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Long-term predictions of ecosystem acidification and recovery

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HIGHLIGHTS

- Modelled the effects of acid deposition on a forested catchment for 500 years.
- Current emission reductions allow 250 year recovery; then acidification resumes.
- Catchment accumulates N, nitrate leaching increases.
- Modelled forest growth reduces stream NO_3 and acidity, but acidifies soil.
- Soil validation data indicate acidification may be faster than model predicts.

ABSTRACT

This paper considers the long-term (500 year) consequences of continued acid deposition, using a small forested catchment in S. England as an example. The MAGIC acidification model was calibrated to the catchment using data for the year 2000, and run backwards in time for 200 years, and forwards for 500. Validation data for model predictions were provided by various stream and soil measurements made between 1977 and 2013. The model hindcast suggests that pre-industrial stream conditions were very different from those measured in 2000. Acid Neutralising Capacity (ANC) was +150 µeq L^{-1} and pH 7.1: there was little nitrate (NO_3). By the year 2000, acid deposition had reduced the pH to 4.2 and ANC to c. -100 µeq L^{-1}, and NO_3 was increasing in the stream. The future state of the catchment was modelled using actual deposition reductions up to 2013, and then based on current emission reduction commitments. This leads to substantial recovery, to pH 6.1, ANC +43 µeq L^{-1}, though it takes c.250 years. Then, however, steady acidification resumes, due to continued N accumulation in the catchment and leaching of NO_3. Soil data collected using identical methods in 1978 and 2013 show that MAGIC correctly predicts the direction of change, but the observed data show more extreme changes – reasons for this are discussed. Three cycles of forest growth were modelled – this reduces NO_3 output substantially during the active growth phase, and increases stream pH and ANC, but acidifies the soil which continues to accumulate nitrogen. The assumptions behind these results are discussed, and it is concluded that unmanaged ecosystems will not return to a pre-industrial state in the foreseeable future.

Keywords
Modeling; catchment; watershed; forest; nitrogen; acidity.

1. Introduction

The effects of acid deposition remain a significant environmental problem, even though deposition has reduced considerably in many parts of the world. Although there is still much to learn, we now have a good understanding of the major acidification and recovery mechanisms for sensitive soils and waters, encapsulated in models of various kinds. We also have some good long-term data, which is becoming commensurate with the timescales of ecological change induced by changes in atmospheric deposition. The time seems right to explore the long-term consequences of acid deposition given current knowledge, and to ask whether the data we have are sufficient to constrain our predictions of those consequences so that meaningful statements

can be made. This paper is an attempt to answer those questions using a calibrated acidification model and long-term data from a catchment in the UK. A single catchment can only serve as an example given the huge variety of climates, vegetation, soils, deposition changes etc., but its reactions can still provide useful insights. For instance, Skeffington and Brown (1992), used this approach to predict that one consequence of declining sulphur deposition would be lower base cation concentrations in recovering surface waters, and that this could cause biological problems. Controversial at the time, this prediction has subsequently been borne out by observations in many places (e.g. Battarbee et al., 2014; Stoddard et al., 1999).

There have been many acidification modelling studies involving projections into the future (e.g. Evans et al., 1998; Ferrier et al., 2003; Helliwell et al., 2003; Jenkins et al., 1990). Usually the time period concerned is 50 years or less, because of a well-justified feeling that predictions become too uncertain over longer periods. This paper is different: it extrapolates for 500 years. It uses data from a small (0.93 km^2) forested catchment in southern England. The MAGIC acidification model was calibrated to the catchment for the year 2000, run back in time for 200 years to assess pre-industrial conditions and forward in time for 500 years to explore future trajectories, given current (2016) knowledge of deposition trajectories. Extrapolating for 500 years may seem unduly speculative in view of the uncertainty over likely environmental change during that time, but the aim of the work is not to make predictions, but rather to explore the implications of current knowledge, and the credibility of current assumptions in the long term. Because observed data on the catchment span 36 years with dramatic changes in deposition, it is possible to apply validation tests to check whether the model predicts the right direction and magnitude of observed change. As well as changes in stream chemistry, a set of soil samples taken in a precise location in 1978 and again in 2013 is used for this purpose. The results are used to discuss the long-term implications of continued low levels of acid deposition for such unmanaged catchments.

2. Methods

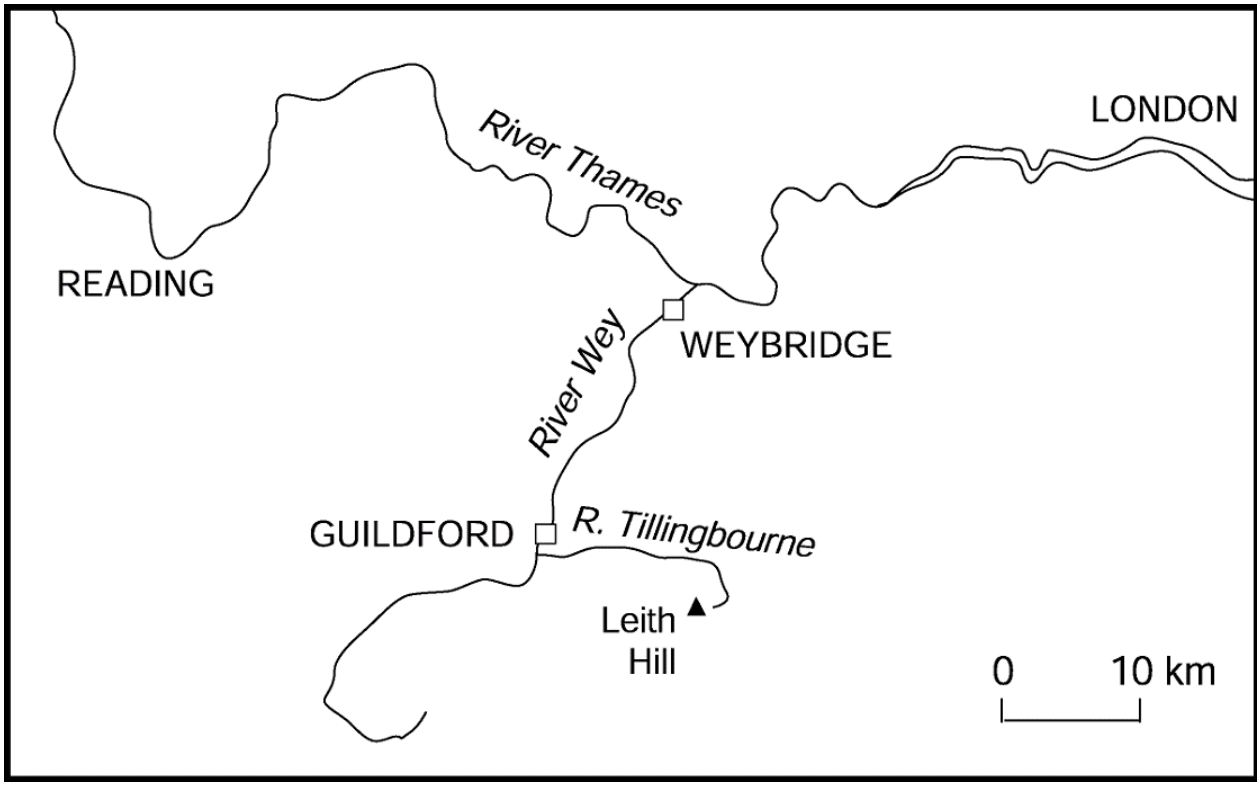

Fig.1. Situation of the Tillingbourne Catchment (triangle) in the UK.

2.1 Study site

The study was conducted in the Tillingbourne Catchment in SE England. The catchment is described in detail in Hill et al. (2002): a brief summary follows. The Tillingbourne catchment is located 7 km south west of Dorking in SE England, Latitude 51° 11′ N., Longitude 0° 22′ W. (Fig.1). It consists of a valley sloping northwards at an angle of about 3º, cut into the dip slope of Leith Hill (297m), the highest point of SE England. There are no motor roads or habitations in the catchment, which is composed of sedimentary rocks of Cretaceous age, the Lower Greensand Group. The Atherfield Clay which outcrops in the bottom of the valley consists of shales and mudstones which weather to a silty clay with a very low permeability to water. The soils that develop on this formation are classified as argillic humic gleysoils (humic gleysols in the WRB System (FAO, 2015)). Overlying the Atherfield Clay is the Hythe Formation, which consists of coarse, porous, non-calcareous sandstones which weather to very acidic humo-ferric podzols (orthic podzols in the WRB System; FAO (2015). The catchment lies south of the glacial limit for any of the Pleistocene glaciations, hence the soils are likely to be older, more weathered, and capable of absorbing more sulphate compared to most UK soils, a situation similar to that found in the USA (e.g. Robison et al., 2013). The vegetation of the area is mixed coniferous-deciduous forest. Trees cover about 89% of the catchment, the main species being Scots pine (*Pinus sylvestris* L.); oak (*Quercus robur* L.) and birch (*Betula pendula* Roth). There are occasional trees of other species, notably a beech (Fagus sylvatica L.) plantation at the N. end of the catchment, and European alder (*Alnus glutinosa* L. Gaertn.) in wetland areas. On the basis of annual ring counts, most trees date from about 1920, indicating that any large trees formerly present were felled during the 1914-18 war, a common fate for British trees. The area was then left to recover spontaneously, so the trees are self-sown, giving an open canopy structure. Ground vegetation is overwhelmingly dominated by bracken (*Pteridium aquilinum* (L) Kuhn), which suppresses other ground cover. There were few changes in vegetation over the three study periods: the trees grew larger but growth rates for mature trees on these infertile soils are slow.

