Transitioning from anthropogenic to natural acidification in a humic catchment in Norway: projections of deposition and climate change effects

Heleen A de Wit¹, Francois Clayer¹, Øyvind Kaste¹, and Magnus Norling¹

¹Norwegian Institute for Water Research

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Abstract

Five decades of monitoring data (1974-2022) at the acidified, acid-sensitive forested catchment of Langtjern in southern Norway document strong chemical recovery and browning of surface water, related to changes in sulfur (S) deposition. We used the process-oriented model MAGIC to simulate water chemistry from 1860 to 2100 using historical and projected deposition and climate. New in MAGIC is i) a solubility control of dissolved organic carbon (DOC) from S deposition, which allows inclusion of the changing role of organic acids in chemical recovery, and ii) climate-dependency of weathering rates. MAGIC successfully described measured chemical recovery and browning, and the change towards organic acid dominated acidification status. Hindcasts of pH suggested lower preindustrial pH than previously modelled with MAGIC, simulated without sulfate-dependency of DOC solubility. Climate scenarios indicated substantially wetter climate, leading to increased base cation losses and slight reacidification of the surface waters. A sensitivity analysis of weathering rates revealed that a doubling of weathering rates is needed to reach pre-industrial ANC in 2100, given that S deposition is expected to be reduced to a minimum. We conclude that impacts of climate change are most likely to lead to slight reacidification of surface waters, and that enhanced weathering rates could partly compensate this trend.

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Heleen A. de Wit^{1,2*}, François Clayer¹, Øyvind Kaste¹ and Magnus Norling¹

1 Norwegian Institute for Water Research, Oslo, Norway

2 Centre for Biogeochemistry in the Anthropocene, Department of Biosciences, University of Oslo, Norway

*corresponding author

Abstract

Five decades of monitoring data (1974-2022) at the acidified, acid-sensitive forested catchment of Langtjern in southern Norway document strong chemical recovery and browning of surface water, related to changes in sulfur (S) deposition. We used the process-oriented model MAGIC to simulate water chemistry from 1860 to 2100 using historical and projected deposition and climate. New in MAGIC is i) a solubility control of dissolved organic carbon (DOC) from S deposition, which allows inclusion of the changing role of organic acids in chemical recovery, and ii) climate-dependency of weathering rates. MAGIC successfully described measured chemical recovery and browning, and the change towards organic acid dominated acidification status. Hindcasts of pH suggested lower preindustrial pH than previously modelled with MAGIC, simulated without sulfate-dependency of DOC solubility. Climate scenarios indicated substantially wetter climate, leading to increased base cation losses and slight reacidification of the surface waters. A sensitivity analysis of weathering rates revealed that a doubling of weathering rates is needed to reach pre-industrial ANC in 2100, given that S deposition is expected to be reduced to a minimum. We conclude that impacts of climate change are most likely to lead to slight reacidification of surface waters, and that enhanced weathering rates could partly compensate this trend.

Keywords: organic acids, weathering, climate change, chemical recovery, forest

Introduction

Reductions in anthropogenic emissions of sulfur (S) and nitrogen (N) to the atmosphere has resulted in widescale chemical recovery of surface waters in acid-sensitive regions in Europe and North America (Garmo et al. 2014; Skjelkvale et al. 2005). Reductions in sulfate (SO₄), rather than in N deposition have been the dominant driver of water chemical recovery since N deposition change has been less distinct than for S, and N-retention in catchments diminish its impact on elemental runoff (Watmough et al. 2005).

