

Assessing Recovery from Acidification of European Surface Waters in the Year 2010: Evaluation of Projections Made with the MAGIC Model in 1995

Rachel C. Helliwell,^{*,†} Richard F. Wright,[‡] Leah A. Jackson-Blake,[†] Robert C. Ferrier,[†] Julian Aherne,[§] Bernard J. Cosby,^{||} Christopher D. Evans,^{||} Martin Forsius,[⊥] Jakub Hruska,[#] Alan Jenkins,[¶] Pavel Kram,[#] Jiri Kopáček,[⊗] Vladimír Majer,[#] Filip Moldan,[∇] Maximilian Posch,[×] Jacqueline M. Potts,[○] Michela Rogora,[◇] and Wolfgang Schöpp⁺

[†]The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, U.K.

[‡]Norwegian Institute for Water Research, 0349 Oslo, Norway

[§]Trent University, Peterborough, Ontario K9J 7B8, Canada

^{||}Environment Centre Wales, Centre for Ecology & Hydrology, Bangor LL57 2UW, U.K.

[⊥]Finnish Environment Institute (SYKE), FI-00251 Helsinki, Finland

[#]Czech Geological Survey, 118 21 Prague, Czech Republic

[¶]Centre for Ecology and Hydrology, Wallingford OX10 8BB, U.K.

[⊗]Institute of Hydrobiology, Biology Centre ASCR, 370 05 České Budějovice, Czech Republic

[∇]IVL Swedish Environmental Research Institute, SE-411 33 Gothenburg, Sweden

[×]Coordination Centre for Effects, RIVM, 3720 BA Bilthoven, The Netherlands

[○]Biomathematics and Statistics Scotland, Edinburgh EH9 3JZ, U.K.

[◇]Institute of Ecosystem Study, CNR, 28922 Verbania, Italy

⁺International Institute for Applied Systems Analysis, 2361 Laxenburg, Austria

S Supporting Information

ABSTRACT: In 1999 we used the MAGIC (Model of Acidification of Groundwater In Catchments) model to project acidification of acid-sensitive European surface waters in the year 2010, given implementation of the Gothenburg Protocol to the Convention on Long-Range Transboundary Air Pollution (LRTAP). A total of 202 sites in 10 regions in Europe were studied. These forecasts can now be compared with measurements for the year 2010, to give a “ground truth” evaluation of the model. The prerequisite for this test is that the actual sulfur and nitrogen deposition decreased from 1995 to 2010 by the same amount as that used to drive the model forecasts; this was largely the case for sulfur, but less so for nitrogen, and the simulated surface water [NO₃⁻] reflected this difference. For most of the sites, predicted surface water recovery from acidification for the year 2010 is very close to the actual recovery observed from measured data, as recovery is predominantly driven by reductions in sulfur deposition. Overall these results show that MAGIC successfully predicts future water chemistry given known changes in acid deposition.



1. INTRODUCTION

During much of the 1900s large regions of Europe suffered from the effects of acid deposition, due to the emissions of sulfur and nitrogen oxides to the atmosphere.¹ Long-range transport of air pollutants caused acidification of surface waters with loss of fish and other damage to biota.² In 1979 the LRTAP Convention under the auspices of the United Nations Economic Commission for Europe (UNECE) was established with the aim to reduce the emissions of sulfur and nitrogen.³ Since the mid-1980s a series of

protocols have been implemented, and the emissions of sulfur and nitrogen have been reduced substantially.^{4,5} In response, acidified surface waters have shown widespread chemical^{6,7} and to a lesser extent biological recovery.^{8–10}

Received: May 29, 2014

Revised: October 14, 2014

Accepted: October 17, 2014

Published: October 17, 2014

Research on the acidification of soils and waters led to the development of process-oriented acidification models. One of these, MAGIC (Model of Acidification Of Groundwater In Catchments),^{11,12} has been extensively used to simulate historical and future trends in surface water acidification at sites and regions around the world.^{13,14}

In 1999 a major European research project, RECOVER:2010,^{14,15} was started with the aims to document the recovery in surface water acidification 1970–2000,¹⁶ and to use MAGIC to forecast the future changes expected if the Gothenburg Protocol to the LRTAP Convention was implemented by the year 2010, as agreed.¹⁷ A total of 202 sites in 10 European regions were studied. At each site MAGIC was calibrated to observed data for the years 1994–1996, and forecasts were made for the year 2010 to represent the time of implementation for the Gothenburg Protocol (average 2008–2010).

Now, 15 years later, we revisit these MAGIC forecasts to determine if the predictions made in 1999 indeed came true. First we compare the projected deposition of sulfur and nitrogen in 2010 with the actual measured values. Then we check that the simulated surface water concentrations of the strong acid anions SO_4^{2-} (sulfate) and NO_3^- (nitrate) agree with the MAGIC forecasts. And finally we compare the simulated with observed values for acid neutralizing capacity (ANC) in the waters. This is the first paper of its kind to report on testing long-term MAGIC model predictions against actual observations at a European scale.

2. MATERIALS AND METHODS

2.1. Sites. The 202 sites in 10 regions cover a wide range of acid-sensitive landscapes, from high-altitude alpine meadows and rocky catchments in the Italian Alps and Tatra Mountains of Slovakia and Poland, to Central European and Scandinavian forests, to peaty moorlands and forested sites in the UK (Figure 1, Table 1). The catchments typically have podzolic soils derived from highly siliceous primary minerals, with low rates of chemical weathering. Waters are dilute with low alkalinity. Additional details are given by Jenkins et al.¹⁷ The number of sites analyzed here differ from the number of sites modeled in the 2003–2004 publications (Table 1) because not all sites were monitored during the period 1995–2010 due to resource limitations.

