

Modelling reversibility of Central European mountain lakes from acidification: Part I - the Bohemian forest

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Abstract

A dynamic, process-based acidification model, MAGIC7, has been applied to three small, strongly acidified lakes in the Bohemian Forest, the Czech Republic. The model was calibrated for a set of experimental records on lake water composition over the 1984–2000 period, and produced hindcast concentrations that compared well, even with older (40-year) irregular determinations of nitrate, chloride and pH. Water and soil chemistry forecasts up to 2050 were based on reductions in S and N emissions presupposed by the Gothenburg Protocol. Modelled sulphate and chloride concentrations were predicted to decrease to the levels at the beginning of the 20th century by 2050. The lake water carbonate buffering system is predicted to be re-established in only two lakes (Cerné and Plešné), with current soil base saturations of 12–15%. Concentrations of ionic aluminium species decreased sharply, from 110 $\mu\text{eq l}^{-1}$ in the mid-1980s to the current $\sim 40 \mu\text{eq l}^{-1}$, and were predicted to decrease below 10 $\mu\text{eq l}^{-1}$ in the 2020s. Diatom-inferred pH in pre-industrial times was substantially lower than modelled pH. It is suggested that the diatom pH, based almost entirely on non-planktonic species, is biased by inwash of diatoms from more acidic tributaries into the sediment of these small lakes. Generally significant results can be summarised as follows: (1) Simulated sulphate levels agree well with observations during acidification progress and retreat only for values of soil SO_4^{2-} adsorption capacity three to six times (20 to 40 meq kg^{-1}) higher than those found experimentally. This implies a further mechanism of S retention and release in addition to physical sulphate adsorption to Fe and Al oxides of soils. (2) The catchments' ability to retain deposited N appeared to decline after ~ 1950 but this was not connected with a sufficient change in the C : N ratio of the soils. Agreement between modelled and observed concentrations of nitrate was therefore achieved by empirical restriction of N retention in the soils. Based on their current ability to retain N, the catchments will remain N-saturated and could, temporarily, produce more inorganic N than they receive due to additional nitrate production from soil N-organic pools. This situation has occurred already in the Cerné Lake catchment. (3) Differences in responses of individual lakes can be attributed to different land usages over the past several centuries as well as to differences in geology and primary production.

Keywords: MAGIC, atmospheric deposition, N retention, diatom-inferred pH, sulphate, nitrate, base cations, aluminium, Czech Republic

Introduction

Extremely high emissions of sulphur (S) and nitrogen (N) compounds ($\sim 280 \text{ mmol m}^{-2} \text{ yr}^{-1}$ each) declined by $>70\%$ and $\sim 35\%$, respectively, in the central European region of Germany, Poland, Czech Republic and Slovakia between the second half of the 1980s and the late 1990s (Barrett *et al.*, 2000). The reduction in atmospheric inputs of S and N to mountain ecosystems has resulted in a pronounced reversal of the acidification of fresh waters in this region (Veselý *et al.*, 2002), including the Tatra Mountains and Bohemian Forest lakes (Kopáček *et al.*, 1998; Veselý *et al.*, 1998a,b). These mountain lakes responded most quickly to a decrease in S input and were the only European lakes

exhibiting significantly decreasing trends in NO_3^- over the 1990s (Evans *et al.*, 2001; Prechtel *et al.*, 2001). Despite this rapid decline in lake water concentrations of strong acid anions, their concentrations were substantially higher than expectations based on observed concentrations at comparable emission rates during the development of acidification (Kopáček *et al.*, 2002a). This hysteresis in chemical reversal from acidification was predominantly associated with a washout of S accumulated in soils and N-saturation of their catchments (Kopáček *et al.*, 2001a). Consequently, mineralisation and desorption of S accumulated in soils and a decreasing ability of N-saturated terrestrial ecosystems to retain N have become the most

important processes affecting soil and water quality in these mountain regions, as has been observed elsewhere (e.g. Stoddard, 1994; Alewell *et al.*, 2000).

The leaching of S to surface waters and the resulting changes in acid-base chemistry can be simulated with the original model of MAGIC (Modelling the Acidification of Groundwater in Catchments, Cosby *et al.*, 1985). On the other hand, the N dynamics oriented model MERLIN (Model of Ecosystem Retention and Loss of Inorganic Nitrogen, Cosby *et al.*, 1997) provides a rigorous treatment of N cycling. The later model, however, requires a large amount of information on N and C pools and cycles, which is usually lacking (Wright *et al.*, 1998). The new MAGIC7 (Cosby *et al.*, 2001) offers a satisfactory compromise between the original MAGIC and MERLIN, allowing the simulation of changes in acid-base water chemistry associated with changing S and N deposition trends (Wright *et al.*, 1998).

The Bohemian Forest and Tatra Mountains represent unique mountain-forest and alpine ecosystems, respectively, with a high potential of lake water reversal from acidification due to the pronounced reductions in S and N deposition since the late 1980s (Kopáček *et al.*, 2001a). In this Part I, MAGIC 7 (Cosby *et al.*, 2001) is applied to modelling historical changes in lake water and forest soil chemistry in three catchments of the Bohemian Forest lakes and to simulating future (until 2050) responses to different scenarios of acid deposition. In Part II (Kopáček *et al.*, 2003), a similar simulation is presented for four representative alpine catchments in the Tatra Mountains.

Methods

SITE DESCRIPTION

In the Bohemian Forest at the Czech-German-Austrian border, there are eight small glacial lakes situated between 48°47' and 49°11' N, and 13°07' and 13°52' E, at elevations of 918–1096 m a.s.l. The following three lakes were included in this study: (1) Cerné Lake (CN), the largest; (2) Certovo Lake (CT), the most acid; and (3) Plešné Lake (PL), with the highest trophic status due to a higher loading of phosphorus (P) and dissolved organic carbon from natural terrestrial sources than in other lakes. The selected lakes are dimictic, drainage, oligotrophic (CN and CT) or mesotrophic (PL) water bodies, with theoretical water residence times between 0.7 and 1.6 years and with three to nine surface tributaries (Kopáček *et al.*, 2001b,c,d).

CT and CN Lakes are situated on opposite sides of the same mountain and their catchments are steep with maximum local reliefs of 313 m and 335 m, respectively.

The bedrock is formed primarily of mica-schist (muscovitic gneiss) in the CN catchment, and mica-schist with quartzite intrusions in the CT catchment (Veselý, 1994). The PL catchment has a maximum local relief of 288 m and its bedrock is formed of granite. All three catchments were covered with local glaciers during the last glacial period (Veselý, 1994). More than 90% of the catchments have 90–160 years old forest cover, dominated by Norway spruce, with a minor contribution of mountain-ash and beech. For more morphological details on the lakes and their catchments see Table 1 and Veselý (1994).

SOIL CHEMISTRY

Soil samples were taken from all major organic and mineral horizons at sites representative for particular parts of the CT, CN, and PL catchments (11, 8, and 12 soil profiles, respectively) between September 1997 and May 2001. More details on heterogeneity in the soil distribution were obtained by grid samplings in regular 50 × 50 m (PL) and 75 × 75 m (CT) grids. The vertical and spatial heterogeneity of soil properties within a soil profile and across the whole catchment, respectively, was 'homogenised' numerically to provide a catchment weighted mean (CWM) composition. This catchment weighting generates a single value for each parameter, representing a hypothetical situation in which all soils are uniformly distributed over the whole catchment. The physical and chemical characteristics of soils in the lake catchments were determined as described in detail by Kopáček *et al.* (2002b,c).

The CT catchment was found to be covered predominantly with ~0.5 m deep spodo-dystric cambisol (58% of area) and podzol (21% of area), and shallow (~0.2 m) undeveloped organic rich soil (17% of area). Wetland covered <3% of the CT catchment area. The dominant contribution of spodo-dystric cambisol and podzol, and negligible wetland areas were also evident in the CN catchment. The PL catchment area was covered with an undeveloped ~0.2 m deep organic rich soil (38% of area), and ~0.45 m deep podzol (29% of area) or spodo-dystric cambisol (27% of area). Wetland and bare rocks covered 1% and 5% of the catchment area, respectively.

