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Modelling long-term changes in stream water and soil chemistry in catchments with contrasting vulnerability to acidification (Lysina and Pluhuv Bor, Czech Republic)

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Abstract

In two Czech catchments covered by Norway spruce forests, the MAGIC model was used to simulate annual stream water and soil chemistry for the period 1851–2030. These two sites represent geochemical end-members of ecosystem sensitivity to acidification (acid-sensitive granitic Lysina catchment vs. acid-resistant serpentinitic Pluhuv Bor catchment). Although the total deposition of sulphur to the catchments declined by 75% between 1990 and 2002, the recovery of stream water pH was relatively small over this period. At Lysina, the annual discharge-weighted mean pH of stream water increased only from 3.92 to 4.01, although SO_4 concentration declined very sharply from 570 μeq L^{-1} in 1990 to 150 μeq L^{-1} in 2002. Stream water buffering was caused mainly by dissociation of organic acids. At Pluhuv Bor, the annual mean pH varied inversely with the annual discharge. Stream water concentrations of SO_4 declined dramatically at Pluhuv Bor, from 1040 μeq L^{-1} in 1992 to 220 μeq L^{-1} in 2002. Using atmospheric deposition as specified in the Gothenburg Protocol, the model predicts that, at Lysina, stream water pH will increase to 4.3 and soil base saturation will increase to 6.0% by 2030 (from 5.6% in 2002); corresponding pre-industrial stream water pH was simulated to be 5.5 and soil base saturation to be 25%. At Pluhuv Bor, the pre-industrial pH was estimated to be 7.2 and the corresponding base saturation was 94%. Large anthropogenic acidification in the 20th century caused only a small decline in pH (to 6.9) and base saturation (to 88%). Simulations in accordance with the Gothenburg Protocol predict that the pH should increase by 0.2 pH units and the base saturation by 1% by 2030. Under this protocol, critical loads of atmospheric deposition for SO_4 and NO_3 will not be exceeded at Pluhuv Bor but will be exceeded at Lysina.

Keywords: MAGIC model, catchment, critical loads, Gothenburg Protocol, soil and water acidification, granite, serpentinite, Czech Republic

Introduction

Environmental disorders resulting from atmospheric deposition of pollutants have been documented in Europe (Moldan and Schnoor, 1992; Evans *et al.*, 2001; Prechtel *et al.*, 2001). In Central Europe, acidic deposition and widespread occurrence of spruce plantations are two major factors causing the acidification and nutrient degradation of forest soils (Cerný and Paces, 1995; Hruška and Cienciala, 2003). Despite high inputs of strong acids, there is site-to-site variability in the response of forested catchments to pollution. There is considerable interest in predicting the chemical responses of soils and stream waters to changes in atmospheric deposition through dynamic acidification models and these have frequently been applied in north-western Europe and North America (e.g. MAGIC model; Cosby *et al.*, 2001). However, modelling for assessment of acidification/recovery problems in heavily polluted Central-Eastern Europe has been used only rarely (Krám and Bishop, 2001). Computer predictions for the future were made using realistic scenarios, e.g. under the Gothenburg Protocol (Wright, 2001; Jenkins and Cullen, 2001; Krám *et al.*, 2001; Jenkins *et al.*, 2003). In this paper, the influence of the contrasting geochemistries of two catchments was tested by computer simulations of long-term chemical changes.

Material and methods

DESCRIPTION OF CATCHMENTS

The Lysina and Pluhuv Bor catchments, situated in western

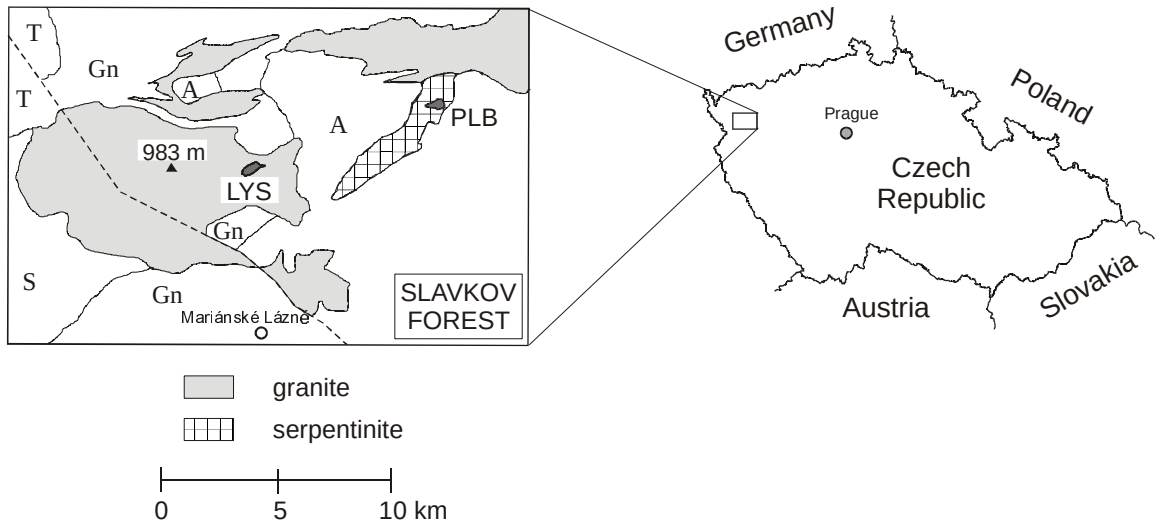

Fig. 1. *Map of the Czech Republic, showing studied region. Left panel: map of the Slavkov Forest with the locations of the catchments Lysina (LYS) and Pluhuv Bor (PLB), and major geologic formations (granite, serpentinite, A – amphibolite, Gn – gneiss, S – mica shist, T – tertiary sediments, dashed line – fault).*

Bohemia, the Czech Republic (Fig. 1) are just 7 km apart in the Slavkov Forest (Slavkovský les). The site selection criteria included proximity; similar climate, atmospheric deposition, topography, catchment size, vegetation cover and chemically differing bedrock (Table 1). The region was not glaciated and is overlain by soil derived from residuum bedrock. The bedrock at Lysina is coarse-grained, light-colour leucogranite. Predominant soils at Lysina are podzolic brown forest earths. Peaty gleys are locally developed, but small areas of stagnogleys and peat also occur. Pluhuv Bor is underlain by serpentinite, consisting primarily of the magnesium-silicates (Krám *et al.*, 1997) and the dominant soils are fine-textured, eutrophic brown forest soils with some peaty gleys locally developed. The catchments are drained by single perennial streams that begin about 900 m from the catchment outlet at Lysina and about 800 m at Pluhuv Bor.