The catchment is drained by a small stream (the Tillingbourne) which is seasonal (drying in summer) in its upper reaches, but perennial at the catchment exit where it is sustained by inputs from groundwater. The hydrogeology of the catchment is described briefly in Hill et al. (2002) and in more detail in Skeffington et al. (2003). Soils on the upper slopes are very permeable, and rainfall quickly passes into a deep vadose zone in the Hythe Formation sandstones, part of the Lower Greensand aquifer. This is a major aquifer in the Thames basin (Shand et al., 2003). Flow in the aquifer is both intergranular and through fissures, and essentially in a northerly direction. The Tillingbourne Catchment is a significant recharge area for the aquifer, estimated overall to be ca. 285 mm yr^{-1} (Shand et al., 2003). The base of the catchment is occupied by the low permeability Atherfield Clay. This brings the phreatic zone to the surface in the valley floor, and causes some of the groundwater to be discharged to the stream via springs and seeps, and generates wetland soils (gleysols and peats) in these areas. The catchment is thus probably watertight to downward percolation, but loses some water in groundwater flows across catchment boundaries. Calculation of a water balance in 1999 – 2003 (Skeffington et al., 2003) showed this to be the case, and this has been taken into account in calibrating the model to the catchment (see Section 2.4).

2.2 Measurements

This paper utilises measurements made during three time periods: atmospheric deposition, soil and water measurements made in 1977-1982 and 1999-2003; and soil measurements made in October 2013 (Section 2.3). Full details of these measurements are given in other publications (Hill et al., 2002; Skeffington and Hill, 2012; Skeffington, 1984; Skeffington et al., 2003). In 1977 – 1982 and 1999 – 2003, measurements included continuous measurements of rainfall at a site just north of the catchment; continuous measurements of stream discharge at the catchment exit; weekly bulk precipitation and throughfall volume and chemical composition; and weekly stream chemical composition. The chemical parameters measured varied between dates: in 1977 – 82 they were pH, conductivity, sulphate, nitrate, chloride, ammonium and dissolved organic

carbon; in 1999 – 2003 all these plus remaining major cations and anions and alkalinity were measured. Gaseous NH_3 and NO_2 concentrations were measured in the catchment in 2001-3 using diffusion tubes, giving a 4-week and 2-week average respectively (Skeffington et al., 2003). The chemistry of the five main soil types in the catchment was analysed in 1979-82 and reported in Hill et al. (2002), and specific measurements of soils were made to test various hypotheses on a campaign basis (Skeffington, 1983; Whitehead et al., 2002).

2.3 Soil sampling around isolated trees

In July 1978, a set of soil samples was taken round isolated individuals of the three major tree species: oak, birch and Scots pine (Section 2.1). The original aim was to assess the relative effect of tree growth and acid deposition on soil acidification. Three individuals of each species growing at least 8m from their nearest neighbour in a gently-sloping area of the catchment were selected. The trees were surrounded by a monoculture of bracken. Soil cores were taken at 0-10, 10-20 and 20-30 cm depth using an Edelman combination auger (now from Rotek A/S, Denmark). Cores were taken on three transects, in the north, southwest and southeast directions from each tree, at distances of 30 cm, 1 m and 6 m from the tree bole, ensuring that the 1m sample was under the tree canopy and the 6 m sample outside. This provides a balanced experimental design of $3^5 = 243$ samples. Soils were transported to the laboratory in sealed polythene bags, kept moist at 4°C, and pH measured within 4 days. 10 g of sample were shaken for 20 minutes in 20 ml 0.01M $CaCl_2$ solution, allowed to settle, and the pH of the supernatant measured electrometrically with a Radiometer pH electrode and meter. Once pH measurement was complete, the remaining soil samples were extracted with water according to the procedure of Ulrich et al. (1980), forming what they termed an “equilibrium soil solution” (ESS). 10 g of moist soil were shaken with 8 ml of distilled water, allowed to stand for 24 h, and the suspension filtered. The ESS was analysed for Ca and Al using an inductively-coupled plasma emission spectrometer. For some of the more organic samples, the extracting volume was doubled to 16 ml to obtain sufficient sample for analysis.

The position of the trees was accurately surveyed. In October 2013, 35 years later, the trees were identified and the exact procedure was repeated. The trees had grown somewhat, but the surrounding landscape had not altered since 1978.

2.4 Modelling

The MAGIC Model (Model of Acidification of Groundwater In Catchments) has been in use for many years in policy and assessment activities around the world (e.g. de Vries et al., 2015), and has even been used to assess the effects of acidic emissions from volcanic eruptions at the end of the Cretaceous period (Schmidt et al., 2016). MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry. The model simulates soil solution chemistry and surface water chemistry and predicts the monthly and annual average concentrations of the major ions in these waters, given catchment characteristics and deposition data. The original structure of MAGIC was described by (Cosby et al., 1985a; Cosby et al., 1985b): the modifications used by the version employed in this study are described in Cosby et al. (2001).

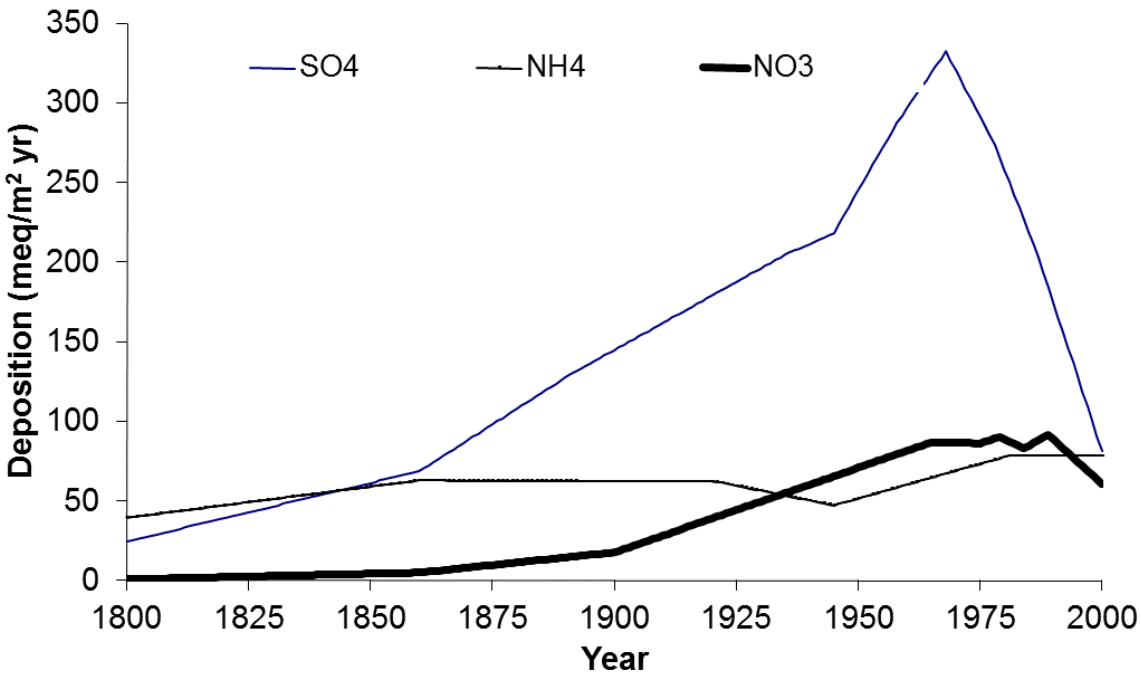

Fig. 2. Historical total (wet and dry) deposition sequences for S and N species

The model requires a number of inputs and state variables, including atmospheric deposition, stream chemistry and soil characteristics. The model was calibrated to fit the data in a baseline year, which was 2000 in this case, chosen because appropriate calibration data were available. Wet deposition for the calibration year was estimated using volume-weighted annual means of the two bulk precipitation collectors in the catchment for the years 1999 and 2000. Dry deposition inputs for the model were calculated by combining the observed annual wet fluxes with measured total annual deposition from throughfall collectors in the catchment. These combined data for 1999-2000 were used to calculate the Dry Deposition Factors (DDFs) for each ion for MAGIC for the calibration year. The DDF is a factor which, when multiplied by the wet deposition flux, gives the total deposition flux for an ion. Though this method does not account for canopy retention of ions, particularly N species, calculations suggest that this is small from 2000 onwards (Skeffington and Hill, 2012).

Historical sequences for the deposition of S and N to the catchment (Fig. 2) were estimated from S and N emissions histories in the UK and continental Europe. This is described in detail in Skeffington et al. (2003), but essentially involves using estimates of emissions in each country and estimating their contribution to the catchment using the EMEP Model for the appropriate time (Tuovinen et al., 1994), constrained to the observed deposition on the catchment in the year 2000. Soils input data for the calibration were derived by vertically and areally averaging the observed soil characteristics in the catchment. The averaging was done using a bulk density weighting scheme and provided aggregated values of soil characteristics for use in the model (Table 1).