Chemical recovery is impacted by other factors than reduced SO₄ deposition and associated changes in inorganic cations and anions. Reduced air pollution has also led to widespread browning of surface waters (de Wit et al. 2021; Monteith et al. 2007), where other factors such as precipitation also impact dissolved organic matter (DOM) concentrations (de Wit et al. 2016). Increases in DOM are relevant for assessing chemical recovery of surface waters since increases in organic acidity partly compensate for declines in mineral acidity (Evans et al. 2008a), also illustrated by the organic-acid adjusted acid neutralizing capacity (ANCoaa) which better describes acidification in humic lakes than ANC only based on major ions (Lydersen et al. 2004). Factors that affect surface water acidification on a more local or regional basis are seasalt spray, through mobilization of protons and aluminium (Hindar et al. 2004), catchment disturbances such as tree die-back from insect attacks, leading to mobilization of S and N (Oulehle et al. 2021), and hydrology through post-drought mobilization of SO₄ (Clark et al. 2006) and variation in flow-paths (Evans et al. 2008b). Possibly, chemical recovery may be enhanced by climate-induced increased weathering rates (Augustin et al. 2015) resulting in higher rates of base cation replenishment in soils, which have lost base cations through decades of mobilization and leaching due to acid deposition (Watmough et al. 2005).

Because of the high success of historical emission reductions of S, the potential for further reductions in Europe will be limited (Grennfelt et al. 2020; Schopp et al. 2003). That implies that other factors such as climate and land use will become relatively more important for future chemical recovery of surface waters (Kopacek et al. 2016; Vuorenmaa et al. 2017) and for the time required for reaching pre-industrial water quality, if at all possible (Helliwell & Simpson 2010).

For assessment of future surface water acidification, the process-oriented model MAGIC (Cosby et al. 1985; Norling et al. this issue) is commonly used (Larssen 2005; Posch et al. 2019). MAGIC has in its core descriptions of acid-base soil chemistry and elemental mass balances and has been further developed to include forest N cycling and C storage which potentially enable simulation of catchment disturbances and climate change effects on element cycling and surface water chemistry (Valinia et al. 2021). A new version of MAGIC called MAGIC-Forest is implemented in the model development framework Mobius (Norling et al. 2021) enabling flexible sensitivity analysis and addition of model features (Norling et al., this issue) , Simulation of effects of 'confounding factors' on expected recovery of surface water is necessary for credible predictions in the current era where factors other than deposition will influence surface water acidification status (de Wit et al. 2023). Until recently, browning of surface waters was not implemented in MAGIC while weathering rates were calibrated to a constant value. In the current era of low S deposition, changes in organic acids and weathering are likely to become more important drivers of surface water acidity status.

Here, we aim to test the MAGIC model on its ability to describe five decades of acidification and recovery

in the acidified, forested Langtjern catchment using new features in MAGIC, e.g. browning (sulfate-control) and climate-dependency of weathering, and predict acidification under further reductions of atmospheric deposition and climate change. Our research questions are the following: i. can we reproduce empirical charge balances at Langtjern, including estimates of organic charge; ii. Given observed increases in DOM at Langtjern, can MAGIC reproduce acidification and recovery, and produce credible hindcasts and forecasts of pre-industrial and future ANC under changes in acid deposition? iii. How high must weathering rates be to reach preindustrial ANC in 2100, given projections of climate and deposition? The model calibration will be anchored in five decades of streamwater monitoring at Langtjern.

Materials and methods

Site description

Langtjern is a forested, boreal lake catchment in southeast Norway (Figure 1) (4.8 km²; 510–750 m.a.s.l; 60.371 N, 9.727 E) where monitoring of water chemistry started in 1972 under the national monitoring programs for air pollution effects on surface waters (Lund et al. 2018; Vogt & Skancke 2022). The catchment includes a lake (0.23 km²) and its land cover is dominated by forest (75% forested with low productivity Scots pine forest and 5% of productive Norway spruce forest), located on shallow mineral soils, and peatland (20%). Since the 1950s, when some small-scale forest harvest was conducted, the catchment has been free from direct human disturbances. The geology consists of till generated from felsic gneisses and granites (de Wit et al. 2018). Mean annual temperature, precipitation, and discharge (1974-2022) are 2.6°C, 834 mm, and 634 mm, respectively.

