Assessment of Uncertainty in Long-Term Mass Balances for Acidification Assessments: A MAGIC Model Exercise

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Abstract Long-term (1860–2010) catchment mass balance calculations rely on models and assumptions which are sources of uncertainty in acidification assessments. In this article, we report on an application of MAGIC to model acidification at the four Swedish IM forested catchments that have been subject to differing degrees of acidification stress. Uncertainties in the modeled mass balances were mainly associated with the deposition scenario and assumptions about sulfate adsorption and soil mass. Estimated base cation (BC) release rates (weathering) varied in a relatively narrow range of 47–62 or 42–47 $\text{meq m}^{-2} \text{ year}^{-1}$, depending on assumptions made about soil cation exchange capacity and base saturation. By varying aluminum solubility or introducing a dynamic weathering feedback that allowed BC release to increase at more acidic pHs, a systematic effect on predicted changes in acid neutralizing capacity (ΔANC ca. 10–41 $\mu\text{eq l}^{-1}$) and pH (ca. $\Delta\text{pH} = 0.1\text{--}0.6$) at all sites was observed. More robust projections of future changes in pH and ANC are dependent on reducing uncertainties in BC release rates, the timing, and extent of natural acidification through BC uptake by plants, temporal changes in soil element pools, and fluxes of Al between compartments.

Keywords MAGIC · Weathering · Modeling · Base cations · Aluminum · Acidification

INTRODUCTION

Studies on the causes and mechanisms of acidification and subsequent recovery have been a major focus of surface water research from the early 1980s to the present (Cosby et al. 1985a, b; Whitehead et al. 1988; Moldan et al. 2004; Aherne et al. 2007). The intricate coupling of nitrogen,

sulfur, and carbon biogeochemistry; recent observed increases in organic matter concentrations in many surface waters (Monteith et al. 2007); and renewed interest in weathering rate estimates in Sweden (Akselsson et al. 2007; Klaminder et al. 2011; Sverdrup 2009) have brought process-based modeling approaches to the forefront.

Due to its simple water and soil chemistry and straightforward mass balance approach, MAGIC (Model of Acidification of Groundwater In Catchments) has been used for a multitude of modeling and assessment purposes (Forsius et al. 1998; Laudon et al. 2005; Wright and Cosby 2003). In Sweden, MAGIC has been adopted as the official tool for classifying acidified waters as those where recent modeled pH values differ from values for the so-called preindustrial period (ΔpH) by more than 0.4 (Fölster et al. 2007). However, MAGIC is often calibrated against 1 year's data of stream water chemistry and soil acidity status using exchangeable base cations (BC) (Moldan et al. 2004; Aherne et al. 2007). While these are clearly defined reference values, measurements from single years or based on single sites within a catchment may be prone to systematic deviations arising from inter-annual, climate-induced variations in water chemistry and spatial heterogeneity of the active pool of exchangeable cations throughout a catchment.

For the four Swedish Integrated Monitoring (IM) sites, a large amount of stream water chemistry data is available for estimating element fluxes over several decades. Both Wright and Cosby (2003) and Whitfield et al. (2007) have demonstrated that MAGIC calibrations are more robust when applied for longer time scales.

Deposition is a key parameter for catchment-scale mass balance calculations, but large uncertainties about dry deposition of BC and its effect on the acid neutralizing capacity (ANC) of precipitation still exist. Based on Swedish deposition data, an alternative approach using

sodium rather than chloride to estimate total deposition was initiated by Persson et al. (2004). Other important factors are aluminum fluxes from the soil to the stream and the amount of exchangeable BC available in the soil. The latter is known to vary spatially within the catchment, and in the absence of measured data, averages from other sites have to be employed (Moldan et al. 2004). Aluminum solubility product constants determine aluminum fluxes and were identified previously as a critical factor in modeling surface water chemistry (Wright and Cosby 2003). Despite this, these constants have rarely been verified with actual stream data, and the quantitative effect of using different values has not been studied systematically. The large amount of available aluminum speciation data at three of the IM sites may allow the definition of realistic boundaries for these sites.

Our aim was to apply MAGIC to the four Swedish IM catchments to (a) test the outcome of calibrating MAGIC parameters to element fluxes available for the time period 1996–2008, (b) test the robustness of the prediction of ΔpH and ΔANC when various key parameters are varied, and (c) estimate apparent present-day BC release rates from the soils for use in future studies on potential acidification effects of forestry practices, e.g., whole tree harvesting.

MATERIALS AND METHODS

The catchment characteristics and biogeochemical sampling programs at the four IM sites Aneboda (N 57° 05' E 14° 32'), Gårdsjön (N 58° 03' E 12° 01'), Kindla (N 59° 05' E 14° 54'), and Gammtratten (N 63° 51' E 18° 06'), are described elsewhere (e.g., Löfgren et al. 2011). The sites are situated in protected non-managed forests dominated by Norway spruce (*Picea abies*), granite bedrock and till, along the South-North climatic and deposition gradient prevailing in Sweden. Marine aerosol deposition affects the Gårdsjön site substantially, due to its location on the Swedish west coast. The sites have been thoroughly investigated for more than a decade. All sites have been intensively monitored for a large number of chemical (Löfgren and Cory 2010), meteorological, and biological (Grandin et al. 2011 a, b) parameters. In this study, we primarily concentrate on the soil and surface water chemical data that are available from the Swedish University of Agricultural Sciences Department of Aquatic Sciences and Assessment databases (<http://info1.ma.slu.se/IM/>).

MAGIC is a dynamic model that uses mass balances and chemical equilibria to estimate element fluxes for different landscape units (recharge areas, discharge areas, streams, and lakes) and different soil horizons (organic and mineral soil) over time (Cosby et al. 2001). Given the variability in catchment characteristics, it is possible to arrange

compartments in the model to resemble a specific catchment. In MAGIC, precipitation water chemistry is altered when passing through a soil box as a consequence of a number of chemical and biological processes, before reaching a stream or a lake. In its simplest default mode, a MAGIC simulation comprises two compartments, a soil/biomass box and a surface water box. Elements may move from the soil to surface water box and are driven by user-defined time series of biomass uptake, weathering, nitrogen immobilization, deposition, and a chemical module that simultaneously solves for charge balance, ion speciation, cation and sulfate (SO_4^{2-}) exchange, degassing of carbon dioxide (CO_2), presence of organic acids, and an unspecified aluminum polyhydroxide ($\text{Al}(\text{OH})_n$) solid phase with a variable stoichiometry. Total mass of solids is defined using soil thickness, bulk density, and porosity. Water fluxes and retention times may be altered allowing bypassing of soil layers.

MAGIC has been widely applied in Europe and North America (Cosby et al. 1985a, b; Wright et al. 1994; Wright and Cosby 2003; Moldan et al. 2004; Whitfield et al. 2007; Aherne et al. 2007 among others), mainly for estimating the potential effects of acid deposition on surface water quality. The exact mathematical formulation of the model can be found elsewhere (Cosby et al. 1985a, b; Cosby et al. 2001). The parameterization and execution of MAGIC requires a large amount of data and ancillary assumptions, which have varying degrees of uncertainty. Input data include time series of total deposition for all major elements, plant growth sequences, and corresponding element uptake in biomass as well as surface water chemistry. Estimates of soil mass, soil chemical parameters, cation exchange capacity (CEC), SO_4^{2-} adsorption characteristics, and base saturation (BS%) are also needed. The results of this study rely on a combination of manual calibration and comparisons of modeled and measured stream export, which may affect the quantitative interpretation of the results. In the following sections, we describe the construction of the aforementioned time series.

Quantification of Element Fluxes

Water chemistry data for the major cations calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), aluminum (Al^{3+}); major anions: sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-), fluoride (F^-); and total organic carbon (TOC), together with runoff data were used to calculate annual element fluxes using the Macro Flownorm (Grimvall 2004) for the period 1996–2008. Daily element fluxes were estimated by multiplying linearly interpolated concentrations by the measured daily water discharge. Total runoff was then used to transform the annual flux (mass per area and year) into

flow-weighted annual average ion concentrations (meq m^{-3}). Equivalent charges for TOC were recalculated using the same organic acid model as used in MAGIC (Hruska et al. 2003) but with a slightly higher site density of $11.6 \mu\text{eq mg}^{-1}$ (Sjöstedt et al. 2010).