Table 1 Soil characteristics and parameter values used in the calibration of MAGIC

Parameter	Units	Value
Ave. soil depth	m	1.01
Soil porosity	fraction	0.50
Bulk Density	kg/m^3	1299
SO_4 Adsorption Maximum	meq/kg	20
SO_4 Adsorption Half-saturation	μeq/L	300
$Al(OH)_3$ solubility	log_{10}	7.00
CEC	meq/kg	128.8
ECa	meq/kg	6.4
EMg	meq/kg	1.6
ENa	meq/kg	0.7
EK	meq/kg	3.7
Base Saturation	percent	9.6
pH		3.6
Soil C content	mol/m^2	1063
Soil N content	mol/m^2	36.5
N uptake upper threshold	C/N	32
N uptake upper threshold	C/N	12
Weathering Ca	$meq/m^2.yr$	45
Weathering Mg	$meq/m^2.yr$	26
Weathering Na	$meq/m^2.yr$	12
Weathering K	$meq/m^2.yr$	2
Ca-Al Selectivity Coefficient	log_{10}	-0.3
Mg-Al Selectivity Coefficient	log_{10}	1.3
Na-Al Selectivity Coefficient	log_{10}	0.6
K-Al Selectivity Coefficient	log_{10}	-5.3

The sulphate content of the soil was based on estimates made during work for an unpublished MSc thesis (D. Hussey, pers. comm.) but the maximum sulphate adsorption capacity and the DDF for seasalt excess SO_4 were adjusted to calibrate stream sulphate concentrations. Base cation weathering rates and Gaines-Thomas selectivity coefficients were adjusted to calibrate the base cations in the stream and on the soils rather than considering soil mineralogy and hydrogeology, although the calculated rates are consistent with measured values for these variables. This is standard practice in running the MAGIC model (Cosby et al., 2001; Cosby et al., 1985a). The thresholds for N retention in the soil organic pool, and the historical C/N ratio were adjusted to calibrate nitrate and ammonium concentrations in the stream and the current N content of the soil. Streamwater concentrations for the lower stream sampling site were used as the target for calibration, which thus represents the entire study catchment. The annual average volume weighted streamwater concentrations for 1999 and 2000 were averaged to provide the calibration data. The runoff volume used in the model simulations was calculated from the annual average precipitation volume used for calibration assuming a streamwater yield of 50%. This runoff is higher than the observed streamwater discharge, but is intended to represent soil water losses to both the stream and recharge to groundwater. The value was chosen based on discharge from adjacent larger catchments without significant groundwater outputs, and calculations of evapotranspiration from the catchment using the Penman-Monteith method (Skeffington et al., 2003).

The calibration of MAGIC for the Tillingbourne catchment was successful with good fits to the observed data obtained for both the calibration year 2000 and the period of earlier observation in 1980-81 (Table 2).

Table 2. Comparison of simulated and observed streamwater and soil values for the calibration year (2000) and for observed conditions 20 years earlier (1981). The earlier observations were not used in the model calibration (base cation observations are not available for 1981).

Year 2000 (Calibration Year)					
Streamwater (µeq/L)			**Soils**		
Constituent	**Simulated**	**Observed**	**Constituent**	**Simulated**	**Observed**
Ca	176	176			
Mg	143	143	Exch Ca %	5.0	5.0
Na	363	363	Exch Mg %	1.2	1.2
K	22	22	Exch Na %	0.5	0.5
NH4	0.2	1	Exch K %	2.8	2.8
SO4	350	351			
Cl	410	410	Base Sat %	9.5	9.6
NO3	42	41	C/N (mol)	29	29
pH	4.2	4.2	pH	3.7	3.6
ANC	-98	-98			

Year 1981					
Streamwater (µeq/L)			**Soils**		
Constituent	**Simulated**	**Observed**	**Constituent**	**Simulated**	**Observed**
NH4	0.1	1			
SO4	404	405	C/N (mol)	31	38
NO3	14	15			

The calibrated model was used to construct the history of streamwater acidification in the Tillingbourne River and the soils of the catchment (hindcast simulation) and project trends into the future (forecast simulation). Forecast deposition sequences were based on actual UK deposition reductions from 2000-2013, and the reductions necessary to meet the UK's commitments for the second UNECE Gothenburg Protocol in 2020, and held constant thereafter. The resulting fluxes are shown in Table 3.

Table 3. Total S and N depositions used in forecast simulations, together with percentage reductions on the year 2000. Deposition in intermediate years was linearly interpolated.

Substance	**Deposition (meq m^{-2} yr^{-1}) / % reduction on 2000**					
Year	**2000**	**2010**	**(%)**	**2020**	**(%)**	**2500**
SO_4	81.1	43.9	(65.0)	37.5	(74.1)	37.5
NO_3	60.6	37.9	(39.5)	24.1	(61.3)	24.1
NH_4	78.4	67.4	(14.0)	67.4	(14.0)	67.4

The effects of forest growth were also simulated. The dynamics of nutrient uptake into forest will vary considerably depending on management strategy, tree species and soil fertility, but a typical pattern for the local area might be clear-felling followed by re-planting. Nutrient uptake increases sharply in the early years of a forest rotation, reaching a peak 20-40 years after planting, and thereafter slowly declines to a low level (e.g. Nilsson et al., 1982). This is simulated in the model by setting a maximum N uptake rate of 70 meq N m^{-2} yr^{-1} (9.8 kg ha^{-1} yr^{-1}), which corresponds to a forest growing at a moderate rate. N uptake increases to this value over the first 10 years of the forest rotation and stays there for 20 years. Over the next 20 years it declines to a net value of zero, where it remains for 50 years until harvest. Forests also take up base cations, which will have an acidifying effect. As it is assumed in this simulation that all nitrogen is taken up as nitrate, an exactly equivalent uptake of base cations is required to maintain electrical neutrality.

(The assumption that all uptake of N is nitrate is unlikely but will not affect the acidification or eutrophication calculations provided there is no ammonium output in the stream). Base cation uptake is thus assumed to follow the same trajectory as N uptake, with maximum values of Ca, 40 meq m^{-2} yr^{-1}; Mg, 20 meq m^{-2} yr^{-1}; Na, 5 meq N m^{-2} yr^{-1}; and K, 5 meq N m^{-2} yr^{-1}. This scenario was applied three times, representing three forest growth cycles, starting in 2001, 2101 and 2201. These data were derived from estimates of uptake fluxes in Nilsson et al. (1982), followed by whole-tree harvesting which removes all elements from the system.

3. Results and Discussion

3.1 Hindcast simulation

Figure 3 shows the modelled sulphate and nitrate concentrations in the stream from 1800 to 2000, together with averaged observed annual means for the two study periods.

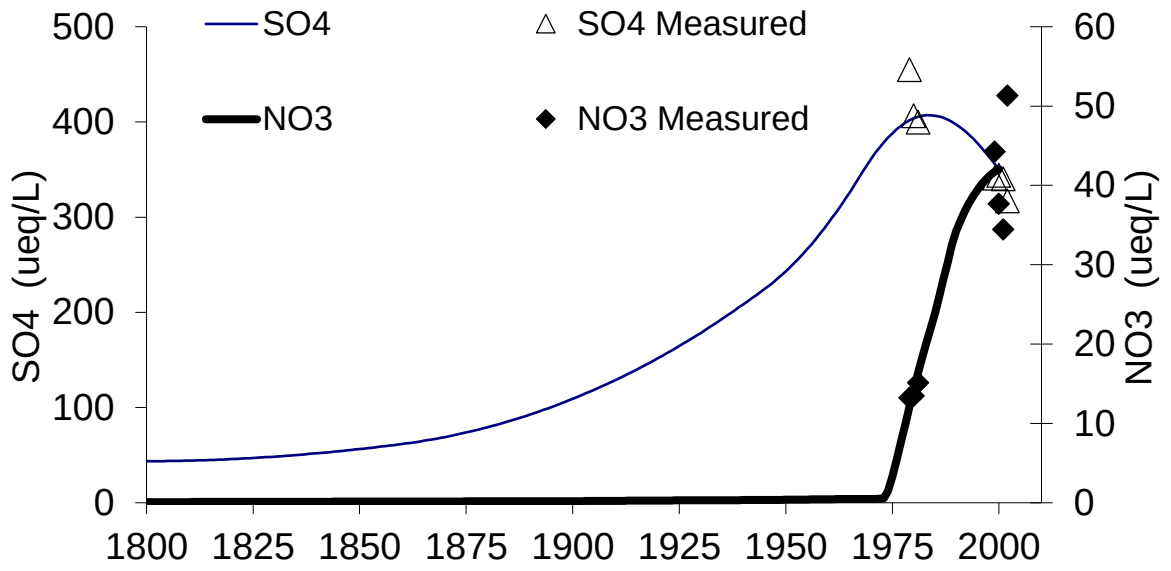

Fig. 3. Simulated (lines) and measured (points) stream sulphate and nitrate concentrations, 1800 – 2000. Measured values are volume-weighted annual means: model runs were calibrated to the mean volume-weighted concentrations 1979-1981 and 1999-2003.

Averaging reduces the variation due to differences in rainfall between years, and hence provides a better comparison with modelled values. Stream sulphate concentration is a smoothed version of atmospheric S deposition, with the peak occurring in 1984, 16 years after the deposition peak in 1968. The reason for this behaviour is the large sulphate adsorption capacity of the catchment soils, which tend to adsorb sulphate while S deposition is rising and release it when deposition is falling. This will delay both acidification and recovery. Nitrate in contrast starts in 1800 at a very low concentration and increases very slowly until 1973, when the concentration takes off abruptly. This marks the point in the model at which the soil C:N ratio reaches the upper limit of 32 $mol.mol^{-1}$ after which it is assumed that soil microorganisms cannot assimilate all the N, and nitrate starts to leak into the soil and streamwater (see below). Although even in 2000 nitrate concentrations are low compared to those in water draining agricultural areas, the modelled results represent a change in water type, and the increase in nitrate reduces the rate of recovery due to the decrease in sulphate. Ammonium concentrations remain negligible in the stream throughout the simulation.

The effects of these changes on acidity are seen in Figure 4. Stream pH in 1800 is approximately neutral and remains so through the nineteenth century. ANC remains above about 150 μeq L-1, both these parameters indicating good conditions for fish and other aquatic organisms, perhaps surprisingly in view of the low base status of the catchment soils. After 1900, acidification becomes progressively worse, and the water becomes unsuitable for most organisms in the mid-

1960s. After reaching a low of 4.18 in 1991, pH begins to recover slightly, as does ANC. Conditions are still unsuitable for all but the most hardy invertebrate species, as confirmed by observation.