Fine soil was sandy, with a low (1–4%) content of clay, and CWM soil pools were 225, 143, and 92 kg m⁻² in the CT, CN, PL catchments, respectively. Soil pH was generally low, with the lowest pH_{CaCl2} values (2.5–3.3) in the humus horizon. The CWM cation exchange capacity of the CT and CN soils was 104 and 123 meq kg⁻¹, respectively, and was dominated by exchangeable Al³⁺ (62% and 55%). The CWM base saturation of the CT and CN soils was 9% and 15%, respectively. It was primarily based on exchangeable Ca²⁺

Table 1. Major morphological characteristics and measured or estimated soil parameters for the Bohemian Forest lakes (Kopáček *et al.*, 2001b,c,d) and their catchments (Kopáček *et al.*, 2002b,c; Kana, personal communication).

Parameter	Units	Lake		
		CERNÉ	CERTOVO	PLEŠNÉ
<i>Morphology</i>				
Latitude (N)		49°11'	49°10'	48°47'
Longitude (E)		13°11'	13°12'	13°52'
Water level elevation	m	1008	1028	1090
Lake volume	10 ⁶ m ³	2.88	1.85	0.62
Maximum depth	m	40	36	18
Lake area	ha	18.4	10.3	7.5
Retention time	yr	1.63	1.58	0.73
Catchment area (including lake)	ha	129	86	67
<i>Soil Parameters</i>				
Soil depth	m	0.53	0.65	0.33
Porosity ¹⁾	%	50	50	50
Bulk density	kg m ⁻³	269	345	281
Fine soil pool	kg m ⁻²	143	225	92
Cation exchange capacity	meq kg ⁻¹	125	106	130
Ca saturation	%	6.6	4.3	8.8
Mg saturation	%	2.6	1.8	2.3
Na saturation	%	1.1	1.0	2.2
K saturation	%	2.2	2.1	1.9
Used SO ₄ ads. half-saturation ¹⁾	meq m ⁻³	100	100	100
Measured SO ₄ ads. max-capacity	meq kg ⁻¹	12	6.4	6.0
Used SO ₄ ads. max-capacity ¹⁾	meq kg ⁻¹	40	20	40
Total organic acid ²⁾	mmol m ⁻³	85	85	85
C pool	mol m ⁻²	1120	1350	936
N pool	mol m ⁻²	50	59	39
Average C:N of soil profile	mol mol ⁻¹	22	23	24
<i>In-lake sedimentation velocity</i>				
Ca	m yr ⁻¹	0.09	0.18	0.32
Mg	m yr ⁻¹	0.09	0.33	0.37
N	m yr ⁻¹	1.37	2.02	6.80

¹⁾Fitted in the model calibration procedure or set (porosity).

²⁾Estimated according to Hruška *et al.* (2002) for the measured soil organic content.

(~50%), and the contribution of Mg²⁺ and K⁺ was roughly equal (~20%). The CWM cation exchange capacity of the PL soils was 129 meq kg⁻¹, 15% of which was base saturated, and was dominated by exchangeable Al³⁺ (57%) and protons (28%). The CWM carbon to nitrogen (C:N) ratio was 23, 22, and 24 for the whole CT, CN, and PL soil profiles, respectively, and varied between 23 and 33 in the forest floor. The CWM pools of C and N are given in Table 1.

The SO₄²⁻ sorption characteristics of catchment soils were determined in batch experiments according to Alewell

(1998). Sorption experiments were conducted with fresh samples at the original soil pH in the sulphate concentration range of 0-100 µmol l⁻¹.

LAKE WATER CHEMISTRY

The historical data (before 1984) on lake water concentrations come from Jírovec and Jírovcová (1937), Veselý (1994), and Procházková and Blažka (1999) and have been found to be reasonably reliable (Veselý and Majer,

1992; Procházková and Blažka, 1999). Lake water concentrations in the 1984–2001 period are from a regular monitoring programme (Veselý *et al.*, 1998a,b; unpublished data). Data on terrestrial and in-lake sources and sinks of elements were based on their mass budgets in the 2000 hydrological year (Kopáček *et al.*, 2001b,c,d). The concentration of organic acid anions (A) in lake water was assumed to be proportional to DOC (42 meq per mol of DOC; Kopáček, unpublished data). Since 1984, concentrations of total aluminium (Al_T) were determined by inductively coupled plasma atomic emission spectrometry. In parallel, Al fractionation according to Driscoll (1984) has been analysed in a filtrate ($<0.4 \mu\text{m}$ pore size) regularly since 1993 to determine the proportion of dissolved inorganic Al (Al_i), organically bound Al (Al_o), and particulate ($>0.4 \mu\text{m}$) Al (Al_{part}) in the total Al pool. Equivalent concentrations of Al_i (Al_i^{n+}) were obtained from their molar concentrations and the average charge of Al hydroxocomplexes (n) at the sample pH (Stumm and Morgan, 1981). In-lake concentrations of Al_i before 1993 were estimated from the measured Al_T concentrations, assuming a similar $Al_T : Al_i$ ratio as observed after 1993. These $Al_T : Al_i$ ratios were 1.04, 1.14, and 1.28 for CT, CN, and PL Lake, respectively. The Al_i^{n+} concentrations before 1993 come from: 1984, Veselý *et al.* (1998b); and 1988–1989, Fott *et al.* (1994).

ATMOSPHERIC DEPOSITION

The 1860–2000 trends in bulk and throughfall deposition of SO_4^{2-} , NH_4^+ , and NO_3^- come from Kopáček *et al.* (2001a).

The respective trends in the Cl^- deposition were assumed to be proportional to the deposition of S, with the S : Cl ratios obtained for the bulk and throughfall deposition in the catchments studied. The trend in the bulk deposition of BC was based on (1) relationships between BC concentrations in precipitation in the Bohemian Forest (Hruška *et al.*, 2000; Kopáček, unpublished data) and at long-term monitored sites in the Czech Republic, and (2) the emission rate of particulates from Czech industrial sources, taken from Yearbooks of the Czech Statistical Office (data after 1980) and was assumed to be proportional to the S emission before 1980. Then, the deposition trend of BC was calculated as the sum of background BC deposition (originating from agricultural sources) plus industrial BC deposition. The background bulk deposition of BC ($\sim 25 \text{ meq m}^{-2} \text{ yr}^{-1}$) was estimated by extrapolating the relationship between bulk BC and S depositions (for the 1985–2000 period) to the S deposition equalling zero.

Throughfall deposition of Ca^{2+} , Mg^{2+} , K^+ , and NH_4^+ is usually affected strongly by canopy processes (e.g. Lovett, 1992; Dise *et al.*, 1998). In the Bohemian Forest, the average ratio between concentrations of conservative ions (SO_4^{2-} , Cl^- , and Na^+) in throughfall and bulk deposition was ~ 1.7 in the 1997–2000 period (Kopáček *et al.*, 2001b). This ratio was used to estimate the proportion of dry deposition of Ca^{2+} , Mg^{2+} and K^+ ions, concentrations of which were increased in throughfall by canopy leaching. The same approach was used to estimate dry deposition of NH_4^+ , which was negatively affected by canopy interactions (its concentration was only 20% higher in throughfall than in bulk samples). Consequently, atmospheric inputs of BC and

