

Voyage without constellation: evaluating the performance of three uncalibrated process-oriented models

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ABSTRACT

Three process-oriented dynamic acidification models were applied to a long-term monitoring site without calibration to evaluate the influence of model structural differences on simulation. The models were simplified to share as many commonalities as possible so that the main structural differences could be investigated. The models differed in sub-models for cation exchange, organic acids and acid anion speciation. All models were populated with 'equivalent' parameters by systematic input mapping. The influence of input variability was addressed through Monte Carlo parameter sampling. The three models behaved exactly the same for tracers (e.g. sulphate and chloride), indicating successful cross-parameterization of the models. Differences in model structure had an impact on some of the simulated chemical parameters. In particular, models using Gapon cation exchange simulated higher base saturation levels in the long run than their Gaines-Thomas counterparts, but simulated lower base cation concentration and acid neutralizing capacity in soil solution when acid deposition levels were high. Multiple-model evaluation frameworks as presented here allow for greater certainty in model predictions; ultimately, this type of framework should be employed when evaluating the impacts of future climate and environmental changes on soil and surface water hydrogeochemistry.

Key words | acidification, hydrogeochemistry, input mapping, model evaluation, Monte Carlo simulation, process-oriented models

INTRODUCTION

For more than two decades dynamic soil chemical models have been used to assess the impacts of acid deposition on soil and surface waters. In recent years, such models have been increasingly used to support the development of emission reduction policies e.g. in Europe (Hettelingh *et al.* 2007). There are numerous dynamic soil chemistry (or acidification) models: see Table 1 for a list of models. These models are used to assess ecosystem response to

changes in land use or atmospheric deposition (e.g. recovery from acidification) and/or climate change impacts on ecosystem biogeochemistry (e.g. see Wright *et al.* 2006; Posch *et al.* 2008).

Many of these models are based on the same conceptual formulation with respect to soil and soil water acidification (Reuss & Johnson 1986) and include similar processes. However, they differ widely in structural

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details (e.g. simulation time-step, representation of the soil horizons) and input requirements, which could potentially lead to different forecasts for the same deposition scenario.

Several attempts have been made to evaluate or compare the performance of multiple models (ILWAS, MAGIC and ETD: Rose *et al.* 1991a,b; MAGIC, SAFE and SMART: Warfvinge *et al.* 1992; Forsius *et al.* 1998; 16 models: Tiktak & van Grinsven 1995; see Table 1 for acronym definitions); however, many of these studies suffer from (subjective) model calibration. While calibration can be used to increase the confidence in the performance of a particular model application, it suffers from non-uniqueness (Page *et al.* 2004). Accordingly, comparison of several independently calibrated models may confound the objective evaluation of simulation results. Moreover, differences in model input requirements, e.g. spatial and temporal resolution, may further confound model assessment.

These factors have generally limited cross-model performance evaluation. One notable exception is the study conducted by Rose *et al.* (1991a,b) who employed Monte Carlo and input mapping techniques in the assessment of ILWAS, MAGIC and ETD. Monte Carlo techniques can be used to account for the variability in input parameters and data (e.g. spatial heterogeneity in site properties or measurement uncertainty). Input mapping ensures that site data (model inputs) are translated ('mapped') consistently to several models; procedures range from trivial unit conversions to

algebraic lumping of spatial and temporal data. Consequently, all models receive (approximately) the same data.

The purpose of this study was to objectively evaluate three widely used dynamic models: MAGIC, SAFE and VSD. Simplified model configurations were used to maximize consistency among models. Variability in input parameters was addressed using Monte Carlo and input mapping techniques. All model input data were taken from the long-term monitoring site at Hubbard Brook, New Hampshire, USA, to ensure simulations were 'grounded' in reality; however, the models were not calibrated as the study focused on the relative differences between the candidate models.

METHODS AND MATERIALS

Study site

All model inputs were derived from the extensive long-term observations (precipitation chemistry, soil solution chemistry and soil physical properties) at the Hubbard Brook Experimental Forest (HBEF) Watershed 6 (e.g. Likens & Bormann 1995 for site description). In principle, the current study could have been carried out using trivial site data; however, the site observations at Hubbard Brook ensured consistency between model input data and facilitated quality control of the input mapping procedure. The current