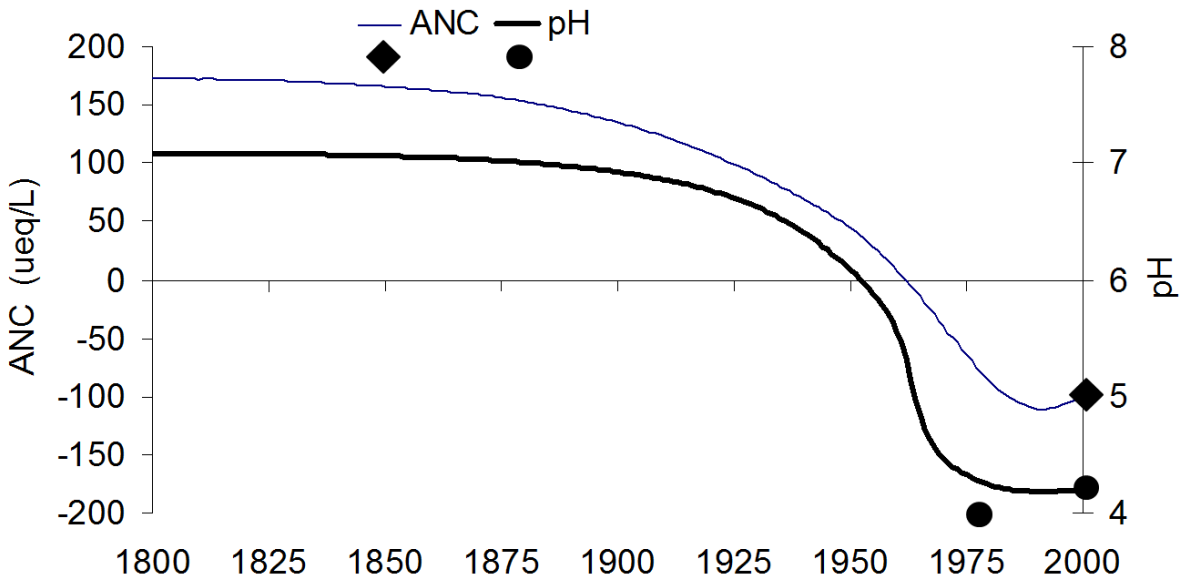

Fig. 4. Simulated (lines) and measured (points) ANC concentrations and pH, 1800 – 2000. Values are annual means: points are the mean volume-weighted concentrations 1979-1981 and 1999-2003. ANC was not measured in 1979-81.

The nitrogen parameters underlying these trends are shown in Fig. 5. The catchment soils retain 99.9% of the incoming deposition until 1973, and even by 2000 are still retaining 83%. The amount retained becomes progressively less after 1973, however, demonstrating the start of the process of "nitrogen saturation" (e.g. Aber et al., 1998). As with nitrate leaching, the process is triggered by the decline of the C:N ratio below the upper limit of 32 mol.mol^{-1}. In 1800, the C:N ratio is 58 mol.mol^{-1}, characteristic of a very N-poor system, but by 2000 it has declined in the simulation in close to linear fashion to the observed value of about 29 mol.mol^{-1}.

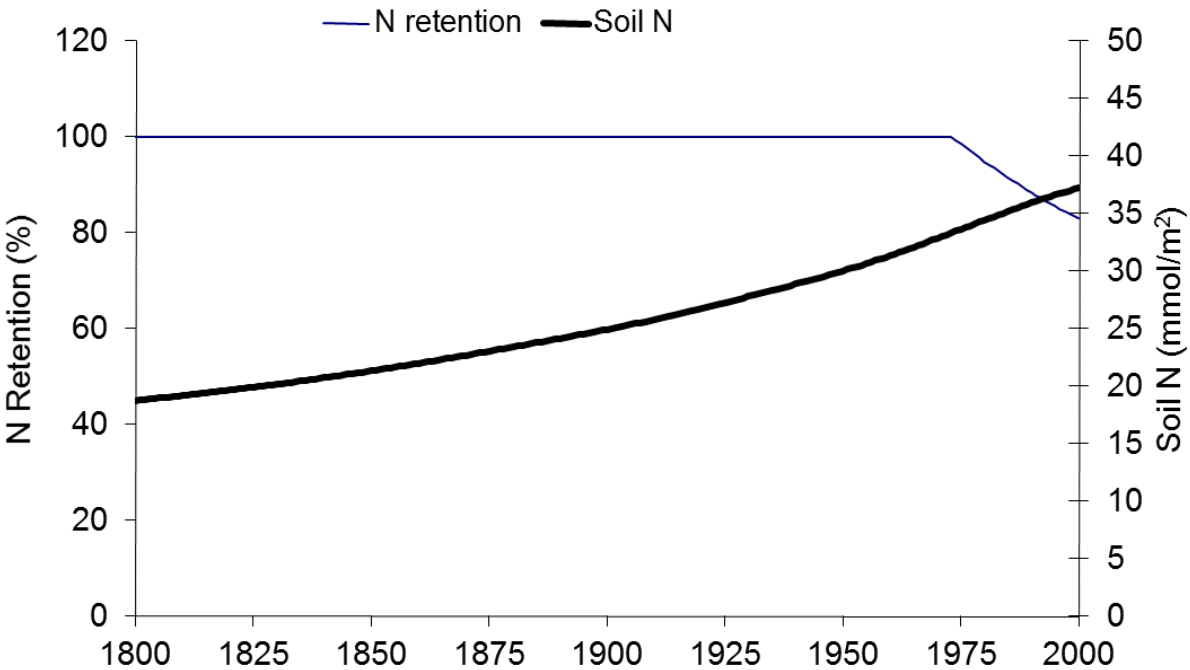

Fig. 5. Simulated catchment N retention and soil N content, 1800 – 2000.

The hindcast results suggest that soil and water chemistry in this small catchment was radically different in the past compared to the late 20th Century. The soil was base-poor (base saturation c. 12% throughout the 19th Century, results not shown) and deficient in nitrogen, implying low fertility which accords with historical records. By the end of the 20th Century it was even poorer in bases but richer in N, allowing acid-tolerant species to grow well. The change in the stream was even greater. In the past according to MAGIC it was circumneutral, had a high acid neutralising capacity, and little dissolved inorganic N, whereas by the end of the 20th Century it was highly acidic and had ecologically-significant nitrate concentrations. It would have supported a very different set of organisms than it does presently. This assessment is of course dependent on the assumptions embedded in the MAGIC Model, and there are no palaeoecological data against which to test it. It is however consistent with present views of acidification and the development of nutrient cycles.

3.2 Forecast simulations

The calibrated catchment model was then used to forecast the effects of a number of deposition reduction scenarios. Here we describe the results of reducing deposition in line with the reduction in UK emissions from 2000 to 2013, followed by reduction to the UK's commitment in the second Gothenburg Protocol by 2020, keeping emissions constant thereafter (Section 2.4). The simulations were run for 500 years from the year 2000, to investigate the long-term behaviour of the catchment. The 20th century rise in stream sulphate now appears as a sharp peak, falling away exponentially in response to a decline in sulphate deposition, but buffered by S release from the catchment soils. Although sulphate concentration approaches its limit asymptotically, it is close to equilibrium with deposition by the year 2500, having fallen by only 0.5 μeq L^{-1} in the previous 50 years. From 2003 to 2020 stream nitrate concentrations decrease, responding to the sharp decrease in N deposition, but thereafter continue to rise as catchment N stores fill up. Nitrate concentration on the other hand continues to increase, though at a decreasing rate. Nitrate exceeds sulphate from the year 2201, a trend currently being observed in other UK catchments (Battarbee et al., 2014).

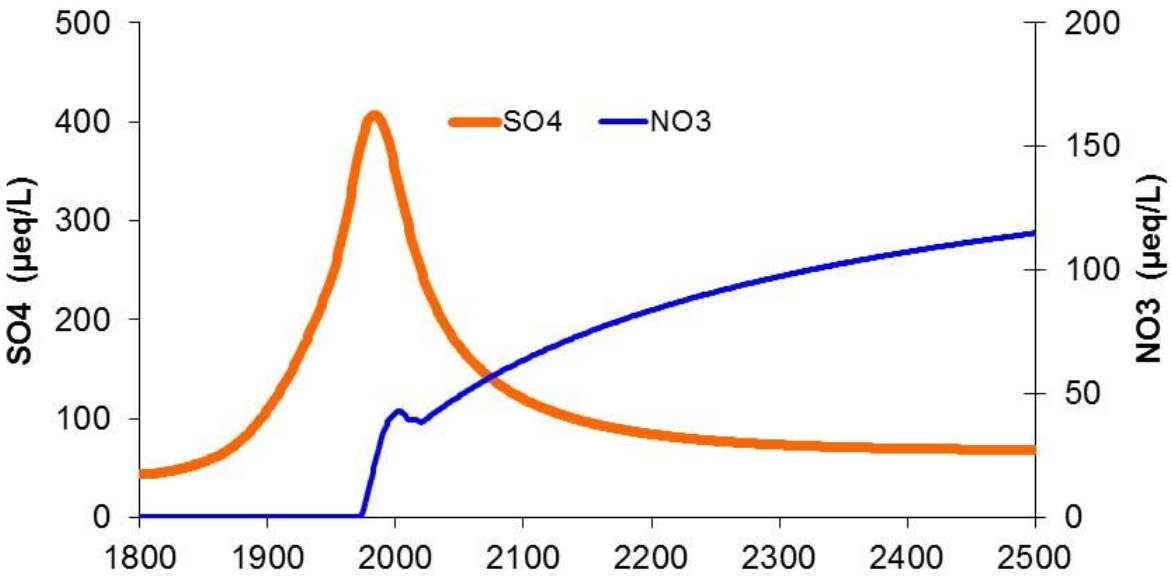

Fig. 6. Simulated stream sulphate and nitrate concentrations, 1800-2500.

