcium, magnesium (Figure 2c, d) and aluminium concentrations also increase in response to sulphate input whilst soil exchangeable bases (top layer) decrease (Figure 3). Exchangeable magnesium decreases most quickly, relative to the other exchangeable cations. This is a direct consequence of the Gaines - Thomas expression used to model ion exchange, whereby the most abundant ion is preferentially leached.

The model has also been used to estimate changes in stream, soil and deep water components into the future under two sulphate deposition reduction scenarios (Figure 2a-d); a reduction to 30% and 60% of present day levels by the year 2000 and held at a constant level thereafter.

Stream water pH improves in response to increasing pH in both soil layers and the greatest recovery occurs in response to the larger deposition reductions. Sulphate concentration in both endmembers decreases and the model predicts a reversal in sulphate concentration gradient between the upper and lower soils. Prior to the 1970's, modelled groundwater sulphate concentrations are lower than in the upper soils. In future years, as a consequence of the chosen sulphate adsorption constants sulphate concentration in groundwater takes longer to decline than the upper soil water. By the year 2100 the sulphate concentrations have equilibriated with the lowered input and there is no longer a variation between the layers.

Simulated aluminium concentrations fall, in line with sulphate reduction. The results give only a broad indication of likely trends since the cubic equilibrium conditions assumed in MAGIC may well not hold during episodes (Neal et al, 1989); this does not affect hydrogen ions or other base cations to any significant degree. The response of the base cation concentrations is more complex (Figure 2c, d). As sulphate input is reduced, fewer cations are exchanged from the soils and so cation concentrations decrease in both endmembers. The decrease is rapid for the first 10-20 years and then slows, directly reflecting the mobile anion input to the system. Under a 60% deposition reduction, some long term recovery is predicted but a 30% reduction is insufficient for any recovery in the model. In terms of the catchment soils (upper box), a 60% reduction in sulphate input produces a significant improvement in cation exchange capacity (Figure 3).

To assess the performance of the two layer model, a basic one-layer version of MAGIC was also calibrated to the Gwy catchment. Where possible identical values of the fixed parameters were chosen. The parameters for the aggregated soil layer were lumped according to standard practice (Jenkins and Cosby, 1989). As expected, the results show a broadly similar pattern of behaviour. The one-layer stream water chemistry falls well within the range spanned by the predicted endmembers from the two-layer model (Figure 4). However, the optimised one layer model estimates a significantly lower weathering rate than was found for the two layer version. As a consequence, the simulated background and predicted future stream chemistries from the one layer model are more acidic and the one layer model is less responsive to the variations in atmospheric deposition. The major differences between the approaches result from the inclusion of an additional body of well buffered water in the two-layer model.

DISCUSSION

During the next 140 years the predicted changes in endmember chemistry will produce a significant improvement, relative to present conditions, in the chemistry of the streamwater, especially at high flows. For example, the model predicts that whereas the difference in cation concentrations at high and low flows will remain the same, relative to each other, the predicted recovery in the upper soil water chemistry and the assumed dominant contribution from that source at high flows will lead to a decrease in the peak concentrations of hydrogen and aluminium. Concentration of both hydrogen and aluminium at baseflow is currently low and this situation will continue.

The incorporation of short term stream chemistry dynamics into models of long term response to changing acid deposition has obvious benefits in determining critical loads to ecosystems. At present, critical load estimation is based only on predictions of mean chemistry (Nilsson and Grennfelt, 1988) and yet stream biota can be seriously affected by short term acid pulses. This is not neccesarily a result of the peak levels of toxic species reached during an event, but may also be a function of the duration of the toxic conditions. If the critical load is to accurately represent the point at which biological life becomes seriously at risk then it must account for these dynamics. Through the technique developed here short term water quality responses can be quantified.

The two layer MAGIC model predicts enhanced recovery relative to the one layer model. Further work is required to see if this result holds in general as present day regional assessments may be too pessemistic.

CONCLUSIONS

1. A simple 2-layer model structure gives a good fit to observed endmember and stream water chemistry.

2. The model predicts that the chemistry of the endmembers has changed historically. Both soil waters and deep waters have acidified and the cation exchange capacity of the soils shows a large decrease.