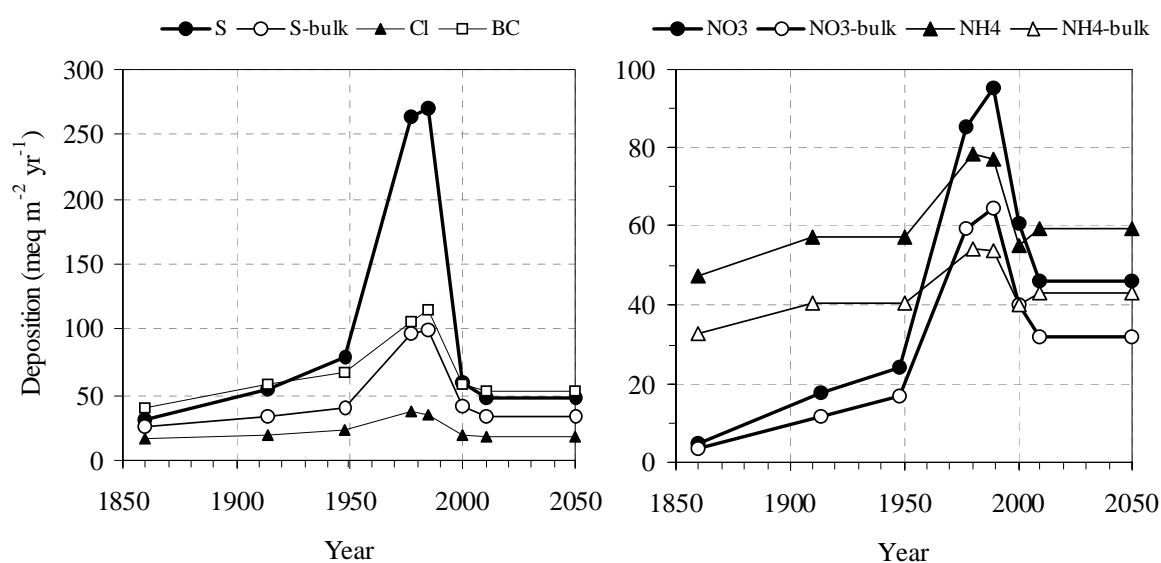


Fig. 1. Long-term trend in total (and bulk SO_4 -S and NO_3 -N) atmospheric deposition of major ions in the catchments of the Bohemian Forest used for MAGIC modelling.

NH_4^+ into the forested parts of catchments were assumed to be 1.7-fold higher than bulk deposition and this constant was used for the whole 1860–2000 period.

Two scenarios of element deposition were used for future (2000–2050) predictions: (1) Constant trends at 2000 deposition levels and (2) decreasing deposition until 2010 and then constant until 2050. The decrease in deposition of S and N compounds from 2000 to 2010 was assumed to be proportional to the decrease in their respective emission levels in the central European region (Germany, Poland, Czech Republic, and Slovakia) as required by the Gothenburg Protocol (UN-ECE, 1999). This simplified approach was used because atmospheric deposition of S and N compounds in central Europe originates predominantly (65% to 85%) from emissions within the region (Berge, 1997). The future changes in the Cl^- and BC deposition were assumed to be proportional to changes in S deposition.

Total chemical input into the catchment-lake ecosystem of the Bohemian Forest lakes from atmospheric sources was calculated from the estimated trends in throughfall and bulk deposition onto the respective areas of forest and bare surface (including the lake). This input was assumed to be roughly equal for all three lakes studied, because the morphological parameters of their catchments (Table 1), as well as precipitation chemistry at CT and PL Lakes (Kopáček *et al.*, 2001b,d), were similar. The resulting trends in total atmospheric input of SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , and BC, including their decrease according to the Gothenburg Protocol, are given in Fig. 1.

The average annual precipitation height and runoff was assumed to be 1.50 and 1.35 m, respectively, constant over the 1860–2050 period. These values were based on (1) the average throughfall deposition in the CT catchment in the 1992–2001 period, (2) long-term (1961–2001) precipitation in the central part of the Bohemian Forest (Churánov station, 49°04' N; 13°37' E; 1122 m a.s.l.), and (3) water balance (evaporation) calculated for the catchment-lake ecosystems studied (Kopáček *et al.*, 2000, 2001b,c,d).

Results and discussion

MODEL CALIBRATION

The MAGIC (version 7) model by Cosby *et al.* (2001) was calibrated using measured deposition, long-term data on lake water chemistry from 1984 to 2000, and soil composition for the year 2000 (Table 1). The fixed parameters (Table 2) were selected or set empirically and calibrations at each site proceeded by the following sequential steps:

(1) Trends in the total deposition of SO_4^{2-} , Cl^- , NO_3^- , NH_4^+ ,

and BC into the catchments were applied as shown in Fig. 1. At the beginning of the Industrial Revolution, reduced nitrogen compounds dominated the sum of emitted and deposited S and N compounds in central Europe. Atmospheric inputs of SO_4^{2-} and NO_3^- increased steadily until the late 1950s and then, very sharply (3 to 4-fold) between the 1950s and 1980s to ~ 270 and ~ 95 $\text{meq m}^{-2} \text{ yr}^{-1}$, respectively. The increase in NH_4^+ deposition was less than that of NO_3^- , which led to a change in deposition quality of dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) from that dominated by $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ domination since the 1960s (Fig. 1). Hence, the total DIN deposition and its $\text{NO}_3\text{-N}:\text{NH}_4\text{-N}$ ratio increased 2 and 3-fold, respectively, between the 1950s and 1980s.

In the 1990s, atmospheric inputs of S and DIN decreased by 80% and $\sim 30\%$ to 60 and ~ 110 $\text{meq m}^{-2} \text{ yr}^{-1}$, respectively, in the Bohemian Forest. Due to this rapid decline, the 2010 target emissions of S and N compounds (Gothenburg Protocol; UN-ECE, 1999) were nearly reached in central Europe by the late 1990s, and only small additional decreases can be expected for SO_4^{2-} and NO_3^- deposition (Fig. 1). In contrast, the current emission rate of NH_3 in central Europe is lower than the 2010 target and the future scenario of NH_4^+ deposition is a slight increase. Around 2010, the SO_4^{2-} , NH_4^+ , and NO_3^- deposition in the Bohemian Forest will reach levels comparable to those in the

Table 2. Fixed parameters (measured* or estimated) for the Bohemian Forest lakes and catchment soils used in calibration of MAGIC 7.

Parameter	For water or soil	Units	All lakes
Precipitation height*		m	1.50
Annual discharge*		m	1.35
Temperature*	water	°C	5.6–6.0
	soil	°C	4.5
CO_2 partial pressure	water	atm	0.0005
	soil	atm	0.0045
pK_1 (organic acids)	soil and water	-Log	2.6
pK_2 (organic acids)	soil	-Log	5.66
pK_2 (organic acids)	water	-Log	5.8
pK_3 (organic acids)	soil	-Log	5.94
pK_3 (organic acids)	water	-Log	7.0
Solubility $\text{Al}(\text{OH})_3$	soil and water	Log	9.0
K(AIA)	water	Log	8.5
K(AIHA ⁺)	water	Log	10.0

1890s, the first half of the 20th century, and the 1950s, respectively (Fig. 1).

- (2) Net annual retention of Ca, Mg, and N in the lakes (Table 1) was estimated from their concentrations in surface sediments and sedimentation rates (Kopáček *et al.*, 2001b,c,d), and were held constant for the whole period.
- (3) The measured SO_4^{2-} adsorption half saturation and maximum adsorption capacity varied from 2000 to 2200 meq m^{-3} and from 6 to 12 meq kg^{-1} , respectively (Kana, personal communication). These adsorption maxima were too low for the model to predict properly the observed delay between SO_4^{2-} deposition and in-lake concentrations during both the acidification advance and retreat. Consequently, in the calibration procedure, soil sulphate chemistry (as well as other ions) was fitted such that modelled concentration equalled the measured concentration in lake water during the 1984–2000 period. The fitted values of SO_4^{2-} maximum adsorption capacity, which simulated, reasonably, the observed trends in lake water chemistry, were 3 to 6-fold higher than the measured adsorption data (20–40 meq kg^{-1}). This pattern suggests other effective mechanisms immobilising S in the forest floor organic matter (Novák *et al.*, 1996; Torssander and Mörth, 1998) or in basic aluminium sulphates (Nordstrom, 1982), which paralleled the physical adsorption of SO_4^{2-} on Fe and Al oxides.