The effect of these trends on stream acidity is shown in Fig. 7. Twentieth century acidification now appears extremely rapid, and recovery somewhat slower. It is also clear that, in the long term, it is a temporary recovery. The surface water critical load criterion of 20 μeq L^{-1} is reached in the year 2076, and ANC rises to a maximum of 47.6 μeq L^{-1} in the year 2200, stays essentially

stable for 80 years, but then starts to decline again at a slowly increasing rate, reaching 35 μeq L^{-1} by the end of the modelled period. The response of pH is similar, reaching a maximum of 6.12 in the same period, but falling below 6.0 in the year 2493. Even the maximum pH and ANC values are well short of their initial levels of 7.08 and 172 μeq L^{-1} respectively, implying an essentially irreversible change.

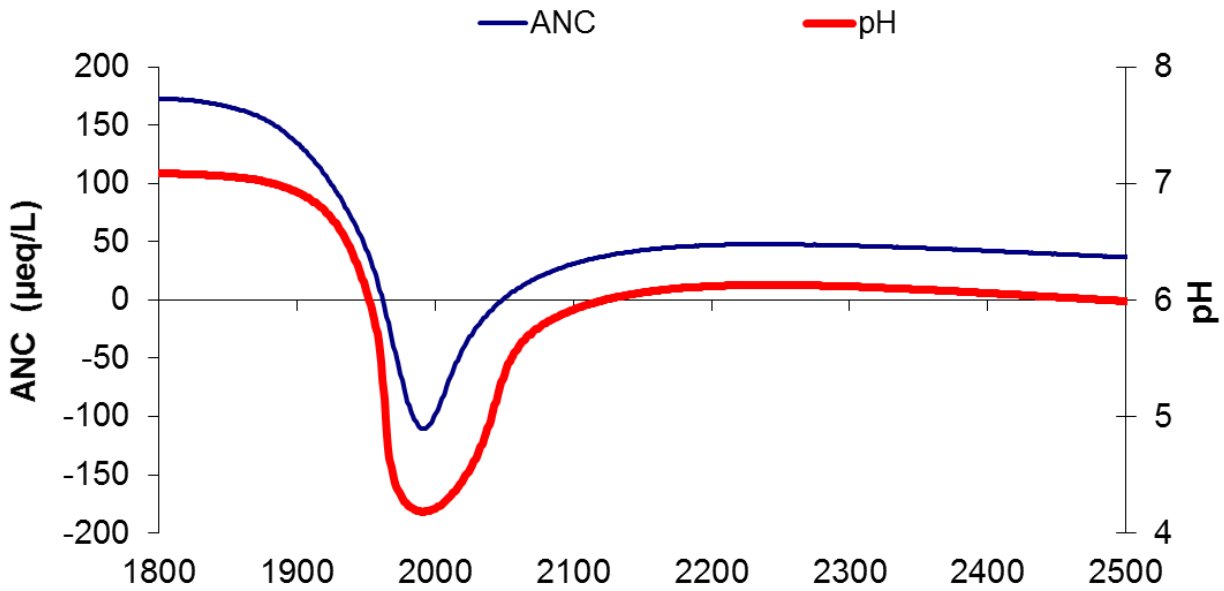

Fig. 7 Simulated stream ANC and pH, 1800-2500

The reason that recovery stops is the continued increase in nitrate. The reason the nitrate continues to increase is the narrowing C:N ratio in the catchment soils, which allows more and more of the incoming nitrate to leach into the stream while the soil N continues to build up (Fig. 8).

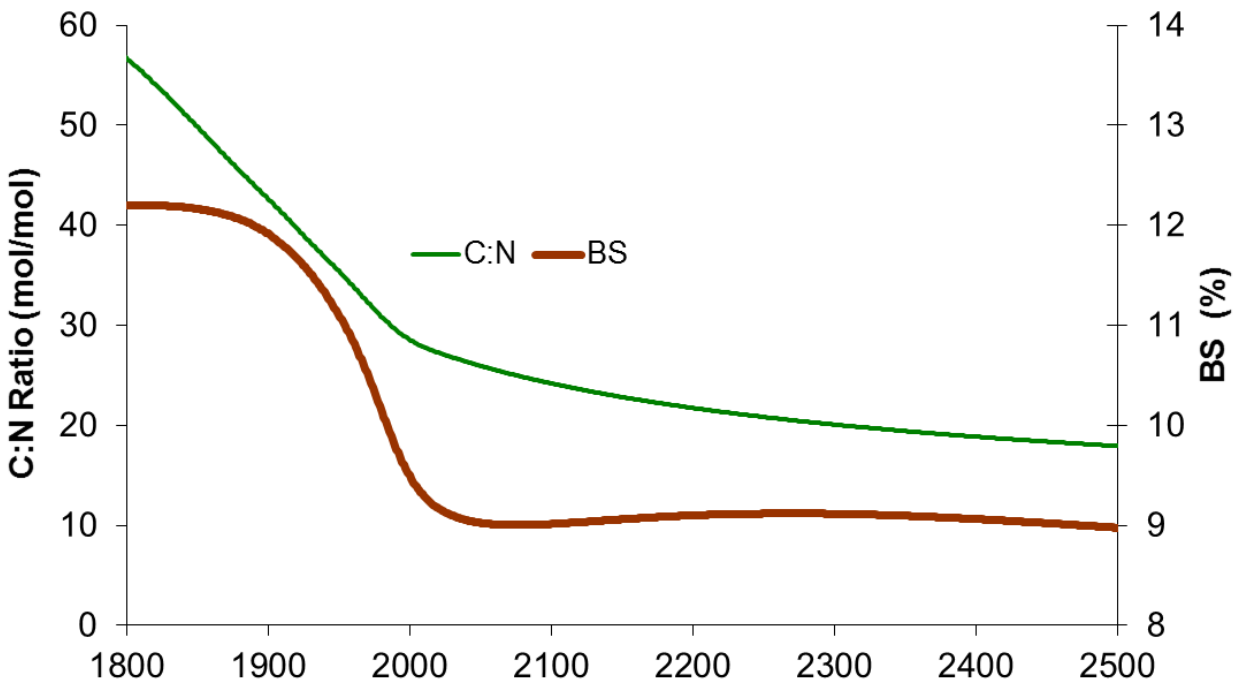

Fig. 8. Simulated C:N Ratio and base saturation, 1800-2500.

The soil continues to acidify, slowly, until the year 2076, but then starts to recover for the following 200 years as the acidification pressure caused by the fluxes of sulphate and nitrate falls below the weathering rate. Recovery is only slight, 0.1 percentage point, and acidification subsequently resumes, falling by another 0.14 percentage points by 2500. The official most stringent acidity critical loads for unmanaged deciduous woodland on the site are $CL_{max}S$, 1.72 keq ha^{-1} yr^{-1}, $CL_{min}N$, 0.142 keq ha^{-1} yr^{-1} (see Skeffington (1999) for an explanation of these terms). Compared with modelled deposition, the combined S + N critical load was first exceeded in the year 1885, reached a peak exceedance of 3 keq ha^{-1} yr^{-1} in 1968, and ceased to be exceeded in 2005. From 2020, deposition has been 0.57 keq ha^{-1} yr^{-1} less than the critical load, which should have led to a sustained recovery, which is clearly not quite the case.

This feature of the results depends critically on whether nitrate leaching is actually controlled by the C:N ratio of soil organic matter. Rowe et al. (2006) pointed out the importance of the quality of organic carbon, and how this may vary with different vegetation types. Oulehle et al. (2012) suggested an alternative formulation for shorter-term simulations, but their review suggested that using the bulk C:N ratio was the best option for longer-term studies, such as the present one.

3.3 Model corroboration data: trends in soil acidity and nitrogen

Although the model was successfully calibrated to the year 2000, and gave good predictions of the observed data in 1978-82 (Section 2.4), comparing model predictions with more modern data would give extra corroboration. Unfortunately there are no stream chemistry data after 2003, but some soil data are available. In 1978, 243 soil samples were taken under nine specific trees (Section 2.2) to investigate the influence of trees on soil acidity: this exercise was repeated in 2013 using exactly the same methods. The presence of the trees allowed the sampling sites to be re-located exactly. Table 4 shows the changes in relevant soil properties predicted by MAGIC using the actual changes in deposition, and the changes observed, with percentage change where this is meaningful.

Table 4: Predicted and observed changes in soil properties between 1978 and 2013

[a]Variable	Predicted (MAGIC)			Observed			
	1978	**2013**	**Change (%)**	**Canopy**	**1978**	**2013**	**Change (%)**
Ca	3.73	3.16	-15	Outside	4.12 (73)§	0.84 (27)	-80
				Under	6.60 (144)	1.30 (54)	-80
Al	2.66	2.41	-9	Outside	6.60 (73)	1.18 (27)	-82
				Under	5.61 (144)	1.68 (54)	-70
Ca/Al	0.95	0.88		Outside	0.42 (73)	0.48 (27)	
				Under	0.79 (144)	0.52 (54)	
pH	3.73	3.73					
pH ($CaCl_2$)				Outside	2.95 (81)	2.46 (81)	
				Under	2.82 (164)	2.38 (162)	
Base Sat (%)	10.12	9.25	-9				
C:N	26.4	24.5*			32.8 (6)	26.4* (6)	

[a] Ca and Al are soil solution concentrations, units, mg L^{-1}; soil solution Ca/Al ratio, units $mol.mol^{-1}$; predicted pH is soil solution pH, measured is pH in 0.01M $CaCl_2$; units of C:N ratio are gC gN^{-1}, *year of assessment was 2001 (Whitehead et al., 2002). §Values in brackets are numbers of soil samples. All differences between years are statistically significant: C:N ratio ($p<0.05$*), the remainder ($p<0.001$***).