HISTORY OF FOREST MANAGEMENT

Intensive forest cutting in the Slavkov Forest started in the 15th century due to the demand for wood, especially

Table 1. Characteristics of the Lysina and Pluhuv Bor catchments.

	LYSINA	*PLUHUV BOR*
Location	50°03'N, 12°40'E	50°04'N, 12°46'E
Altitude (m)	829-949	690-804
Average altitude (m)	884	774
Drainage area (km^2)	0.273	0.216
Mean slope (%)	11.5	13.0
Aspect	North-East	South-East
Forest stands structure	Forest >20 years (70%), Young forest (30%)	Forest >20 years (93%), Young forest and grass (7%)
Tree species	Norway spruce *(Picea abies)* (>99%) European beach (*Fagus sylvatica)* (<1%)	Norway spruce *(Picea abies)* (92%) Scots pine *(Pinus sylvestris)* (8%)
Average age of spruce trees (yr)	50	120
Prevailing soils	Podzolic brown forest earth	Eutrophic brown forest earth
Bedrock	Leucogranite	Serpentinite
Throughfall 1992-2002 (m)	0.715	0.529

associated with tin mines in the area, and remained active and erratic until the end of 18th century. Planned silvicultural management in Bohemia dates back to the reign of Josef II, Austrian emperor in 1780–1790. The first generation of Norway spruce monoculture was planted at Lysina in the middle of 19th century. The catchment originally had a mixed forest of European beech (*Fagus sylvatica*), Norway spruce (*Picea abies*) and silver fir (*Abies alba*). Approximately 30% of catchment area is covered by young spruce plantation (10–15 years old), 60% of the catchment is covered by 30–70 year old plantation spruce. Very small areas of the Lysina catchment are forested by stands close to the rotation age (100–120 years).

Pluhuv Bor catchment was originally forested by Scots pine (*Pinus silvestris*) stands which are typical for serpentinite areas. As at Lysina, spruce monocultures were planted on most of the catchment in the 19th century. Spruce monoculture stands, usually over 100 years old, occupy the major part of the catchment; the remainder, at higher elevation, is covered by Scots pine (Table 1). Annual wood increment for the same age forest is only about one-third at Pluhuv Bor of that at Lysina due to nutrient imbalances of the serpentinite substrate (Krám *et al.*, 1997).

HISTORY OF ATMOSPHERIC EMISSIONS

There is a close correlation between coal mining and emissions of SO_2 in the Czech Republic (Hruška *et al.*, 2002). Significant mining activities in the Bohemian coal basins started in 1870. The period after the World War II was accompanied by a massive production of energy from burning soft coal (lignite). Emissions of SO_2 peaked in 1982 and the decrease since then can be attributed to the declining volume of coal mined in 1982–1992. However, there is a distinct break point in 1993 when the first power plants in Bohemia were equipped with flue-gas desulphurisation, a process that was completed in the Czech Republic in 1999. Sulphur emissions declined from 2.4 Tg of SO_2 in 1982 to 1.4 Tg in 1993 and then to 0.26 Tg in 1999. According to *The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone* (http://www.unece.org/env/lrtap/protocol/99multi.htm), the target SO_2 emission in 2010 is 0.283 Tg for the entire Czech Republic. Emissions of SO_2 measured in 1999 already meet the 2010 target, so SO_2 emissions in the Czech Republic are unlikely to decrease further during the next decade. Beyond 2002, the deposition reductions of SO_4, NO_3, and NH_4 according to the Gothenburg scenario supplied from the CIAM/CCE (Posch *et al.*, 2002), were used for modelling purposes. As a result, deposition reduction was calculated as a fraction of deposition relative to 1990 for 2010 (scale factor). For the EMEP coordinates (i, j) = (23, 17) the scale factor is 0.18 for SO_4, 0.53 for NO_3 and 0.96 for NH_4 for both catchments.

FIELD SAMPLING

Two bulk precipitation collectors situated in clearings in the middle of each catchment were sampled fortnightly since August 1990 (Lysina) and December 2001 (Pluhuv Bor). Throughfall has been collected monthly from five collectors in each of two plots at Lysina (since June 1991) and, at Pluhuv Bor, at one plot (since November 1991) and at a second plot since December 2001. Dry deposition of sulphur under the spruce canopies in both catchments was estimated from measured throughfall fluxes. Dry deposition of base cations was estimated according to Bredemeier (1988), assuming negligible internal flux of Na in a spruce stand. The ratio of Na in throughfall to Na in bulk flux was used to estimate dry deposition for Ca, Mg and K. Stream water runoff from the catchments has been monitored continuously since September 1989 (Lysina) and since November 1991 (Pluhuv Bor) at a V-notch weir with a water level recorder. Grab runoff samples were collected, usually weekly but more frequently during some floods. Reported annual mean concentrations are volume-weighted and are based on water years (November–October). Spruce tissue samples were obtained from four representative trees within each catchment in July 1994. Soils were sampled at nine locations at Lysina and at four locations at Pluhuv Bor. Soil physical properties were estimated by excavating five 0.5 m^2 pits (four at Lysina, one at Pluhuv Bor) in June 1993. Procedures for analysis of soil, water and spruce tissue chemistry are described in detail in Krám (1997) and Krám *et al.,* (1997, 1999).

MODEL DESCRIPTION

The MAGIC model can reconstruct past and predict future stream and soil water and soil chemistry (Cosby *et al.*, 1985, 2001), using a lumped representation of physical and chemical properties (Table 2) because the stream water runoff integrates runoff from the entire catchment. Water fluxes, wet and dry atmospheric deposition, net vegetation uptake and a description of organic acids are required as external inputs to MAGIC.

INPUT DATA DESCRIPTION

The most important parameters used in the modelling at Lysina and Pluhuv Bor are summarised in Table 2. Soil bulk density and concentrations of exchangeable cations were weighted according to the measured thickness of soil

Table 2. Values for the MAGIC model calibration at the Lysina and the Pluhuv Bor catchments.