2.2. Data Sources. For this study we used the MAGIC forecasts made in 1999 for the individual sites. The 1999 forecasts were driven by the projected sulfur and nitrogen deposition over the period 1995–2010 as calculated by the EMEP (European Monitoring and Evaluation Programme) Lagrangian acid deposition model.²⁷ EMEP is part of the LRTAP Convention. This old version of the EMEP model gave estimates of average deposition for sulfur and nitrogen in each $150 \text{ km} \times 150 \text{ km}$ grid square covering Europe. Data were supplied at 5-year intervals²⁷ and were computed by assuming identical average meteorological conditions each year. Values were obtained for the calibration year 1995 and the year 2010 under the assumption that the Gothenburg Protocol and other current legislation were fully implemented (the CLE scenario).⁴ The regional estimates of 1995 sulfur deposition were scaled to match observed concentrations of SO_4^{2-} in surface water at each site, after first subtracting the seasalt contribution and the natural background contribution (details in ref 17). The deposition of NO_x (sum of oxidized species of nitrogen) and NH_y (sum of reduced species of nitrogen) were then calculated from the NO_x/S and NH_y/S ratios in the EMEP data and the scaled sulfur

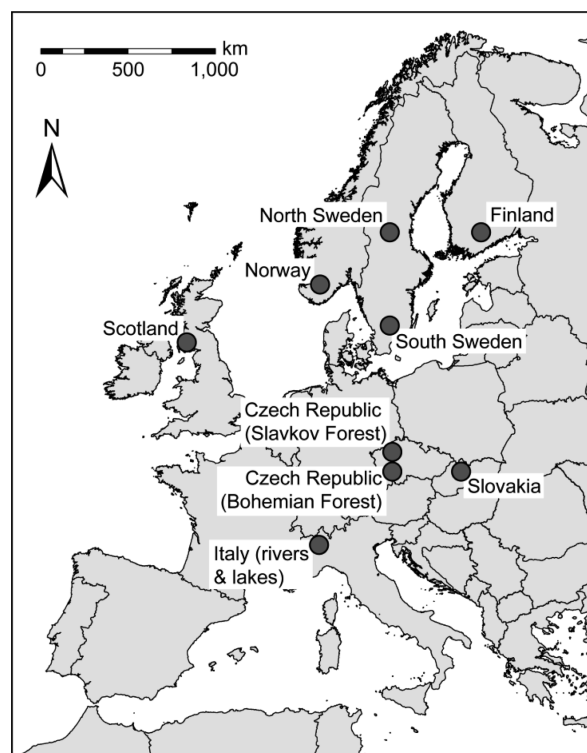


Figure 1. Map of Europe showing the location of regions.

Table 1. Study Regions with Key References for Previously Published MAGIC Forecasts

region	waterbody	no. of sites	ref(s) for MAGIC forecasts
Scotland, UK	lakes	42	18
Norway	lakes	31	19,20
northern Sweden	lakes	32	21
southern Sweden	lakes	32	21
Finland	lakes	24	22
Slavkov Forest, Czech Republic	rivers	2	23
Bohemian Forest, Czech Republic	lakes	3	24
Tatra Mountains, Slovakia	lakes	30	25
Alps, Italy	lakes	4	26
northern Italy	rivers	2	26

deposition at each site. Total inorganic nitrogen (TIN) is defined as $\text{NO}_x + \text{NH}_y$. Depositions for the year 2010 were calculated from the percentage change between 1995 and 2010 in the EMEP data sets.

To check if changes in sulfur and nitrogen deposition at the sites from 1995 to 2010 were similar to the declines projected by the EMEP model under the CLE scenario, we obtained measured deposition data for one or more stations in each of the 10 study regions. These stations are operated by various national agencies, in most cases as part of the EMEP network.

Measurements of lake and stream chemistry for the period 1995–2010 likewise came from national monitoring programs, in many cases as part of the International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP-Waters), part of the LRTAP Convention. Where hydro-chemical analysis took place outside the ICP-Waters network, standard protocols were followed in quality assured laboratories.

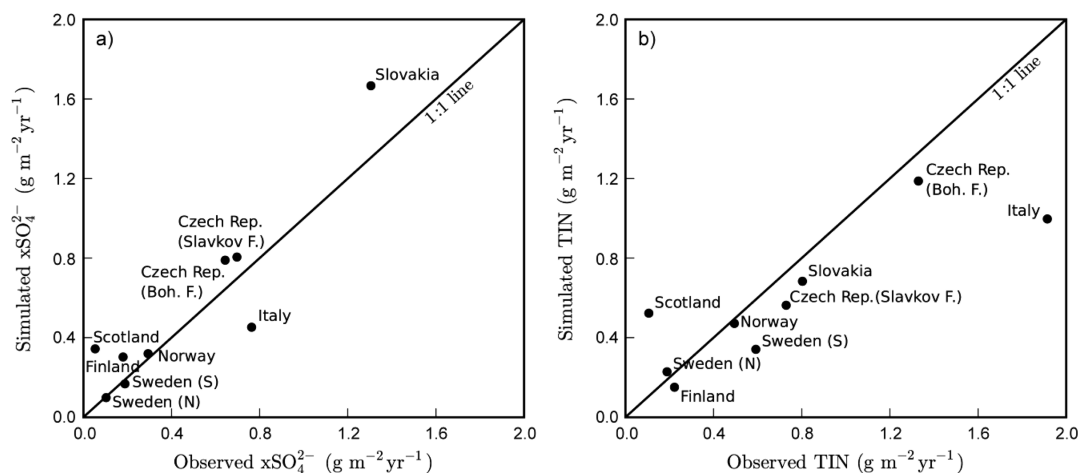


Figure 2. Deposition of (a) $x\text{SO}_4^{2-}$ and (b) total inorganic nitrogen (TIN) for 2009 as projected by the EMEP model assuming full implementation of the Gothenburg protocol and other legislation (CLE scenario) and as observed at one or more stations in each of the 10 regions studied.

For surface waters, a set of three key variables are considered: acid neutralizing capacity (ANC), $x\text{SO}_4^{2-}$ (non-marine sulfate), and NO_3^- . ANC was defined as the difference in the equivalent sum of base cations (calcium (Ca), magnesium (Mg), sodium (Na), potassium (K)) and acid anions (chloride (Cl), sulfate (SO_4^{2-}), nitrate (NO_3^-)). The variables selected illustrate the main surface water responses to changes in acid deposition, with $x\text{SO}_4^{2-}$ and NO_3^- representing the major acidifying anions, and ANC providing a measure of surface water acidity and a link to biota. Gran alkalinity was used instead of ANC to evaluate the model performance for Bohemian Forest sites.²⁴ Gran alkalinity was determined according to Mackereth et al.²⁸ All references to SO_4^{2-} in deposition and surface water in this paper refer to $x\text{SO}_4^{2-}$ except for sites in Italy, Czech Republic, and Slovakia, where SO_4^{2-} is reported as these sites are remote from coastal areas with negligible sources of Cl. River and lake sites in Italy share the same deposition data.

2.3. Data Analysis. The changes in observed and simulated deposition (flux) and surface water chemistry (concentration) between 1995 and 2009 were calculated as the average of values in 2008–2010 minus the average of 1994–1996. For surface water chemistry, this was performed per site in the region (as defined as a collection of sites within a country), and values were averaged to give the regional mean (Δ). The standard deviation (σ) between sites within each region (where the number of sites is >4) was also calculated (Table 2). Simulated deposition fluxes (EMEP with CLE scenario) were generally only available on a 5 year basis, so the start year was taken as 1995. The 2009 value was gained by linear interpolation between the 2005 and 2010 points. 2009 was chosen as the end year, as the majority of regions had observed deposition data until 2009 only. These start and end years were chosen to maximize the data interval while also maximizing the number of regions with observations. As a result, not all regions had data to be averaged for all three of the start/end years, in which case the average of the available years was used. The number of sites used in the regional averaging is given (Table 2, below).