Derivation of Growth Sequences

Forest-growth sequences were created for each site based on known land-use history, current forest age and measured standing biomass. Tree growth varied as a function of age and geographical location. In general, it was assumed that the growth rate was fast during the first 25–40 years and then leveled off. With the exception of Aneboda, where net forest growth was set to zero for a short period after a major storm in 2005, all stands are assumed to grow over time. Stand thinning and clear cutting were negligible (<10%) at all sites. The same information was used to estimate canopy closure, which is important for determining dry-deposition factors (DDF). Prior to canopy closure, we assumed that DDF increased linearly from a value of 1 to the final site and element specific values. Growth sequences for the IM sites are shown in Fig. 1.

Deposition Measurement, Interpretation of Deposition Date and Derivation of Time Series

Estimates of Total Deposition From the Atmosphere to the Forest

Total annual input of major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , Cl^- , and NO_3^-) by wet and dry deposition for the calibration years (1996–2009) were derived from open field (bulk) and throughfall measurements. Methods for sampling, analysis and data validation of deposition are described in the ICP-Forests manual, part XIV (<http://www.icp-forests.org/Manual.htm>).

In contrast to wet-only collectors, open-bulk collectors collect both wet and dry deposition. Traditionally, the contribution of dry to bulk deposition has been ignored, partly due to lack of data from wet-only collectors (Lövblad et al. 2000). Earlier comparisons between wet-only

and bulk precipitation in Sweden recorded small differences between the two types of collectors (Granat 1988). However, other studies have indicated that dry deposition can be high, especially for sea-salt components (Persson et al. 2004; Hellsten and Westling 2006). Values for wet deposition were calculated by subtracting average dry deposition contributions of 25% (Na^+) and 10% (Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , SO_4^{2-} , and NO_3^-) from bulk deposition values (product of precipitation amounts and concentrations), according to Persson et al. (2004) and Hellsten and Westling (2006). A similar approach is used for modeling deposition in Sweden using the MATCH-model (pers. comm. Christer Persson, Swedish Meteorological and Hydrological Institute). Measures of F^- are not included in the chemical analysis and were set to zero. Wet deposition of Cl^- was estimated (normalized) by multiplying wet deposition values for Cl^- by 0.858, according to the molar Na/Cl ratio of sea water (Sverdrup et al. 1942) and assuming the contribution from non-marine sources of Na^+ (e.g., wind-borne mineral dust) was negligible. However, an analysis of precipitation chemistry of 5000 samples from 7 European laboratories resulted in a mean Na/Cl ratio of 0.94–1.08, which is close to the marine ratio of 0.858 (Mosello et al. 2005). Consequently, the Na/Cl ratio of deposition is reasonably similar to that of sea salt, and hence normalization may be performed using either Na^+ or Cl^- . Dry deposition was calculated by subtracting wet deposition from total deposition. Total deposition was estimated using several techniques. Sodium and SO_4^{2-} are generally accepted as inert ions that are neither taken up nor leached from tree canopies. Thus, throughfall depositions of Na^+ and SO_4^{2-} were assumed to represent total depositions of Na^+ and SO_4^{2-} . The total deposition of Cl^- was estimated by multiplying the total deposition of Na^+ by 1.165 (Mosello et al. 2005). As other major ions including Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , and NH_4^+ are either taken up or leached from the canopy, their total deposition cannot be calculated directly from throughfall deposition. Instead, estimates of Ca^{2+} , Mg^{2+} , and K^+ deposition followed the Na-ratio method described by Ulrich (1983) using the following equation:

$$\text{TD}_x = (\text{TF}_{\text{Na}^+} / \text{WD}_{\text{Na}^+}) \times \text{WD}_x \quad (1)$$

Fig. 1 Estimated development of standing biomass at the four IM sites (**a**, left) and applied sequences for ANC in total deposition at the four IM sites (**b**, right). The small inset in figure a displays the assumed history and increase of BC dry deposition over time in meq m^{-3} at one of the sites

where TD_x is the total deposition of ion, TF_{Na+} is the throughfall deposition of Na^+ , WD_{Na+} is the wet deposition of WD_{Na+} , and finally, WD_x is the wet deposition of ion x . The total deposition of NO_3^- and NH_4^+ were estimated from wet deposition scaled up by a factor (1.3, 1.2, 1.1, and 1.01 for Gårdsjön, Kindla, Aneboda, and Gammtratten, respectively), varying from south to north (Karlsson et al., in prep.). Finally, the DDF used for scaling up wet deposition to total deposition on forest-covered surfaces in MAGIC were estimated by dividing total by wet deposition. For all parameters except NO_3^- and NH_4^+ , the DDF varied annually during the calibration years.

Establishing Time Series for the Time Period 1860–2010

Modeled long-term deposition time series for SO_4^{2-} , NO_3^- , and NH_4^+ from 1860 to 2010 are available in a grid database from the Coordination Centre for Effects, Netherlands Environmental Assessment Agency (Anon 2008). This is referred to as EMEP deposition in the following. For each site, the corresponding grid was chosen as a reference for scaling the temporal patterns of deposition. Initially, marine background concentrations were estimated from average measured Cl^- concentrations. At Aneboda, these values were adjusted at a later stage so that incoming Cl^- from deposition would match outgoing Cl^- in the stream during the observation period (1996–2008). No changes were necessary at the other sites. Soil sources of Cl^- were set to zero at all sites as no independent validation data were available. It is possible that very small amounts of Cl^- are derived from mineral dissolution of hornblende, muscovite or apatite or via mineralization and decomposition of organic chlorine. Anthropogenic sources of SO_4^{2-} , NO_3^- , NH_4^+ , and BC were added to the marine background using linear-step functions established between time points (1880, 1950, 1970, 1980, 2003, and 2010) to reflect the temporal evolution of the EMEP-predicted deposition. A comparison of measured and estimated total deposition during the whole 8–12 year observation period was used to scale deposition depending on when the site was established. Between 1950 and 1970, extra BC deposition was added to partly compensate for anthropogenic acids and to match the present observed BC and ANC in deposition as closely as possible (see inset in Fig. 1). Relative to the predicted marine background in 1950, BC were multiplied by 1.7 (Gammtratten), 1.5 (Kindla), 1.1 (Aneboda), and 1.2 (Gårdsjön).

Soil Physical and Chemical Parameters

To investigate element release and retention, a MAGIC simulation including two soil boxes, representing an upper organic and a lower mineral layer with different adsorption–desorption characteristics, was performed. We

initially assumed a constant hydraulically active soil depth of 1 m separated into 15 cm top and 85 cm thick bottom layers (SET I). The top layer represented a combined O-, E-, and upper B-horizon, whereas the bottom layer represented a combined lower B- and C-horizon. The assumption of a two-layer hydraulically active soil was consistent with hydrological studies at boreal Swedish sites dominated by till (Rhode 2003; Lind and Lundin 1990). The soil depth and layer thicknesses were adapted to the measured soil depth at the four sites during the calibration process (SET II) and the final estimated values are displayed in Table 1. Soil temperature was set 2° below average air temperature, while stream water temperature was set to the average air temperature at the site. These assumptions mostly affect carbon dioxide and the apparent $Al(OH)_3$ equilibria, but otherwise have only minor effects on aqueous equilibrium concentrations.

For all the aqueous phases, the chemical equilibria can allow for the presence of a triprotic organic acid (Hruska et al. 2003) and Al binding as described by Cosby et al. (2001). The Al binding constants in this study were calibrated against an existing triprotic analog model assuming different acid analogs but the same relative binding of Al as a function of pH. The fitting was done using the USGS freeware PHREEQC (Parkhurst 1998). As Al speciation data were available for all sites, we adjusted the two binding constants so that organically bound Al would not exceed 90% of the total mobile Al, in accordance with measured data available in the pH range 4–5.5. No effort was made to fit the cation selectivity constants; instead, they were automatically calculated assuming a given distribution of the ion exchange complex, as set by one of the two default options in MAGIC. Partial pressure of CO_2 was estimated from alkalinity and pH using the first carbonic acid constant and Henry's constant at 5°C after accounting for the contribution of organic acids to alkalinity. Soil CO_2 partial pressure was set to ten times the stream water partial pressure. This assumption results in a lower pH in the soil water compared with the stream water.