3. Under reduced deposition the model predicts that the most significant changes in stream chemistry will occur at peak flow with greatly reduced levels of acidity and aluminium. Baseflow chemistry will also improve slightly. Recovery is greatly enhanced by a 60% reduction as opposed to a 30% reduction.

4. The approach may be expanded to model dynamic storm response using mixing principles and can provide valuable information for establishing an episodic basis for critical load estimation.

5. Greater recovery from reduced emission strategies are suggested with the two layer model in comparison with the one layer MAGIC model.

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Table 1.

Rainfall, stream water, soil water and baseflow water chemistry. Units are µEq/l except Al and Si (µmol/l) and pH.

	Rainfall	Stream	Baseflow	Soils		
				Oh	Eag	Bs
Ca	8	36	58	14	20	14
Mg	10	54	70	40	44	40
Na	85	143	166	100	187	173
K	2	3	2	8	4	4
NH_4	17	<5	<5	<5	<5	<5
Si	<2	35	54	18	42	36
SO_4	42	72	74	68	87	71
Cl	106	155	170	124	209	184
NO_3	12	15	4	29	39	28
H	21	13	1	77	55	44
pH	4.7	4.9	6.3	4.1	4.3	4.4
HCO_3	<1	35	27	-	-	-
Al	<2	3	2	10	18	15

Table 2.

Stream water, soil water and baseflow Acid Neutralisation Capacity. Units are µEq/l.

	Stream	Soil			Baseflow
		Oh	Eag	Bs	
Sum cations	236	162	255	231	295
Sum anions	242	221	335	283	248
ANC	-6	-59	-80	-52	47

Table 3.

Soil characteristics used in the two-layer MAGIC model

	Units	Top Layer	Bottom Layer
depth	m	0.4	1
porosity	frac	0.55	0.35
bulk density	kg/m^3	1060	1460
CEC	meq/kg	70	0.1
Organics	μmol/l	56	10
Temperature	°C	7.6	7.6
PCO$_2$	atm	0.009	0.009
$\log_{10}(K_{Al(OH)_3})$		7.8	8.6

Table 4.

Calibrated parameters for the two-layer MAGIC model

		Top Layer	Bottom Layer
SO_4 Halfsat	μEq/l	80	5
SO_4 MAXcap	μEq/l	2	9
pk1 (organics)		4	4

Weathering/Uptakes	Top Layer	Bottom Layer
NH_4	-92	0
NO_3	0	-88
Ca	2	43
Mg	14	28
Na	0	36
K	0	0

Selectivity coefficients

Ca	2.7
Mg	3.27
Na	-0.65
K	-4.7

Initial base saturation: 35.0

Table 5.

Modelled stream and endmember chemistry. Bracketed values are the field measurements. A range is given for the O-B horizons in the soil. Units are µEq/l except pH.

	Stream		Top Layer		Bottom Layer	
Ca	36	(36)	16	(14-20)	55	(58)
Mg	54	(54)	41	(40-44)	66	(72)
Na	143	(143)	126	(100-183)	159	(166)
K	3.2	(3)	3.2	(4-8)	3.3	(2)
NH_4	1.5	(<5)	1.5	(<5)	1.5	(<5)
SO_4	72	(72)	71.0	(68-87)	73	(74)
Cl	155	(155)	155	(124-209)	155	(170)
NO_3	16	(15)	29	(28-39)	3.5	(4)
H^+	18	(13)	60	(44-77)	3.6	(1)
pH	4.8	(4.8)	4.2	(4.1-4.4)	5.4	(6.3)
Al^{3+}	7	(9)	46	(28-55)	1.0	(5)
ANC	-5	(-6)	-69	(-52 - -80)	54	(47)