Correlations between projected and observed surface water chemistry for 2009, and for differences between 2009 and 1995, were calculated, and the significance of the correlation coefficient was assessed. Where there were sufficient sites in a region, this was done for individual regions (Table 3, below). A high correlation between projected and observed values simply

indicates the ability of the model to predict relative concentrations at different locations, while the correlation between predicted and observed changes provides a better indicator of the predictive ability of the model. Paired *t* tests were also carried out to assess whether there were significant differences between the means of the observed and projected values for 2009 and of changes from 1995 to 2009.

2.4. MAGIC Model. The MAGIC model was developed to predict long-term effects of acid deposition on soil and surface water chemistry.^{11–13} MAGIC calculates annual or monthly concentrations of ions in soil solution and surface water using mathematical solutions to simultaneous equations describing sulfate adsorption, cation exchange, dissolution–precipitation speciation of aluminum, and dissolution–speciation of inorganic and organic carbon. The model accounts for the mass balance of major ions by simulating ionic fluxes from atmospheric inputs, chemical weathering, net uptake in biomass, and loss to runoff.

3. RESULTS

3.1. Deposition. The first step in the analysis is to compare the year 2009 deposition of sulfur and nitrogen, and the decreases in deposition from 1995 to 2009, projected by the EMEP model given the CLE scenario, with the actual observed deposition (average values for the years 1994–1996 and 2008–2010). This is to check how closely the actual measured deposition from the calibration year (i.e., 1995) to the present (i.e., 2008–2010) match the deposition sequences used in the MAGIC forecasts. The projected surface water chemistry cannot be expected to match the observed, if the driver of change, the deposition of sulfur and nitrogen, used in the model was not similar to the observed (Supporting Information, Figure S1). A large deposition gradient is represented in this European assessment with the lowest deposition in Scandinavia and Scotland and the highest in Slovakia, Czech Republic, and Italy (Figure 2). Sites that historically received high anthropogenic deposition also exhibit the highest reduction in sulfur and nitrogen emissions and deposition (Figure S1). For example, the present sulfur emissions in central Europe (mostly in post-communist countries) decreased by 90% and are lower than in 1900. Also NO_x emissions declined by $\sim 50\%$ (to the levels of the 1960s), and NH_3 emissions are lower than in 1850s, due to a drastic reduction in cattle production.²⁹

Table 2. Change in Simulated and Observed Surface Water and Deposition Chemistry between 1995 and 2009^a

		Surface Water Chemistry ^b											
		xSO ₄ ²⁻				NO ₃ ⁻				ANC			
region	no. sites	MAGIC		obsd		MAGIC		obsd		MAGIC		obsd	
		Δ	σ	Δ	σ	Δ	σ	Δ	σ	Δ	σ	Δ	σ
Czech Rep. (Slavkov F.)	2	-458	-10	-509	47	-7	-1	21	-1	80	6	194	88
Czech Rep. (Bohemian F.)	3	-57, -70, -68		-44, -60, -81		-17, -16, -9		-8, -5, 60		8, 15, 9		7, 8, 5	
Finland	24	-29	16	-31	21	0	1	0	2	7	4	12	17
Italy (lakes)	4	-10	-10	47	12	-1	-2	-1	-3	6	8	88	75
		-17	-19	-16	-17	-2	-2	-7	-4	11	12	9	3
Italy (rivers)	2	-26	-26	-14	-19	-3	3	-4	3	-3	-18	12	45
Norway	31	-21	8	-26	12	-2	2	-6	5	19	7	26	10
Scotland	42	-46	13	-52	20	2	5	-14	10	17	10	32	42
Slovakia	30	-29	4	-21	11	-8	3	-9	7	13	5	35	18
Sweden (N)	32	-43	26	-22	25	-1	1	0	3	11	6	22	37
Sweden (S)	32	-103	41	-82	30	-2	2	2	3	26	13	13	50
		Deposition Chemistry ^c											
		xSO ₄ ²⁻				TIN							
region	no. sites	EMEP		obsd		EMEP		obsd					
Czech Rep. (Slavkov F.)	2	-1.96 (71%)		-1.95 (74%)		-0.13 (16%)		-0.22 (19%)					
Czech Rep. (Bohemian F.)	3	-0.83 (51%)		-1.38 (68%)		-0.26 (15%)		0 (0%)					
Finland	24	-0.05 (13%)		-0.1 (36%)		-0.13 (41%)		-0.01 (5%)					
Italy (lakes, rivers)	6	-0.62 (58%)		-1.05 (58%)		-0.22 (15%)		-0.24 (9%)					
Norway	31	-0.23 (41%)		-0.09 (21%)		-0.04 (7%)		-0.2 (25%)					
Scotland	42	-0.28 (45%)		-0.8 (94%)		-0.24 (26%)		-0.94 (88%)					
Slovakia	30	-1.09 (40%)		-1.56 (54%)		-0.27 (24%)		-0.44 (31%)					
Sweden (N)	32	-0.07 (42%)		-0.1 (49%)		0.07 (-30%)		0.01 (-5%)					
Sweden (S)	32	-0.32 (65%)		-0.24 (56%)		-0.16 (27%)		0.05 (-8%)					

^aCalculated as the average of values in 2008–2010 minus the average of values in 1994–1996, such that negative values indicate a decrease. xSO₄²⁻ is non-marine SO₄²⁻, TIN is total inorganic nitrogen, and ANC is acid neutralizing capacity. ^bΔ indicates regional mean, and σ is the standard deviation of values for individual sites around the regional mean. Units are μequiv L⁻¹. ^cUnits are g m⁻² yr⁻¹. Percentage reduction in simulated (CLE scenario) and observed deposition is shown in parentheses (negative values indicate an increase). Data from individual sites are reported for sites in Italy and the Czech Republic.