Measurements of cation exchange capacity (1 M NH_4Cl exchangeable cations and 1 M KCl exchangeable acidity) and base saturation were available for 5–10 locations at each site for several soil horizons down to a depth of 80 cm. Given the measured bulk density, these depth-dependent values were used to estimate the total CEC and amount of BC bound in the whole soil profile in the two hypothetical soil layers (Table 1). In addition, average ($\pm$ standard deviation) CEC data for both O (ca. 0–3 cm) and B (ca. 20–60 cm) horizons from the Swedish Forest Soil Inventory (<http://www.slu.se/en/collaborative-centres-and-projects/swedish-forest-soil-inventory/>) were calculated within the same EMEP grid (± 50 km, ≈ 15 –20). These values are available for Gammtratten (799 ± 202 ;

Table 1 List of MAGIC parameters that were calculated or manually optimized (mod, SET II)

Parameter	Compartment	Gammtratten		Kindla		Aneboda		Gårdsjön	
		Mod	Mea	Mod	Mea	Mod	Mea	Mod	Mea
T (°C)	Soil	1		2		3		5	
	Stream	3		4		5		7	
CO ₂ (vol%)	Soil	5		5		16		5	
	Stream	0.5		0.5		1.6		0.5	
CEC (meq kg ⁻¹)	Upp. soil	50		70		100		120	
	Low. soil	5		8		18		35	
BS%	Upp. soil	65		48		54		52	
	Low. soil	13		50		41		39	
Ca (ppm)	Biomass	1600		2100		2300		1800	
Mg (ppm)	Biomass	280		290		340		310	
K (ppm)	Biomass	1100		880		960		1100	
Na (ppm)	Biomass	50		22		32		21	
Smax (meq kg ⁻¹)	Upp. soil	3		5		2.5		5	
	Low. soil	0.5		5		2.5		3	
Halfsat	Upp. soil	25		150		150		100	
Halfsat	Low. soil	25		150		150		100	
Log K_{sp}	soil	9.3		9.5		7.5		9.2	
Slope	soil	3		3		3		3	
K_{AlA}	soil	−7.8		−6.8		−4.9		−6.8	
K_{AlHA}	soil	−11.8		−11.8		−9.6		−11.8	
log K_{sp}	Stream	9.3		9.3		8		8.5	
Slope	Stream	3		3		3		3	
K_{AlA}	Stream	−7.8		−6.8		−6.8		−6.8	
K_{AlHA}	Stream	−11.8		−11.8		−11.6		−11.8	
DOC (mM m ⁻³)	Upp. soil	158		115		304		153	
	Low. soil	22.2		19.2		49		24.5	
	Stream	38.3		27.6		74.3		37.4	
mass (kg m ⁻²)	Upp. soil	56	124	51	108	56	105	37	123
	Low. soil	760	768	593	639	759	793	584	804
	Total	816	892	644	747	815	898	621	927
CEC (meq kg ⁻¹)	Upp. soil	2800	3300	3570	3500	5600	5500	4464	7100
	Low. soil	3800	2400	4744	3565	13 662	6200	20 440	12 600
	Total	6600	5700	8314	7065	19 262	11 700	24 904	19 700
BC (meq kg ⁻¹)	Upp. soil	1817		1717		3032		2348	
Initial	Low. soil	533		2413		5731		8097	
	Total	2350		4130		8763		10 445	
BC (meq kg ⁻¹)	Upp. soil	1351	726	722	1317	1652	1414	932	1785
Final	Low. soil	209	158	486	242	1807	758	775	1137
	Total	1560	884	1208	1559	3459	2172	1707	2922
Soil depth (m)	Upp. soil	0.15		0.15		0.15		0.1	
	Low. soil	0.65		0.55		0.65		0.5	
	Total	0.8		0.7		0.8		0.6	

The second column for each site show estimates of soil weight, BC pools, and CEC based on measured values (Mea), using the 5–10 data points available at each site. Element contents for Ca, Mg, K, and Na are given as parts per million (ppm) dry weight biomass. K_{sp} is the solubility product of the $Al(OH)_3(s)$ solid phase, Halfsat and Smax the sulfate adsorption factors, DOC is the concentration of dissolved organic carbon and K_{AlA} , K_{AlHA} are the complexation constants of aluminum to the triprotic organic acid analog

$65 \pm 38 \text{ meq kg}^{-1}$), Kindla (906 ± 304 ; $51 \pm 19 \text{ meq kg}^{-1}$), and Aneboda (755 ± 360 ; $\text{BC} = 89 \pm 42 \text{ meq kg}^{-1}$). In these surveys, the thickness of the B horizon was estimated to be between 23 and 27 cm.

Average values of CEC within the same EMEP grid and those measured at the IM sites did not differ substantially (i.e., they varied by a factor of less than threefold). In the absence of other data and given the large standard deviation of both CEC and BS% in both datasets, we arbitrarily selected starting CEC values for all sites of around 100 meq kg^{-1} for the upper and 25 meq kg^{-1} for the lower horizons. For the SET II calibration at the Gårdsjön site, we started with the value published by Jenkins et al. (2003) and Forsius et al. (1998).

Around 5–10% of the weathering fluxes were assumed to originate from the upper layer with the remaining 90–95% from the lower layer. All corresponding parameters and initial values are shown in Table 1. Variable N dynamics were not used. Instead, 90% of NO_3^- and NH_4^+ from deposition sources was assumed to be biologically consumed in both horizons.

Element Uptake

Element uptake was calculated from growth sequences and repeated element inventories available for the four sites. Element-uptake sequences were then calculated from estimated growth sequences and the measured average elemental content from several (≥ 2) inventories such that the integrated amount of standing biomass at the inventory matched the integrated estimate over time. The element uptake was divided between the two soil layers in a ratio of 30:70%. The resulting uptake curves are displayed in Fig. 1.

Manual Calibration

The initial step of the manual calibration involved small adjustments to the marine background concentrations of Na^+ and Cl^- . The final average deviation between measured and modeled ANC in deposition was below $3 \mu\text{eq l}^{-1}$ (except for Gårdsjön $< 8 \mu\text{eq l}^{-1}$). In all cases, modeled ANC was consistently below the measured ANC. Thereafter, SO_4^{2-} adsorption, soil depth, CEC, and BC release rates were subsequently adjusted. This process involved a large number of manual tests with higher and lower values for CEC, SO_4^{2-} adsorption, and weathering, as the export of desorbed SO_4^{2-} leads to leaching of cations as co-ions. Finally, solubility product constants of the hypothetical Al phases were changed. This process was stopped when a number of conditions were fulfilled simultaneously, notably when the modeled element fluxes for SO_4^{2-} , Cl^- and the sum of BC deviated by less than 10% from the measured export, and measured and modeled

Al concentrations were within 15% on average. Measured pH was not used as a criterion nor was stream water ANC because all its major components (BC , SO_4^{2-} , and Cl^-) were included in the calibration. The calibration procedure was undertaken for two different sets. For one set (SET I), soil CEC was chosen arbitrarily (upper layer = 100 meq kg^{-1} , lower layer = 15 meq kg^{-1}) and soil depths of 15 and 85 cm were used for the upper and lower soil horizons, respectively. For this set, initial BS was varied and only slight changes were made to CEC. For the second set (SET II), soil CEC and soil depth were chosen to be as close as possible to measured values. Therefore, the starting pools of BC available in the soil differed by a factor of up to 2.5 between SET II and SET I. The exact values for SET II (SET I) in meq m^{-2} are as follows: Gammtratten 2300 (4900), Kindla 4100 (9500), Aneboda 8800 (12 000), and Gårdsjön 10 000 (15 000) (Table 1).