	Units	*LYSINA*		*PLUHUV BOR*	
		Value for Soil	*Value for Stream*	*Value for Soil*	*Value for Stream*
FIXED PARAMETERS					
Discharge, annual	m		0.432		0.253
Precipitation, annual	m		0.953		0.783
Soil depth	m	0.90		0.99	
Bulk density	kg m^{-3}	530		781	
CEC	meq kg^{-1}	59		140	
SO_4 adsorption half saturation	meq m^{-3}	500		100	
SO_4 maximum adsorption capacity	meq kg^{-1}	3		3	
pCO_2	atm	0.022	0.0011	0.022	0.002
Temperature	°C	5	5	6	6
pK_1 of organic acids	–log 10	2.5	2.5	2.5	2.5
pK_2 of organic acids	–log 10	4.4	4.4	4.4	4.4
pK_3 of organic acids	–log 10	6.7	6.7	6.7	6.7
Organic acids	mmol m^{-3}	110	58	100	58
Ca saturation 1993	% of CEC	3.7		3.6	
Mg saturation 1993	% of CEC	0.8		84.4	
Na saturation 1993	% of CEC	0.4		0.1	
K saturation 1993	% of CEC	1.9		0.5	
Total base saturation 1993	% of CEC	6.8		88.6	
Vegetation uptake Ca 1994	meq m^{-2}	12.5		1.2	
Vegetation uptake Mg 1994	meq m^{-2}	3.8		0.4	
Vegetation uptake Na 1994	meq m^{-2}	0.1		0.1	
Vegetation uptake K 1994	meq m^{-2}	2.3		0.2	
OPTIMISED PARAMETERS					
$Al(OH)_3$ solubility constant	log 10	7.7	7.1	7.7	7.1
Weathering Ca	meq m^{-2}	29		10	
Weathering Mg	meq m^{-2}	10		230	
Weathering Na	meq m^{-2}	22		1	
Weathering K	meq m^{-2}	4		0.1	
Weathering of Σ(Ca+Mg+K+Na)	meq m^{-2}	65		241	
Weathering F	meq m^{-2}	5		1	
Selectivity coeff. Al-Ca	log	0.78		9.77	
Selectivity coeff. Al-Mg	log	1.08		9.44	
Selectivity coeff. Al-Na	log	–0.48		5.49	
Selectivity coeff. Al-K	log	–4.21		–0.043	
Ca saturation 1851	%	16		3.5	
Mg saturation 1851	%	5		90.5	
Na saturation 1851	%	1		0.1	
K saturation 1851	%	2.7		0.5	
Total base saturation 1851	%	24.7		94.6	

horizons and on measured fine soil pools (< 2 mm for the mineral soil, < 5 mm for the organic soil). Stream water concentrations of organic acids (Table 2) were calculated from the mean concentration of DOC (dissolved organic carbon) 17.0 mg L^{-1} (1400 mmol m^{-3}) at both studied catchments between 1993–2000. The DOC and TOC (total organic carbon) values were almost identical indicating negligible contribution of particulate organic carbon. Dissociation constants (pK_a's) of triprotic organic acids with a site density of 10.2 µeq of carboxylic groups/mg TOC (Hruška *et al*, 2003) derived from titration of stream water (Hruška *et al.*, 1996, 2001, 2003) were used to derive the

concentration of organic acids (58 mmol m^{-3}, Table 2). For the modelling, the total amounts of organic acids were set constant at both catchments for the entire period (1851–2030). Sulphate adsorption parameters, the $Al(OH)_3$ solubility constants and weathering rates were fitted in the MAGIC calibration procedure. Net uptake of base cations fixed to above-ground tree biomass (usually harvested after the rotation period) was calculated from the tissue chemistry of stem wood and bark multiplied by increment per year. Curves for tree uptake of base cations (Moldan *et al.*, 1999), where the maximum rate of uptake occurs at canopy closure (*c*. 30 years for spruce monocultures), were adopted. Historical changes of uptake were estimated from the history of forest management in the catchments, using relevant areas of different forest age classes. Annual values of uptake of nitrate and ammonium were calculated by MAGIC using the fitted (for 1991) or estimated (for 1851) fraction of the total atmospheric deposition of nitrogen compounds. The future N uptake in 2003–2030 was set at the same value as for 1991–2002.

The future atmospheric deposition (2003-2030) of all elements was modelled using four different scenarios:

(a) Continuation of the average of 2000 and 2001 deposition projected to 2003-2030 ('Deposition 2001' in Fig. 2).

b) The requirements of implementation of the Gothenburg Protocol in 2003–2010. The concrete parameters of this scenario for the studied area were supplied from the CIAM/CCE (Posch *et al.*, 2002). As a result deposition reduction was calculated as a fraction of deposition relative to 1990 for 2010 (scale factor). For the EMEP coordinates (i, j) 23, 17 the scale factor is 0.18 for SO_4, 0.53 for NO_3 and 0.96 for NH_4 for both of catchments. Constant deposition from 2010 is used for 2011–2030 ('Gothenburg' in Fig. 2).

c) Continuation of 1991 deposition in 1992–2030 ('Deposition 1991' in Fig. 2).

d) Deposition estimated for 1850 applied to 2003–2030 ('Deposition 1850' in Fig. 2).