Data sources

Streamwater discharge and chemistry

Annual values for discharge and flow-weighted streamwater chemistry (1974–2022) were derived from the routine monitoring conducted by NIVA as part of the Norwegian national environmental monitoring programmes (Vogt & Skancke 2022). Water level is monitored continuously by a weir at the outlet and converted to discharge using standardized stage-discharge relationships. Streamwater samples are collected weekly at lake outlet and analysed for major chemical components (pH, labile Al, alkalinity), major anions (SO₄, Cl, NO₃), major cations (Ca, Mg, Na, K) and TOC at NIVA. Analytical methods have evolved since monitoring began in 1973 and currently entail automated ion-chromatography. In 1986, monitoring of TOC started. Acid Neutralizing Capacity (ANC) is calculated as the sum of base cations minus the sum of strong acidic anions. ANC corrected for organic acidity, ANCoaa (Lydersen et al. 2004), is calculated as ANC $+ 1/3^{*}$ site density of TOC, where site density is $-10.2 \,\mu eq/mg$ C. The charge balance of the streamwater chemistry was estimated as the difference between the equivalent sum of all major cations and major anions, and the anion deficit was attributed to organic acidity (OA). Charge density (CD) of TOC was calculated as the anion deficit divided by TOC. For NH_4^+ and F, no full time series were available, but earlier data show that their concentrations are low and that they largely outweigh each other in terms of equivalent concentrations. Labile Al was assumed to have charge density of 2^+ while the contribution of bicarbonate was set at zero, an acceptable assumption at pH below 5.5.

Element fluxes at the catchment outlet were calculated for each day using measured water discharges at the sampling point multiplied by the solute concentration interpolated from the weekly samples. The daily calculated data were then aggregated to annual fluxes of each element.

Soil element pools

Soils were sampled with the purpose to estimate catchment soil pools of exchangeable cations, and following the same sampling design, in 1983 (Reuss 1990), 1991 (Stuanes et al. 1995) and 2001 (SFT 2001) and reported in Larssen (2005). Standard soil depth for Langtjern was estimated to be 40 cm, including the O horizon. Catchment exchangeable base cation soil pools were calculated by multiplying bulk density with

layer depth and soil base cation concentration, where the B horizon was assumed to extend to 40 cm soil depth. Only mineral forest soils were sampled, and the soil base cation stores reported in in Larssen (2005) only represent forest soils.

Atmospheric deposition

Total annual deposition inputs (the sum of wet and dry deposition of SO₄, NH₄, NO₃, Cl and major cations) to MAGIC for the period 1850-2100 are derived from air quality monitoring at the station Brekkebygda (390 masl., 60.29° N, 9.76° E, 7 km south of Langtjern) for 1974-2022, a hindcast for 1860-1973 and projections for 2023-2100. The air quality and deposition monitoring for 1974-2022, resulting in annual wet deposition, follows analytical methods, quality control and flux calculations are described in Aas et al. (2022). The mass balance approach incorporated in the MAGIC model requires adjustment of the wet deposition data, since the deposition station data are not entirely representative for the catchment: dry deposition is not measured, and precipitation amounts may differ from the catchment given the lower elevation of the deposition station. The adjustment is done in two steps. First, dry deposition is estimated using Cl as a conservative tracer. assuming that all Cl originates from sea salt aerosols. For the 1974–2022, the ratio of inputs of Cl (wet deposition) to outputs (streamwater flux of Cl) was 0.898, where the difference (1-0.102) is assumed to be from dry deposition. The dry deposition of Cl is assumed to be associated with dry deposition of cations and marine sulphate (mSO_4) following their relative proportions in seawater (as given by the following molar elemental ratios: Ca/Cl: 0.037, Mg/Cl: 0.196, Na/Cl: 0.856, K/Cl: 0.018, SO₄/Cl: 0.103). Second, we assume that long term catchment outputs of S (in streamwater) equal anthropogenic (SO₄^{*}) and marine inputs (mSO_4) to the catchment, resulting in the scaling factor 0.98 for anthropogenic SO₄ deposition. Historical (1860-1973) and future (2023-2100) deposition of sea salts and base cations was assumed to equal averaged total deposition over 1974-2022. For SO₄*, NH₄ and NO₃, historical deposition was estimated from the modelled deposition for the Langtjern grid square by EMEP based on historical emissions of air pollutants in Europe (Schopp et al. 2003), and scaled to Langtjern using the ratio of the long term averaged EMEP deposition of the grid square and Langtjern deposition, estimated as described above. Future deposition of SO_4^* , NH_4 and NO_3 was assumed to follow the European emissions of the CLRTAP current legislation scenario (CLE) for the Langtjern grid square forward to the year 2050 and then held constant to the year 2100. The scenarios were supplied by the Coordination Centre for Effects of the CLRTAP. Future deposition was scaled to Langtjern deposition 1974-2022 data to follow the same relative trends as in the CLE grid square.