Table 1 | Dynamic soil acidification models

Model	Reference
CHESS: Chemical Equilibrium in Soil Systems	(Santore & Driscoll 1995)
CHUM: CHemistry of the Uplands Model	(Tipping 1996)
DayCent-Chem	(Hartman <i>et al.</i> 2007)
ETD: Enhanced Trickle Down	(Nikolaidis <i>et al.</i> 1989)
ForSAFE: Forest SAFE	(Wallman <i>et al.</i> 2005)
ILWAS: Integrated Lake Watershed Acidification Study	(Gherini <i>et al.</i> 1985)
MAGIC: Model of Acidification of Groundwater in Catchment	(Cosby <i>et al.</i> 1985, 2001)
PnET-BGC: Photosynthesis and Evapotranspiration – Biogeochemistry	(Gbondo-Tugbawa <i>et al.</i> 2001)
SAFE: Soil Acidification in Forested Catchment	(Warfvinge <i>et al.</i> 1993)
SMART: Simulation Model for Acidification's Regional Trends	(De Vries <i>et al.</i> 1989)
Trickle Down	(Schnoor <i>et al.</i> 1986)
VSD: Very Simple Dynamic	(Posch & Reinds 2009)

study is part of a larger model evaluation study at the HBEF, in which the relationship between calibration and model inputs and multiple-model ensemble forecasts are being investigated.

Dynamic acidification models

The three models (MAGIC, SAFE and VSD) have been previously described (see *Cosby et al. 1985, 2001; Warfvinge et al. 1993; Alveteg 1998; Posch & Reinds 2009*). To a large extent, the three models are based on the conceptual formulation developed by *Reuss & Johnson (1986)*. All models consider a similar suite of processes such as mineral weathering, cation exchange between soil solution and exchangeable sites on soil particles, nitrification and pH-dependent processes such as gibbsite dissolution, organic anion dissociation (e.g. *Oliver (Oliver et al. 1983)* and triprotic models (*Santore et al. 1995*)) and other acid dissociation equilibria including carbon dioxide. However, the models differ in how these processes are implemented; e.g. SAFE includes a weathering rate sub-model whereas weathering is supplied as an external input to the other models (*Table 2*).

For the purpose of this study the models were simplified to elucidate model structural differences (*Table 2*). For example, the base cation weathering rate sub-model in SAFE was disabled. Base cation weathering rate estimates from the PROFILE model (*Warfvinge & Sverdrup 1992*) were used as input for all models. A one-layer lumped soil was used for all models. Only nitrification (constant: 100%) and nitrogen immobilization (varying proportion to soil nitrogen pool) were considered among the nitrogen cycle processes. Forest dynamics such as forest growth, nutrient cycling and net uptake were also not considered. The study focused solely on simulating soil chemistry, and any existing surface water compartment was excluded from the analysis. The VSD model allows soil base cation exchange to be described using either *Gaines & Thomas (1953)* or *Gapon (1933)* exchange models. In the current study both ‘models’ (VSD–Gaines–Thomas and VSD–Gapon) were evaluated. Thus, four models (MAGIC, SAFE, VSD–Gaines–Thomas and VSD–Gapon) were evaluated in the current study.

Evaluation framework

All observation data are associated with variability and this variability arises both from the inherent spatial heterogeneity of forested ecosystems and uncertainties associated with measured data. In the current study, the simplification of the models reduced the number of parameters with uncertainty. For example, nitrification rate may vary but was set to a constant (100%). However, uncertainties associated with other processes such as deposition flux were considered using a Monte Carlo randomization technique (*Tables 3 and 4*).

The overall design of the current study (see *Figure 1*) follows *Rose et al. (1991b)*. First, primary parameters were repeatedly sampled (1,000 times) from defined distributions based on literature and observation (see *Tables 3 and 4* for detailed descriptions and justifications for selected parameter distributions). Normal distributions were used to represent parameters with sufficient data to estimate mean and standard deviation (for example, current deposition concentration and soil DOC concentration). Uniform distributions were used to represent parameters with less observational data (for example, partial pressure of CO₂ in soil solution). At each iteration, a parameter set together with fixed variables was translated into individual model inputs, ensuring that models were given the same deposition chemistry and soil physicochemical properties (see next section).

It is important to note that, even though parameters were randomly selected for each iteration, translated parameters within a single iteration were chemically equivalent among the models. Subsequently, the models were run for all iterations for a 300-year period 1800–2100 to predict soil exchangeable cation fraction and the concentrations of major ions in the soil solution at the bottom of B-horizon. While not essential for the model comparison, a realistic deposition scenario was used (*Figure 2*). Historic deposition sequences were based on emission inventories and site observations (*Husar 1994; Galloway 1995; Lovett et al. 1996; Lefohn et al. 1999; EPA 2002*) following *Aherne et al. (2003)*. Future deposition was based on current legislated emission under the Canada-US Air Quality Agreement. Model outputs were collated for comparison using probability density distributions and time-series plots. In particular, commonly used variables