The results show that the actual decreases in deposition of xSO₄²⁻ over the period 1995 to 2010 was, for the regions together, about the same as those expected under the CLE scenario (Table 2). The correlation between the predicted and observed changes in xSO₄²⁻ was 0.92 ($p < 0.001$). However, for TIN, although the correlation between predicted and observed values in 2009 was 0.85 ($p = 0.004$), the correlation between the predicted and observed changes was only 0.42 ($p = 0.257$). There are several possible explanations for the differences between projected and observed deposition:

1. Measurements at a single site do not (and cannot, except by chance) represent modeled deposition for a grid cell of 22,500 km².
2. Emissions of sulfur and nitrogen did not decrease as expected, or the decreases did not occur in the geographic locations (within a country) as expected.
3. The meteorological conditions in the years of interest (1995 and 2008–2010) differed from the meteorology used in the EMEP model, thus the deposition of sulfur and nitrogen was not distributed geographically as expected.
4. The EMEP model does not (and cannot) capture all the local (within-grid) variability of orography, land cover and meteorology and thus might give an inaccurate deposition at certain sites.

3.2. Surface Water Chemistry. For the period 1995–2009, large decreases of the concentrations of xSO₄²⁻ in surface waters

were forecast by MAGIC, and these forecasts agreed well with the actual measured concentrations (Figure 3a, Supporting Information Figures S2 and S3, Tables 2 and 3). However, although there were significant correlations between the observed and projected changes in concentrations, there were also significant differences in the mean values (Table 3).

Unlike xSO₄²⁻, the observed NO₃⁻ trends in surface waters were highly variable with no evidence of a consistent Europe-wide trend from 1995 and 2009. This result complements recent European trend analysis as part of the ICP Waters program³⁰ as well as a previous European assessment of surface water NO₃⁻ trends.³¹ In some regions NO₃⁻ concentrations increased (Slavkov Forest and Bohemian Forest, Czech Republic), and in other regions no major changes were observed (Finland, northern Sweden), while concentrations decreased in Scotland (Galloway), Slovakia (Tatra Mountains), and Norway (Table 2, Figure 3d, Supporting Information Figures S4 and S5).

The simulated changes in concentrations of NO₃⁻ from 1995 to 2010 in general did not match the observed (Table 3). In most regions the correlation between the predicted and observed changes was not significant, and in some regions there was a significant difference between the mean predicted and observed changes. The simulations assumed that the fraction of incoming nitrogen retained in the terrestrial catchments remained constant from 1995 to 2010. As nitrogen deposition decreased over most of Europe during this period, the simulations forecast a proportional decline in NO₃⁻ concentrations in surface waters.

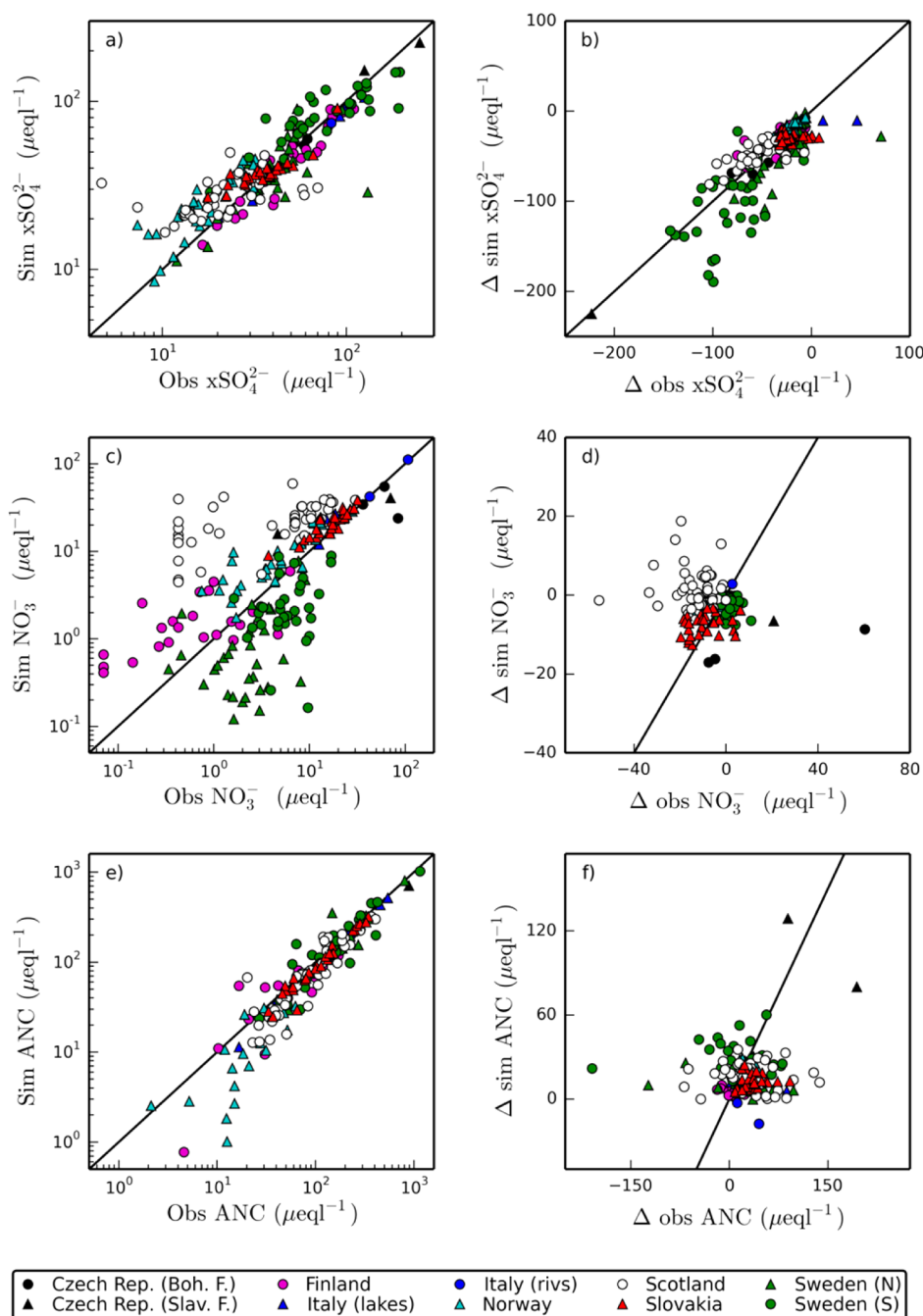


Figure 3. Left: Simulated versus mean observed surface water concentrations for the years 2008–2010 at each site. A range of years was chosen as not all sites had observations for all years of interest. Right: Change in simulated and observed surface water concentrations over the period 1995–2009. Sites within a region have the same symbol and color, while black lines show the 1:1 relationship. For delta change in $x\text{SO}_4^{2-}$, one point with a delta change of $>400 \mu\text{equiv L}^{-1}$ in both simulated and observed was excluded for clarity. Note the log scale in the left-hand plots, and that gran alkalinity is presented instead of ANC at the Bohemian Forest sites (panel e and f).