An exact match between observed and predicted values would not be expected, particularly because MAGIC is calibrated to the whole catchment whereas these samples were taken on only one of the catchment soil types – Type D (Hill et al., 2002) which is a transitional soil between the orthic podzols and argillic gleysols, and covers only 1% of the catchment. Nevertheless the observed and predicted trends should be similar to each other, and Table 1 shows that this is the

case. Samples taken under the tree canopies (at 0.3m and 1.0 m from the trunks) are presented separately from samples outside the canopy where the tree influence should be minimal. Modelled soil solution calcium and aluminium show downward trends and this is also shown by the soil data, except that the decline is much sharper. The calcium / aluminium ratio, used as a risk factor in critical load calculations (Skeffington, 1999; Sverdrup and De Vries, 1994), declines in the model and under the tree canopy, but outside it increases slightly due to the precipitous decline in Al. In both model and data the ratio is <1.0, indicating the trees are at risk of long-term damage, though they appear healthy currently. Modelled soil pH, which is buffered by high CO_2 concentrations in soil, does not change. Measured pH in $CaCl_2$, which is a measure of exchangeable H^+ and thus inversely related to base saturation (Rowell, 1994), declines sharply, matching the modelled decline in base saturation. Finally both modelled and measured C:N ratios decline, as previously described by Whitehead et al. (2002).

Thus the trends predicted by MAGIC appear by and large to be reflected in the data, except the latter appear more extreme. Though there are always methodological concerns when studies are repeated, even if they are done by the same people, the large number of samples, structured sampling programme, and precise sample location gives confidence that these trends are real, as evidenced by the statistical significance of the differences (Table 4). The large decline in Ca concentrations both under and outside the tree canopies must raise concerns about threats to tree health in these nutrient-poor soils (e.g. Schaberg et al., 2001; Schaberg et al., 2006), even though in a maritime climate like the UK there are significant atmospheric inputs of Ca and other base cations (Roberts et al., 1989). Consideration of these results led us to incorporate forest growth into modelling effects as explored in Section 3.4.

3.4 Long-term modelling with forest growth

The long-term modelling described in Section 2 showed that continuing acidification of the catchment resumed after a period of recovery, essentially due to the build-up of N in the catchment soils. The rise in nitrogen is inevitable with the model parameters used, because there is no sink for nitrate other than output in the stream and accumulation in the soil organic matter, thereby decreasing the C:N ratio. Real catchments have other sinks for N, of which the most important is uptake into vegetation. For a forested area like Leith Hill, forest growth and harvest of the timber provides a long-term sink for N which might make a considerable difference to the reactions of the catchment. The effect of incorporating three 100-year forest growth cycles starting in the year 2000 (Section 2.4) is described in this section. MAGIC has been used previously to assess the effects of forestry on acidification (e.g. Helliwell et al., 2014; Wright et al., 1994; Zetterberg et al., 2014), but mostly concentrating on the effects on waters and never with more than one forest rotation.

Fig. 9 shows the influence of forest uptake of nitrogen and base cations on stream nitrate and base cation concentrations.

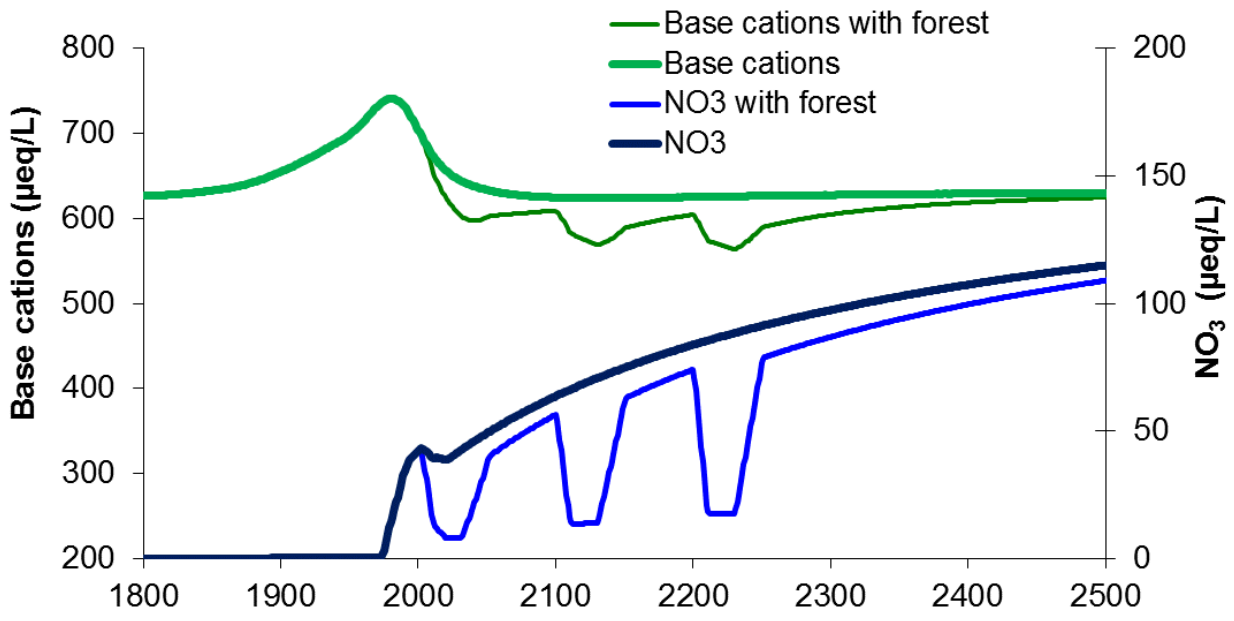

Fig. 9. Modelled stream nitrate and base cations, with and without forest uptake.

Nitrate concentrations are reduced during the peak forest growth phases, but afterwards recover towards their values in the absence of forest growth. The export of N from the catchment in biomass permanently reduces the overall NO_3 concentrations in the stream, by 11 µeq L^{-1} by the end of the last cycle, but the difference steadily reduces to 6 µeq L^{-1} by 2500. Stream NO_3 concentrations continue to rise in both scenarios. Base cation uptake and export likewise reduce stream base cation concentrations during the period of forest growth, but recovery is quicker, the difference between scenarios being < 1 µeq L^{-1} after 150 years. The effects of these opposing tendencies on stream acidity parameters is shown in Fig. 10.

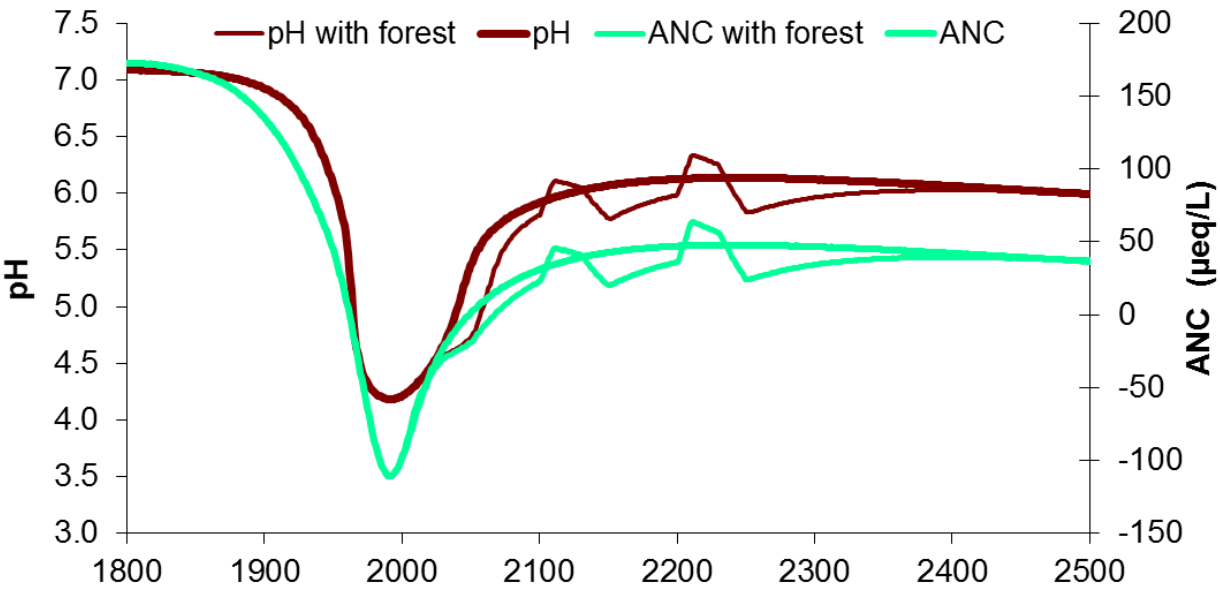

Fig. 10. Modelled stream pH and ANC, with and without forest.

The pH and ANC values follow each other. Though base cations and N are taken up at the same rate, which should mean there is no effect on pH and ANC, various non-linearities in the catchment response make pH and ANC dependent on the rate of change of uptake. When uptake is increasing, pH and ANC increase rapidly so they exceed the "no forest" case, by as much as 15 µeq L^{-1} and 0.2 pH unit. Once uptake stabilises, pH and ANC start to fall slowly, and once uptake declines they fall more rapidly, so that they are less than the "no forest" case by up to 22 µeq L^{-1} and 0.3 pH unit. Once uptake returns to zero, pH and ANC approach the "no uptake" value again, taking just over 200 yr to do so after the last period of forest growth, and eventually stabilising just above the "no forest" case. This behaviour can be seen most clearly in Fig. 10 during the last episode of forest growth, from 2201 onwards. This somewhat unexpected pattern of behaviour is due to the soil solution strong acid anions (nitrate in this case) responding more quickly to uptake changes than the soil solution strong base cations, whose response is buffered soil ion exchange complex. The implications for the effects of forest growth on stream acidity is that they are likely to be complex and significant even when, as in this case, there is no long-term effect. Periods when forest growth depresses pH and ANC seem to last longer than periods when they are increased, which only occur when growth is increasing. Even though the responses are temporary, on even a rapid forest growth cycle they may last longer than an observer's lifetime.