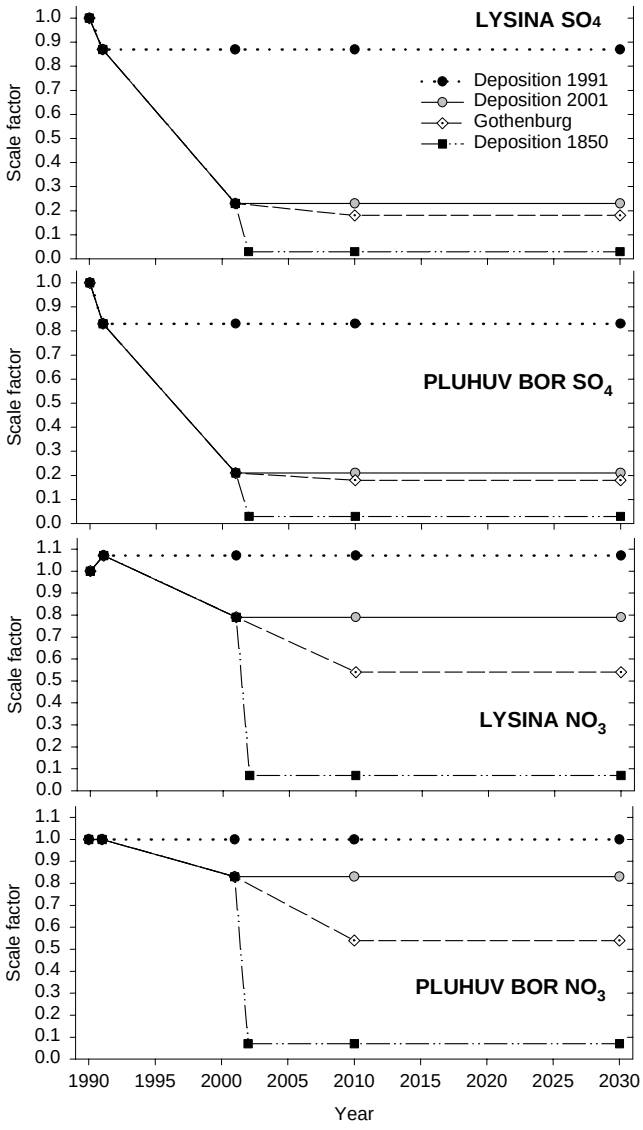

Fig. 2. *Four scenarios of total atmospheric deposition at Lysina and Pluhuv Bor shown as the scale factors, relative to the observed deposition from 1990. Note, observed deposition from the period 1990–2002 have been used in all simulations (data not shown in the figure). For details about scenarios, see the section "Input data description".*

Results and discussion

COMPARISON TO REGIONAL STREAM WATER PATTERNS

The atmospheric deposition received in the catchments studied is near the median acidity for the Czech Republic (Hruška *et al.*, 2002). However, the mean pH of streamwater at Lysina (in low-flow conditions) represented only the 8% quantile of values measured in surface waters sampled regionally at elevations above 700 m a.s.l., the elevation similar to the outflows from these catchments (Fig. 3). Only *c.* 1% of the whole area of the Czech Republic had surface waters with a pH lower than the Lysina stream (Veselý and Majer, 1998). In contrast, Pluhuv Bor represented the 95% quantile of available regional streamwater pH values at elevations above 700 m a.s.l. (Fig. 3). Approximately 40% of the surface waters in the entire Czech Republic have higher pH values than Pluhuv Bor (Veselý and Majer, 1998). The main reason for the contrast between Lysina and Pluhuv Bor is differing bedrock and soil geochemistry of the catchments (Table 1, Krám *et al.*, 1997).

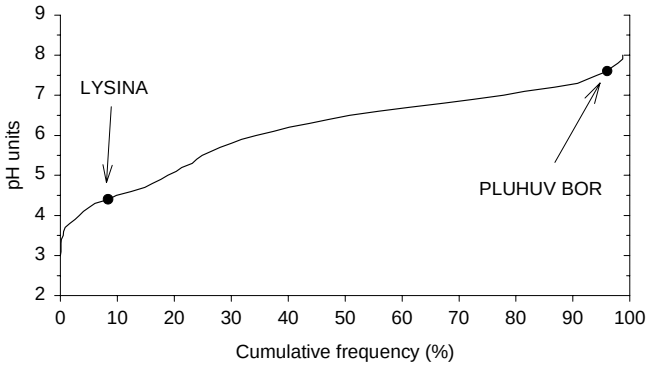

Fig. 3. *Frequency distribution of stream water pH at altitudes >700 m a.s.l. from the regional survey of Czech surface waters conducted during baseflow conditions (891 samples, derived from Veselý and Majer, 1998). Dots represent the Lysina and Pluhuv Bor catchment data from the baseflow conditions as well.*

OBSERVED ATMOSPHERIC DEPOSITION

The mean annual concentration of airborne SO_2 was 32 μg m^{-3} for the period 1980–1990 (Station Lazy, 3 km northwest of the Lysina catchment, Forestry and Game Management Research Institute, Prague, unpublished data). The SO_2 concentrations declined markedly in the 1990s and, in 1999–2000, the average SO_2 at Lazy was only 3 μg m^{-3}.

The atmospheric deposition of S and other major ions increased in different proportions over the modelled historical period from the middle of the 19th century up to the peak values around 1980 (Hruška *et al.*, 2002). Total S deposition measured at the beginning of the 1990s ranged from 30–40 kg ha^{-1} yr^{-1} (170–220 meq m^{-2} yr^{-1}) at Lysina and Pluhuv Bor. Dry deposition contributed about 60% of total deposition of S in that period. After a decade of S deposition reduction, only approximately 7–11 kg ha^{-1} yr^{-1} (40–60 meq m^{-2} yr^{-1}) was measured at the sites studied at the beginning of the 2000s and the dry deposition fraction was about 20–30%. Thus, the total deposition of S declined by approximately 75%. Bulk deposition of NO_3 ranged between 43–47 meq m^{-2} yr^{-1} in 1991–1993 and 32–39 meq m^{-2} yr^{-1} between 2000-2002, a decline of 21%. Similarly, bulk deposition of NH_4 was 43–57 meq m^{-2} yr^{-1} (1991–1993) and 32–37 meq m^{-2} yr^{-1} (2000–2002), a decline of 35%.

Atmospheric deposition of the sum of base cations (SBC = Ca^{2+}+Mg^{2+}+K^++Na^+) was relatively stable between 1991–2002; it varied between 25 and 37 meq m^{-2} yr^{-1} at Lysina and between 21 and 31 meq m^{-2} yr^{-1} at Pluhuv Bor. Dry deposition was estimated to be between 11% and 91% (average 30%) of bulk deposition of these elements at Lysina. At Pluhuv Bor, the dry deposition fraction varied from 0 to 60% and averaged only 10%.

OBSERVED RUNOFF CHEMISTRY IN THE CATCHMENTS

The annual runoff varied between 327 and 747 mm at Lysina and between 191 and 451 mm at Pluhuv Bor. Long-term stream water runoff averages used in the MAGIC model are shown in Table 2. Stream water chemistry changed predominantly in response to changing deposition over the measured period 1990–2002 (Figs. 4a, b).

Stream water sulphate declined steadily from 568 μeq L^{-1} in 1990 to 145 μeq L^{-1} in 2002 at Lysina (Fig. 4a). This 74% decline parallels that in SO_4 deposition (75%). Sulphate declined even more dramatically from 1035 μeq L^{-1} in 1992 to 215 μeq L^{-1} in 2002 at Pluhuv Bor (Fig. 4b). Such dramatic reductions in sulphate concentrations in stream water have not been documented in any other European catchment (e.g. Evans *et al.*, 2001; Prechtel *et al.*, 2001; Alewell *et al.*, 2001; Fölster and Wilander, 2002). It appears that sulphur stores in the upper soil horizons at Pluhuv Bor declined markedly in the last decade (Shanley *et al.*, 2004). Concentrations of organic acid anions were highly variable (annual average concentrations between 60–140 μeq L^{-1} at Lysina and 100-200 μeq L^{-1} at Pluhuv Bor). High runoff, originating mainly from upper soils, transported more DOC to the streams. Therefore, the annual concentrations of organic anions were higher during years of elevated discharge.