In reality NO_3^- concentrations over the 15-year period in many cases did not follow the decline in nitrogen deposition. Of many possible explanations:

1. Nitrogen saturation may have increased over the 15 years (lower fraction of N retained).^{32,33}
2. Forest damage from severe weather/disease/infestation (i.e., bark beetle).^{34,35}
3. Recovery of the forest may have promoted growth and uptake of nitrogen.³⁶
4. Warmer climate may have promoted uptake of nitrogen.³⁷

Observed surface water ANC mirrored the same general pattern of simulated ANC, with a universal tendency toward a rising ANC in surface waters from 1995 to 2009. The ANC at sites that have historically received high deposition inputs, and then experienced the most pronounced reduction in anthropogenic acidic deposition, recovered the most (Table 2, Figure 3e, Supporting Information Figures S6 and S7). However, the magnitude of the rise in ANC was not so well predicted, with many regions not showing a significant correlation between the observed and projected changes, or showing a significant difference in the mean change (Table 3).

Table 3. Correlation (r) between Predicted and Observed Values and Difference in Mean between Predicted and Observed Values (diff.) for Surface Water Chemistry in 2009 and for Changes in Surface Water Chemistry between 1995 and 2009^a

region	no. sites	xSO ₄ ²⁻			NO ₃ ⁻			ANC					
		2009		Δ	2009		Δ	2009		Δ			
		r	diff	R	r	diff	r	diff	r	diff			
Finland	24	0.96 (<0.0001)	6.30 (<0.0001)	0.84 (<0.0001)	-2.02 (0.400)	0.81 (<0.0001)	-0.76 (0.03)	0.60 (0.002)	0.36 (0.175)	0.93 (<0.0001)	10.22 (0.022)	-0.14 (0.523)	5.10 (0.172)
Norway	31	0.90 (<0.0001)	-7.67 (<0.0001)	0.95 (<0.0001)	-5.36 (<0.0001)	0.90 (<0.0001)	-3.61 (<0.0001)	0.72 (<0.0001)	-3.78 (<0.0001)	0.88 (<0.0001)	13.28 (<0.0001)	0.36 (0.049)	6.79 (0.001)
Scotland	42	0.42 (0.006)	-4.03 (0.041)	0.72 (<0.0001)	-6.49 (0.005)	0.54 (<0.0001)	-16.89 (<0.0001)	-0.01 (0.998)	-15.9 (<0.0001)	0.92 (<0.0001)	13.43 (0.016)	-0.09 (0.570)	15.74 (0.027)
Slovakia	30	0.90 (<0.0001)	-1.47 (0.207)	-0.001 (0.994)	8.23 (<0.0001)	0.90 (<0.0001)	-3.90 (<0.0001)	0.27 (0.158)	-1.90 (0.155)	0.99 (<0.0001)	13.43 (<0.0001)	0.08 (0.684)	22.6 (<0.0001)
Sweden (N)	32	0.60 (<0.0001)	2.12 (0.587)	0.68 (<0.0001)	20.6 (<0.0001)	0.61 (<0.0001)	1.64 (<0.0001)	-0.10 (0.582)	0.69 (0.212)	0.91 (<0.0001)	2.91 (0.789)	-0.30 (0.099)	10.67 (0.135)
Sweden (S)	32	0.78 (<0.0001)	-0.20 (0.970)	0.56 (<0.0001)	21.0 (0.002)	0.44 (0.012)	3.82 (<0.0001)	-0.18 (0.332)	4.12 (<0.0001)	0.96 (<0.0001)	8.10 (0.443)	-0.07 (0.722)	-12.56 (0.186)
all	202	0.89 (<0.0001)	-0.89 (0.455)	0.89 (<0.0001)	5.70 (<0.0001)	0.73 (<0.0001)	-3.53 (<0.0001)	-0.10 (0.177)	-2.88 (<0.0001)	0.96 (<0.0001)	11.04 (<0.0001)	0.12 (0.098)	9.36 (<0.0001)

^aThe corresponding p -values are indicated in parentheses. Regions with fewer than five sites were not analyzed separately.

We used an ANC threshold of 20 $\mu\text{equiv L}^{-1}$ to indicate water quality sufficient to support viable populations of brown trout.³⁸ Jenkins et al.¹⁷ and Wright et al.³⁹ used ANC thresholds and MAGIC simulations to estimate the number of sites in three ecologically significant ANC categories in response to acid deposition across Europe for key years (1860, 1980, 2000, and 2016). Here we used a similar approach to compare the number of sites in the ANC categories predicted in 2009 (based on the mean data from 2008 to 2010) to those observed in 2009 (based on the mean data from 2008 to 2010), and assessed these against the situation in 1995 (mean 1994–1996) (Figure 4). The simulated and observed ANC in 2009 show very similar classifications into the three categories.

4. DISCUSSION

Good models are the foremost tools for projecting future changes; this is the case for making projections of future acidification of soils and waters given alternative possible scenarios for acid deposition. A continuing concern in using models either to summarize our current knowledge or to assist in making policy decisions is the level of confidence that can be placed in the model projections. The “verification” or “validation” of a mathematical model of a natural system is problematic because natural systems are never closed, model results are non-unique, and “truth” cannot be proved absolutely.⁴⁰ Model evaluation is, however, feasible when the model is tested against observations from a range of heterogeneous ecosystems at multiple sites, and confidence in the models is increased if it is found to produce satisfactory results.⁴¹ This was the premise of the current study.

The MAGIC model has been subjected to several types of evaluations during the 30 years since its launch in 1985:

1. Compare model hindcasts with independent historical data records of acid deposition and water chemistry, such as the study of Larssen,⁴² a comparison of MAGIC simulations with 30-years of observations from four small calibrated catchments in Norway.
2. Compare MAGIC hindcasts with other types of observed historical data, such as paleo-limnological data for diatoms.⁴³
3. Compare the results from large-scale whole ecosystem acidification experiments with MAGIC simulations.⁴⁴

To these we now add a fourth type of test: Use MAGIC to project future water chemistry, wait 15 years, and then test if the projections actually came true.

The prerequisite for this test is that the CLE deposition scenario for 2010 used in the MAGIC projections did indeed happen. For sulfur deposition this appears to be approximately the case, but not so for nitrogen deposition. Differences in simulated and observed deposition were attributed to the following factors: (a) Bulk deposition was monitored at all study sites except those in the Czech Republic (Bohemian Forest) and Finland, where only the wet component was recorded. (b) In central Europe (Czech Republic and Slovakia) and northern Italy, marine inputs in deposition are minor, therefore xSO₄²⁻ (non-marine sulfate) is approximately equal to SO₄²⁻.