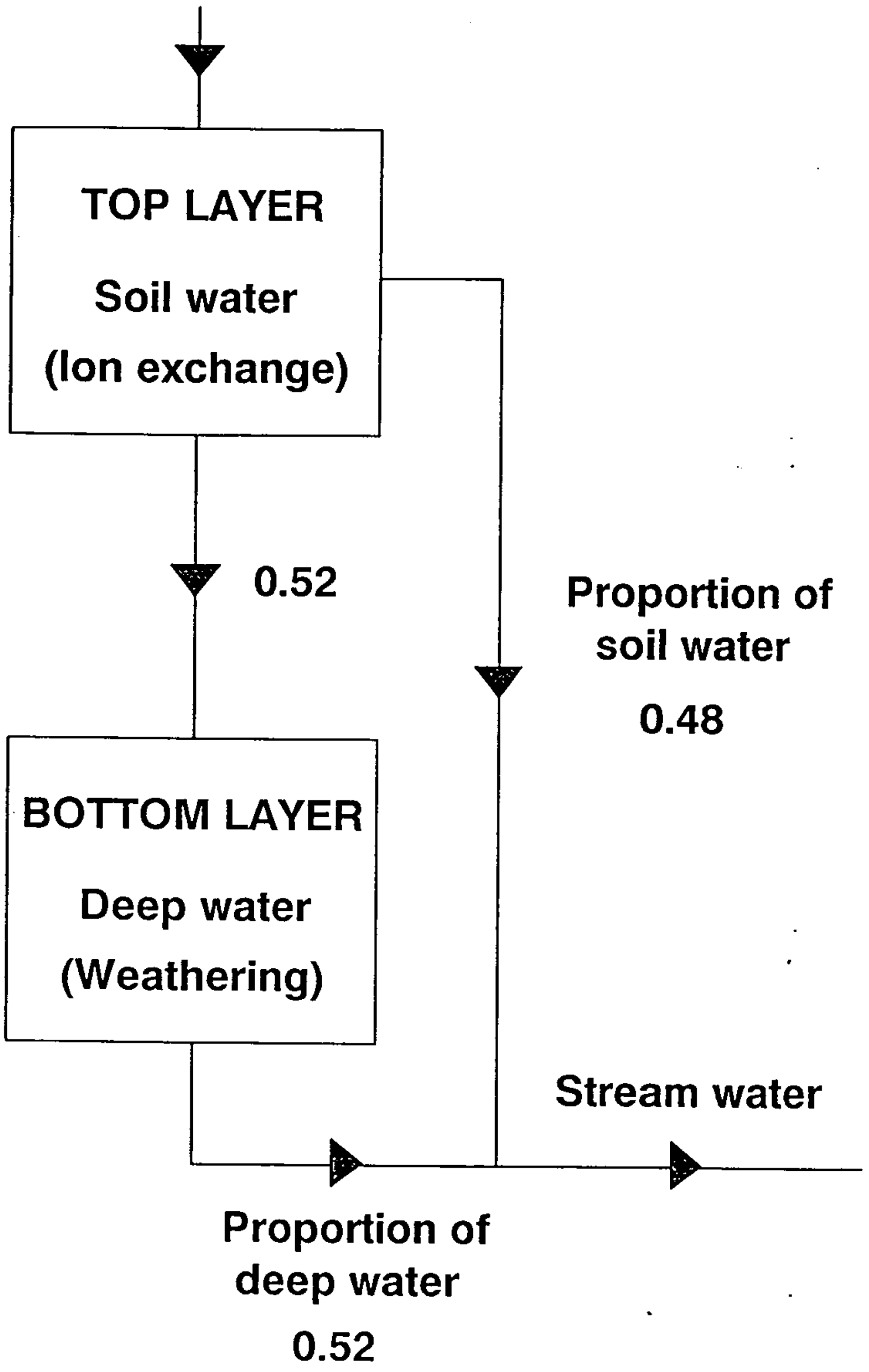
Figure Legends

Figure 1. Flow routing for the two-layer MAGIC model.