Table 2 | Features of the models and their configurations used in this study

	In this study	MAGIC	SAFE	VSD
Number of soil layers	1	Up to 3	Up to 20	1
Temporal resolution	Annual	Annual or monthly	Annual	Annual
Weathering	External input	Calibrated	Sub-model	External input
Forest nutrient uptake	None	External input	External input	External input
Variable hydrology	Fixed ratio	External input	Fixed ratio	External input
Sulphate adsorption	No	Langmuir isotherm	Yes	No
N immobilization in soil	Fraction of deposition	Fractional or fixed	Available in previous versions	Fractional or fixed
Nitrification	100%	Fractional	Always or own submodel	100%
Denitrification	None	Fractional	Own submodel	Fractional or fixed
Surface water chemistry	Ignored	Stream or lake	Stream	Stream or lake
Base cations (Ca, Mg, K)	Varied	Individual ions	Lumped	Lumped
DOC dissociation model	Varied	Triprotic	Oliver	Oliver or simple monoprotic
DOC-Al	Varied	Yes	No	No
Cation exchange model	Varied	Gaines-Thomas	Gapon	Gaines-Thomas or Gapon
Exchange considered between	Varied	Ca vs. Al Mg vs. Al K vs. Al Na vs. Al	(Ca + Mg + K) vs. H	(Ca + Mg + K) vs. Al (Ca + Mg + K) vs. H
Ions considered in charge balance in addition to H, Ca, Mg, K, Na, Cl, SO ₄ , NO ₃ , NH ₄ , Al, HCO ₃ , and organic acid	Varied (see individual descriptions to the right)	Al(OH), Al(OH) ₂ , Al(OH) ₄ , Al(SO ₄), Al(SO ₄) ₂ , OH, CO ₃ (This study; possible to include F complexations)	Al(OH), Al(OH) ₂ , OH, CO ₃	None

such as soil solution Acid Neutralizing Capacity (charge balance ANC) and soil base saturation were compared. Probability density and (median) time-series plots were derived from the 1,000 model simulations for each model.

Input mapping

All four models require that acid dissociations in soil solution are at equilibrium, that soil solution is in charge balance and that cation exchange processes between soil solution and the soil particle surface are also at equilibrium. These conditions pose a challenge to translating (mapping) initial soil solution chemistry among the four models, as different sets of acid dissociation equilibria and different representations of cation exchange equilibria are implemented in the models (see

Table 2 for details). As such, both soil solution chemistry and exchangeable cation fractions cannot be identical across all models, as it would violate the equilibrium requirements.

In the current study, equivalent starting soil conditions among the models during each iteration were guaranteed, as they are calculated using the same Monte Carlo-sampled initial exchangeable cation fractions, deposition flux and weathering flux (in year 1800). This enabled systematic determination of consistent initial soil chemistry (exchangeable and solution chemistry). Initial soil solution concentrations were determined using the pH dependence of charged ions and charge balance; Al³⁺, aluminium hydroxides, HCO₃⁻, CO₃²⁻, RA⁻ (charged organic acid) and OH⁻. Due to charge balance requirements, all models can be numerically solved for H⁺.

Since the set of ions considered in the charge balance differs among models, and also the pH dependence of some ions differs slightly, the initial soil solution concentrations were calculated individually for each model during each Monte Carlo simulation. Further, as charge density for DOC differs between the Oliver model (Oliver *et al.* 1983) and the triprotic model (Santore *et al.* 1995), the ratio of the charge densities for the two sub-models was kept constant. This was done in an attempt to ensure similar charge from dissolved

Table 3 | Input variables (deposition and hydrology) and their sources

Input parameter	Monte carlo probability distribution*
Rainfall (mm yr ⁻¹) [†]	Constant: 1418.53
Percolation (mm yr ⁻¹) [†]	Constant: 738.44
Current deposition (μeq l ⁻¹) [‡]	[SO ₄ ²⁻]: Normal, 28.55, 0.99 [Cl ⁻]: Normal, 4.95, 0.47 [K ⁺]: Normal, 0.90, 0.12
Deposition ratio [H]:[SO ₄] [¶]	Normal, 1.173, 0.014
Deposition ratio [NH ₄]:[SO ₄] [¶]	Normal, 0.279, 0.007
Deposition ratio [Ca]:[NH ₄] [¶]	Normal, 0.364, 0.010
Deposition ratio [Mg]:[Ca] [¶]	Normal, 0.366, 0.011
Deposition ratio [NO ₃]:[H] [¶]	Normal, 0.496, 0.009
Deposition ratio [Na]:[Cl] [¶]	Normal, 0.720, 0.012
Dry deposition factor [¶]	Ca: uniform, 1.1, 1.2 Mg: uniform, 1.1, 1.2 K: uniform, 1.1, 1.2 Na: uniform, 1.1, 1.2 NH ₄ : uniform, 1.0, 1.1 SO ₄ : uniform, 1.1, 1.2 Cl: uniform, 1.5, 1.6 NO ₃ : uniform, 1, 1.1

*Normal distribution is defined by mean and standard deviation. Uniform distribution is defined by minimum and maximum.