Fortunately most of the ANC changes in the sites studied here have been driven by changes in SO₄²⁻, and heretofore nitrogen has played a lesser role. The MAGIC model performed particularly well at those sites where the long-term hydrochemical trends were driven primarily by sulfur deposition and terrestrial geochemical (abiotic) processes. For nitrogen, refine-

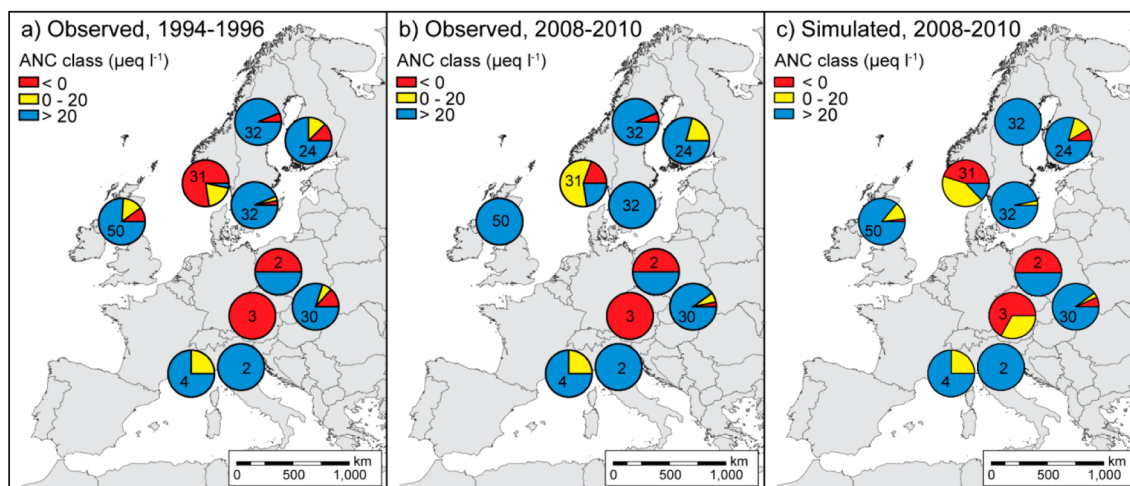


Figure 4. Pie charts summarizing the number of sites within three ecologically relevant ANC classes which correspond to the probability of viable populations of brown trout. Red: ANC < 0, barren of fish; yellow: ANC 0–20, sparse population; blue: ANC > 20, good population. Pies are annotated with the number of sites per region.

ment to the model structure, setup, and parameterization is required to more readily capture biological processes and especially those processes driven by climate.⁴⁵ More detail is given on the importance of abiotic and biotic processes at site level in the references supplied in Table 1.

Non-marine sulfur deposition was the principal cause of acidification of the majority of surface waters in this study.³⁹ Of the strong acid anions, concentrations of sulfate (SO_4^{2-}) were commonly 3–10 times higher than that of nitrate (NO_3^-). Since the 1990s, due to effective abatement policies, it is clear that xSO_4^{2-} has lost its role as the dominant acidifying anion, and NO_3^- and reduced forms of nitrogen (TIN) deposition are becoming a greater concern for all countries except Slovakia (Figure S1).

Nonetheless, the strong declining trend in observed surface water xSO_4^{2-} was successfully simulated at the majority of sites throughout Europe (Figure S2 and S3), and this is attributed to the calibration of SO_4^{2-} adsorption parameters based on input/output budgets⁴⁶ and valid EMEP deposition forecasts. Slight discrepancies with the model performance were observed. For example, simulated xSO_4^{2-} was overpredicted as a consequence of the possible desorption of sulfur from soil; the mismatch between surface water xSO_4^{2-} concentrations in the Galloway region of Scotland was attributed to disturbance of the soil from intensive forest management during ground preparation, tree planting, and felling operations in catchments dominated by forestry; and the clear increasing SO_4^{2-} trend in the Italian lakes (Boden Inferiore and Superiore) can be linked to the high content of carbonate and SO_4^{2-} minerals in the bedrock. It is hypothesized that the increasing SO_4^{2-} trend in the Italian lakes results from enhanced mineral weathering induced by the direct and indirect effects of climate change.⁴⁷ Similarly, the long-term variability in ANC of the Italian rivers is mainly driven by weathering processes and factors influencing them (e.g., climate change driving less snow cover in the higher portions of the catchments and a greater export of base cations from weathering processes.⁴⁷ Such climate-induced geochemical processes were not represented in the model.

In general, NO_x deposition has played a secondary role in the acidification of surface waters in semi-natural systems throughout Europe, although TIN ($\text{NO}_x + \text{NH}_y$) has become the dominant form of deposition for the majority of regions as xSO_4^{2-}

concentrations decrease (Figure S1). Most nitrogen deposition is retained in the terrestrial catchments at the majority of sites, and thus leaching of NO_3^- has played a lesser role in water acidification.^{48,49} Simulated changes in NO_3^- concentrations from 1995 to 2010 were poorly represented by the model. This was particularly evident in catchments where the nutrient cycle had been disrupted as a result of unforeseen environmental perturbations (extreme climatic conditions, disease or infestation).

Our study provides strong evidence that the MAGIC model is a robust management tool capable of forecasting changes in surface water chemistry, primarily driven by geochemical processes, in response to changes in acid deposition following the implementation of abatement technologies. This multi-site evaluation confirms the value of dynamic modeling studies for integrating and synthesizing scientific understanding of natural resources management and future policy development. The credible prediction of the future recovery trajectories of sensitive surface waters is a key element in political decisions regarding revisions to existing protocols and potential new protocols to the LRTAP Convention. However, despite a number of refinements, adjustments, and extensive testing of the MAGIC model prior to the RECOVER:2010 project, this evaluation has demonstrated a clear need to improve the representation of climate driven processes responsible for the simulation of nutrients in surface waters.

■ ASSOCIATED CONTENT

📄 Supporting Information

Observed and simulated atmospheric deposition and water quality data from 10 regions in Europe. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +44 (0)1224 395152; fax: +44 (0)844 9285429; e-mail: rachel.helliwell@hutton.ac.uk.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded primarily by the Scottish Government's Rural and Environment Science and Analytical Services Division (RESAS), Norwegian Institute for Water Research, Natural Environment Research Council (NERC), and a number of other European Institutes and funding agencies. The modeling was performed as part of the EU project RECOVER:2010 (EVK1-CT-1999-00018).