The measured in-lake reduction of SO_4^{2-} varied between 143 and 214 $\text{meq m}^{-2} \text{yr}^{-1}$ (on a lake surface area basis), representing 13% of the total (terrestrial and atmospheric) SO_4^{2-} input in CT and PL Lakes and 22% in CN Lake in 2000 (Kopáček *et al.*, 2001b,c,d). These values were too high to model the SO_4^{2-} concentration maxima in the 1980s satisfactorily. Alternatively, a ~5% in-lake reduction of SO_4^{2-} was estimated from SO_4^{2-} loading and mass transfer coefficient of 0.54 m yr^{-1} according to Kelly *et al.* (1987). The best agreement between the measured and simulated concentrations was obtained with a 5% in-lake reduction of SO_4^{2-} in PL and CT Lakes and a 20% reduction in CN Lake. The lower in-lake reduction of SO_4^{2-} (both measured and simulated) in PL and CT Lakes was due to anoxic conditions in their hypolimnion. Sulphate reduction in the sediment is the most effective in-lake sink of SO_4^{2-} when water above the sediment is under oxic conditions (Kelly and Rudd, 1984). Under anoxia, sulphate concentrations decreased above the bottom of CT and PL Lakes (Kopáček *et al.*, 2001b,d), which limited the SO_4^{2-} diffusion into

sediments and, consequently, its more effective reduction.

- (4) Nitrogen leaching to surface water depends on the difference between N-input via deposition and its uptake by plants, denitrification loss, and net immobilisation in the soil (Cosby *et al.*, 2001). Net immobilisation of N in the soil is assumed to be governed in the model by the C : N ratio. The estimated relatively small change in the soil C:N ratios from ~25 to 22–24 in the 1930–2000 period (Kopáček *et al.*, 2001a), however, did not allow the model to simulate the observed dramatic changes in lake water NO_3^- concentrations. There are no data available to evaluate historical changes in the ability of terrestrial parts of the Bohemian Forest catchment-lake ecosystems to immobilise or lose N (e.g. changes in plant uptake of N or mineralisation rate of soil organic N pools). Hence, net retention of DIN in the catchment was set empirically such that modelled NO_3^- concentrations equalled the measured concentrations throughout the study period (Fig. 2). For the 2000–2050 period, the net N retention in the catchment was assumed to be the same as in 2000.
- (5) Weathering rates, cation-exchange selectivity coefficients for base cations, and the original base saturation of soils were determined by a trial-and-error procedure such that the modelled pools and

Table 3. Calibrated parameters for the Bohemian Forest lakes obtained from MAGIC 7.

	Units	Lake		
		CERNÉ	CERTOVO	PLEŠNÉ
<i>Cation exchange selectivity coefficients</i>				
Al-Ca	Log	-1.82	-1.87	-1.68
Al-Mg	Log	-0.57	-0.53	-1.09
Al-Na	Log	-3.37	-3.66	-3.81
Al-K	Log	-5.43	-5.68	-5.28
<i>Weathering rates</i>				
Ca^{2+}	$\text{meq m}^{-2} \text{yr}^{-1}$	16.0	1.8	33.2
Mg^{2+}	$\text{meq m}^{-2} \text{yr}^{-1}$	41.5	32.4	18.2
Na^+	$\text{meq m}^{-2} \text{yr}^{-1}$	12.0	2.1	21.4
K^+	$\text{meq m}^{-2} \text{yr}^{-1}$	2.0	0.0	1.3
Initial base saturation (1860)				
Ca	%	11.9	5.4	17.4
Mg	%	6.0	3.4	4.9
Na	%	1.4	1.0	2.7
K	%	2.2	1.8	1.9

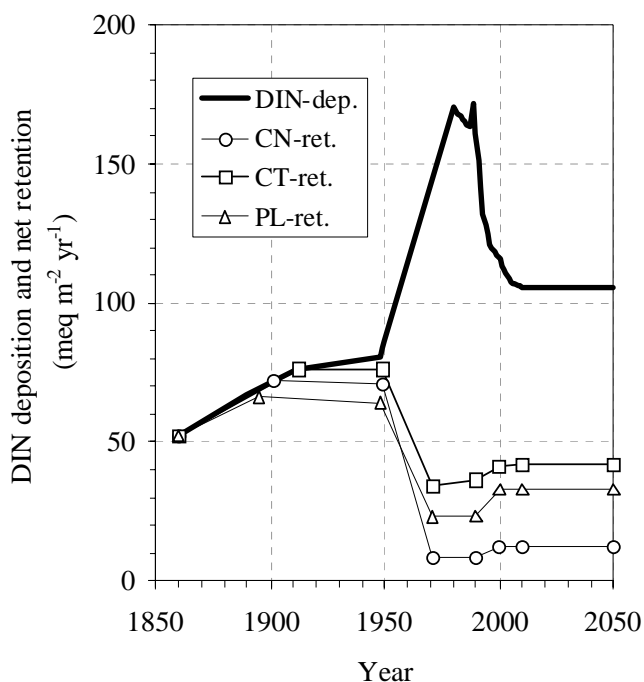


Fig. 2. Trends in atmospheric deposition of dissolved inorganic nitrogen ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$; DIN-dep.) and the assumed DIN retention in the catchments of Cerné, Certovo, and Plešné Lakes (CN-ret., CT-ret., and PL-ret., respectively).

concentrations equalled the measured soil exchange pools and lake chemistry concentrations of each base cation for the year 2000. This step was performed using an automated optimisation routine and the results are given in Table 3. Because the vegetation uptake of BC was set equal to zero in the optimisation, the resulting weathering rates represented a net difference between the BC supply by the real weathering processes and the BC sink by vegetation uptake.

- (6) Fixed parameters (Table 2): Dissociation constants of tri-protic organic acids and $\text{Al}(\text{OH})_3$ solubility were selected within widely used ranges (e.g. Sullivan *et al.*, 1996; Wright *et al.*, 1998) and further fitted in the MAGIC calibration procedure. Stability constants of organic-Al complexes ($\text{K}(\text{AlA})$ and $\text{K}(\text{AlHA}^+)$) were set empirically within the set of published data (e.g. Browne and Driscoll, 1993; Nordstrom and Howard, 1996), such that the modelled concentrations equalled the measured concentrations of Al_1^{III} and Al_0 in lake water. Concentrations of A^- were adjusted by optimising the pK values of the tri-protic organic acid such that modelled concentrations equalled the measured concentrations.

MODELLING OF NITROGEN DYNAMICS

The observed lake water concentrations of NO_3^- in 1936 were below the detection limit of the analytical method used at the time ($< 2 \mu\text{eq l}^{-1}$) (Jírovec and Jírovcová, 1937; Veselý and Majer, 1992). The elevated NO_3^- concentrations in the beginning of 1960s (Procházková and Blažka, 1999) were determined by a more reliable method, based on the colorimetric determination of NO_2^- after NO_3^- reduction with alkaline hydrazine (Procházková, 1959). The changes in these values suggest that catchments of the Bohemian Forest lakes started to leach NO_3^- between the 1930s and the late 1950s, in the period of sharp increase in NO_3^- deposition (Fig. 1). Consequently, the net retention of DIN was set equal to its deposition in the 1860–1900 period and slightly lower than its deposition (to fit the observations from the 1930s) in the 1900–1950 period (Figs. 2 and 3). For these two periods, it was assumed that the terrestrial ecosystem was adapted to a relatively high and stable NH_4^+ deposition, for more than a hundred years before the 1950s (Fig. 1). The hypothesis is that the terrestrial ecosystems were N-limited or in steady state conditions in respect of DIN deposition, which was dominated by NH_4^+ and around the empirical threshold of $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$, below which NO_3^- leaching from European forest soils is usually low (e.g. Dise *et al.*, 1998).

The catchments studied were unable to retain and assimilate the rapidly increasing NO_3^- input already present in 1960s, which resulted in the elevated terrestrial export of NO_3^- (Fig. 3). This change was probably not associated with any significant change in the soil C:N ratios (Kopáček *et al.*, 2001a) and more likely reflected a simple dose-response function. Nitrate is a more mobile ion than NH_4^+ and its relatively short residence time in the catchments studied (shallow soils and steep terrain) probably disables its assimilation. However, the decreasing ability of the catchments to assimilate N (Kopáček *et al.*, 2002a) suggests that this simple dose-response function changed with time. While the ecosystems assimilated $\sim 70 \text{ meq m}^{-2} \text{ yr}^{-1}$ of DIN at the beginning of 20th century, the DIN assimilation was substantially lower ($< 20 \text{ meq m}^{-2} \text{ yr}^{-1}$) in the late 1990s. The PL catchment still assimilated $\sim 16\%$ of the deposited DIN but the CT catchment exported nearly all deposited DIN, and the CN catchment produced $\sim 28\%$ more DIN than it received by atmospheric input (Kopáček *et al.*, 2001b,c,d). This suggests that the net terrestrial production of NO_3^- was higher than the retention of atmospheric NH_4^+ in the CN catchment, probably due to additional NO_3^- production from the pool of soil organic N.