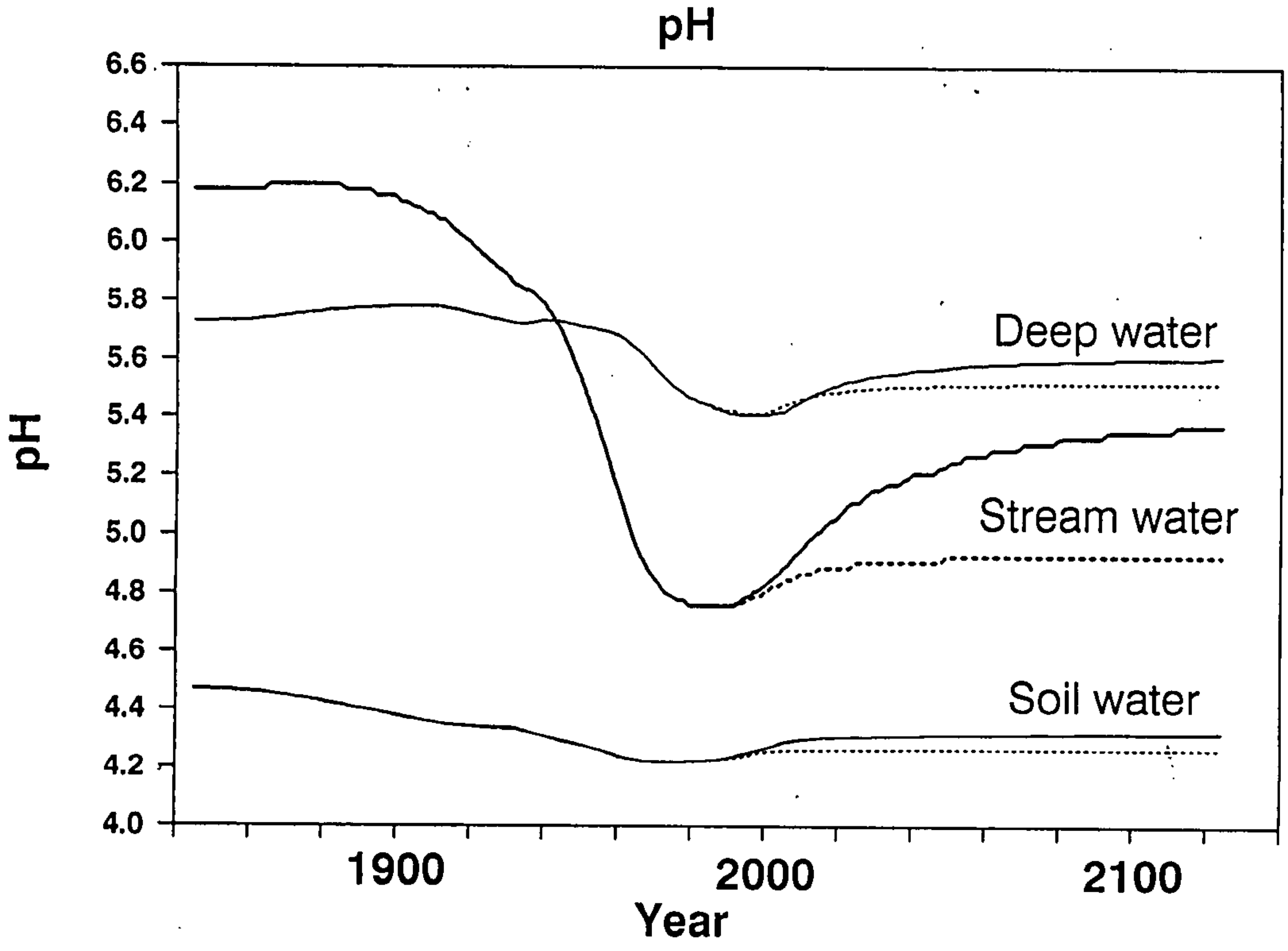
Figure 2. Modelled stream and endmember chemistry; (a) pH, (b) sulphate, (c) magnesium, (d) calcium. For a, c and d solid lines show the predictions for 60% and the dotted lines for 30% reduction.