Climate

Weather data, including daily average temperature (tm, [?]C), daily precipitation (rr, mm) and evaporation (gwb_eva, mm), was downloaded using NVE's Grid Time Series (GTS) API. The catchment area of Lake Langtjern was first delineated based on a 10×10 m digital elevation model for Norway (https://www.geonorge.no/, DTM 10 Terrengmodell (UTM33)) as described by de Wit et al. (2023). Weather data were then downloaded for each 1x1km grid (partially or entirely) overlapping with the catchment area and then area-weighted averaged to one value for the catchment. Projected 90% confidence interval of changes in temperature, precipitation, and evaporation for scenario RCP8.5 for 2071-2100 relative to reference period 1971-2000 were taken from Hanssen-Bauer et al. (2015) to generate climate data over 2023-2100. Temperature (delta T), precipitation (delta P) and discharge (delta Q) increases from 1971-2000 to 2071-2100 were +3.0°C to +5.6°C (median: +4.2°C), +8% to +29% (median: +15%) and -2% to +16% (median: +8%), respectively. A locally adapted scenario RCP8.5* was derived by adding delta T, P and Q to 2023 based on the difference between averaged T, P and Q at Langtjern for 2000-2022 and the reference period 1971-2000.

Model description and calibration

MAGIC (Model of Acidification of Groundwater In Catchments) is a process-oriented semi-distributed mass balance model for biochemical processes involving ions and nutrients at catchment scale (Cosby et al. 2001; Cosby et al. 1985), originally used to predict air pollution effects on surface waters and further developed to also include effects of land use and climate change. This setup of MAGIC includes two connected compartments, e.g., soil and surface water (stream or lake), where the soil runoff is sent to the surface water compartment. The solutes (SO₄, NO₃, NH₄, Cl, Ca, Mg, Na, and K) concentrations are computed as the mass balance between atmospheric deposition, bedrock weathering, retention (for N species) and export through runoff. A new version of MAGIC, MAGIC-Forest (Norling et al. this issue) with modules for hydrology, forest growth, soil carbon accumulation and SO₄-dependent organic matter solubility, has been implemented in the open-source Mobius modelling framework (Norling et al. 2021). The Mobius framework has a modern graphical user interface and scripting for interaction with models, allowing for user-friendly advanced auto-calibration and sensitivity analysis.