[†]Source: on-site measurements. Average amount was used as a constant value throughout the simulation period.

[‡]Modelled with Brook90 (Federer *et al.* 2003). Average modelled amount was used as a constant value throughout the simulation period.

[¶]Hindcast and forecast scenario was set as ratio to the current. This was constant for Ca, Mg, K, Na and Cl throughout the simulation period. Scale sequences for SO₄, NO₃, and NH₄ were estimated using recent deposition chemistry data, as well as emission histories (see sources). These scale sequences were multiplied by current bulk concentration and by bulk deposition to total deposition ratio (dry deposition factor). Current bulk deposition concentration was considered to distribute normally with mean = (max + min)/2 and with standard deviation = (max - min)/4. Where a strong proportional relationship is observed between two ions, their *ratio* was estimated using linear regression, instead of using the observed deposition chemistry directly. The ratio was assumed to distribute normally, with mean = regression-estimated ratio, and with standard deviation = standard error for the estimated ratio. Dry deposition factor was estimated from Draaijers and Erisman (1995).

Table 4 | Input variables (soil properties) and their sources

Input parameter	Probability distribution*
Organic soil depth (cm) [†]	Uniform, 5.34–7.42
Mineral soil depth (cm) [‡]	Uniform, 40–49
Porosity, organic [¶]	Uniform, 0.85–0.95
Porosity, mineral [¶]	Uniform, 0.61–0.71
Water content, organic [¶]	Uniform, 0.27–0.37
Water content, mineral [¶]	Uniform, 0.23–0.44
Bulk density, organic (kg m ⁻³) [§]	Uniform, 130–158
Bulk density, mineral (kg m ⁻³) [§]	Uniform, 617–755
CEC, organic (meq kg ⁻¹) [¶]	Uniform, 157.5–192.5
CEC, mineral (meq kg ⁻¹) [¶]	Uniform, 34–77
[DOC], organic (μmol l ⁻¹) [#]	Normal, 1305, 72
[DOC], mineral (μmol l ⁻¹) [#]	Normal, 279, 15
DOC charge density for Oliver (mmol g ⁻¹ C) ^{**}	Normal 13.27, 1.087
pCO ₂ , organic (times atmospheric pCO ₂)	Uniform, 9, 11
pCO ₂ , mineral (times atmospheric pCO ₂)	Uniform, 19, 21
Gibbsite dissolution constant, organic (log ₁₀ (mol l ⁻¹) ⁻²) ^{††}	Uniform, 6, 7
Gibbsite dissolution constant, mineral (log ₁₀ (mol l ⁻¹) ⁻²) ^{††}	Uniform, 8.1, 9.1
Weathering rate for Ca (meq m ⁻² yr ⁻¹) ^{‡‡}	Normal, 9.34, 0.934
Weathering rate for Mg (meq m ⁻² yr ⁻¹) ^{‡‡}	Normal, 1.97, 0.197
Weathering rate for K (meq m ⁻² yr ⁻¹) ^{‡‡}	Normal, 14.87, 1.487
Weathering rate for Na (meq m ⁻² yr ⁻¹) ^{‡‡}	Normal, 3.84, 0.384
Exchangeable fraction for Ca	Uniform, 0.10, 0.20
Exchangeable fraction for Mg	Uniform, 0.05, 0.075
Exchangeable fraction for K	Uniform, 0.025, 0.05
Exchangeable fraction for Na	Uniform, 0.025, 0.05
Exchangeable fraction for H	Uniform, 0.15, 0.25
Nitrogen immobilization fraction	Uniform, 0.3, 0.7

*Normal distribution is defined by mean and standard deviation. Uniform distribution is defined by minimum and maximum.

[†]Johnson *et al.* 2000.

[‡]Lysimeter depth.

[¶]T. Federer (pers. comm.).

[§]Johnson *et al.* 2000. + / - 10% added.

[#]Johnson *et al.* 1991. + / - 10% added.

[¶]Lysimeter data, Palmer *et al.* 2004. mean and standard deviation.

^{**}Calculated from lysimeter data using Oliver (1983) and Hruska *et al.* (2003) parameters.

^{††}Warfvinge & Sverdrup (1995).

^{‡‡}Calculated using PROFILE model using mineral species analysis. standard deviation was calculated to be 10% of the PROFILE estimate.