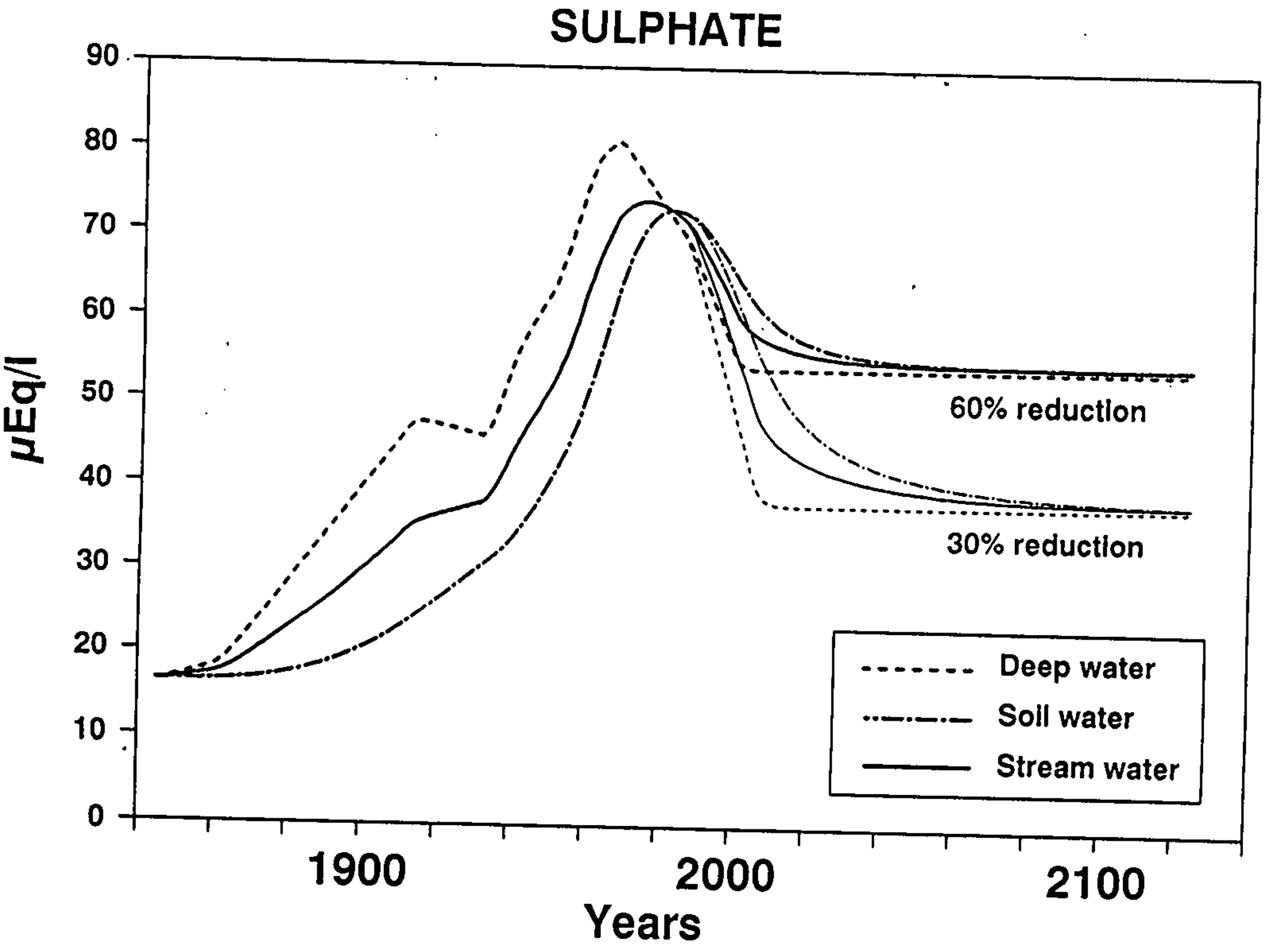
Figure 3. Simulated cation exchange capacity in the top soil layer.

Figure 4. Comparison of Acid Neutralisation Capacity for the one layer (line with markers) and two layer (no markers). Solid lines show the predictions for 60% reduction and dotted lines for 30% reduction.