In the current MAGIC application, we start from the calibration conducted by Larssen (2005) which described streamwater chemistry responses to reductions in S deposition during the period 1974–2003. We included monitoring data for the subsequent period 2004–2022. New features in MAGIC used in the current application are i) the SO₄-solubility control of TOC ($c_{OA} = c_{OA,0} - c_{SO_4} f_{SO_4}$) background concentrations of organic acids reduced with factor f_{SO4} multiplied with SO_4) (Norling et al. this issue) and ii) a factor to change weathering rates (only used in a sensitivity analysis; $w_y = w_0(1 + max(0, (y - y_0))\alpha_w)$, i.e. the rate stays constant at w_0 until year y_0 , and increases by a linearly with slope α_w after that). Table SI 1 describes which parameters are fixed and which are calibrated. Soil characteristics are based on soil element pools as described earlier. The model was calibrated manually, and optimization of the model parameters (Table SI 1) was done by comparing observed and modelled annual FWM concentrations of ANC, H⁺, labile Al, SO₄, NO₃, Cl, Ca and Mg and organic acids. During calibration, we also ensured that other modelled variables were showing an acceptable fit to observations such as total and cation-specific soil base saturation and FWM concentrations of Alⁿ⁺, Na and K. The best set of parameters was selected using expert judgement anchored in an evaluation of combined performance metrics: the Nash-Sutcliffe Efficiency (NSE), the root-mean square error (RMSE), the coefficient of determination (r^2) and the bias (summation of difference between model and empirical estimate, divided by nr of estimates), in addition to comparison with soil base saturation. The automated optimization implemented in Mobius resulted in similar model performance as the manual calibration for base cation weathering rates, but manual optimization was chosen over automated since the automated optimization did not result in converging parameter values.

Scenarios

Scenarios for future climate and deposition always used CLE for future deposition. The scenarios are referenced as ConstantClimate (CLE deposition and no climate change), RCP8.5 (CLE scenario and RCP8.5) and RCP8.5* (CLE scenario and RCP8.5*).

Results

Acidification and chemical recovery

Deposition of S and N at Langtjern peaked during the late 1960s at 9.8 kg S ha⁻¹ yr⁻¹ (61 meq m⁻² yr⁻¹) and 8.8 kg N ha⁻¹ yr⁻¹ (63 meq m⁻² yr⁻¹) (averaged over 1965-1969) (Figure 2). After the 1960s, S deposition gradually declined towards the current level of 1.1 kg S ha⁻¹yr⁻¹ (6.6 meq m⁻²yr⁻¹) (2018-2022 average) and is expected to remain more or less constant towards 2100 under the emission scenario of current legislation (CLE). Deposition of N was more variable, showing two other peaks after the 1960s, and is currently (2018-2022) at 3.7 kg N ha⁻¹ yr⁻¹ (26.5 meq m⁻² yr⁻¹).

Streamwater chemistry follows patterns that are typical for acidified, but recovering, streams (Figure 3): strong declines in SO₄ and SAA, following the temporal change in S deposition; declines in base cations (and SBC), in particular in Ca and Mg, and increases in pH and TOC. Labile Al shows the strongest decline. The other strong acid anions Cl and NO₃ also decline, where Cl is currently at a fairly constant level of circa 10 μ eq l⁻¹, similar to SO₄. Nitrate is present in very low concentrations relative to SO₄because of high retention in the catchment. pH, ANC and ANCoaa are currently at 5.16, 61.5 μ eq/L and 24.0 μ eq/L,

respectively (averaged over 2018-2022), which is below MAGIC-simulated preindustrial levels (5.38 (pH), 73.6 μ eq/L (ANC) and 34.7 μ eq/L (ANCoaa), respectively) (Table 1).

Organic acidity, calculated from the charge balance between strong acid anions and major cations, increased markedly over time, balancing 33% of the base cations during the end of the 1980s and 73% for 2018 to 2022 (Figure 4). On an equivalent basis, organic acids have dominated SAA at Langtjern since 2000-2004. Charge density of TOC increased from 4.3 to 5.7 μ eq/mg C since the end of the 1980s (Figure 5).

MAGIC hindcasts of historical acidification and recovery

Model performance for individual and compound variables were evaluated for a set of performance statistics (Table 2). MAGIC described levels and variations for major cations, major anions, pH and ANC well (Figure 3). The variation was described best ($r^2>0.7$) for the SAA and its constituents, dominating base cations Ca and Mg, ANC, ANCoaa, organic acids and pH. These variables also had low normalized RMSE's (<0.7), except for variables associated with, or affected by, organic acidity such as ANCoaa, labile Al, and organic matter charge density – these variables also had relatively low values for NSE, illustrating systematic overestimation (organic acids, ANCoaa, charge density). The overestimation of organic acidity was primarily related to an overestimation of the TOC charge density with on average ca 1 µeq mg⁻¹ TOC (Table 1; Figure 5). The variables that were described with least bias (|bias| < 1) were those that showed least temporal variation (Figure 3), while those described with a large bias (|bias| > |5|) were ANC, ANCoaa and organic acids.