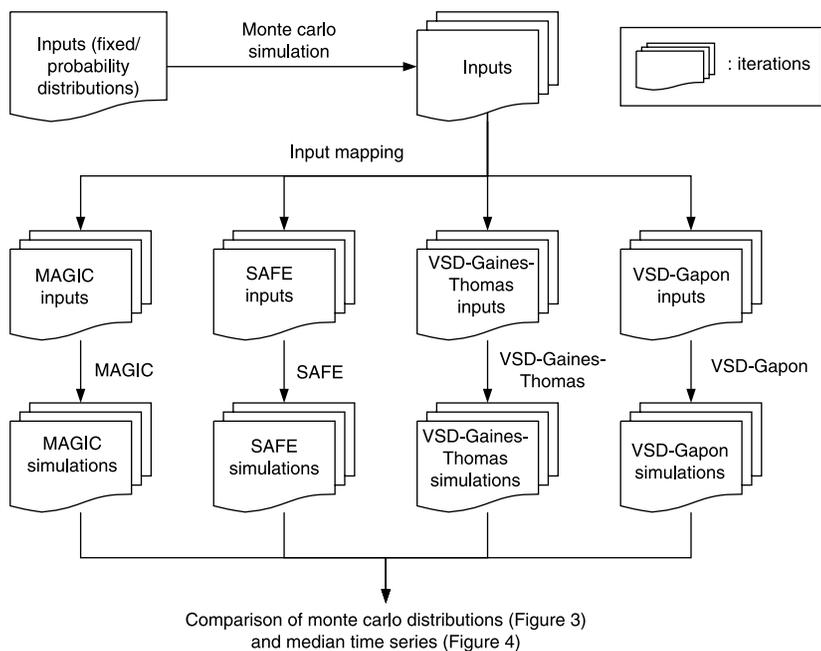


Figure 1 | Schematic work-flow chart for the multiple-model evaluation framework combining Monte Carlo and input mapping (translation) procedures.

organic acid. As a result, the initial soil solution concentration differs slightly among the models, but the equilibrium at the initial stage is guaranteed for all the models.

The models differ in the cation exchange formulation: MAGIC uses Gaines–Thomas, SAFE uses Gapon and VSD can be run using either model (Table 2). Exchangeable sodium (leaching from soil exchange medium) is modelled only in MAGIC. In the current study, the model-specific cation exchange coefficients were calculated using the 1800 soil solution concentrations and independently (Monte Carlo) sampled initial exchangeable cation fractions (Cosby *et al.* 1985; Alveteg 1998; De Vries & Posch 2003). These model-specific cation exchange coefficients were then kept constant for every 300-year (1800–2100) simulation.

RESULTS AND DISCUSSION

Initial soil solution chemistry

Solid phase chemistry, i.e. exchangeable pools, at the start of the simulation (year 1800) was identical in all models. However, due to differences in model structure (i.e. cation exchange sub-model, DOC dissociation sub-model and acid speciation), soil solution chemistry varied slightly

(Figure 3). For example, the $Bc (= Ca^{2+} + Mg^{2+} + K^+)$ concentration density distribution varied by up to 5 meq m^{-3} between the models. Such variability at the start of the simulation is minor compared to the temporal changes in these variables. For example, median Bc concentration varies from below 50 meq m^{-3} to greater than 100 meq m^{-3} over the 300-year simulation period (Figure 4).

Simulated response to acid deposition

Since no sorption process was included in the model configurations, SO_4^{2-} and Cl^- in the deposition fluxes are ‘concentrated’ by evapotranspiration, and directly relate to their soil solution concentrations. Consequently, changes in soil solution concentrations mirrored their deposition concentrations over the 300-year simulation period (Figures 2 and 4). Thus, the SO_4^{2-} concentration in soil solution initially increased during the simulation period, but Cl^- did not (input flux assumed constant).

Nitrogen dynamics were simplified in all model configurations such that deposition of NO_3^- and NH_4^+ were combined (complete nitrification) and a fixed fraction of that was removed from the soil system (immobilization). Accordingly, the simulated NO_3^- concentration in the soil

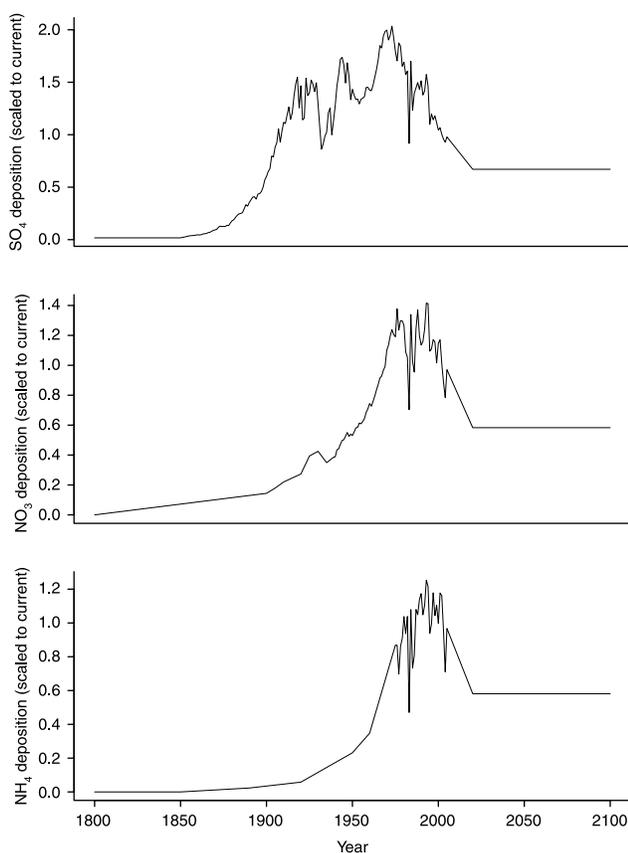


Figure 2 | Deposition scenarios for sulphate, nitrate and ammonium scaled to current deposition.