RESULTS

The deposition sequences from the EMEP-estimated time series required some changes to the total amount of SO_4^{2-} deposition. The simulated total SO_4^{2-} deposition was 89, 93, 72, and 172% of the EMEP data values for Aneboda, Gammtratten, Kindla, and Gårdsjön, respectively. The final deposition sequences at the four sites produced an input of ANC of -1500 , -4200 , -4200 , and $-11\,900 \text{ meq m}^{-2}$ at Gammtratten, Kindla, Aneboda, and Gårdsjön (Fig. 1), respectively, from 1860 to 2010.

The parameters for the manually optimized MAGIC simulations using soil CEC that were as close as possible to the measured values (SET II) are shown in Table 1. These parameter sets resulted in four time series of predicted stream water ANC that are compared to the measured values in Fig. 2. Absolute average deviations of stream water ANC (pH) were 4 (0.14), 7 (0.29), 19 (0.33), and 34 (0.49) meq m^{-3} (no unit) for Gammtratten, Kindla, Aneboda, and Gårdsjön, respectively. The largest relative discrepancy occurred at Aneboda where the optimized parameter sets did not capture the steep increase in ANC (Fig. 2). At Kindla, early field data also indicated that the actual increase in ANC up to 1998 might be underestimated. At Gårdsjön and Gammtratten, the model-predicted ANC followed the observed trend.

Given the estimated total SO_4^{2-} deposition sequence, adsorption of SO_4^{2-} onto the soil mass had to be included into the model. The total amount of potentially adsorbed SO_4^{2-} varied between 500 and 2000 meq m^{-2} . The maximum SO_4^{2-} adsorbed into the lower soil layer varied between 307 and 1631 meq m^{-2} , corresponding to between 10 and 20% of the total amount of SO_4^{2-} deposited at the four sites.

Fig. 2 Time series of modeled (solid squares) and measured (open diamonds) values of ANC at each site Gammtratten (GAM), Kindla (KIN), Aneboda (ANE), and Gårdsjön (GAR) for the period 1980–2010 using SET II

Mass balances of estimated total deposition and stream flux for 1997–2008 indicated a significant internal source of SO_4^{2-} at all sites. Exports during that period were 2.5 (Gammtratten), 2.0 (Kindla), 2.3 (Aneboda), and 1.3 (Gårdsjön) times higher than inputs. At Gårdsjön, this number may be significantly underestimated as the EMEP deposition data were scaled up by a factor of 1.7.

Measured and modeled concentrations of SO_4^{2-} , BC, Al, and pH indicate that the chosen parameters for SET II in MAGIC (Table 1) adequately describe the time series of water chemistry given the calculated deposition scenario (Fig. 3). Mass balances of SO_4^{2-} and BC were mostly within 15% of the measured values or better (Table 2). The largest discrepancy occurred at Gårdsjön where modeled SO_4^{2-} fluxes were on average 15% higher than measured. The closest fit was achieved at Gammtratten.

The resulting modeled changes of pH over time depended on the chosen scenario. The largest differences occurred when the apparent solubility product constant of the $\text{Al}(\text{OH})_3$ phase was reduced systematically and the smallest occurred when a weathering feedback was introduced (Table 3).

Aluminum fluxes from the soil to stream were simulated at all sites. The highest fluxes ($\text{meq m}^{-2} \text{ year}^{-1}$) were modeled at Aneboda (45) and Gårdsjön (45), followed by Kindla (34) and Gammtratten (13). In the model simulation, significant amounts (i.e., 40–80%) of the soil-leached Al re-precipitated in the stream giving rise to additional stream acidity as discussed below.

Base cation fluxes in the stream, plant uptake, weathering, release from the exchange complex, and deposition were calculated for the whole period to estimate their relative importance at each site. These results are displayed

for SET II in Table 4. When considering the total amount of BC, fluxes decreased in the order: runoff in the stream > release due to weathering > release from the soil exchanger > deposition = plant uptake. The corresponding modeling results for stream water fluxes, model parameters, and calculated fluxes of parameter SET II are shown in Table 2.

Changes in BC pools were often larger for SET I than for SET II. The respective values given in meq m^{-2} for SET II (SET I) are 732 (1327) at Gammtratten, 2860 (4336) at Kindla, 4698 (10366) at Aneboda, and 8365 (8265) at Gårdsjön. Large changes in BC pools occurred from 1860 to 1920, which accounted for 76% (Gammtratten), 55% (Kindla), 51% (Aneboda), and 34% (Gårdsjön) of the total change in BC pool shown in Table 1. We also evaluated the change in the BC pool between 1985 and 2010 at all sites, using the SET II scenario. These data were expressed as % change of the total initial amount of the base cations present in 1860. Thus, a value of 5% for BC corresponded to a buildup of 5% in the BC pool during the last 25 years. Values for Gammtratten, Kindla, Aneboda, and Gårdsjön were +12, +2, +15, and +15%, respectively.

The apparent BC release rates differed when weathering feedback was included. The apparent rates ($\text{meq m}^{-2} \text{ year}^{-1}$) decreased from 50 to 39, 46 to 32, 53 to 36, and 62 to 39 at Gammtratten, Kindla, Aneboda, and Gårdsjön, respectively.

DISCUSSION

The application of MAGIC to the available long-term data from the four IM sites allows the effect of varying driving variables and input data on the outcome of the acidification

Fig. 3 Comparison between MAGIC modeled (solid squares) and measured (open squares) annual flow-weighted equivalent concentration for selected elements (SO_4^{2-} , BC, Al^{3+} , and pH from top to

bottom) at the IM sites Gammtratten (GAM), Kindla (KIN), Aneboda (ANE), and Gårdsjön (GAR) from left to right for calibration SET II

Table 2 Comparison of measured (Mea) and MAGIC-simulated (Mod) element fluxes (meq m^{-2}) in the streams at the Swedish IM sites for the two calibrations (SET I and SET II)

IM site	BC			SO_4^{2-}			Cl^-		
	Mea	Mod	R	Mea	Mod	R	Mea	Mod	R
SET II									
GAM	658	656	0.96	191	186	0.95	84	84	0.97
KIN	874	799	0.97	701	621	0.91	318	305	0.97
ANE	1678	1507	0.90	660	605	0.92	725	717	1.00
GÅR	6486	6239	0.96	1988	2277	1.15	4992	4726	0.97
SET I									
GAM	658	631	0.93	191	191	0.98	84	84	0.97
KIN	874	842	0.92	701	641	0.89	318	305	0.97
ANE	1678	1573	0.95	660	642	0.97	725	717	1.00
GÅR	6486	5978	0.92	1988	1996	1.00	4992	4726	0.97

R is the ratio of the modeled/measured flux of element during the period 1996–2008

assessment to be studied by comparing ΔpH and ΔANC . This modeling exercise revealed that systematic differences in MAGIC-predicted ΔpH may be as large as 0.5

(Table 4), which is greater than the 0.4 criterion for acidification of Fölster et al. (2007). Large systematic effects on ΔpH and ΔANC were observed at all sites when the reference year was varied, comparing of ANC from 1860 to 1920. Given the small effects of deposition on incoming ANC in 1920 (Fig. 2), the large modeled changes in surface water ANC and pH between 1860 and 1920 in our runs are almost entirely caused by regrowth after prior harvesting. Interestingly, predicted ΔANC between earlier MAGIC model (Magic Library 2010) runs and those modified comparisons are surprisingly similar at all sites. Similar large differences in modeled ΔANC and ΔpH occurred when the apparent solubility product constant of the $\text{Al}(\text{OH})_3$ phase was reduced systematically. Much smaller changes occurred when either weathering feedback was introduced (Table 4) or the available BC pool was changed by a factor of two. It is difficult to explain the large differences between earlier predicted ΔpH and our model runs. Given that the current Swedish criterion for a stream being classified as acidified is $\Delta\text{pH} = 0.4$, we propose that a margin of error of at least 0.2 pH units should be added to the predicted ΔpH to allow acidified sites to be distinguished from potentially acidified sites.