REFERENCES

- (1) Rodhe, H.; Grennfelt, P.; Wisniewski, J.; Ågren, C.; Bengtsson, G.; Johansson, K.; Kauppi, P.; Kucera, V.; Rasmussen, L.; Rosseland, B.; Schotte, L.; Sellén, G. Acid reign '95?—Conference summary statement. *Water, Air, Soil Pollut.* **1995**, *85*, 1–14.
- (2) Overrein, L.; Seip, H. M.; Tollan, A. *Acid precipitation—Effects on forest and fish*, Final report of the SNSF project 1972–1980; SNSF Project: Ås, Norway, 1980; p 175.
- (3) UNECE. Convention on Long-Range Transboundary Air Pollution, 2014 <http://www.unece.org/env/lrtap/>.
- (4) Schöpp, W.; Posch, M.; Mylona, S.; Johansson, M. Long-term development of acid deposition (1880–2030) in sensitive freshwater regions in Europe. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 436–446.
- (5) Rafaj, P.; Amann, M.; Siri, J.; Wuester, H. Changes in European greenhouse gas and air pollutant emissions 1960–2010: decomposition of determining factors. *Climatic Change* **2013**, *124*, 477–504.
- (6) Skjelkvåle, B. L.; Evans, C. D.; Larssen, T.; Hindar, A.; Raddum, G. G. Recovery from acidification in European surface waters: A view to the future. *Ambio* **2003**, *30*, 170–175.
- (7) Stoddard, J. L.; Jeffries, D. S.; Lükewille, A.; Clair, T. A.; Dillon, P. J.; Driscoll, C. T.; Forsius, M.; Johannessen, M.; Kahl, J. S.; Kellogg, J. H.; Kemp, A.; Mannio, J.; Monteith, D.; Murdoch, P. S.; Patrick, S.; Rebsdorf, A.; Skjelkvåle, B. L.; Stainton, M. P.; Traaen, T. S.; van Dam, H.; Webster, K. E.; Wieting, J.; Wilander, A. Regional trends in aquatic recovery from acidification in North America and Europe 1980–95. *Nature* **1999**, *401*, 575–578.
- (8) Hesthagen, T.; Fjellheim, A.; Schartau, A. K.; Wright, R. F.; Saksgård, R.; Rosseland, B. O. Chemical and biological recovery of Lake Saudlandsvatn, a highly acidified lake in southernmost Norway, in response to decreased acid deposition. *Sci. Total Environ.* **2011**, *409*, 2908–2916.
- (9) Kernan, M.; Battarbee, R. W.; Curtis, C. J.; Monteith, D. T.; Shilland, E. M. *Recovery of lakes and streams in the UK from the effects of acid rain*, UK Acid Waters Monitoring Network 20 Year Interpretative Report, Report to Defra. Environmental Change Research Centre; University College London: London, 2010; p 133.
- (10) Krogglund, F.; Kaste, O.; Rosseland, B. O.; Poppe, T. The return of the salmon. *Water, Air, Soil Poll.* **2001**, *130*, 1349–1354.
- (11) Cosby, B. J.; Ferrier, R. C.; Jenkins, A.; Wright, R. F. Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 499–518.
- (12) Cosby, B. J.; Hornberger, G. M.; Galloway, J. N.; Wright, R. F. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* **1985a**, *21*, 51–63.
- (13) Cosby, B. J.; Wright, R. F.; Hornberger, G. M.; Galloway, J. N. Modelling the effects of acid deposition: estimation of long term water quality responses in a small forested catchment. *Water Resour. Res.* **1985b**, *21*, 1591–1601.
- (14) Ferrier, R. C.; Jenkins, A.; Wright, R. F.; Schöpp, W.; Barth, H. Assessment of recovery of European surface waters from acidification 1970–2000: An introduction to the Special Issue. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 274–282.
- (15) Ferrier, R. C.; Wright, R. F.; Jenkins, A.; Barth, H. Predicting recovery of acidified freshwaters in Europe and Canada: an introduction. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 431–435.
- (16) Evans, C. D.; Cullen, J. M.; Alewell, C.; Kopacek, J.; Marchetto, A.; Moldan, F.; Prechtel, A.; Rogora, M.; Vesely, J.; Wright, R. Recovery

from acidification in European surface waters. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 283–297.

(17) Jenkins, A.; Camarero, L.; Cosby, B. J.; Ferrier, R. C.; Forsius, M.; Helliwell, R. C.; Kopáček, J.; Majer, V.; Moldan, F.; Posch, M.; Rogora, M.; Schöpp, W.; Wright, R. F. A modelling assessment of acidification and recovery of European surface waters. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 447–455.

(18) Helliwell, R. C.; Jenkins, A.; Ferrier, R. C.; Cosby, B. J. Modelling the recovery of surface water chemistry and the ecological implications in the British uplands. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 456–466.

(19) Wright, R. F.; Cosby, B. J. Future recovery of acidified lakes in southern Norway predicted by the MAGIC model. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 467–483.

(20) Wright, R. F.; Cosby, B. J. Recovery of acidified mountain lakes in Norway as predicted by the MAGIC model. *J. Limnol.* **2004**, *63* (1), 101–110.

(21) Moldan, F.; Kronnäs, V.; Wilander, A.; Karlton, E.; Cosby, B. J. Modelling acidification and recovery of Swedish lakes. *Water, Air, Soil Pollut.: Focus* **2004**, *4*, 139–160.

(22) Posch, M.; Forsius, M.; Johansson, M.; Vuorenmaa, J.; Kämäri, J. Modelling the recovery of acid-sensitive Finnish headwater lakes under present emission reduction agreements. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 484–493.

(23) Hruška, J.; Kram, P. Modelling long-term changes in stream water and soil chemistry in catchments with contrasting vulnerability to acidification (Lysina and Pluhuv Bor, Czech Republic). *Hydrol. Earth Syst. Sci.* **2003**, *7*, 525–539.

(24) Majer, V.; Cosby, B. J.; Kopáček, J.; Vesely, J. Modelling reversibility of Central European mountain lakes from acidification Part 1: The Bohemian forest. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 494–509.

(25) Kopáček, J.; Hardekopf, D.; Majer, M.; Pšenáková, P.; Stuchlík, E.; Vesely, J. Response of alpine lakes and soils to changes in acid deposition: the MAGIC model applied to the Tatra Mountain region, Slovakia-Poland. *J. Limnol.* **2004**, *63* (1), 143–156.

(26) Rogora, M.; Marchetto, A.; Mosello, R. Modelling the effects of atmospheric sulphur and nitrogen deposition on selected lakes and streams of the Central Alps (Italy). *Hydrol. Earth Syst. Sci.* **2003**, *7*, 540–551.