solution was the same for all the models and mirrored the historical total N deposition (see [Figure 4](#)). While not surprising, the results help confirm that input mapping was implemented properly. Moreover, it provides an independent verification for each model (cross-validation). Simulated variability in soil chemical parameters among (Monte Carlo) iterations changes over time, and is highest during times of rapid change. For example, during the 1970s, a period of sharp SO_4^{2-} deposition decrease, the variability among iterations for soil SO_4^{2-} concentration was greater than during the starting year (1800).

As acid deposition increased (starting ca. 1900), all models simulated a decrease in soil base saturation, pH and ANC and an increase in soil solution concentration of Bc (and also Na^+ for MAGIC, the only model that includes Na cation exchange). The decrease in pH led to an increase in aluminium due to gibbsite dissociation, while dissociated DOC decreased ([Figure 4](#)). With the rapid

decline in the SO_4^{2-} deposition starting in the 1970s, soil solution chemistry responded rapidly as Bc concentration fell and pH and ANC increased. In contrast, base saturation exhibited very little increase following the SO_4^{2-} reduction. In the current study, all depositions were kept constant after 2020 and, consequently, there was little change in soil solution chemistry. At the end of the simulation period, the soil solution chemistry seemed to approach another steady state; Bc concentration in soil solution was similar to that at the beginning of the simulation period, but pH and ANC were also lower, reflecting the higher acid deposition flux at the end of the simulation period. These are expected (and previously observed) behaviours of the models (e.g. [Warfvinge *et al.* 1993](#); [Hruska *et al.* 2002](#); [Posch *et al.* 2003](#)).

Model differences

The discrepancies in simulation among models can be explained by the model structural differences: cation exchange sub-model, organic acid sub-model and weak acid dissociation. Previous model evaluation studies (e.g. [Warfvinge *et al.* 1992](#); [Forsius *et al.* 1998](#)) suggested that model simulations were similar for multiple models, but not precisely the same. Nonetheless, their results are not comparable to the current study because they calibrated the models and hence model inputs were not equivalent across the models.

The two cation exchange sub-models describe the equilibrium between cations adhered to negatively charged soil particle surfaces (solid-phase cations) and cations in soil solution (liquid-phase cations). These sub-models are similar in formulation (e.g. both use cation exchangeable fraction and soil solution concentration for equilibrium constant) but differ in magnitude or the exponents for the variables ([Reuss 1983](#); [De Vries & Posch 2003](#)). The Gapon-based models (SAFE and VSD-Gapon) exhibited less severe depletion of Bc under elevated acid deposition (ca. 1900–2100) than their Gaines–Thomas counterparts (MAGIC and VSD-Gaines–Thomas) ([Figures 3 and 4](#)). Consequently, simulated Bc in soil solution resulted in lower concentration using the Gapon sub-models ([Figure 4](#)). Acid leaching in all models is identical, so the difference in Bc results in lower soil solution ANC for the Gapon