Table 3 Comparison of MAGIC-simulated changes in ANC (Δ ANC in meq m^{-3}) and pH (Δ pH) at the Swedish IM sites from 1860–2000 or 1920–2000, assuming several scenarios as indicated using SET II if not mentioned otherwise

IVL were obtained from the MAGIC library as described in the text. K_{sp} refers to the solubility product constant of $\text{Al}(\text{OH})_3(\text{s})$ in the stream

	Gammtratten	Kindla	Aneboda	Gårdsjön
Original (SET I) (1860–2000)				
Δ pH	0.4	1.0	0.7	1.4
Δ ANC	55	156	150	211
Variation (1860–2000)				
Δ pH	0.4	1.0	0.9	1.1
Δ ANC	50	145	243	189
Variation (1920–2000)				
Δ pH	0.2	0.6	0.4	0.9
Δ ANC	27	97	99	147
Weathering feedback (1860–2000)				
Δ pH	0.3	0.8	0.5	1.2
Δ ANC	42	130	127	170
$\log K_{\text{Al}(\text{OH})_{\text{stream}}} \Delta \log K_{\text{sp}} = -1$ (1860–2000)				
Δ pH	n.d.	1.3	0.9	1.7
Δ ANC	n.d.	156	150	212
IVL (1860–2000)				
Δ pH	0.4	1.4	1.1	n.d.
Δ ANC	31	100	95	n.d.

Specific effects of uncertainties in various input data and variables driving MAGIC will be discussed in detail below.

Estimating Dry Deposition Using Sodium

Efforts have been made to estimate dry deposition to forest in Kindla using surrogate surfaces, a technique developed by Ferm and Hultberg (1995) and modified by Ferm and Hultberg (1999). Reliable measurements are available for 2005–2008. Dry deposition of an ion (DD_x) can be calculated using the equation given in Ferm and Hultberg (1999):

$$\text{DD}_x = \text{SS}_x / \text{SS}_{\text{Na}} \times \text{NTF}_{\text{Na}^+} \quad (2)$$

where SS denotes the leaching of ion x or Na^+ from the surrogate surface and NTF_{Na^+} is the net throughfall of Na^+ (throughfall deposition minus wet deposition). A comparison of total deposition of Ca^{2+} , Mg^{2+} , and K^+ estimated using Eq. 2 (added to wet deposition to produce total deposition) with values estimated using Eq. 1 shows that Ca^{2+} and Mg^{2+} are about 30% higher (7.9 vs. 10.6 $\text{meq m}^{-2} \text{ year}^{-1}$ for Ca^{2+} and 6.1 vs. 7.9 $\text{meq m}^{-2} \text{ year}^{-1}$ for Mg^{2+}) and K^+ is about 25% lower (5.9 vs. 4.5 $\text{meq m}^{-2} \text{ year}^{-1}$) using Eq. 2. With the limited data available, it is not possible to determine which method produces the most accurate results. Since dry deposition measured via surrogate surfaces is only available for one site, the Na ratio (Eq. 1) was used to calculate total deposition at all four sites. The accuracy of using the Na ratio is questionable in some environments since recent studies have shown that canopy leaching of Na^+ (and Cl^-) occur seasonally and are most pronounced in alpine environments

(Thimonier et al. 2008). Thus, the general assumption that Na^+ (and Cl^-) is neither taken up nor leached from the tree crowns may not be valid. Future studies in environments similar to the ones considered here would help determine whether this assumption is appropriate for Scandinavian coniferous forests. Estimating total deposition from sodium rather than chloride fluxes is an alternative approach that is worth exploring more systematically, especially as Bastviken et al. (2006) and Viers et al. (2001) have shown that short-term mass balances of chloride are not necessarily closed, even on an annual basis. The long-term (1999–2008) Cl^- mass balances are closed at all the sites within an error margin of 15%, except at Aneboda where Cl^- fluxes are around 60% higher than incoming Cl^- from wet and dry deposition. An analysis of the water chemistry revealed that the extra Cl^- correlates strongly with additional Na^+ . Hence, we chose to significantly increase the marine background concentration at Aneboda. Water chemical analysis from an intermittent stream and a groundwater source revealed very high concentrations of both Na^+ and Cl^- that could at least partly explain this discrepancy. Estimated uncertainties arising from differences in nitrate and ammonia deposition scenarios were very small as their contributions to ANC were almost balanced and the ANC flux due to nitrogen export was minor at all sites.

Sulfate Fluxes and Retention

Incoming negative ANC from rainfall must be counter-balanced by cations either directly, in the absence of SO_4^{2-} adsorption, or by dampening over time when

Table 4 Total annual base cation (BC) fluxes (meq m^{-2}) from the different compartments calculated using the modeled data between 1860 and 2010 using SET II

IM site	Flux	BC
KIN	EXPORT	−76.7
	UPTAKE	−21.6
	WEATH	46.5
	DEPO	32.4
	EXCHANGE	18.9
ANE	EXPORT	−131
	UPTAKE	−24.9 (−19)
	WEATH	52.5
	DEPO	68.2
	EXCHANGE	31.1
GAM	EXPORT	−55.9
	UPTAKE	−9.1
	WEATH	50.5
	DEPO	9.5
	EXCHANGE	4.8
GAR	EXPORT	−372
	UPTAKE	−18.3
	WEATH	62.3
	DEPO	272
	EXCHANGE	55.4

Fluxes away from the soil solution are shown as negative values. EXPORT is the calculated stream export, UPTAKE is the assumed incorporation of elements into biomass, WEATH is the assumed release of elements from weathering, DEPO is the assumed atmospheric element input, and EXCHANGE is the calculated change of elements on the base cation exchanger. Values in parenthesis for Aneboda are average values taking account of the significant element release due to storm felling in January 2005 (storm Gudrun) and the subsequent bark beetle infestation

SO_4^{2-} adsorption is considered. The temporal storage of SO_4^{2-} will dampen instantaneous acidification and retard recovery. This has profound consequences for calculated ΔpH and ΔANC , and thus the modeled acidification status. Given that we have no analytical data on ANC in incoming precipitation at any of the sites from the period 1860–1980, we had to make various assumptions. Our analysis of modeled ANC may indicate that the final model scenarios are not perfectly matched with observations from the four sites. Deviations between measured and modeled ANC tend to be larger when multi-year calibration techniques are applied (Wright and Cosby 2003) compared with single year fitting procedures (Moldan et al. 2004). One could envision increasing modeled SO_4^{2-} deposition at Aneboda or decreasing it at Gårdsjön, which is a site that is heavily impacted by sea spray. This in turn would influence the choice of SO_4^{2-} adsorption factors.

Sulfate adsorption has been used in a number of previous MAGIC applications (Forsius et al. 1998; Martinson

et al. 2003; Moldan et al. 2004; Whitfield et al. 2007, 2011) with SO_4^{2-} adsorption capacities varying between 0.1 and 2.5 meq kg^{-1} soil. Martinson et al. (2003) used the SAFE model at the Gårdsjön site and found that when adsorption of significant amounts of SO_4^{2-} was included in the model the fit to measured data improved. Sulfate has been handled in various ways for different sites; some authors tend to disregard SO_4^{2-} desorption and assume steady state (Wright and Cosby 2003) or use small values (Whitfield et al. 2007).

An analysis of SO_4^{2-} fluxes revealed that export always exceeded the sum of inputs from wet and dry deposition. At Gammtratten, this might be explained by direct SO_4^{2-} uptake by trees because the data indicate lower sulfate concentrations in throughfall compared with values measured in open field. Given the low sulfate fluxes at Gammtratten, small changes in direct plant uptake potentially have the largest systematic effect on the calculated deposition at this site. At the other sites, the higher export of SO_4^{2-} compared with input may be due to a number of reasons, e.g., a significant systematic underestimation of SO_4^{2-} in precipitation, desorption of previously bound SO_4^{2-} from mineral surfaces or SO_4^{2-} release from the oxidation of organic sulfur. At Gårdsjön, Aneboda, and Kindla, soil water studies have indicated that these processes occur and that the mineralization and oxidation of organically bound S is most important (Mörth et al. 1999; Löfgren et al. 2001).