(27) EMEP. *Transboundary Acidifying Air Pollution in Europe*, EMEP/MSC-W Report 1/98; Norwegian Meteorological Institute: Oslo, Norway, 1998, 150 pp.

(28) Mackereth, F. J. H.; Heron, J.; Talling, J. F. *Water analysis: Some revised methods for limnologists*, FBA Scientific publication no. 36; Titus Wilson & Sons Ltd.: Kendal, 1978, 120 pp.

(29) Kopáček, J.; Posch, M. Anthropogenic nitrogen emissions during the Holocene and their possible effects on remote ecosystems. *Global Biogeochem. Cycles* **2011**, *25*, No. GB2017.

(30) Garmo, Ø. A.; Skjelkvåle, B. L.; de Wit, H. A.; Colombo, L.; Curtis, C.; Fölster, J.; Hoffmann, A.; Hruška, J.; Høgåsen, T.; Jeffries, D. S.; Keller, W. B.; Krám, P.; Majer, V.; Monteith, D. T.; Paterson, A. M.; Rogora, M.; Rzychon, D.; Steingruber, S.; Stoddard, J. L.; Vuorenmaa, J.; Worsztynowicz, A. Trends in Surface Water Chemistry in Acidified Areas in Europe and North America from 1990 to 2008. *Water, Air, Soil Pollut.* **2014**, *225*, 1–14.

(31) Wright, R. F.; Alewell, C.; Cullen, J. M.; Evans, C. D.; Marchetto, A.; Moldan, F.; Prechtel, A.; Rogora, M. Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 299–310.

(32) Phoenix, G. K.; Emmett, B. A.; Britton, A. J.; Caporn, S. J. M.; Dise, N. B.; Helliwell, R.; Jones, L.; Leake, J. R.; Leith, I. D.; Sheppard, L. J.; Sowerby, A.; Pilkington, M. G.; Rowe, E. C.; Ashmore, M. R.; Power, S. A. Impacts of atmospheric nitrogen deposition: responses of multiple plant and soil parameters across contrasting ecosystems in long-term field experiments. *Global Change Biol.* **2012**, *18*, 1197–1215.

(33) Curtis, C. J.; Evans, C. D.; Helliwell, R. C.; Monteith, D. T. Nitrate leaching as a confounding factor in chemical recovery from acidification in UK upland waters. *Environ. Pollut.* **2005**, *137*, 73–82.

(34) Oulehle, F.; Chuman, T.; Majer, V.; Hruška, J. Chemical recovery of acidified Bohemian lakes between 1984 and 2012: the role of acid

deposition and bark beetle induced forest disturbance. *Biogeochemistry* **2013**, *116*, 83–101.

(35) Huber, C.; Baumgarten, M.; Göttlein, A.; Rotter, V. Nitrogen turnover and nitrate leaching after bark beetle attack in mountainous spruce stands of the bavarian forest national park. *Water, Air, Soil Pollut.: Focus* **2004**, *4*, 391–414.

(36) Jandl, R.; Smidt, S.; Mutsch, F.; Fürst, A.; Zechmeister, H.; Bauer, H.; Dirnböck, T. Acidification and nitrogen eutrophication of Austrian forest soils. *Appl. Environ. Soil Sci.* **2012**, No. 632602.

(37) Shaver, G. R.; Canadell, J.; Chapin Iii, F. S.; Gurevitch, J.; Harte, J.; Henry, G.; Ineson, P.; Jonasson, S.; Melillo, J.; Pitelka, L.; Rustad, L. Global warming and terrestrial ecosystems: A conceptual framework for analysis. *BioScience* **2000**, *50*, 871–882.

(38) Lien, L.; Raddum, G. G.; Fjellheim, A.; Henriksen, A. A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. *Sci. Total Environ.* **1996**, *177*, 173–193.

(39) Wright, R. F.; Larssen, T.; Camarero, L.; Cosby, B. J.; Ferrier, R. C.; Helliwell, R. C.; Forsius, M.; Jenkins, A.; Kopáček, J.; Majer, V.; Moldan, F.; Posch, M.; Rogora, M.; Schöpp, W. Recovery of acidified European surface waters. *Environ. Sci. Technol.* **2005**, *39*, 64A–72A.

(40) Oreskes, N.; Shraderfrechette, K.; Belitz, K. Verification, validation, and confirmation of numerical-models in the earth-sciences. *Science* **1994**, *263*, 641–646.

(41) Klemeš, V. Operational testing of hydrological simulation models. *Hydrol. Sci. J.* **1986**, *31*, 13–24.

(42) Larssen, T. Model prognoses for future acidification recovery of surface waters in Norway using long-term monitoring data. *Environ. Sci. Technol.* **2005**, *39*, 7970–7979.

(43) Jenkins, A.; Whitehead, P. G.; Cosby, B. J.; Birks, H. J. B. Modelling long-term acidification: a comparison with diatom reconstructions and the implications for reversibility. *Philos. Trans. R. Soc. London B* **1990**, *327*, 435–440.

(44) Wright, R. F.; Cosby, B. J.; Flaten, M. B.; Reuss, J. O. Evaluation of an acidification model with data from manipulated catchments in Norway. *Nature* **1990**, *343*, 53–55.

(45) Oulehle, F.; Cosby, B. J.; Wright, R. F.; Hruška, J.; Kopáček, J.; Krám, P.; Evans, C. D.; Moldan, F. Modelling soil nitrogen: The MAGIC model with nitrogen retention linked to carbon turnover using decomposer dynamics. *Environ. Pollut.* **2012**, *165*, 158–166.

(46) Cooper, D. Evidence of sulphur and nitrogen deposition signals at the United Kingdom Acid Waters Monitoring Network sites. *Environ. Pollut.* **2005**, *137*, 41–54.

(47) Rogora, M.; Colombo, L.; Lepori, F.; Marchetto, A.; Steingruber, S.; Tornimbeni, O. Thirty years of chemical changes in alpine acid-sensitive lakes in the Alps. *Water, Air, Soil Pollut.: Focus* **2013**, *224*, 1746.

(48) Emmett, B. A. Nitrogen saturation of terrestrial ecosystems some recent findings and their implications for our conceptual framework. *Water, Air, Soil Pollut.: Focus* **2007**, *7*, 99–109.

(49) Curtis, C. J.; Emmett, B. A.; Grant, H.; Kernan, M.; Reynolds, B.; Shilland, E. Nitrogen saturation in UK moorlands: the critical role of bryophytes and lichens in determining retention of atmospheric N deposition. *J. Appl. Ecol.* **2005**, *42*, 507–517.