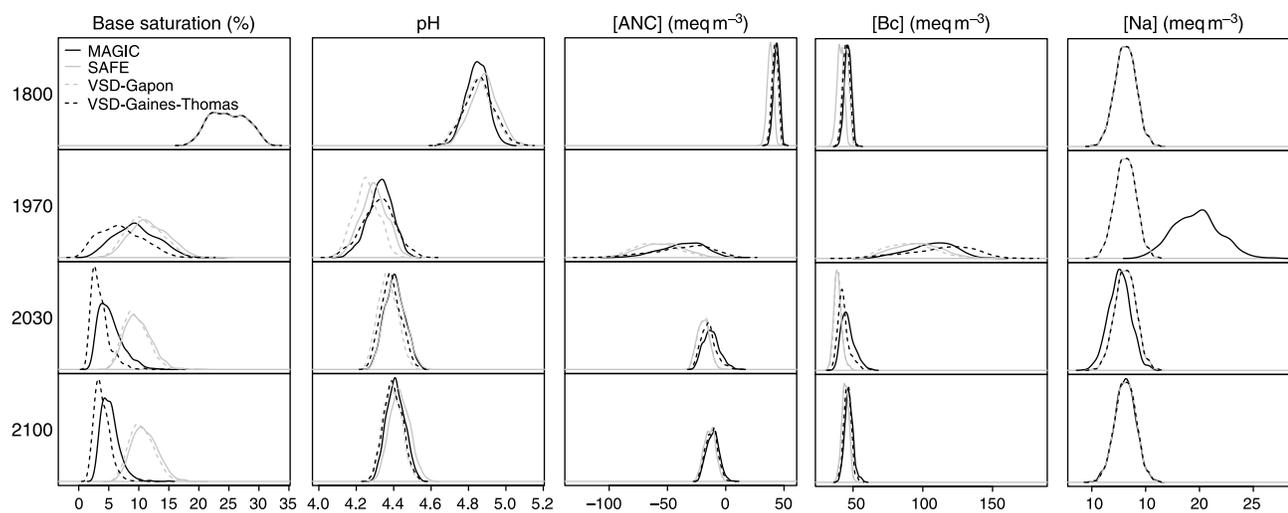


Figure 3 | Probability density plots of soil base saturation (%) and soil solution Acid Neutralizing Capacity (ANC), pH, base cation ($Bc = Ca^{2+} + Mg^{2+} + K^{+}$) concentration and sodium (concentration: $meq\ m^{-3}$) in selected years (1800, 1970, 2030 and 2100) for 1000 Monte Carlo simulations.

models (Figure 4). MAGIC is the only model that considers soil solution Na^{+} originated from cation exchange in addition to deposition, which is considered by all models. Not surprisingly, in the current study MAGIC simulated higher Na^{+} than the other models (Figure 3).

The three models differ in the pH-dependent ions that they consider in soil solution (carbonate, aluminium hydroxide species and organic acids). Such differences could potentially lead to differences in the base cations, DOC and pH owing to charge balance constraints in soil solution. Differences in pH and Al^{3+} were relatively small and, overall, it appears that differences in soil solution chemistry simulated by the models were influenced to a greater extent by the cation exchange model as opposed to the acid speciation.

The amount of DOC that dissociates and therefore contributes to negative charge in soil solution is also modelled differently in MAGIC (triprotic) compared with the other models (Oliver). However, both are pH dependent and the charge associated with DOC decreases as pH decreases in a similar fashion. In the current study, two different DOC charge density values were used for each of the two sub-models (constant over the 300 year simulation period) so that the negative charge from the DOC was consistent or similar across all models. The difference in DOC charge was very small (up to $1.5\ meq\ m^{-3}$) and the pattern over the 300-year simulation period was uniform (Figure 4).

Monte Carlo variability

The variability of many of the simulated variables within each model, i.e. the range in Monte Carlo iterations, changed over time (Figure 3). The range of base saturation within models narrowed after the period of high acid deposition (after 2000). Bc , Na^{+} (for MAGIC), Al_{tot} , SO_4^{2-} , NO_3^{-} and hence ANC concentrations seemed to vary more when these concentrations underwent a rapid change (1900–2000), primarily driven by acid deposition flux. This high variability resulted from the buffering of incoming acid deposition. These parameters were randomly and independently sampled from probability distributions (based on observations) in each Monte Carlo simulation (Tables 3 and 4), and they determine when exchangeable base cations start leaching, how fast leaching occurs, when leaching ends and when soil chemistry starts recovering. The magnitude of the uncertainty surrounding these events (1900–2000) is higher than the uncertainty during more stable periods. Variability of pH and DOC charge did not change much over time. This perhaps indicates that input parameter uncertainty on simulated pH and DOC charge is not relevant to the base cation leaching process, as they are constrained even during the time of rapid change.

Model calibration is a common (and necessary) model application procedure as it provides process-oriented models with prediction capability into the future. Cali-