Since organic acidity is such an important part of the total charge balance, model simulation of other ions is very sensitive to its level. Decreasing of organic acidity in MAGIC leads to lowering of the base cation concentrations, so optimizing organic acidity in MAGIC can come at the cost of good optimization of SBC and therefore pH and ANC. However, the upward trend in organic acidity was described well, which is a novel aspect of MAGIC modelling.

The hindcast of all the elements, from 1850 to 1973, was driven by the change in deposition (Figure 2). Preindustrial pH, ANC, ANCoaa, and TOC were higher than current-day values and much higher than their values during the period when acidification peaked (Table 1). Base saturation decreased from 23.2% (preindustrial) to 19.4% (present-day).

MAGIC projections of future acidification and recovery

Deposition of S and N in 2050 under the CLE deposition was 56% and 67% of 2015 deposition, respectively, where 2015 was used as the reference year. The catchment became warmer and wetter during 1974-2022, as indicated by trends (Sen slopes, MK test (Sen 1968)) in annual temperature, precipitation and discharge, which are $+0.38^{\circ}$ C decade⁻¹ (p<0.0001), +39 mm decade⁻¹ (p<0.1) and +40 mm decade⁻¹ (p<0.01), respectively. The climate scenario RCP8.5 predicted less climate change than these empirical climate data, but the locally adapted climate scenario RCP8.5* gave a higher mean discharge (+80mm) compared with average discharge for 1974 to 2022 (Figure 6).

The Constant Climate scenario did not result in more chemical recovery in 2050 and 2100 than observed for 2018-2022 (Figure 3), while locally adapted RCP8.5^{*} and RCP8.5 resulted in a slight reacidification (Table 1). RCP8.5^{*} had a slightly stronger effect on acidification than RCP8.5, as a consequence of higher discharge and thus higher base cation export. Chemical acidification status in 2100 was markedly below the preindustrial water quality indicators pH, ANC and ANCoaa. The reacidification is driven by the depletion of base cation stores from the catchment soils due to increased element export related to the increased discharge. The three future scenarios give rather similar results, with organic acidity dominating over mineral acidity (Figure 4) and where the strongest climate change scenario results in a slight reacidification (reduction of ANC with 5.2 μ eq/l (Table 1)).

Sensitivity analysis

We tested the necessary increase in weathering rates to obtain preindustrial base saturation and ANC in 2100 in a sensitivity analysis (Table 3) where the weathering rates were increased with a fixed percentage from year 2000 for three climate scenarios. The uncertainty intervals for both RCPs are related to uncertainty intervals for future precipitation, illustrating the importance of precipitation for estimation of weathering rates. For the 'constant climate' scenario, the annual increase was 0.54%, and the two RCPs had median increases in weathering rates of 0.59% and 0.96%, resulting in weathering rates in 2100 that were a factor 1.7 to 2.5 higher than in 2000. Interestingly, it took relatively less weathering to reach preindustrial ANC than for preindustrial BS% as a consequence of lower expected acid deposition in the future compared to pre-industrial. The cumulative excess contribution of base cations from enhanced weathering were 33% (ConstantClim), 36% (RCP8.5) and 68% (RCP8.5*), to reach preindustrial base saturation. To reach preindustrial ANC, these numbers were 35% (RCP8.5) and 59% (RCP8.5*).