The sum of base cations (SBC) in streamwater at Lysina declined markedly between 1990 and 2002 (Fig. 4a) from 434 μeq L^{-1} to 159 μeq L^{-1}, a decline of 63%. Calcium declined from 234 to 63 μeq L^{-1} (by 73%), Mg^{2+} from 78 to 23 μeq L^{-1} (71%), K^+ from 25 to 11 μeq L^{-1} (56%), and Na^+ from 97 to 62 μeq L^{-1} (36%). Divalent cations (Ca^{2+} and Mg^{2+}) declined much more sharply than monovalent K^+ and Na^+. Streamwater pH was very low (Fig. 4a) over the period of observations. Annual averages increased only slightly, from 3.92 to 4.01, only a 18% decrease of H^+ concentration, compared to the substantial decline of SO_4 concentrations. Total Al declined by 60% at Lysina (from 62 μmol L^{-1} in 1990 to 25 μmol L^{-1} in 2002) (Fig. 4b).

Also the SBC in runoff at Pluhuv Bor declined steadily between 1990 and 2002 (Fig. 4a). The decrease from 1588 μeq L^{-1} to 1032 μeq L^{-1}, represents a decline of 35%. Concentrations of Ca^{2+} declined from 90 to 52 μeq L^{-1} (by 42%), Mg^{2+} from 1441 to 938 μeq L^{-1} (35%), K^+ from 5.3 to 4.1 μeq L^{-1} (23%), and Na^+ from 52 to 38 μeq L^{-1} (27%). Divalent cations (Ca^{2+} and Mg^{2+}) at Pluhuv Bor declined again much more sharply than monovalent K^+ and Na^+. Annual streamwater pH values were high (Fig. 4a) during the period and varied slightly (between 6.6–7.3) according to the annual water budget. Lower discharge-weighted annual pH values were observed in wetter years. Total Al

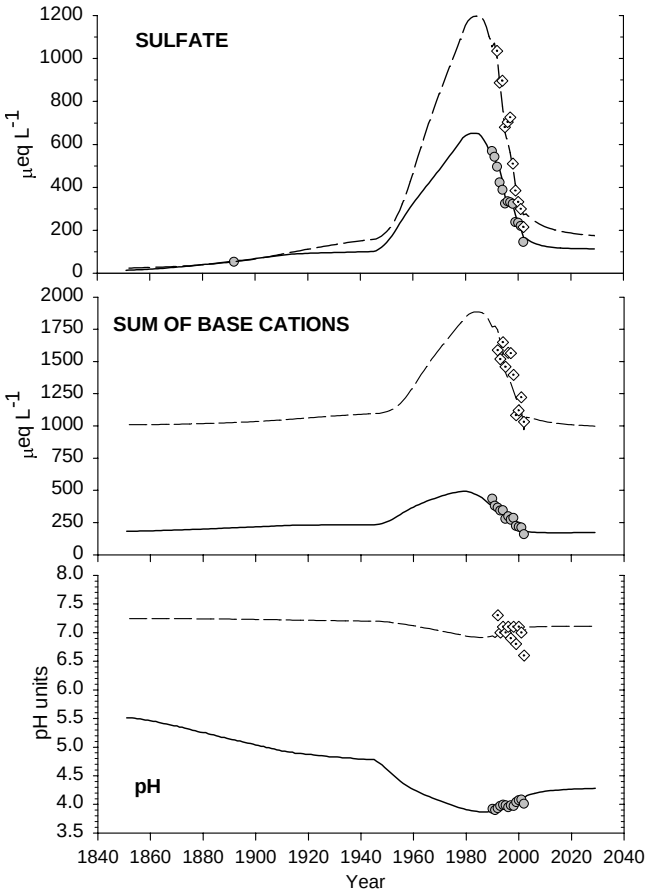

Fig. 4a. *Measured (1990–2002, gray dots) and simulated (1851–2030, solid line) changes in stream water chemistry at Lysina. Measured (1992–2002, diamonds) and simulated (1851–2030, dashed line) changes in stream water chemistry at Pluhuv Bor. Estimated sulphate concentration in 1892 at Lysina (grey dot) was derived from the data of Hanaman, 1896 (Hruška* et al, *2002). The sum of base cations includes calcium, magnesium, potassium and sodium. Deposition measured in 2000–2001 was used for the forecast.*

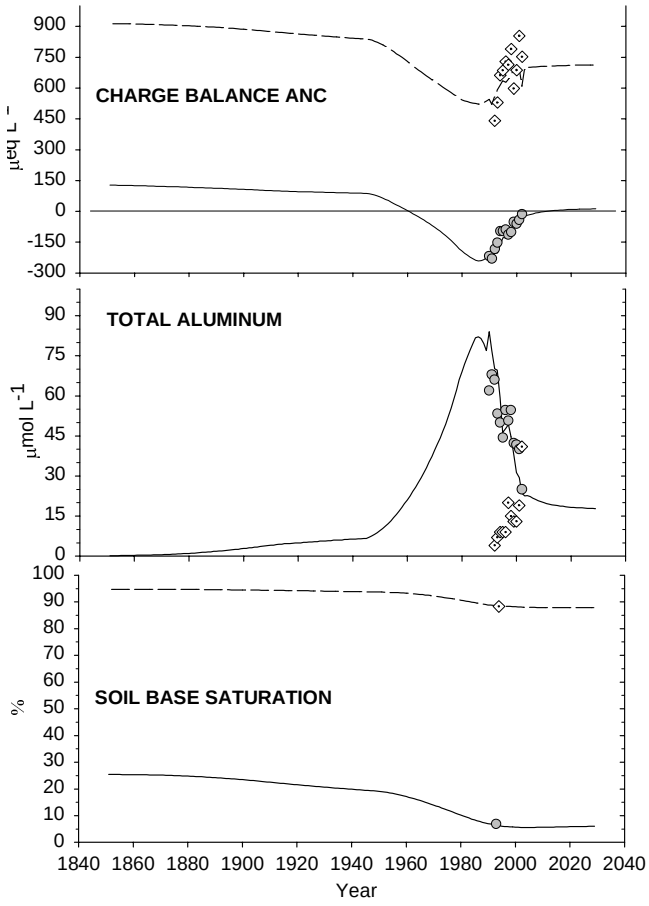

Fig. 4b. *Measured (1990-2002, gray dots) and simulated (1851–2030, solid line) changes in stream water and soil chemistry at Lysina. Measured (1992–2002, diamonds) and simulated (1851-2030, dashed line) changes in stream water and soil chemistry at Pluhuv Bor. ANC means acid neutralising capacity. Simulated aluminium by MAGIC at Pluhuv Bor was close to zero. Deposition measured in 2000–2001 was used for the forecast.*