In the model, it is assumed that the elevated deposition of NO_3^- after the 1950s (Fig. 1) led to a gradual transition of

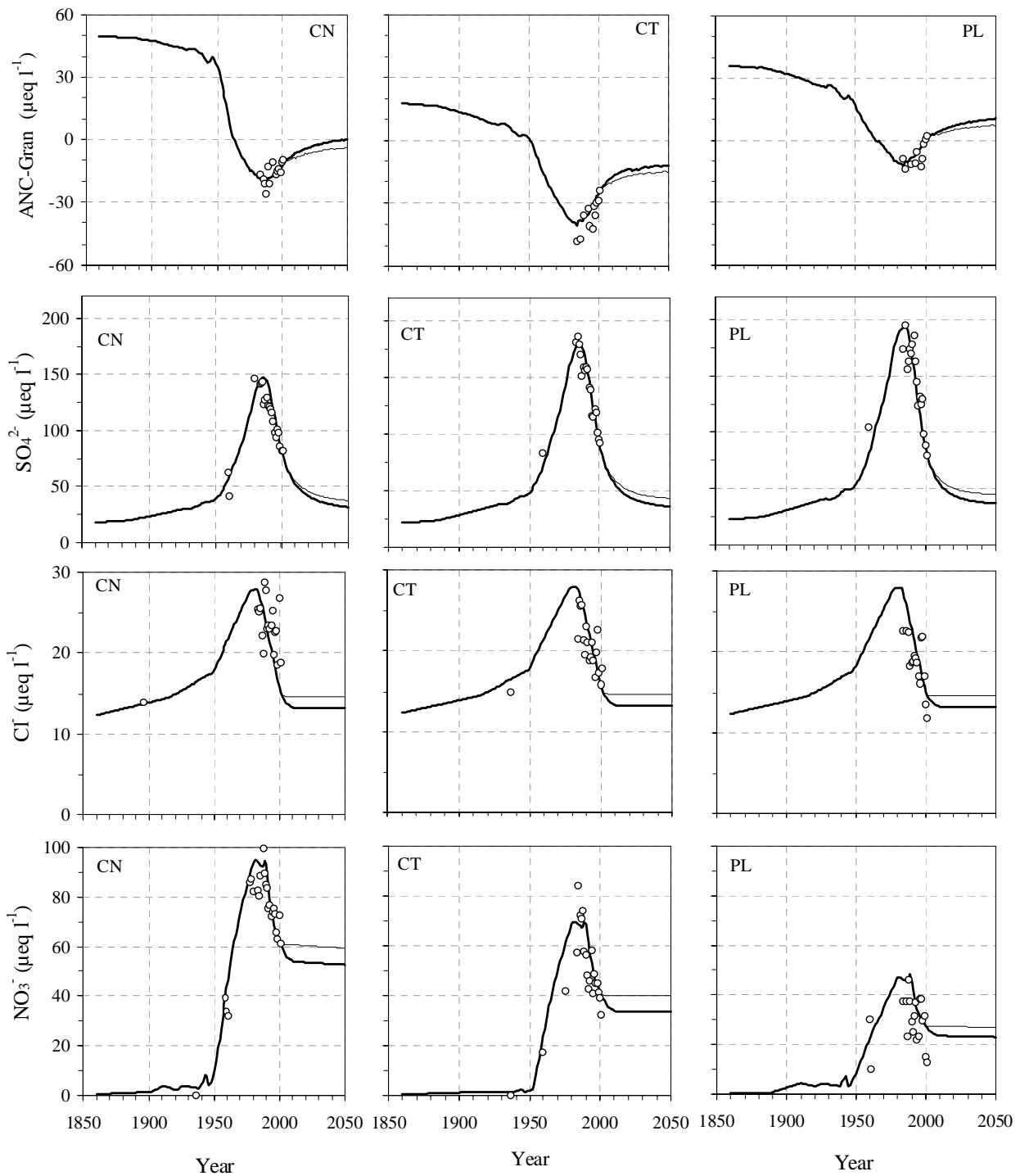


Fig. 3. Measured (open circles) and modelled (lines) trends in major anions in the Bohemian Forest Lakes. Forecasts are based on the 2000 deposition level (thin line) and the decreased S and N deposition proportionally to their emission rate in central Europe according to Gothenburg Protocol (UN-ECE, 1999) (heavy line). ANC-Gran represents measured and/or modelled Gran alkalinity. Lake abbreviations refer to: CN, Cerné; CT, Certovo; and PL, Plešné.

the forest ecosystems from N-limitation to N-saturation and to a decreasing ability to retain N (Fig. 2). The elevated terrestrial NO_3^- export may be associated with a decreased ability of the catchments to assimilate N, e.g. due to

unfavourable soil conditions for forest growth (extremely low Ca : Al ratios in soil solutions; see later), or with changes in the mineralisation rate of soil organic N due to elevated DIN deposition, as has been observed elsewhere (e.g.

Gundersen *et al.*, 1998a). Thus, the empirical DIN retention within the Bohemian Forest soils (Fig. 2) represents a net difference between the potentially reduced sinks and the elevated internal sources of nitrogen.

The NO_3^- concentrations in the Bohemian Forest lakes decreased more than the DIN deposition during the 1990s. A similar response of ecosystem export of NO_3^- to declining DIN deposition was observed in other mountain areas of the Czech Republic (Veselý *et al.*, 2002). To simulate the current lake water concentrations of NO_3^- , a slight recovery in the ecosystem's ability to retain N was expected in response to the decline in DIN deposition (Fig. 2).

The prediction of lake water NO_3^- concentrations was set to the current N cycling situation within the ecosystems and was based on the assumption that the ecosystem N retention characteristic would not change (Fig. 2). However, any future changes in the ecosystem ability to immobilise N (e.g. in the vigour of forest microbial activity) can bias the forecasts given in Fig. 3 (see also Norton and Veselý, 2003).

The current characteristics of NO_3^- leaching from the Bohemian Forest soils fit well the empirical relationships (e.g. Dise and Wright, 1995; Gundersen *et al.*, 1998a,b) which link the N leaching from European sites to N deposition, soil C : N ratios, and pH (Kopáček *et al.*, 2001a). Nevertheless, none of these factors can explain fully the observed differences between the catchments and historical changes in N export from the Bohemian Forest soils during the periods of increasing or decreasing DIN deposition. Modelling of these trends is based here on empirical experience and not on causalities and processes. Although this approach enables a detailed reconstruction of lake water chemistry, it can predict the future changes with only limited significance until the processes involved in N cycling are better understood.

MODELLED V. OBSERVED LAKE WATER COMPOSITION

Observed and modelled lake water concentrations of major anions are shown in Fig. 3. Concentrations of SO_4^{2-} and Cl^- paralleled deposition trends, increasing from their respective background concentrations of 18–23 and 12 $\mu\text{eq l}^{-1}$ to maxima in the 1980s, and then decreasing to the current concentrations of 84–98 and 13–18 $\mu\text{eq l}^{-1}$. The modelled trends predicted an additional sharp decrease in SO_4^{2-} concentrations by the late 2010s (Fig. 3). With no additional reduction in S and Cl emission in central Europe after 2010, concentrations of Cl^- ions will stabilise at $\sim 13 \mu\text{eq l}^{-1}$, and SO_4^{2-} concentrations will decrease slowly to 32–37 $\mu\text{eq l}^{-1}$ over the next 40 years, approaching new steady state conditions in the soil S pool. Simulated trends in SO_4^{2-} and

Cl^- concentrations agree reasonably well with observations both during the acidification advance and retreat.

Simulated trends in ANC (Gran alkalinity) fit the observations reasonably and follow inverse pattern to the trends in strong acid anions (Fig. 3). The modelled lake water ANC values vary between 17 and 49 $\mu\text{eq l}^{-1}$ in 1860. Compared to the current situation, the model predicts a relatively rapid additional increase in ANC by the late 2010s, after which ANC concentrations level off at substantially lower than pre-acidification levels. According to these predictions, positive ANC can be expected only in the PL and CN lakes (Fig. 3).