Discussion

The monitoring data demonstrate strong chemical recovery from acidification at Langtjern, similar to other strongly acidified surface waters in Norway (De Wit et al. 2023), elsewhere in Europe and North America (Bukaveckas 2021; Garmo et al. 2014; Houle et al. 2022; Kopacek et al. 2021; Lawrence et al. 2021; Sterling et al. 2022) and in Japan (Sase et al. 2021). Simultaneously, DOC at Langtjern has increased and now contributes more to the total anion charge in the streamwater than the strong acid anions. The site is thus moving towards a state dominated by natural-, rather than anthropogenic acidification. Browning is a common feature for surface waters in boreal regions, primarily related to reduced acid deposition (de Wit et al. 2021; Monteith et al. 2007). To what extent and at what time scale organic acidity will dominate anthropogenic acidification is not well-known, however. Assumptions about natural levels of organic acidity (Erlandsson et al. 2011) and the necessity of liming to accelerate recovery (Laudon et al. 2021). Humic charge density for DOM increased, as found earlier (De Wit et al. 2007), suggesting that both increased solubility and decreased deprotonation of humic and fulvic acids control the return to naturally acidified systems and pre-industrial water quality.

The last MAGIC application for Langtjern was done based on the period 1974 to 2003 (Larssen 2005). We used the same soil and historical deposition data. In our study, we optimized for 1974 to 2022 and captured the trend in chemical recovery with hardly any bias, which is considerably better than Larssen (2005), where MAGIC underestimated the positive trend in ANC, overestimating peak acidification ANC and underestimating ANC in the early 2000s. Larssen (2005) reported relatively poor model performance for K, Na, Mg and Cl compared with MAGIC applications for two other acidified catchments in southernmost Norway, which could indicate that the relatively poor simulation of ANC levels at Langtjern were related to other major cations and anions than SO_4 and Ca. Also, an internal source of S in the Langtjern catchment (6 meq m⁻² yr⁻¹) was assumed by Larssen, contrary to our study, which could lead to overemphasizing the importance of background SO_4 at the cost of anthropogenic SO_4 and anthropogenic acidification. This is illustrated by the substantially higher hindcast for preindustrial ANC in our study (e.g. ANC of 80 μ eq l⁻¹ (Figure 3) than in Larssen (2005) (e.g. ANC of 40 μ eq l⁻¹). Furthermore, the longer time series in our study presents a stronger dataset for model calibration. The inclusion of changing organic acidity in our study, where Larssen assumed constant organic acidity, cannot explain the poorer description of recovery by Larssen since organic acidity counteracts changes in mineral acidity, leading to a lower response in ANC to changes in SAA.

The increases in DOC and organic acidity were described tolerably well by MAGIC albeit more poorly than mineral acidity. The levels of organic acidity at Langtjern were somewhat overestimated possibly indicating that organic acid properties at Langtjern are outside the range for values for organic acid deprotonation reported by Hruska et al. (2003). The organic charge density estimated in our study was between 4.4 and 5.7 μ eq g⁻¹ C, which agrees with the values previously calculated for Langtjern (De Wit et al. 2007).

The MAGIC-forecasted pH, ANC and ANCoaa under reduced S deposition and current climate were not yet back at preindustrial levels in 2100, which to a great degree was related to depleted base cation stores. Climate change acted through increasing discharge and thereby further depleting base cation stores and thereby leading to a slight reacidification. Such tendencies have already been observed in humus-rich acidified lakes in Eastern Norway (de Wit et al. 2023), which was attributed to organic acidity rather than climate change. However, TOC and organic acidity are also climate-sensitive, in particular to precipitation (de Wit et al. 2016), a feature that is currently not included in MAGIC. Increased catchment base cation export related to discharge is textbook knowledge, but changes in soil base cation stores for periods shorter than 3 to 5 decades are typically difficult to measure (Ahrends et al. 2022).