increased markedly from 4 μmol L^{-1} in 1990 to 41 μmol L^{-1} in the wettest year 2002 (Fig. 4b). Acid neutralising capacity (ANC), calculated as the difference between the sum of base cations (Ca^{2+}+Mg^{2+}+K^{+}+Na^{+}) and the sum of strong inorganic anions (SO_4^{2-}+NO_3^{-}+Cl^{-}+F^{-}), increased significantly from –241 μeq L^{-1} in 1990 to –22 μeq L^{-1} in 2002 at Lysina and similarly from +435 μeq L^{-1} in 1990 to +746 μeq L^{-1} in 2002 at Pluhuv Bor (Fig. 4b).

MODELLING OF SULPHUR

Historic changes in atmospheric deposition of sulphur were the main factor causing changes in the biogeochemical patterns in the catchments examined. Sulphur deposition was estimated as proportional to the regional coal mining over the period 1851-1990 (Hruška *et al*, 2002). Estimates of SO_4 concentrations in stream water at Lysina in the past were verified by examining historic surface water data from 1892 published by Hanaman in 1896 (Fig. 4a, Hruška *et al*, 2002). Desorption of soil sulphate caused a lag in the response of sulphate fluxes in runoff to decreasing sulphate deposition in both catchments (Fig. 5).

If atmospheric deposition remains at 2000/2001 values (scenario Deposition 2001 in Figs. 2, 6a), predicted streamwater SO_4 concentrations at Lysina will decrease to 120 μeq L^{-1} around 2010 and to 110 μeq L^{-1} in 2030 (Fig. 4a). This last value is similar to concentrations simulated at the beginning of the 1950s but only about 15% of the highest streamwater SO_4 simulated for 1983 (640 μeq L^{-1}). However, SO_4 will still remain the dominant inorganic anion in stream water. Under the scenario of the Gothenburg Protocol implementation (Fig. 2), streamwater SO_4 will decline to

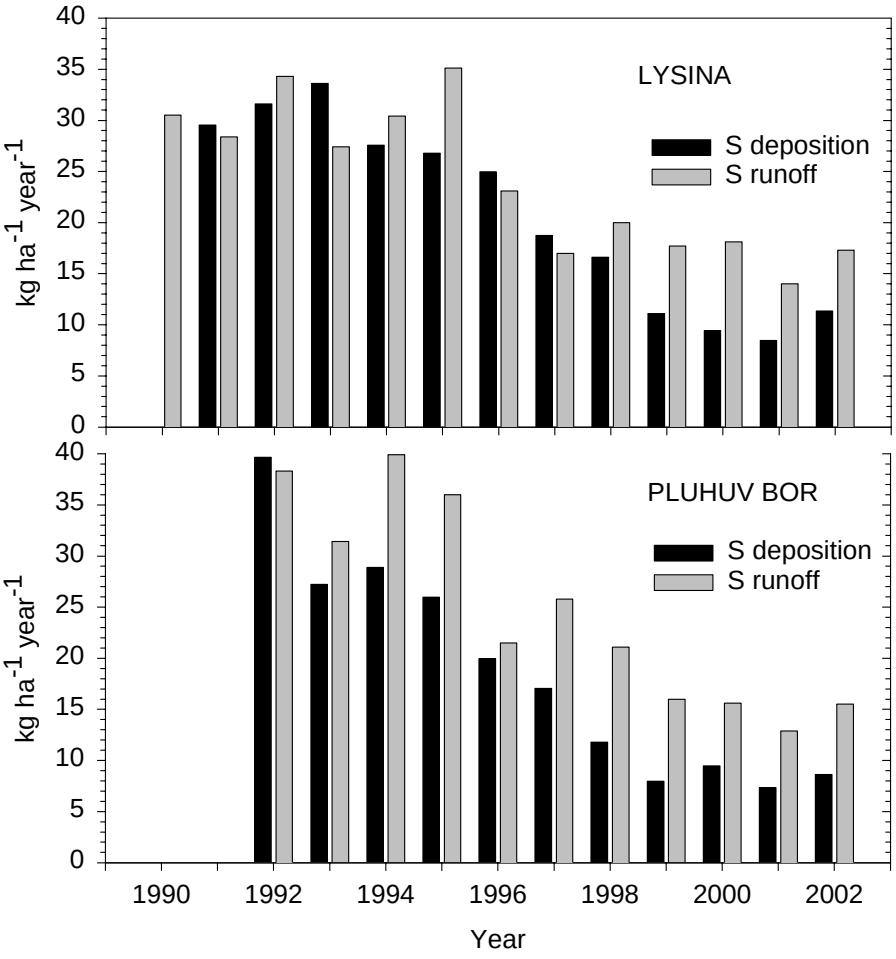

Fig. 5. *Sulphur budgets for the Lysina and Pluhuv Bor catchments measured from 1990 to 2002.*

100 μeq L^{-1} in 2010 and to 90 μeq L^{-1} in 2030 ('Gothenburg' in Fig. 6a). This concentration equals the amount of organic anions in the stream predicted for years 2010–2030. The scenario based on continuation of deposition measured in 1991 ('Deposition 1991' in Figs. 2 and 6a) results in stable values of SO_4 around 450 μeq L^{-1} in the period 2000–2030, similar to those in the 1970s. The scenario based on deposition estimated for 1850 (applied since 2003), results in a substantial decline in SO_4 and the predicted concentration for 2030 (18 μeq L^{-1}) is close to the pre-industrial 1850s estimate of 14 μeq L^{-1}.