The changes in concentration of strong acid anions and ANC are partly compensated for by changes in BC, H^+ , and Al_i^{n+} concentrations (Fig. 4). All the modelled cation concentrations fit the observations during the acidification retreat. The only reliable historical results on cation analyses are those with colorimetric pH determinations (Procházková and Blažka, 1999). With the exception of slightly higher measured pH in CN Lake in 1936 and 1947, MAGIC also simulates, reasonably, the in-lake pH decline during the acidification progress. The simulated pre-acidification pH values vary between 6.0 and 6.7 in 1860. These values are surprisingly more than one pH unit higher than diatom-inferred pH, which indicates a pre-industrial pH of around 4.7 in CT Lake (Veselý *et al.*, 1993) and 5.0–5.3 in CN lake (Schmidt *et al.*, 1993). Such a difference is atypically high compared to other sites where the MAGIC and diatom-inferred pH trends exhibited comparable values (Cumming *et al.*, 1992; Sullivan *et al.*, 1996).

This discrepancy indicates that the processes controlling acidity in small lakes may be more complex than previously thought. The diatom-inferred pH of the lakes is based almost entirely on non-planktonic (benthic, epilithic, periphytic and metaphytic) species. The actual lake water pH may be underestimated because: (1) Benthic or epilithic diatoms could grow in tributaries (or at their mouths), which are generally more acidic and have higher P concentrations than lake water (e.g. Kopáček *et al.*, 2001b,c,d). (2) Periphytic or metaphytic diatoms could grow on macrophytes in littoral zones, also affected by more acidified tributaries. (3) In small lakes, with a high shoreline to area ratio, these diatom sources are relatively more important for the total in-lake diatom production than in larger lakes. Moreover, these diatoms can be more easily transported secondarily to the sediments in the deepest parts of small lakes. Such processes could contribute significantly to the observed prevalence of acidobiontic or acidophilous diatoms in the sediment cores and, therefore, to the underestimation of inferred pH of the lakes studied.

The modelled concentrations of dissolved Al (sum of Al_i

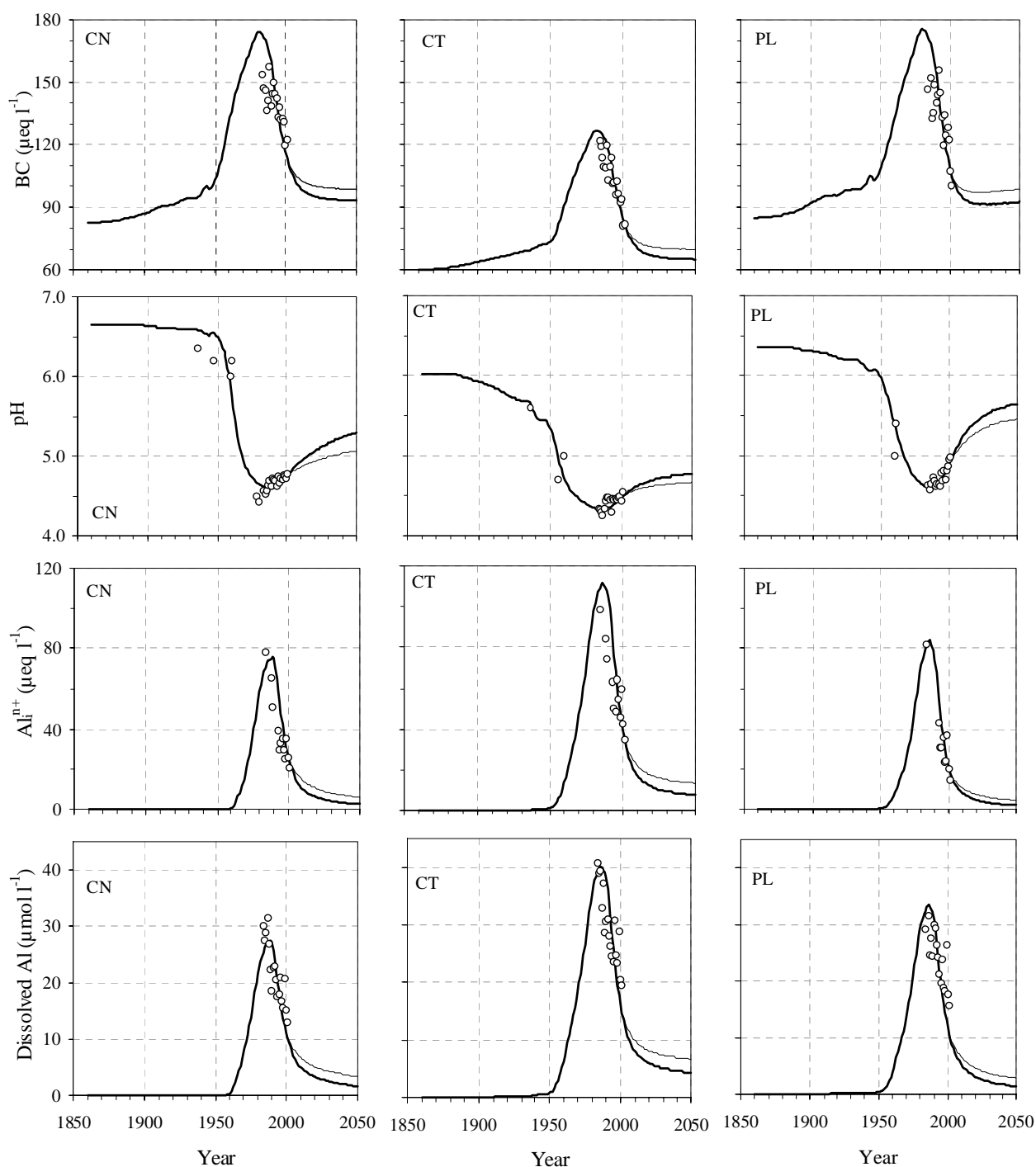


Fig. 4. Measured (open circles) and modelled (lines) trends in major cations in the Bohemian Forest Lakes. Forecasts are based on the 2000 deposition level (thin line) and the decreased S and N deposition proportionally to their emission rate in central Europe according to Gothenburg Protocol (UN-ECE, 1999) (heavy line). Lake abbreviations refer to: CN, Cerné; CT, Certovo; and PL, Plešné.

and Al_0) and Al_1^{n+} were $<1 \mu\text{mol l}^{-1}$ and $<2 \mu\text{eq l}^{-1}$, respectively, before 1950 and reached their maxima of 27–40 $\mu\text{mol l}^{-1}$ and 75–111 $\mu\text{eq l}^{-1}$ in the mid-1980s (Fig. 4). The current Al concentrations have declined ~50–70% compared to these maxima. The model predicts a further

sharp decline in Al concentrations by 2010, after which the Al_1^{n+} concentrations will be comparable to those in the late 1950s ($<10 \mu\text{eq l}^{-1}$). Such a decline in concentrations of the most important toxicant in lake water is promising for the biological recovery of the lakes studied. Biological recovery

of the lakes, however, is delayed substantially compared to the chemical reversal. Up to the present, increasing numbers of only *Ceriodaphnia quadrangula* in CN Lake and planktonic rotifers in PL Lake have been observed (Vrba *et al.*, 2003).