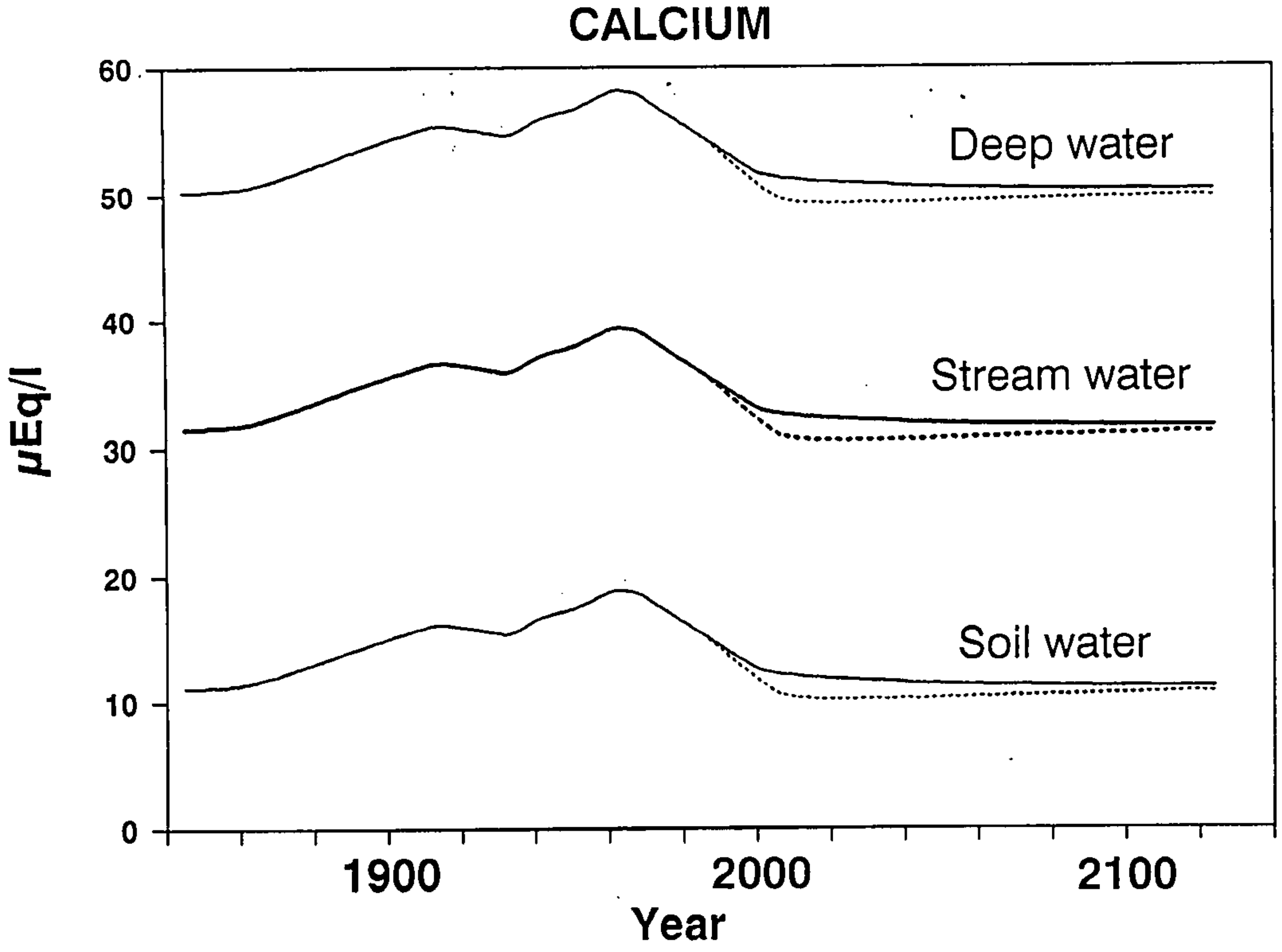

TOP LAYER
Soil water
(Ion exchange)
0.52
Proportion of soil water
0.48
BOTTOM LAYER
Deep water
(Weathering)
Stream water
Proportion of deep water
0.52