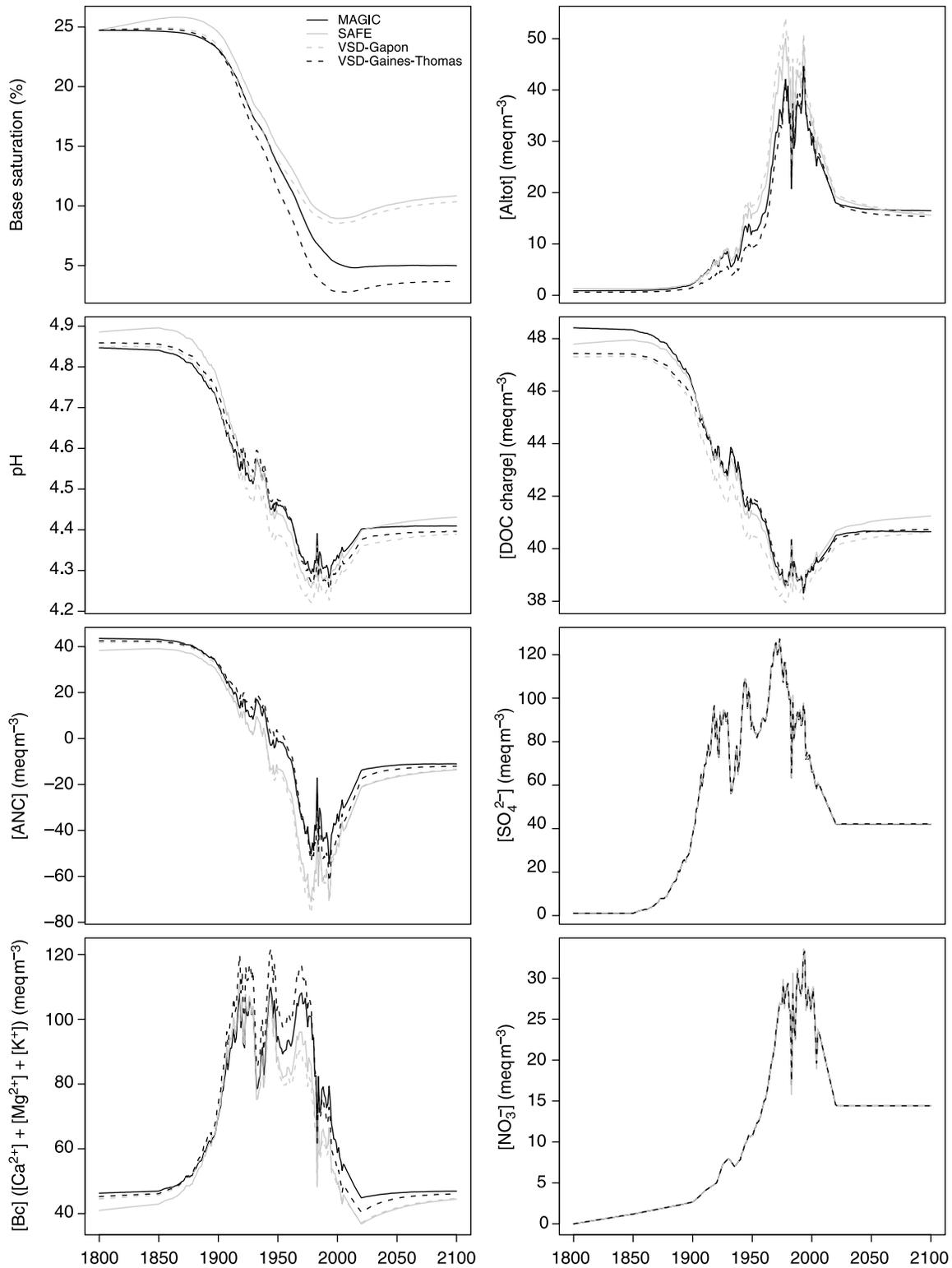


Figure 4 | Median time-series outputs for selected variables using uncalibrated model runs (1800–2100) based on 1000 Monte Carlo simulations.

bration was absent from the current study, as it focused on evaluating the impact of model structural differences on simulation, irrespective of accurately predicting the future soil chemistry at the study site. Model hindcasts and forecasts presented here do not present ecologically relevant uncertainty between model predictions, as simulations were not constrained by observations. However, the model evaluation framework can be further used to objectively include the calibration procedure by selecting Monte Carlo simulations that successfully reproduce observation counterparts (behavioural simulations). As each model is valid in its own right, this approach will result in a range of plausible future chemical conditions from multiple models. This approach could ultimately be coupled with climate models to provide the range and uncertainty in future chemical conditions under potential climate, deposition or land use scenarios.

Such multiple model frameworks have been used in atmospheric and climate simulations (Eyring *et al.* 2007; Randall *et al.* 2007) and shown to provide more reliable and robust forecasts (Dentener *et al.* 2006).

CONCLUSIONS

Input mapping and Monte Carlo sampling can be used to objectively evaluate process-oriented models provided that the models can be configured for consistency. In this study, this was achieved by reducing features that are generally used to customize model applications. Such features included variable percolation, multi-layer soil profile, sulphate sorption in soil and forest nutrient uptake. Future work is required to incorporate these important processes (structures) for a more complete model evaluation.

In the current study, the greatest differences in model outputs were attributed to the cation exchange sub-model, with Gapon-exchange based models retaining more base cations on the exchange complex and releasing less into solution, resulting in lower soil solution ANC values. Differences in acid-base equilibria were relatively minor and had less impact on model predictions. This study demonstrates that, given the same deposition scenario, the three models (without calibration) simulate changes in soil

and soil solution chemistry differently, but the basic patterns were similar. These models are usually calibrated before being used to predict ecosystem response to environmental or climate change; future work should address questions such as whether differences in simulation are still observed for calibrated multiple model ensembles.

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