Underlying the stream responses are changes in the soil. Fig.11 shows that the soil decidedly acidifies during the forest growth periods, as expressed by the reduction in base saturation, which reaches a maximum of 1.5 percentage points in the third forest growth episode. Acidification, which is due to base cation uptake, continues during forest growth, but recovery begins as soon as this stops (Fig.11), because the soil exchanger is now out of equilibrium with the soil solution.

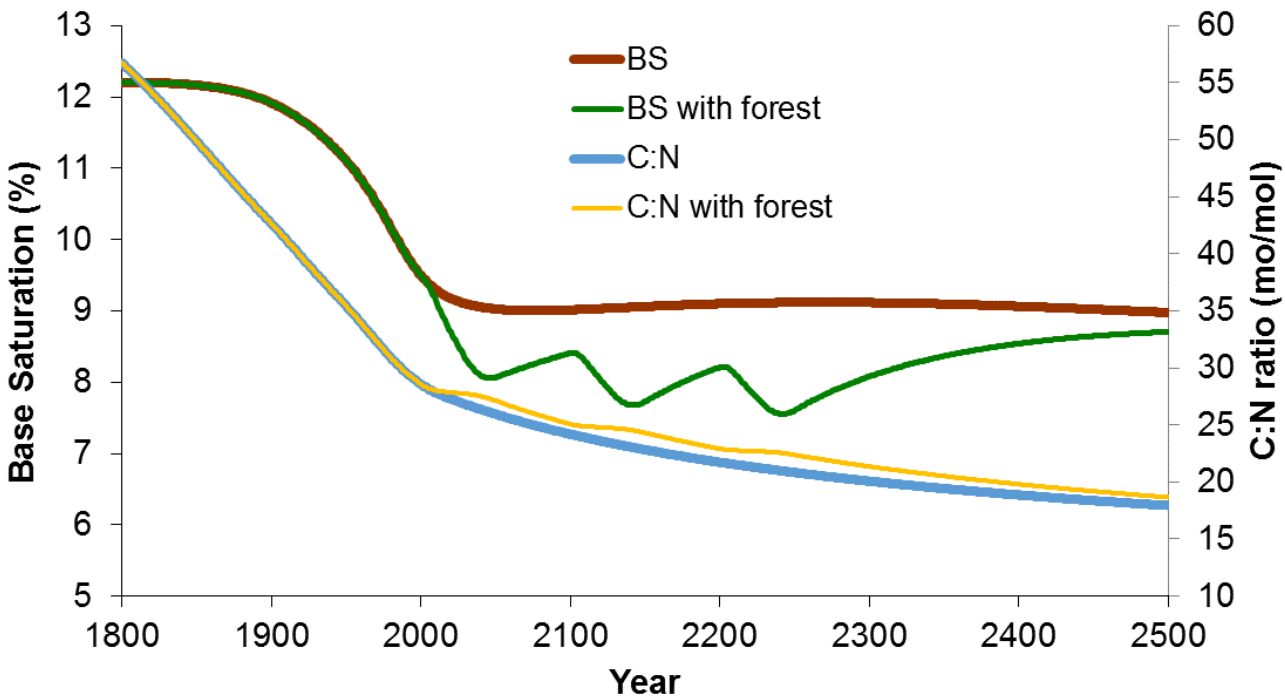

Fig. 11. Modelled soil base saturation and C:N ratio, with or without forest

The recovery is, however, slow, reducing to a difference of 0.27 percentage points compared to the "no forest" condition by 2500. The C:N ratio shows a similar pattern. The decline in C:N ratio is slowed relative to the "no forest" case, but the N uptake by the trees is not quite sufficient to completely arrest the decline in C:N with time, even at maximum uptake. The largest difference that develops between the "forest" and "no forest" case is 1.6 mol mol^{-1} in the third forest rotation: again this slowly reduces over time, but is still 0.73 mol mol^{-1} by 2500.

4. Discussion and Conclusions

These results should be seen not as a prediction of what will happen to this particular catchment, but as an exploration of the consequences of current understanding of acidification and recovery processes given present commitments to emission reduction. A number of caveats need to be taken into account, because the model formulation has been kept as simple as possible to maintain a tight focus on understanding of acidification and recovery. Firstly, soil carbon content has been kept unchanged, whereas it might in practice accumulate which would increase the catchment's ability to retain N. Secondly, weathering rates are fixed, whereas over a long period soil weatherable minerals might be depleted, and decreasing ambient acidity may reduce rates. Thirdly, the climate may change in unpredictable ways, affecting all biogeochemical processes. Fourthly, the model could almost certainly be calibrated differently given the limited data available in relation to the complexity of the system. All these would affect the detail of model outputs, but some robust conclusions can still be drawn.

The first conclusion is that in the pre-industrial era the model predicts that though the soil was still acidic the stream was very different, with circumneutral pH and ANC > 150 µeq L^{-1}, in contrast with the modern pH of 4.2 and ANC c. -100 µeq L^{-1}. Though there are no palaeoecological data to validate this, it is consistent with historical records which show the land use as heathland (implying acidic soil), but that just N. of the catchment there were some late 17th century fishponds constructed on the Tillingbourne stream (Hill et al., 2002). The mean stream pH is a little higher here but these ponds are currently unsuitable for most fish due to acid episodes, whereas better water quality in historical times made them a viable proposition.

The second conclusion is that in spite of the large emission reductions since 1970, the catchment stream is not predicted to achieve its pre-industrial state. This is a common feature of long-term predictions (e.g. Helliwell et al., 2014; Wright and Hauhs, 1991). There are a number of reasons for this. One is that pre-industrial water quality implies pre-industrial emissions and deposition. Although UK S emissions required by 2020 should be only a little more than those in 1800 after a 95% reduction from 1970; those for oxidised N (73% reduction on 1970) and reduced N (30% reduction on 1970) are substantially greater than in 1800. A second reason is the continued accumulation of N in the catchment soils, leading to a continued increase in nitrate outputs, whereas according to MAGIC stream nitrate was negligible before 1973. A third reason is the depletion of soil base cations, which will reduce the output of bases and hence stream ANC. Though the deposition reduction is sufficient to allow a small increase in base saturation driven by weathering rates (Fig. 8), the acidification due to the increased nitrate output eventually overtakes this and acidification resumes. Different deposition reductions would lead to quantitively different outcomes, but given the practical and political difficulties of reducing deposition much further, it can be said that the Tillingbourne Catchment, and by default similar areas, will not return to its pre-industrial state but will exist in a state where the soil is poorer in bases but richer in nitrogen, and the stream lower in ANC and pH, but having measurable nitrate concentrations.

The model predicts that over the 35 years between soil samplings, most parameters which are both measured and modelled (i.e. soil solution calcium, aluminium, Ca : Al ratio; plus base saturation and C:N ratio) should have declined in value, and this is the case (Table 4), the only exception being Ca:Al ratio outside the tree canopy which has increased slightly. This gives some credence to the model predictions, although the observed changes are much more extreme. As explained in Section 3.3, the modelled and observed predictions relate to the catchment soils as a whole and an individual soil respectively, and thus cannot be compared directly, but the re-sampled soil would not be expected to be more sensitive to acid deposition that the catchment soils as a whole. Another difference between model and observed data is that the model is operating over the whole soil depth (1m) whereas only the top 30 cm of the soil was sampled,

and this may account for the greater than predicted response of Ca in particular. Although the H and A_h horizons have the highest Ca concentrations (Hill et al., 2002) and are the most important layers for tree nutrient uptake, especially for the more shallow rooted pines (e.g. Nilsson et al., 1982), the store of Ca in the lower horizons is still significant and could account for the difference between model and observation. However, the decline in Ca in the upper horizons is of concern, and was one of the destabilising effects of acid deposition on forest ecosystems predicted for instance by Meiwes et al. (1986). Another factor not taken into account in the modelling is any change in the availability of organic anions apart from straightforward acid-base chemistry, whereas it now seems clear that the large reductions of S deposition such as have occurred on this catchment (Skeffington and Hill, 2012) are likely to have increased organic anion availability (e.g. Monteith et al., 2007). It would be interesting to see if the model could take these more detailed changes into account and explore the implications for the future.

The fourth conclusion is that continued N accumulation in the catchment will eventually (given current deposition reduction commitments) lead to a resumption in soil and stream acidification, and an increase in nitrate flux to surface waters. Growing trees on the catchment and removing the resulting timber will slow this process considerably, reducing nitrate outputs while trees are growing quickly (Fig. 9). However as soon as forest growth slackens the acidification process resumes. The C:N ratio which underlies these responses never ceases to decline (Fig. 11). We should consider whether these model predictions are realistic in the long term, and in particular whether there are sinks for N which have been neglected. Denitrification is one such sink. Measurements on the catchment wetlands indicate that they appear to have become more efficient at retaining N, retaining about 35% of input in 1979-82 and 93% in 1999-2003 (Skeffington et al., 2003). This may be due to reduced acidity allowing denitrifying organisms to function better. However, wetlands occupy only a small proportion of the catchment, and this increase in efficiency did not prevent a reduction in C:N ratio (Whitehead et al., 2002) and an increase in stream nitrate (Hill et al., 2002). Another possibility is fire – although fire is rare in this humid area, in the long-term fires would be expected – one burned about 4 ha of the catchment in the very dry summer of 1976. Though fires have long been known to reduce soil organic N, they can also increase N availability (Raison, 1979). Wan et al. (2001) conducted a meta-analysis of the effects of fire on N availability using 185 published datasets and concluded that though an increase in N availability after fire was common it was also short-lived: less than a year in most cases. In the long-term, Wan et al. (2001) concluded that fire had no significant effects on soil N amounts or concentrations. This may not be true in every environment – one reason for the finding was that in many grassland environments the soil N occurs deep into the profile and a surface burn will remove only a small proportion of it. Forest soils with much of the N in the surface horizons may be more vulnerable. In terms of the controlling C:N ratio, fire will burn off the C as well. Johnson and Curtis (2001), in another meta-analysis, found fire had no immediate significant effect on C and N in forest ecosystems, though some did demonstrate an initial increase in C:N followed by rapid re-equilibration. Overall, the literature on fire does not seem to indicate that the accumulation of N in such nutrient-poor forest soils is likely to be substantially reduced by sporadic fires, not least because fire will be controlled in environments such as the Tillingbourne Catchment. It appears that the data and long-term modelling credibly predict the continuing eutrophication of these systems.