2a

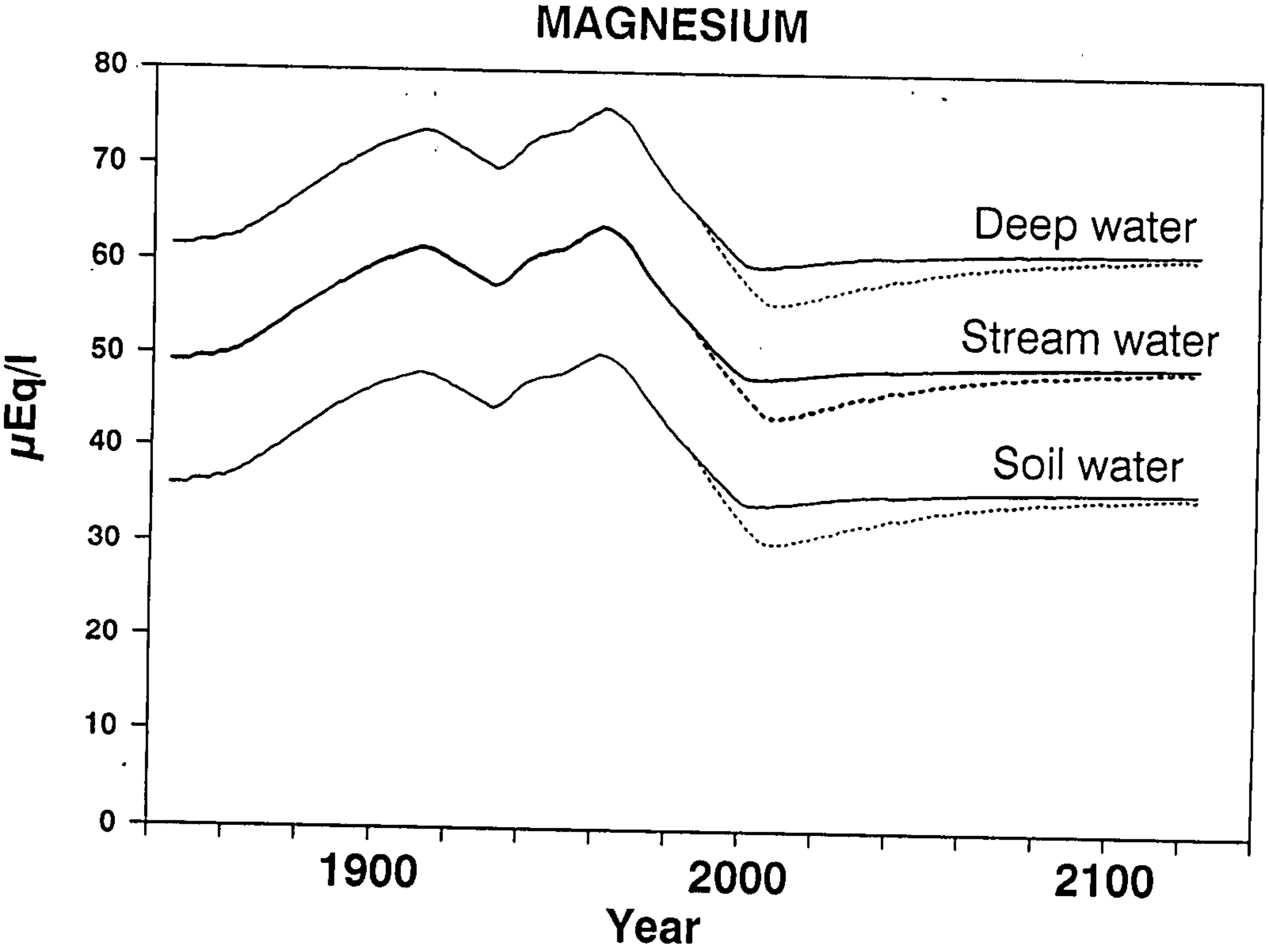

pH
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
pH
Deep water
Stream water
Soil water
1900
2000
2100
Year