Despite the relatively advanced chemical reversal from

acidification, all the lakes are still acidic. The changes in relative ionic composition of the lakes (Fig. 5) suggest that bicarbonate was depleted in CN and PL Lakes before the 1960s and in CT Lake even a decade earlier. During the acidification peak, SO_4^{2-} dominated (55–70%) the anionic pool and Al_i^{n+} was the major cation (30–40% of the sum of

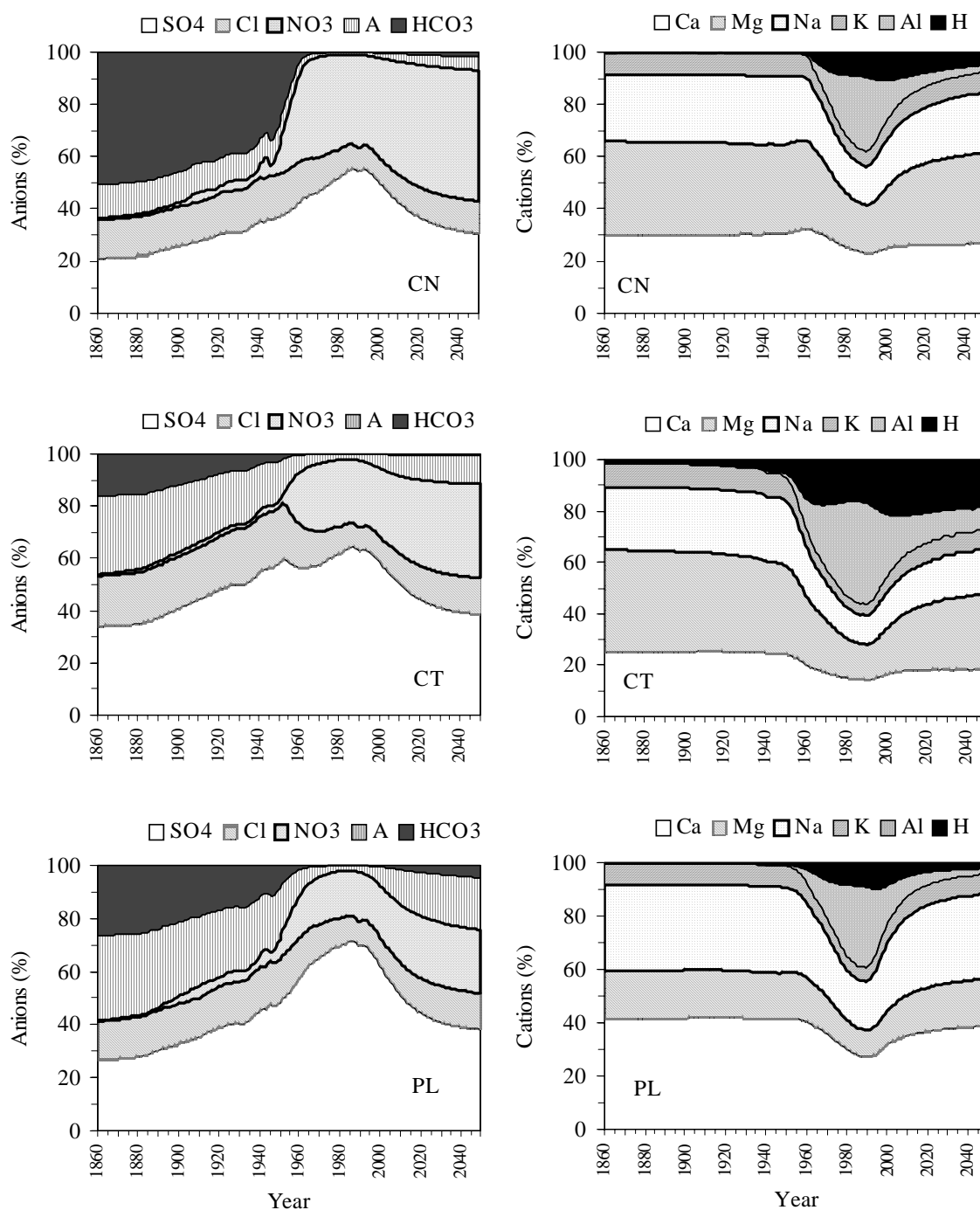


Fig. 5. Relative composition of water in the Bohemian Forest Lakes as simulated by MAGIC model. The 2000–2050 forecasts is based on S and N deposition level proportional to central Europe emission rate according to Gothenburg Protocol (UN-ECE, 1999). Lake abbreviations refer to: CN, Cerné; CT, Certovo; and PL, Plešné.

cations). The modelled changes predict the increasing importance of NO_3^- to become the dominant anion in CN and CT Lakes around 2050, and a partial recovery of the bicarbonate buffering system in CN and PL Lakes. These changes will be accompanied by a rapidly decreasing importance in the Al_1^{n+} contribution and an increasing contribution of BC to the cationic pool. A pronounced increase in pH will probably occur in PL Lake only (Figs. 3 and 4).

TRENDS IN SOIL CHEMISTRY

Among the lakes studied, the chemical composition of soil and soil solutions differ significantly (Fig. 6). The modelled pre-acidification soil base saturation is highest (27%) in PL Lake and lowest (11%) in CT Lake. Similarly, loss of BC from the soil cation-exchange sites is most pronounced in PL Lake while relatively flat in CT Lake. Both the current and 'Gothenburg' scenarios of the future emission rates of S and N compounds in central Europe result in similar trends in base saturation of the Bohemian Forest soils (Fig. 6). These predictions suggest a gradual accumulation of BC in

the CN and PL soils, resulting in a slow increase in their base saturation. Even in 2050, however, base saturation of the CN and PL soils will be ~40% lower than levels in 1860. No increase in base saturation is predicted for the CT soils (Fig. 6), suggesting that the decreases in emissions expected by the Gothenburg protocol will only stop the depletion of the exchangeable BC pool, but will be insufficient for its recovery. Similar results are also evident from other very strongly acidified forest sites (e.g., Hruška *et al.*, 2002).

A low molar Ca to Al ratio in soil solutions ($\text{Ca} : \text{Al} < 1$) is another ecologically important parameter, indicating possible adverse impacts of soil chemistry on tree growth and tissue nutrient concentrations (e.g. Puhe and Ulrich, 2001). The modelled Ca : Al values are >1 only in the CN and PL soils and only until the 1950s and 1970s, respectively, while lower values obtain for CT soils throughout the whole 1860–2050 period (Fig. 6). Similarly to base saturation of soils, the trend in soil solution Ca : Al ratio, most pronounced in the PL catchment and flattest in the CT catchment, exhibits signs of a future increase only in the PL and CN soils.