Effect of Varying Estimates of Exchangeable BC Pools

Measured CEC and BC pools may vary as much as threefold within 50 km of the catchment, according to data from the Swedish forest soil inventory. Based on the four IM soil inventories, an average variation of 40% was found within a catchment. A comparison of the modeled and measured CEC in the soil at all sites from SET (I) are within 25% except at Aneboda. Larger discrepancies of up to 76% relative to the measured values of BC pools occur when comparing these pools at the end of the simulation period. The difference was largest at Gammtratten (76%), followed by Aneboda (59%), Gårdsjön (42%), and Kindla (23%). There are many possible reasons for these larger discrepancies.

Factors that strongly affect the estimation of BC pools are buildup or degradation of organic matter in the soil, changes in pH that affect CEC, and additional root growth or decay that increase plant uptake or cation release. However, none of these effects could be quantified in this study. Another possible explanation for the discrepancies is that the soil pits where the BC pools were determined are disconnected from the major flow pathways. In addition, deeper soils than those sampled may

contribute significantly to stream flow at all the sites. The importance of BC fluxes via deep groundwater flow paths has been shown in Kindla (Löfgren and Cory 2010). Nevertheless, the two different parameter sets (SET I and SET II) highlight that comparable estimates of ΔpH and ΔANC may be obtained even if the BC pools in the soils are significantly overestimated. This latter result is reassuring as large variations in both CEC and base saturation have been observed within catchment soils when upslope or downslope soils have been sampled.

No significant differences between modeled and measured element fluxes were observed when a soil CEC as much as three times higher (SET I) than the actual value (SET II) was used. A systematic overestimation of BC buffering through the CEC exchanger complex produced a slightly lower ΔpH and ΔANC and required lower apparent BC release rates to fit the model to the measured data. The predicted change in the BC pool was more than 100% higher for SET I than SET II at all sites except at Gårdsjön. At Aneboda, the modeled changes were close to the total amount of measured CEC present. Therefore, it is important to evaluate potential systematic errors, especially for sites where small changes in ΔpH or ΔANC may sway the decisions of policy makers. Methodological differences when estimating key parameters and input data, such as those discussed above, between different MAGIC calibrations may be the reason for the large differences between estimates for ΔpH (up to 0.6) or ΔANC (up to 45 meq m^{-3}) reported here and values estimated earlier for the same sites (MAGIC library 2010).

Calculated Changes in BC Pools and BC Release Rates

Results from the model simulations indicate that the growth scenarios considered result in significant acidification between 1860 and 1910, whereas the actual effect of acid deposition is deemed minor for this period. An evaluation of the simulated changes in BC pools during the early period 1860–1920 showed that the estimated BC release rates cannot supply enough cations with respect to the given biomass uptake scenario. In the model outcomes, up to 76% (Gammtratten) and at least 34% (Gårdsjön) of the BC depletion occurs during the first 60 years. Similar but much less pronounced trends have been documented by Wright and Cosby (2004) for sites in Norway but have not been observed in MAGIC applications at any other Swedish monitoring sites (Kram et al. 2001).

Our findings are somewhat puzzling as the impact of acid deposition during the period 1860–1920 is generally considered to be of minor importance. If only part of this scenario is actually correct then BC depletion during this

“pre-acidification period” would result in significant overestimation of the severity of anthropogenic acidification (ΔANC) at all sites from 1920 to 2010. The choice of an arbitrary reference condition where the forest is assumed to be at steady state in 1860 in the MAGIC simulation might then introduce a systematic bias and pose mass balance problems. Thus, natural soil acidification due to forest growth prior to the intensive atmospheric deposition acidification period must be taken into account and quantified. Analysis of recent changes in BC pools in scenario SET II shows that the BC pools are replenishing at all sites. High rates of replenishment may occur at sites which are very low in exchangeable BC, such as Gårdsjön or Kindla where the model scenario SET II predicted large changes in BC pools (from 10445 down to 1707 at Gårdsjön and 4130 down to 1208 at Kindla (Table 1). The mass balances for SET II may also be used to constrain maximum apparent BC release rates at the four sites. Assuming, hypothetically, that none of the modeled cation exchange occurs, the corresponding BC release rates ($\text{meq m}^{-2} \text{ year}^{-1}$) would have to increase from 43 to 71 at Kindla, from 41 to 77 at Aneboda, from 45 to 54 at Gammtratten, and from 47 to 120 at Gårdsjön to account for the same BC supply. Assuming that 50% of cation exchange occurs, the corresponding BC release rates ($\text{meq m}^{-2} \text{ year}^{-1}$) become 57 at Kindla, 59 at Aneboda, 50 at Gammtratten, and 84 at Gårdsjön. Rates between 30 and 50 $\text{meq m}^{-2} \text{ year}^{-1}$ are reasonable for some of the sites considering values obtained in previous models (Forsius et al. 1998). Therefore, it is probable that at least 50% of the modeled BC exchange actually occurred at the sites. Interestingly, the corresponding BC release rates would only just supply sufficient K, even at the Kindla site. Assuming that only 50% of the BC supply originates from exchange sites, the probable error boundaries for the BC release rate were estimated to be below 50% for all sites except Gårdsjön, for which it was 80%. This is a surprisingly narrow error estimate given the large geographical variation of the four catchments and the large differences in weathering rates reported in the literature (Hodson and Langan 1999).

The choice of model structure in MAGIC affects BC release rates by up to 20% when using one-box or two-box models (Aherne et al. 2007). The study described herein reveals that similar differences arise if weathering feedback is allowed to occur. The fact that the rate of mineral weathering increases under increased acid concentration has been known for at least 50 years (Berner 1967; Schott et al. 1981). Most standard models (SAFE, PROFILE, WITCH) have included this process in an expression similar to Eq. 3:

$$r = k * [\text{H}^+]^N \quad (3)$$

which assumes the rate of destruction of minerals (Rate) increases non-linearly with pH, where N is a number which

is adjusted to fit the data. The rate of destruction of minerals (Rate) in contact with increased amount of protons (pH) increases nonlinear (N). Given a constant rate at a fixed pH of 5, this equation predicts that the rate increases to 250% if the soil solution acidifies to pH 4 and N is set to 0.4. This behavior is in line with a large number of experimental studies which used values between 0.3 and 0.6 in the acid pH range depending on the type of mineral studied (Wieland et al. 1988; Oelkers 2001; Köhler et al. 2003).

Increased soil acidity will trigger increased weathering, which in turn increases soil pH, thus constituting a negative feedback loop. While this “weathering feedback” is implemented in the MAGIC model (Cosby et al. 2001), it is not used when calculating the acidity status of surface waters (F. Moldan IVL pers. com.). Our study indicates that including this feedback may have significant effects on the predicted values of ΔpH and ΔANC (Table 4). Interestingly, including this feedback mechanism may allow a better fit to the observed time series of cations, e.g., the Ca time series at Gårdsjön (Fig. 4). This improvement might have also been achieved by changing the initial BS or potentially by changing the Al–Ca exchange constants. This is by no means proof that weathering feedback is actually occurring, but this process can be verified by experiment in contrast to changing the initial unmeasured base saturation for 1860 or the apparent Ca–Al exchange constant. The model-fitted BC release rates were affected significantly when weathering feedback was included; the weathering rate required to reproduce the same BC balance were on average 30% lower than in the absence of such a process.

The Effect of Modeled Aluminum Fluxes on Surface Water pH and ANC

Changes in pH per se are often less of a concern than increases in inorganic Al with decreasing pH, which is why

the mobility and fluxes of Al were incorporated into MAGIC. Aluminum may be mobilized from soil under acidic conditions or bound to triprotic organic acid analogs (anions: H_2A^- , HA_2^- , A_3^-) in the form of AlA or AlHA^+ , which can be taken into account in MAGIC (Eqs. 4, 5). When these organic Al complexes are exposed to a different ambient pH, such as may arise through degassing of CO_2 in MAGIC, or released to an environment with an apparent lower solubility of $\text{Al}(\text{OH})_3(\text{s})$ in the stream compartment, the following reactions may occur:

An analysis of modeled proton transfer from the soil to the stream using the above reactions indicates that around 37 meq m^{-2} of protons are produced per year on average at the Aneboda site (18 meq m^{-2} on average at Kindla and Gårdsjön and 6 meq m^{-2} at Gammtratten). Analysis of the net reaction for the precipitation of $\text{Al}(\text{OH})_3$, after correction for the average runoff in 1860 and 2000, indicated that this process tends to decrease the calculated ΔANC at Gårdsjön, Gammtratten, and Kindla by 15, 11, and 7 meq m^{-3} . On the other hand, inclusion of the hypothetical $\text{Al}(\text{OH})_3$ precipitation process at the Aneboda site resulted in a decrease of more than 25% in the total ANC, depending on which scenario was considered.