At Pluhuv Bor, the reduction in deposition resulted in a sharper decline in streamwater SO_4 compared to Lysina (Fig. 4a). Pluhuv Bor is more completely forested by closed canopy trees (Table 1) and the reduction in dry deposition probably had a more pronounced effect, as well as calibrated lower sulphate adsorption capacity of catchment soils (Table 2). Streamwater SO_4 declined from its simulated peak in the 1980s (1200 μeq L^{-1}) to measured 215 μeq L^{-1} in 2002 a reduction to 18% of the peak value. Assuming the scenario 'Deposition 2001' (Fig. 2), streamwater SO_4 will decline to *c*. 170 μeq L^{-1} in 2030 representing only 14% of the 1980s peak (Fig. 6b). Under the scenario 'Gothenburg' (Fig. 2), a further reduction in deposition is negligible between 2001 and 2010, because S deposition measured in 2001 was 19% of that in 1990 and the Gothenburg Protocol requirement for this area is only slightly lower (18%) for 2010. Continuation of deposition measured in 1991 ('Deposition 1991' in Figs. 2 and 6b) would result in SO_4 concentrations of about 800 μeq L^{-1} between 2000–2030, four times higher than the present level. Scenario 'Deposition 1850' will result in a further decline to 80 μeq L^{-1} in 2030.

The soil pool of adsorbed SO_4 is predicted to decrease rapidly under the deposition scenarios 'Gothenburg' and 'Deposition 1991' and, by around the year 2010, the soil-adsorbed SO_4 will approach a new steady state with atmospheric deposition. From the year 2010 to 2030, the predicted decrease in the adsorbed SO_4 pool will be small.

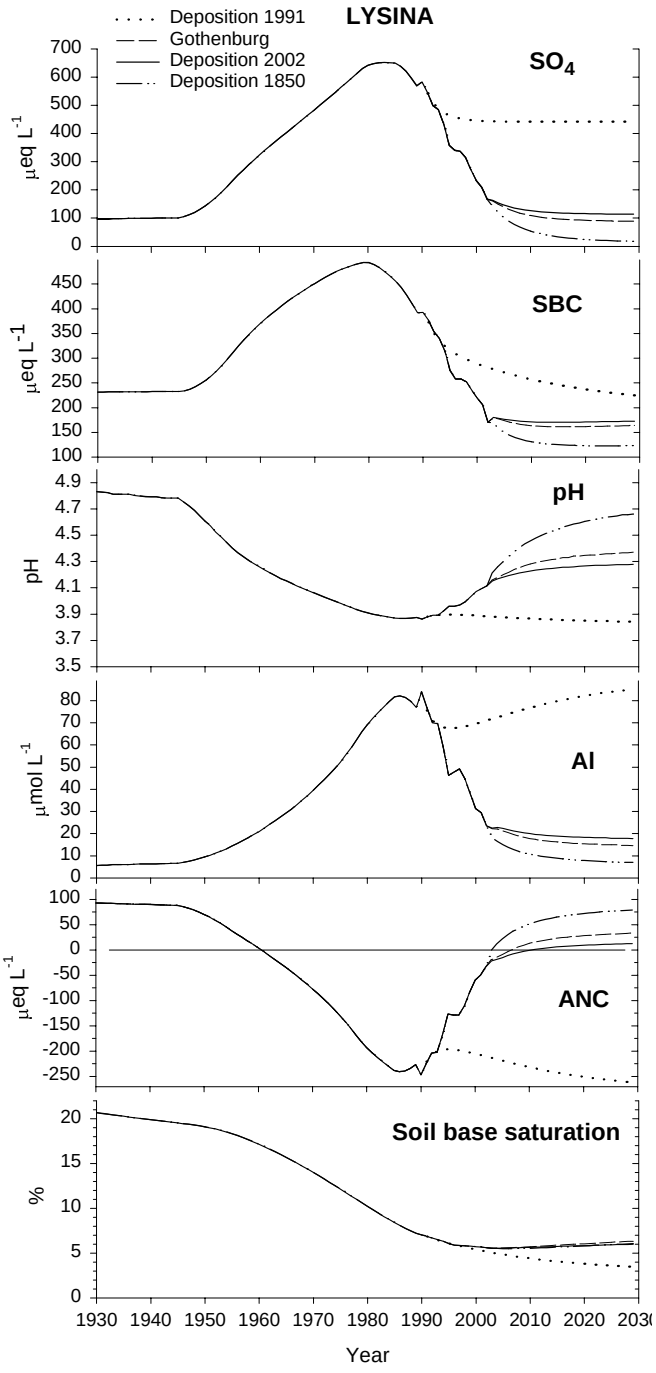

Fig. 6a. *Simulated concentrations of sulphate, sum of base cations, pH, aluminium and acid neutralising capacity in stream water and soil base saturation at Lysina from 1930 to2030. Solid line depicts observed deposition in 1990–2002 and deposition observed in 2000–2001 is used in the forecast for 2003–2030. Dotted line represents deposition measured in 1991 and used in 1992–2030. The impact of implementing the Gothenburg Protocol on atmospheric deposition reductions of sulphate, nitrate and ammonium in 2003–2010 is shown by dashed lines. Dash-dot-dot line shows hypothetical scenario with the preindustrial deposition (1850) used in 2003–2030.*