We showed in a sensitivity analysis, using new features of MAGIC-Forest, that a doubling in weathering rates would be required to achieve preindustrial base saturation and associated water quality in 2100. An even higher weathering would be necessary to compensate for enhanced soil base cation loss under higher runoff from climate change. While it is clear that mineral weathering rates are higher under forested versus non-forested sites (Berner 1997), generally higher in moist versus dry climates (West et al. 2005), and are promoted by higher pCO_2 and organic acids (Bargrizan et al. 2020), it is difficult to constrain weathering rates based on empirical measurements (Koseva et al. 2010; Kronnas et al. 2019). However, unexpected widespread increases in dissolved silicates and calcium have been observed in Norwegian lakes (de Wit et al. 2023), possibly providing indirect evidence of recent, enhanced weathering rates. We conclude that chemical recovery at Langtjern may be impacted – positively and negatively – by climate change. Continued monitoring is needed to evaluate which drivers will prove to be strongest.

Our study illustrates that a combination of long-term monitoring and process-oriented modelling is key for predictions of water quality under changing environmental conditions. Our assessment points towards an ongoing transition from anthropogenic to natural acidification in surface waters, due to reduced acid deposition and stronger impact of climate, humic compounds, and possibly land use change as drivers determining the surface water acidity status.

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Conflict of interest

The authors declare no conflicts of interest

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Figure 1 Map of the Langtjern catchment

Figure 2 Total atmospheric deposition of SO_4 and N (sum of NO_x and NH_y) at the Langtjern catchment in meq m⁻² yr⁻¹. Historical (1850-1973) and future deposition, following current legislation policy (CLE), provided by EMEP. Deposition of SO_4 is corrected for seasalt contribution.

Figure 3 Empirical flow-weighted mean annual element concentrations from 1974 to 2022 (open circles) and MAGIC-simulations for 1850 to 2100, for SO_4 , Cl, NO_3 , pH (and H+), Na, K, TOC (expressed on an equivalent basis), ANC, ANCoaa, labile Aluminum (IAI) SBC and SAA. The future scenarios include EMEP deposition according to current legislation (CLe) in combination with constant climate (dotted line), RCP8.5 (blue line) and locally adapted RCP8.5* (red line).

Figure 4 Five-year averages of the equivalent sum of strong acid anions (SAA), organic acids and sum of base cations (SBC) in μ eq/l. Hatched and plain bars show simulated data by MAGIC in a preindustrial decade, at peak acidification and for future (2090-2100) scenarios (ConstantClim: CLe deposition, no climate change; CLe+RCP8.5, CLe+RCP8.5*).

Figure 5 Simulated and empirical TOC charge density ($\mu eq/mg$ TOC, top panel) and organic acidity (in $\mu eq/l$) (bottom panel). Open circles show empirical estimates, open squares and lines show MAGIC simulation.

Figure 6 Annual runoff (mm) at Langtjern for 1850-2100. Open circles: empirical data; 1850-1973: modelled runoff using averaged climate for 1971–2000. Future runoff 2023-2100: dotted line, constant climate (discharge equal to pre-1974); blue line, RCP 8.5 (change relative to predefined period 1971-2000); red line, RCP8.5* (change relative to empirical runoff for 2000 to 2022).

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Table 1 Key MAGIC model results for preindustrial time (mean 1850-1860), peak acidification (1965-1974), current situation (2018-2022), and future (2090-2100), and for the different climate scenarios. All with CLe deposition (constant climate; RCP8.5, RCP8.5*), all with constant weathering. Last column shows results sensitivity analysis (for RCP8.5* only, increased weathering).

Table 2 MAGIC calibration performance statistics over 1974-2022 including Nash-Sutcliffe efficiency (NSE), root mean squared error (RMSE), coefficient of determination (r^2) , standardized root mean squared error (RMSE/std) and bias (the mean signed difference between modeled and observed values).

Table 3 Estimation of required increase in weathering rates (in %) and resulting cumulative additional base cation input from weathering over 2000–2100 (expressed as % of base cation inputs from weathering for 2000-2100 under constant weathering), to return soil base saturation, ANC or pH back to their pre-industrial levels, for three climate scenarios. The intervals show interquartile range based on the interquartile range of predicted precipitation under the RCPs.

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