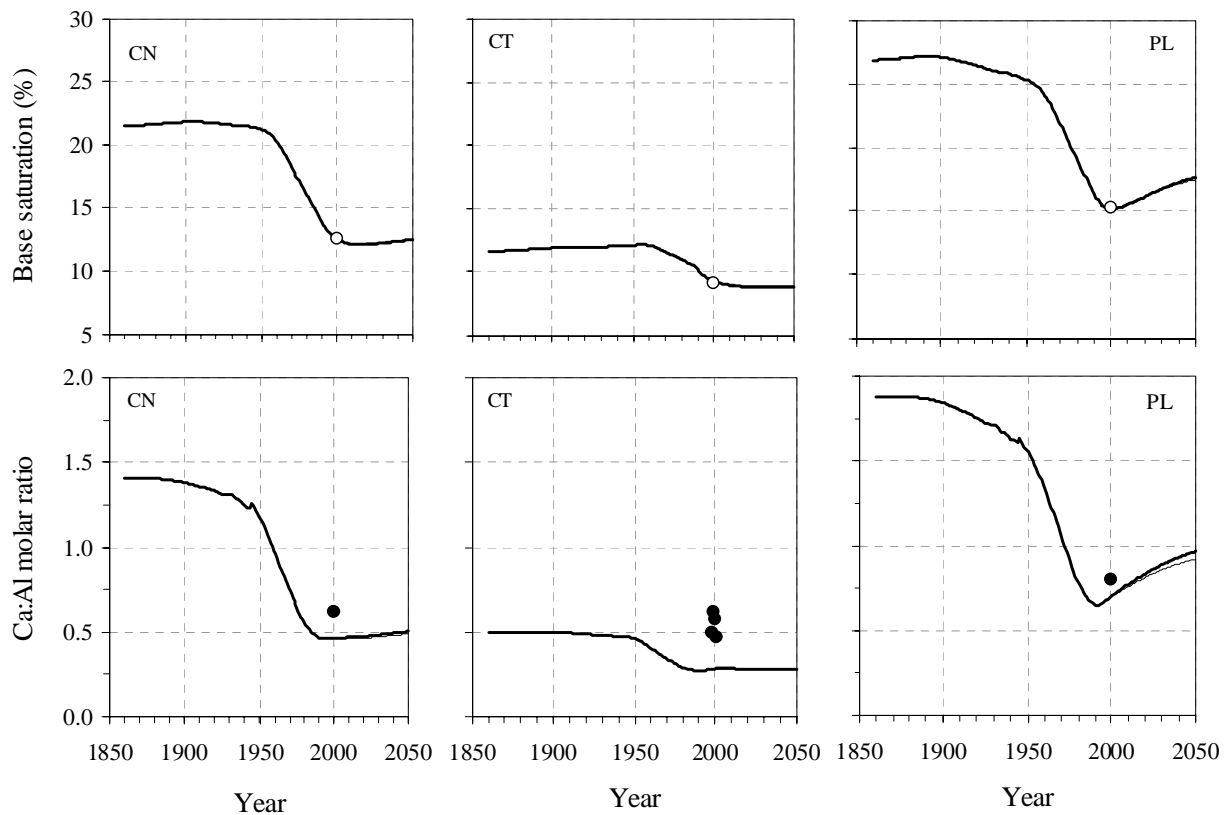


Fig. 6. Measured (open circles) and modelled (lines) trends in soil chemistry in the Bohemian Forest Lakes. Forecasts are based on the 2000 deposition level (thin line) and the decreased S and N deposition proportionally to their emission rate in central Europe according to Gothenburg Protocol (UN-ECE, 1999) (heavy line). Black circles in lower panel represent the Ca:Al ratios in lake tributaries (annual discharge weighted means). Lake abbreviations refer to: CN, Cerné; CT, Certovo; and PL, Plešné.

Soil solutions were not analysed in this study. Instead, the modelled data have been compared with annual discharge weighted mean values of Ca : Al ratios in the lake tributaries (Kopáček *et al.*, 2001b,c,d). These values (black points in Fig. 6), are higher than the Ca:Al ratios in soil solutions due to a partial contribution of overflow to the runoff without percolating through the mineral soil horizons. Even the Ca:Al ratios in lake tributaries, however, show a pattern similar to the modelled data, being higher in the CN and PL than in CT tributaries.

According to the MAGIC simulation for the next five decades, the desirable reversal of Ca : Al ratios in soil solutions toward ~ 1 can be expected only in the PL catchment (situated on granite) but will remain < 0.5 in the CT and CN catchments, underlain with mica schist. This difference is due to (i) the lower depletion of the soil exchangeable Ca pools in the PL than CN and CT catchments (Table 1), (ii) the two-fold higher content of Ca in granite than in mica schist (0.11 vs. ~ 0.06 mol kg⁻¹; Kopáček *et al.*, 2002b,c) and (iii) significantly higher repletion of the soil pools of Ca by weathering in the PL catchment (Table 3).

LAKE TO LAKE VARIATIONS IN THE REGION

Atmospheric deposition of S and oxidised N compounds (Fig. 1) is the major driving force governing the in-lake concentrations of major ions, which exhibit similar trends in all lakes (Figs. 3 and 4). Despite the same deposition history and comparable morphological characteristics of the ecosystems studied (Table 1), the chemical composition of lake waters differs significantly. These differences are associated predominantly with bedrock composition, land use history (affecting both soil and water composition), and in-lake processes (associated with nutrient loading) as follows:

(1) *Soils, weathering, and land-use history* – Concentrations of SO₄²⁻ and NO₃⁻ differ among the lakes studied, but lakes with lower NO₃⁻ concentrations have higher SO₄²⁻, which results in comparable concentrations of strong acid anions (e.g. 255–275 µeq l⁻¹ during the acidification peak, Fig. 3). The ecosystems differ in the way this acidity is compensated for with cations. While the responses of the CN and PL catchment-lake ecosystems are comparable despite the different bedrock, CT Lake (with bedrock similar to CN Lake) is most acidified, has lowest concentrations of BC, and highest Al_i^{nat} concentrations (Fig. 4). Moreover, the modelled pH exhibits a continuously decreasing trend in CT Lake from the late 19th century to the 1980s (Fig. 4). The different response of the CT ecosystem to neutralise acid loads resulted from a substantially lower base saturation of soils (Fig. 6).

The difference in soil composition between the geographically adjacent CT and CN Lakes may well result from lower weathering rates and different land-use history. The CT catchment was deforested more than the CN catchment in the first half of the 18th century and was used as pasture for about 100 years. Pasturing and burning of bushes probably contributed to a continual decrease in the base saturation of the catchment soils. Another depletion of the CT soil pools of BC was probably associated with the subsequent draining and re-forestation of the CT catchment with spruce in the middle 19th century. This process led to the accumulation of BC from the soil exchangeable pools in the rapidly growing forest. Moreover, repletion of the soil BC pool from weathering was less effective in the CT than the CN catchment, because part of the CT bedrock is quartzite.

The less rapid acidification-derived changes in CN than in CT Lake could also be attributed partly to return-water pumping by a power station into CN Lake during the 1930–1975 period (water from the lake was partly mixed with less acidified river water). However, the similar patterns of the modelled and measured pH trends in CN and unaffected PL Lake (Fig. 4) suggest that this land-use aspect had probably only a limited effect on the acid-base chemistry of CN Lake.

(2) *In-lake processes* – The most pronounced difference in the chemistry of the lakes studied was associated with NO₃⁻ concentration, which was lowest in PL Lake (Fig. 3). Part of this difference was due to the higher ability of the PL catchment to assimilate N. Consequently, PL Lake had a lower input of DIN compared to the other two lakes. In the 2000 hydrological year, the total DIN input (via tributaries and direct atmospheric deposition) was 780 and 1030 meq m⁻² yr⁻¹ (given on a lake surface area basis) in PL and CN Lakes, respectively (Kopáček *et al.*, 2001c,d). In-lake removal of NO₃⁻, calculated according to Kelly *et al.* (1987) with a mass transfer coefficient for colder lakes (5 m yr⁻¹; Curtis *et al.*, 1998), suggests a 29–35% internal reduction of these DIN loads. The primary mechanism of this DIN reduction is NO₃⁻ diffusion into the sediments followed by denitrification under anoxic conditions. The measured internal reduction of DIN was 28%, 33%, and 50% in CN, CT, and PL Lakes, respectively, in the 2000 hydrological year (Kopáček *et al.*, 2001b,c,d). While the empirical and estimated values are well comparable in CN and CT Lakes, a substantially higher in-lake reduction in the DIN loads was observed in PL Lake. The latter lake received \sim five-fold higher loads of phosphorus (predominantly in the form of soluble reactive P), leading to higher primary production. The resulting assimilation of N by algae and their

sedimentation represents another significant sink for DIN in PL Lake, which is also evident from the higher N sedimentation rate in this lake (Table 1).

Conclusions

The chemistry of Bohemian Forest lakes has exhibited significant changes toward chemical reversal from atmospheric acidification since the late 1980s. The MAGIC model forecasts further advancement in this process for about the next two decades. Sulphate leaching and BC export from soils should decline to their levels at the beginning of the 20th century, and Al_1^{nt} concentrations in lake water to their levels in the 1950s. Only in two of the three lakes studied will these changes be sufficient for the re-establishment of the bicarbonate buffering system and pH increase over the unit of 5. These lakes (CN and PL) have less depleted soil BC pools, which can partly recover in the 2000–2050 period. In contrast, the more acidified CT catchment-lake ecosystem will recover more slowly. Until 2050 (and probably even several decades longer), soil base saturation will not increase in the CT catchment and the lake water bicarbonate buffering system will not be re-established.

While the measured trends in pH and ANC, SO_4^{2-} , Cl^- , Al_1^{nt} , and BC concentrations are simulated reasonably by MAGIC 7, historical simulations of NO_3^- are speculative due to the changing ability of the terrestrial parts of ecosystems studied to assimilate nitrogen, which is not associated with significant changes in the soil C : N ratios. Without more detailed knowledge of current N-cycling within the forest soils and potential mechanisms that can affect the terrestrial immobilisation of N, future predictions of NO_3^- leaching are hypothetical. Undoubtedly, NO_3^- will become the dominant strong acid anion in the Bohemian Forest lakes over the next five decades and the major carrier of BC from soils. Climatic, chemical or physiological (e.g. forest die-off) changes, however, can affect the future terrestrial NO_3^- export significantly and invalidate the prognoses based on the current situation.

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