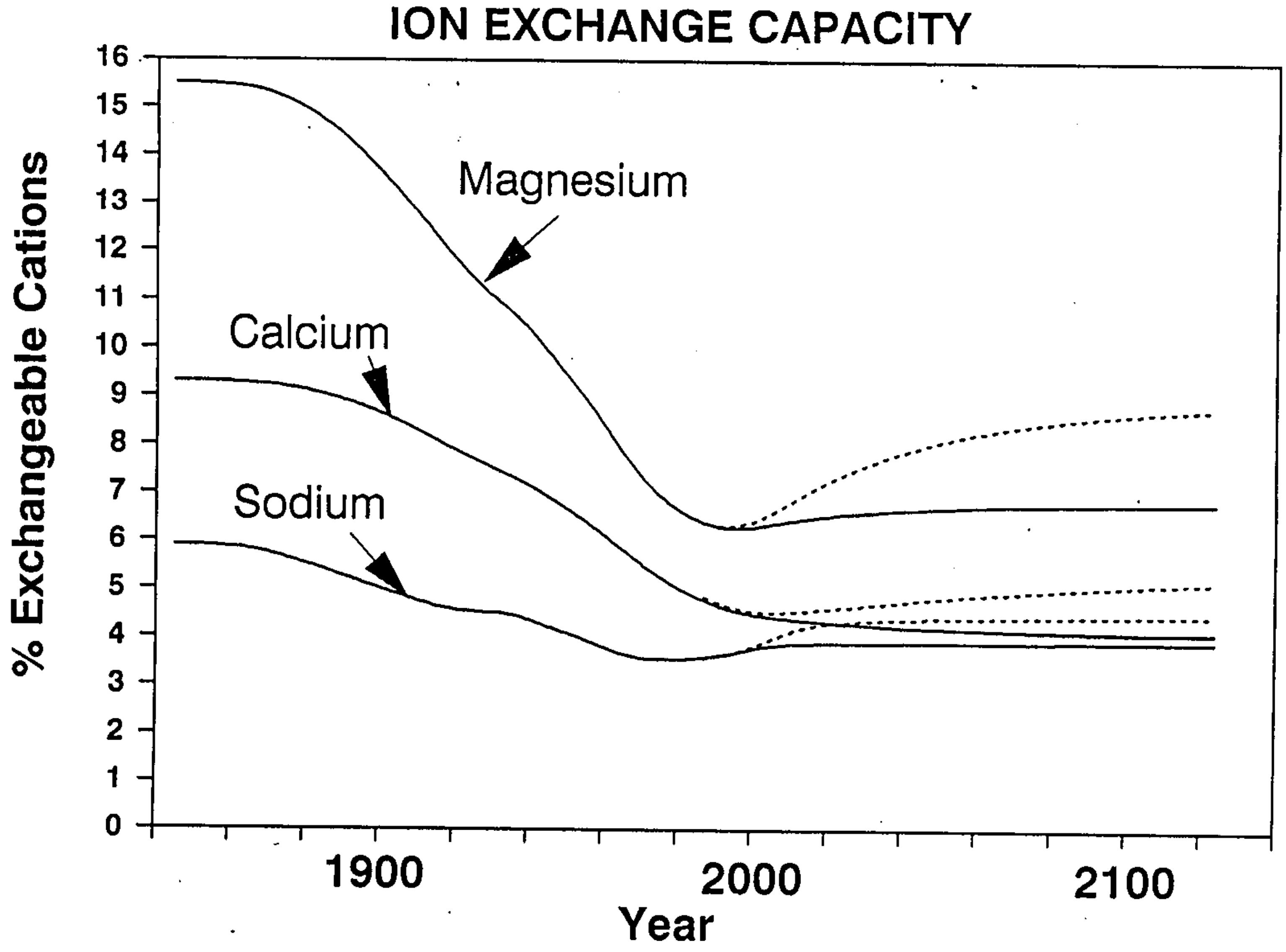

SULPHATE
µEq/l
90
80
70
60
50
40
30
20
10
0
1900
2000
2100
Years
60% reduction
30% reduction
Deep water
Soil water
Stream water

2c


CALCIUM
µEq/l
60
50
40
30
20
10
0
Deep water
Stream water
Soil water
1900
2000
2100
Year

2d


MAGNESIUM
µEq/l
80
70
60
50
40
30
20
10
0
1900
2000
2100
Year
Deep water
Stream water
Soil water


ION EXCHANGE CAPACITY
% Exchangeable Cations
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Magnesium
Calcium
Sodium
1900
2000
2100
Year

ACID NEUTRALISATION CAPACITY

COMPARISON OF ONE-LAYER AND TWO-LAYER MAGIC