Finally, forest growth and harvesting are predicted to further acidify the soil due to base cation uptake. Somewhat unexpectedly, the simulations indicate that this acidifying effect will not appear when base cation uptake is increasing rapidly. On the contrary the initial effect on the stream may be to increase pH and ANC relative to the no “uptake” situation, because the effect on the strong acid anion (nitrate) occurs more quickly than on the base cations. Only when uptake slows or ceases will the acidification effect become apparent. As the uptake phase may last 50 years or more, this illustrates the difficulty of validating predicted trends with short-term data.

Overall, this illustrative study suggests that even with much reduced acid deposition, unmanaged ecosystems like the present one will still be showing effects into the foreseeable future. These include the resumption of a steady deterioration in environmental quality even though there may have been some improvements in the short-term. Some deposition of acidic substances is probably inevitable: managing the effects of this on sensitive ecosystems will remain a substantial challenge.

5. Acknowledgements
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7. References

Aber J, Mcdowell W, Nadelhoffer K, Magill A, Berntson G, Kamakea M, et al. Nitrogen saturation in temperate forest ecosystems - hypotheses revisited. Bioscience 1998; 48: 921-934.

Battarbee RW, Shilland EM, Kernan M, Monteith DT, Curtis CJ. Recovery of acidified surface waters from acidification in the United Kingdom after twenty years of chemical and biological monitoring (1988–2008). Ecological Indicators 2014; 37: 267-273.

Cosby BJ, Ferrier RC, Jenkins A, Wright RF. Modelling the effects of acid deposition: refinements, adjustments, and inclusion of nitrogen dynamics in the MAGIC model. Hydrology and Earth System Sciences 2001; 5: 499-517.

Cosby BJ, Wright RF, Hornberger GM, Galloway JN. Modelling the effects of acid deposition: assessment of a lumped parameter model of of soil and stream water chemistry. Water Resources Research 1985a; 21: 51-63.

Cosby BJ, Wright RF, Hornberger GM, Galloway JN. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. Water Resources Research 1985b; 21: 1591-1601.

de Vries W, Hettelingh J-P, Posch M. Critical Loads and Dynamic Risk Assessments: Nitrogen, Acidity and Metals in Terrestrial and Aquatic Ecosystems. Vol 25: Springer, 2015.

Evans CD, Jenkins A, Helliwell RC, Ferrier R. Predicting regional recovery from acidification; the MAGIC model applied to Scotland, England and Wales. Hydrology and Earth System Sciences 1998; 2: 543-554.

FAO. World Reference Base for Soil Resources 2014. World Soil Resources Reports. 106. United Nations Food and Agriculture Organisation, Rome, 2015.

Ferrier RC, Wright RF, Jenkins A. Predicting recovery of acidified freshwaters in Europe and Canada. Hydrology and Earth System Sciences 2003; 7: 429-617.

Helliwell R, Aherne J, Nisbet T, MacDougall G, Broadmeadow S, Sample J, et al. Modelling the long-term response of stream water chemistry to forestry in Galloway, Southwest Scotland. Ecological Indicators 2014; 37: 396-411.

Helliwell RC, Jenkins A, Ferrier RC, Cosby BJ. Modelling the recovery of surface water chemistry and the ecological implications in the British uplands. Hydrology and Earth System Sciences 2003; 7: 456-466.

Hill TJ, Skeffington RA, Whitehead PG. Recovery from acidification in the Tillingbourne Catchment, southern England: catchment description and preliminary results. The Science of the Total Environment 2002; 282-283: 81-97.

Jenkins A, Whitehead P, Cosby B, Birks H, Charles D. Modelling long-term acidification: a comparison with diatom reconstructions and the implications for reversibility [and

discussion]. Philosophical Transactions of the Royal Society of London B: Biological Sciences 1990; 327: 435-440.
Johnson DW, Curtis PS. Effects of forest management on soil C and N storage: meta analysis. Forest Ecology and Management 2001; 140: 227-238.
Meiwes KJ, Khanna PK, Ulrich B. Parameters for describing soil acidification and their relevance to the stability of forest ecosystems. Forest Ecology and Management 1986; 15: 161-179.
Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T, et al. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 2007; 450: 537-540.
Nilsson SI, Miller HG, Miller JD. Forest growth as a possible cause of soil and water acidification: an examination of the concepts. Oikos 1982; 39: 40-49.
Oulehle F, Cosby B, Wright R, Hruška J, Kopáček J, Krám P, et al. Modelling soil nitrogen: The MAGIC model with nitrogen retention linked to carbon turnover using decomposer dynamics. Environmental Pollution 2012; 165: 158-166.
Raison RJ. Modification of the soil environment by vegetation fires, with particular reference to nitrogen transformations: a review. Plant and soil 1979; 51: 73-108.
Roberts TM, Skeffington RA, Blank LW. Causes of Type 1 spruce decline in Europe. Forestry 1989; 62: 179-222.
Robison AL, Scanlon TM, Cosby BJ, Webb JR, Galloway JN. Roles of sulfate adsorption and base cation supply in controlling the chemical response of streams of western Virginia to reduced acid deposition. Biogeochemistry 2013; 116: 119-130.
Rowe E, Evans C, Emmett B, Reynolds B, Helliwell R, Coull M, et al. Vegetation type affects the relationship between soil carbon to nitrogen ratio and nitrogen leaching. Water, air, and soil pollution 2006; 177: 335-347.
Rowell DL. Soil science: Methods & applications: Routledge, 1994.
Schaberg PG, DeHayes DH, Hawley GJ. Anthropogenic calcium depletion: a unique threat to forest ecosystem health? Ecosystem Health 2001; 7: 214-228.
Schaberg PG, Tilley JW, Hawley GJ, DeHayes DH, Bailey SW. Associations of calcium and aluminum with the growth and health of sugar maple trees in Vermont. Forest Ecology and Management 2006; 223: 159-169.
Schmidt A, Skeffington RA, Thordarson T, Self S, Forster PM, Rap A, et al. Selective environmental stress from sulphur emitted by continental flood basalt eruptions. Nature Geosciences 2016; 9: 77-82.
Shand P, Cobbing J, Tyler-Whittle R, Tooth A, Lancaster A. The Lower Greensand of southern England. Baseline report series. 9. British Geological Survey, Keyworth, UK, 2003.
Skeffington R, Hill T. The effects of a changing pollution climate on throughfall deposition and cycling in a forested area in southern England. Science of the Total Environment 2012; 434: 28-38.
Skeffington RA. Soil properties under three species of tree in Southern England in relation to acid deposition in throughfall. Holland: Reidel Publishing Co, 1983.
Skeffington RA. The chemistry of bulk precipitation at a site in S E England. 1. Small-scale spatial variation, frequency distributions, and variation with time. Atmospheric Environment 1984; 18: 1683-1693.
Skeffington RA. The use of critical loads in environmental policymaking: a critical appraisal. Environmental Science & Technology 1999; 33: 245A-252A.
Skeffington RA, Brown DJA. Timescales of recovery from acidification: implications of current knowledge for aquatic organisms. Environmental Pollution 1992; 77: 227-234.
Skeffington RA, Cumberland SA, Flynn NJ, Cosby B, Whitehead PG. Recovery of Acidified Catchments in Southern England: Final Report. University of Reading, Reading, UK, 2003.

Stoddard JL, Jeffries DS, Lukewille A, Clair TA, Dillon PJ, Driscoll CT, et al. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 1999; 401: 575-578.

Sverdrup H, De Vries W. Calculating critical loads with the simple mass balance method. Water, Air and Soil Pollution 1994; 72: 143-162.

Tuovinen J, Barrett K, Styve H. Transboundary acidifying pollution in Europe: calculated fields and budgets 1985-93 EMEP, Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe. EMEP/MSC-W Report 1/94, Det Norske Meteorologiske Institutt, Technical Report, 1994.

Ulrich B, Mayer R, Khanna P. Chemical changes due to acid precipitation in a Loess-derived soil in Central Europe. Soil science 1980; 130: 193-199.

Wan S, Hui D, Luo Y. Fire effects on nitrogen pools and dynamics in terrestrial ecosystems: a meta-analysis. Ecological Applications 2001; 11: 1349-1365.

Whitehead PG, Lapworth DJ, Skeffington RA, Wade AJ. Excess nitrogen leaching and C/N decline in the Tillingbourne Catchment, southern England. Hydrology and Earth System Sciences 2002; 6: 455-466.

Wright RF, Cosby BJ, Ferrier RC, Jenkins A, Bulger AJ, Harriman R. Changes in acidification of lochs in Galloway, southwestern Scotland, 1979-1988 - the MAGIC model used to evaluate the role of afforestation, calculate critical loads, and predict fish status. Journal of Hydrology 1994; 161: 257-285.

Wright RF, Hauhs M. Reversibility of acidification: soils and surface waters. Proceedings of the Royal Society of Edinburgh 1991; 97B: 169-191.

Zetterberg T, Köhler SJ, Löfgren S. Sensitivity analyses of MAGIC modelled predictions of future impacts of whole-tree harvest on soil calcium supply and stream acid neutralizing capacity. Science of the Total Environment 2014; 494: 187-201.