Geochemical equilibrium calculations using visual Minteq and Al speciation data from Aneboda indicated that gibbsite ($K_{\text{sp}} = 8.29$ at 10°C) was undersaturated at all times. A recent study (Sjöstedt et al. 2010) has shown that gibbsite supersaturation occurs at pH 6 and above. Based on data from Kindla, Löfgren and Cory (2010) suggested cationic Al is formed due to decomplexation of organic Al when the groundwater discharges into the more acidic stream. Assuming equilibrium with gibbsite when running MAGIC at sites with high organic acidity in combination

Fig. 4 Comparison between MAGIC modeled (solid squares) and measured annual flow weighted values (open squares) from various MAGIC scenarios (SET II). Upper graphs: Ca^{2+} concentrations in meq m^{-3} in the stream at Gårdsjön with (a, right) and without weathering feedback (b, left). Lower graphs: pH with (c, right) and without (d, left) decreasing K_{sp} of $\text{Al}(\text{OH})_3$ in the stream at Kindla by one order of magnitude

with a natural low pH (such as may be encountered in many headwater forest streams and mires) would lead to significant systematic errors if a secondary phase is not actually present. Cosby et al. (2001) have commented that the solubility product constant may be implemented in the MAGIC model as an aggregated value of both ion exchange and solubility.

Wright and Cosby (2003) have remarked that the choice of solubility product constant of the $\text{Al}(\text{OH})_3$ phase has a significant effect on runoff chemistry. In the default parameter list of MAGIC 7.77 aluminum solubility is the same in the soil and the stream. Wright and Cosby (2003) used a lower solubility in the soil compared with the stream effectively excluding $\text{Al}(\text{OH})_3$ precipitation, whereas Whitfield et al. (2006, 2011) did the opposite. Varying the solubility product constant of the hypothetical $\text{Al}(\text{OH})_3$ phase resulted in an improved fit for the pH at Kindla (Fig. 4), but this change had a large effect on predicted ΔpH , increasing it by 0.5. The fitting of apparent solubility product constants needs to be verified by other available data such as aluminum speciation or mineralogical analysis.

CONCLUSIONS

MAGIC was used to model element fluxes at the four Swedish IM sites between 1860 and 2010 using a calibration period of 1996–2008. Trends in pH and ANC were driven mostly by deposition and model scenarios and by no means provide a quantitative estimate of historic patterns of acidification. Measured and modeled amounts of soil BC agreed within 75% and element fluxes during the calibration period were within 15%. Varying the model setup using different amounts of BC, adding weathering feedback or changing the apparent solubility of $\text{Al}(\text{OH})_3$, all have significant effects on the outcome of the model. The results of the model indicate that predicted values of pH and ANC have a precision around 0.3 and 20 meq m^{-3} , respectively. Little is known about how natural acidification through BC uptake during periods of forest growth may affect estimates of ΔpH and ΔANC . The arbitrary choice of 1860 as a reference year, where forests are considered to be at steady state, may need to be reconsidered since human impact on forestry was quantitatively important. The model results revealed that allowing weathering feedbacks to occur at more acidic pH has significant effects on weathering rate estimates for all cations, and thus affects assumptions about depletion of the BC pool. Additional systematic differences arise when unrealistic Al fluxes from the soil to the stream are affected by the choice of apparent Al solubility product constants. It would be valuable to investigate the effects of weathering feedback and Al fluxes in more detail.

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REFERENCES

- Aherne, J., R.C. Helliwell, A. Lilly, R.C. Ferrier, and A. Jenkins. 2007. Simulation of soil and surface water acidification: divergence between one box and two-box models? *Applied Geochemistry* 22: 1167–1173.
- Akselsson, C., O. Westling, H. Sverdrup, and P. Gundersen. 2007. Nutrient and carbon budgets in forest soils as decision support in sustainable forest management. *Forest Ecology and Management* 238: 167–174.
- Anon. 2008. Historic deposition data for the EMAP 50*50 km Grid. Coordination Centre for Effects, Netherlands Environmental Assessment Agency, Bilthoven, The Netherlands.
- Bastviken, D., P. Sandén, T. Svensson, C. Ståhlberg, M. Magounakis, and G. Öberg. 2006. Chloride-retention and release in a boreal forest soil: effects of soil water residence time and nitrogen and chloride loads. *Environmental Science and Technology* 40: 2977–2982.
- Berner, R.A. 1967. Comparative dissolution characteristics of carbonate minerals in the presence and absence of aqueous magnesium ions. *American Journal of Science* 265: 45–70.
- Cosby, B.J., G.M. Hornberger, J.N. Galloway, and R.F. Wright. 1985a. Modeling the effects of acid deposition—assessment of a lumped parameter model of soil-water and streamwater chemistry. *Water Resources Research* 21: 51–63.
- Cosby, B.J., R.F. Wright, and E. Gjessing. 1985b. An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. *Journal of Hydrology* 170: 101–122.
- Cosby, B.J., R.C. Ferrier, A. Jenkins, and R.F. Wright. 2001. Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrology and Earth System Sciences* 5: 499–517.
- Ferm, M., and H. Hultberg. 1995. Method to estimate atmospheric deposition of base cations in coniferous throughfall. *Water, Air, and Soil pollution* 85: 229–2234.
- Ferm, M., and H. Hultberg. 1999. Dry deposition and internal circulation of nitrogen, sulphur and base cations to a conifer forest. *Atmospheric Environment* 33: 4421–4430.
- Fölster, J., C. Andrén, K. Bishop, I. Buffam, N. Cory, W. Goedkoop, K. Holmgren, R. Johnson, et al. 2007. A novel environmental quality criterion for acidification in Swedish lakes—an application of studies on the relationship between biota and water chemistry. *Water, Air, and Soil pollution* 7: 331–338.
- Forsius, M., M. Alveteg, A. Jenkins, M. Johansson, S. Kleemola, A. Lükewille, M. Posch, H. Sverdrup, et al. 1998. MAGIC, SAFE and SMART model application at integrated monitoring site: effects of emission reduction scenarios. *Water, Air, and Soil pollution* 105: 21–30.
- Granat, L. 1988. Luft- och nederbördskemiska stationsnätet inom PMK. Rapport från verksamheten 1988. Rapport no 3649. Stockholm (in Swedish, English summary).
- Grimvall, A. 2004. *FLOWNORM 2.0—A visual basic program for computing riverine loads of substances and extracting anthropogenic signals from time series of load data*. Linköping: Department of Mathematics, Linköping University.

- Hellsten, S., and O. Westling. 2006. Försurande och övergödande nedfall i skog. Delprogram Krondropp inom programområdet luft. Sakrapport 2006-06-01 för naturvårdsverket, IVL, Göteborg (in Swedish, English summary).
- Hodson, M.E., and S.J. Langan. 1999. Considerations of uncertainty in setting critical loads of acidity of soils: the role of weathering rate determination. *Environmental Pollution* 106: 73–81.
- Hruska, J., S. Köhler, H. Laudon, and K. Bishop. 2003. Is a universal model of organic acidity possible: Comparison of acid/base properties of dissolved organic carbon in the boreal and temperate zones. *Environmental Sciences & Technology* 37: 1726–1730.
- Jenkins, A., T. Larssen, F. Moldan, J. Hruska, P. Kram, and S. Kleemola. 2003. *Dynamic modelling at integrating monitoring sites—model tested against observations and uncertainty*. Helsinki: Finnish Environment Institute.
- Grandin, U. 2011a. Epiphytic algae and lichen cover in boreal forests—a long-term study along a N and S deposition gradient in Sweden. *AMBIO*. doi:10.1007/s13280-011-0205-x.
- Grandin, U. 2011b. Understorey vegetation stability and dynamics in unmanaged boreal forests along a deposition gradient in Sweden. *AMBIO*. doi:10.1007/s13280-011-0206-9.
- Klaminder, J., R.W. Lucas, M.N. Futter, K.H. Bishop, S.J. Köhler, G. Egnell, and H. Laudon. 2011. Silicate mineral weathering rate estimates: are they precise enough to be useful when predicting the recovery of nutrient pools after harvesting? *Forest Ecology and Management* 261: 1–9.
- Kram, P., K. Bishop, and F. Moldan. 2001. Modeling long-term streamwater chemistry in the Berg catchment, southwestern Sweden. Paper presented at the Nordic hydrological conference (Uppsala, Sweden, June 2000), vol. 32, 249–264.
- Köhler, S.J., F. Dufaud, and E.H. Oelkers. 2003. An experimental study of Illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C. *Geochimica et Cosmochimica Acta* 67: 3583–3594.
- Laudon, H., J. Hruska, S. Köhler, and P. Kram. 2005. Retrospective analyses and future predictions of snowmelt-induced acidification: example from a heavily impacted stream in the Czech republic. *Environmental Science and Technology* 39: 3197–3202.
- Lind, B.B., and L. Lundin. 1990. Saturated hydrological conductivity Scandinavian tills. *Nordic Hydrology* 21: 107–118.
- Löfgren, S., L. Bringmark, M. Aastrup, H. Hultberg, K. Kindbom, and H. Kvarnäs. 2001. Sulphur balances and dynamics in three forested catchments in Sweden. *Water, Air, and Soil pollution* 130: 632–636.
- Löfgren, S., and N. Cory. 2010. Groundwater Al dynamics in boreal hillslopes at three integrated monitoring sites along a sulphur deposition gradient in Sweden. *Journal of Hydrology* 380: 289–297.
- Löfgren, S., M. Aastrup, L. Bringmark, H. Hultberg, L. Lewin-Pihlblad, L. Lundin, G.P. Karlsson, and B. Thunholm. 2011. Recovery of soil water, groundwater and streamwater from acidification at the Swedish Integrated Monitoring catchments. *AMBIO*. doi:10.1007/s13280-011-0207-8.
- Löfblad, G., C. Persson, and E. Roos. 2000. Deposition of base cations in Sweden. Swedish Environmental Protection Agency report 5119, Stockholm.
- MAGIC library 2010. <http://www.ivl.se/tjanster/datavardskap/magicbiblioteket/magicbiblioteket/ingaendesjoarochvattendrag.4.7df4c4e812d2da6a416800077587.htm>. Retrieved 20 Oct 2010
- Martinson, L., M. Alveteg, and P. Warfvinge. 2003. Parameterization and evaluation of sulfate adsorption in dynamic soil chemistry model. *Environmental Pollution* 124: 119–125.
- Moldan, F., V. Kronnäs, A. Wilander, E. Karlton, and B.J. Cosby. 2004. Modelling acidification and recovery of Swedish lakes. *Water, Air, and Soil Pollution, Focus* 4: 139–160.
- Monteith, D.T., J.L. Stoddard, C.D. Evans, H.A. de Wit, M. Forsius, T. Hogasen, A. Wilander, B.L. Skjelkvale, et al. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450: 537–540.
- Mörth, C.M., P. Torssander, and H. Kusakabe. 1999. Sulfur isotope values in a forested catchment over four years: Evidence for oxidation and reduction processes. *Biogeochemistry* 44: 51–71.
- Mosello, R., M. Amoriello, T. Amoriello, S. Arisci, A. Carcano, N. Clarke, J. Derome, K. Derome, et al. 2005. Validation of chemical analysis of atmospheric deposition in forested European sites. *Journal of Limnology* 64: 93–102.
- Oelkers, E.H. 2001. General kinetic description of multioxide silicate minerals and glass dissolution. *Geochimica et Cosmochimica Acta* 65: 3703–3719.
- Parkhurst, D. 1998. PHREEQC (Version2)—A computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical calculations. http://www.bcr.usgs.gov/projects/GWC_coupled/phreeqc/index.html.
- Persson, C., M. Ferm, and O. Westling. 2004. Förbättrad mätning och beräkning av belastningen av försurande och övergödande luftföroreningar. Specialprojekt på uppdrag av Naturvårdsverkets miljöövervakningsenhet, SMHI och IVL. Göteborg (in Swedish).
- Rhode, A. 2003. Flow paths of waters in Swedish forests. *Kungliga Skogs- och Lantbruksakademiens Tidskrift* 142: 23–29.
- Schott, J., R.A. Berner, and E.L. Sjöberg. 1981. Mechanism of pyroxene and amphibole weathering—I. *Experimental studies of iron free minerals*. *Geochimica et Cosmochimica Acta* 45: 2123–2135.
- Sjöstedt, C.S., J.P. Gustafsson, and S.J. Köhler. 2010. Chemical equilibrium modeling of organic acid, pH, aluminum, and iron in Swedish surface waters. *Environmental Science and Technology* 44: 8587–8593.
- Sverdrup, H. U. Johnson & Felming. 1942. The Oceans. In *Handbook of chemistry and physics*, ed. R.C. Weast. Cleveland: Prentice Hall.
- Sverdrup, H. 2009. Chemical weathering of soil minerals and the role of biological processes. *Fungal Biology Reviews* 23: 94–100.
- Thimonier, A., M. Schmitt, P. Waldner, and P. Schleppe. 2008. Seasonality of the Na/Cl ratio in precipitation and implications of canopy leaching in validating chemical analyses of through-fall samples. *Atmospheric Environment* 42: 9106–9117.
- Ulrich, B. 1983. Interaction of forest canopies with atmospheric constituents: CO₂, alkali and earth alkali cations and chloride. In *Effects of accumulation of air pollutants in Forest Ecosystems*, ed. B. Ulrich and J. Pankrath, 13. Boston: Reidel.
- Viers, J., B. Dupre, J.-J. Braun, R. Freydisier, S. Greenberg, J. Ngoupayou, and L. Nkamdjou. 2001. Evidence for non-conservative behavior of chlorine in humid tropical environment. *Aquatic Geochemistry* 7: 127–154.
- Whitehead, P.G., B. Reynolds, M. Hornung, C. Neal, J. Cosby, and P. Paricos. 1988. Modeling long-term stream acidification trends in upland Wales at Plynlimon. *Hydrological Processes* 2: 357–368.
- Whitfield, C.J., S.A. Watmough, S.A. Aherne, and P.J. Dillon. 2006. A comparison of weathering rates for acid-sensitive catchments in Nova Scotia, Canada and their impact on critical load calculations. *Geoderma* 136: 899–911.
- Whitfield, C.J., J. Aherne, P.J. Dillon, and S.A. Watmough. 2007. Modelling acidification, recovery and target loads for headwater catchments in Nova Scotia, Canada. *Hydrology and Earth Systems Sciences* 11: 951–963.
- Whitfield, C.J., J. Aherne, B.J. Cosby, and S.A. Watmough. 2011. Modelling boreal lake catchment response to anthropogenic acid deposition. *Journal of Limnology* 69(suppl. 1): 135–146.
- Wieland, E., B. Wehrli, and W. Stumm. 1988. The coordination chemistry of weathering: III. A potential generalization on

dissolution rated of minerals. Geochimica et Cosmochimica Acta 52: 1969–1981.

- Wright, R.F., B.J. Cosby, R.C. Ferrier, A. Jenkins, A.J. Bulger, and R. Harriman. 1994. Changes in acidification of lochs in Galloway, Southwestern Scotland, 1979–1988: the Magic model used to evaluate the role of afforestation, calculate critical loads, and predict fish status. *Journal of Hydrology* 161: 257–285.
- Wright, R.F., and B.J. Cosby. 2003. Future recovery of acidified lakes in southern Norway predicted by the MAGIC model. *Hydrology and Earth System Sciences* 7: 467–483.
- Wright, R.F., and B.J. Cosby. 2004. Recovery of acidified mountain lakes in Norway as predicted by the MAGIC model. *Journal of Limnology* 63: 101–110.

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