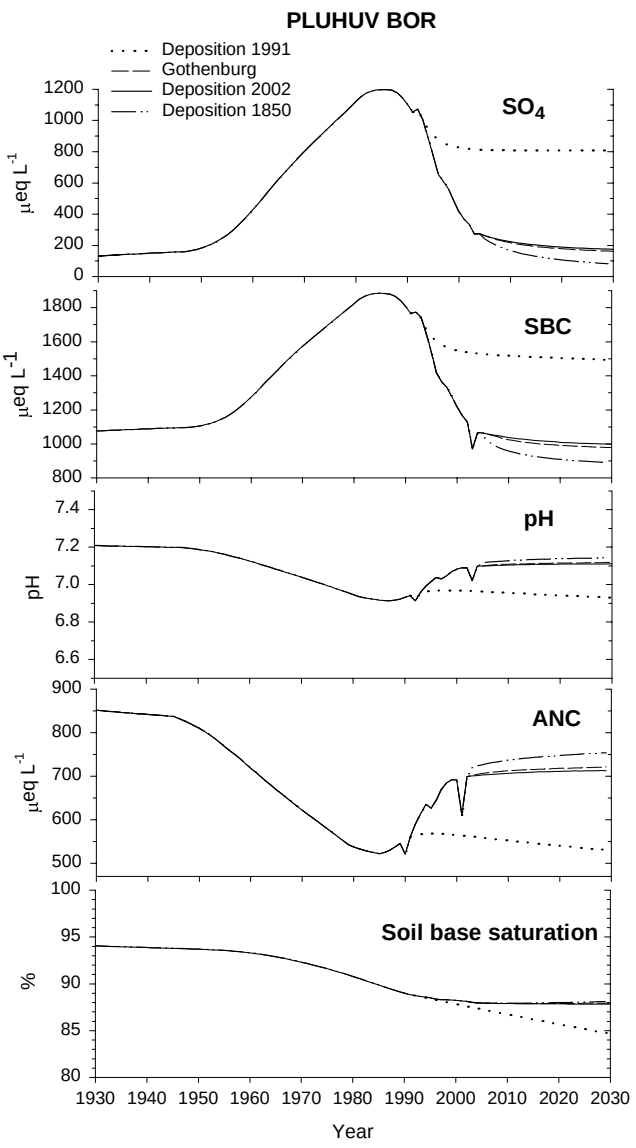

Fig. 6b. *Simulated concentrations of sulphate, sum of base cations, pH, and acid neutralising capacity in stream water and soil base saturation at Pluhuv Bor in 1930–2030. Solid line depicts observed deposition in 1990–2002 and deposition observed in 2000–2001 is used in the forecast for 2003–2030. Dotted line represents deposition measured in 1991 and used in 1992–2030. The impact of implementing the Gothenburg Protocol on atmospheric deposition reductions of sulphate, nitrate and ammonium in 2003–2010 is shown in dashed lines. Dash-dot-dot line shows hypothetical scenario with the preindustrial deposition (1850) used in 2003–2030.*

The MAGIC model simplifies soil S processes by limiting consideration to S inorganic adsorption/desorption on surfaces of oxides. Reactions involving the incorporation of S in soil organic matter and its mineralisation are not considered in the model. Recent work (Novák *et al.*, 2000) showed that release of organic carbon-bonded S could be an important source of stream water SO_4 in regions that had received high S deposition. Therefore, estimates calculated under the deposition scenarios 'Deposition 1850' which

predict a dramatic decrease of SO_4 might significantly underestimate SO_4 concentration in the stream due to missing mineralisation of organic carbon-bonded S.

ORGANIC CARBON AND ORGANIC ACIDS

Measured annual dissolved organic carbon (DOC) concentrations increased during the period with available data (1993–2000) at both catchments. Organic carbon concentrations increased on average 0.1 mg L^{-1} yr^{-1} at Lysina and 0.8 mg L^{-1} yr^{-1} at Pluhuv Bor. For the eight measured years, this represents an increase of 5% at Lysina and 28% at Pluhuv Bor relative to the average concentrations for both catchments. Interestingly, both catchments had identical long-term average DOC of 17.0 mg L^{-1}. A higher standard deviation of annual values was observed at Pluhuv Bor (±2.6 mg L^{-1}) than at Lysina (±1.6 mg L^{-1}).

Krug and Frink (1983) published predictions of increased DOC concentrations during recovery from acidification. However, Lydersen *et al* (1996) found no changes in DOC that were statistically significant during experimental acidification at Lake Skjervatjern in Norway. Similarly, Wright *et al.* (1993) and Skeffington *et al.* (1998) did not observe significant TOC changes during experimental exclusions of acidic precipitation at Risdalsheia, Norway and at Gårdsjön, Sweden. Statistically significant increases of DOC were, however, observed in the UK (Monteith and Evans, 2000; Freeman *et al.*, 2001) but the authors attributed this to climate changes (warming) rather than recovery from acidification. Daily mean air temperature measured at Mariánské Lázne station (700 m a.s.l., Fig. 1) between 1990–2002 showed a weak positive trend (0.06°C yr^{-1}, $p < 0.03$). This increase may contribute to the observed increase of organic carbon at Lysina and Pluhuv Bor.

Anions of the organic acid ($RCOO^-$) were the dominant stream water anions in the 19th century (two-thirds of anionic charge) at Lysina but their contribution declined as anthropogenic SO_4 increased with time. Modelled organic anions fell from 120 μeq L^{-1} to the minimum of 67 μeq L^{-1} in 1983 due to the decrease in organic acid dissociation, which was 69% prior to anthropogenic acidification and 38% during the peak of anthropogenic acidification in the 1980s. The dissociation of 52% was simulated for 2030 under the scenario 'Deposition 2001'. Scenario 'Gothenburg' produces a similar amount of organic anions (97 μeq L^{-1}) and degree of dissociation (54%) in 2030. Under the scenario 'Deposition 1850', the organic anions will increase to 92 μeq L^{-1} in 2030, which represents a degree of dissociation of 61%. All changes in organic acid dissociation are linked to modelled pH changes, because higher pH causes higher dissociation and thus a higher amount of organic anions. Under the scenario 'Gothenburg', the organic anions concentration will be similar to SO_4 concentration around 2010 so that organic anions could slightly dominate streamwater in 2030 (97 μeq L^{-1} *v.* 89 μeq L^{-1}). Scenario "Deposition 1850" produced the highest dissociation due to the highest modelled pH and an organic acids concentration of 108 μeq L^{-1} was modelled for 2030. This value is still less than the pre-industrial estimate, because the modelled pH 4.7 in 2030 is significantly lower than the pH 5.5 value modelled for 1851. Together with $Al(OH)_3$ dissolution, the weak organic acid protonation/deprotonation was the most important stream water pH buffering mechanism at Lysina. Organic acid anions increased in the model prediction only slightly (from 67 to 82 μeq L^{-1}) between 1990-2002. These numbers were within the range of charge balance deficits calculated from the difference in major anions and cations (between 64–138 μeq L^{-1}) at Lysina. Organic acid anions will comprise 40-50% of anionic charge by 2030 under the most realistic deposition scenarios ('Deposition 2001' and 'Gothenburg'), although they comprised less than 10% of anionic charge during the acidification peak.

A substantially different situation was observed and modelled for stream water at Pluhuv Bor. Due to fairly high observed (Fig. 4a) and also modelled pH (Fig. 6b), the organic acids are highly dissociated under all the scenarios examined. $RCOO^-$ concentrations varied between 165–170 μeq L^{-1} which represents a degree of dissociation of 92–95% under all the scenarios, because simulated annual mean pH varied only within the range of 6.9–7.2. Organic anions were the second most abundant anion in the pre-industrial estimate (after HCO_3) and, after HCO_3, they are presently approximately equal to the SO_4 concentration. During the acidification peak in the 1980s, they were the third most abundant anion after SO_4 and HCO_3 at Pluhuv Bor.

MODELLING OF pH, ALUMINIUM AND ACID NEUTRALISING CAPACITY

Chronic soil acidification caused a large decline in pH and boosted Al mobilisation at Lysina (Figs. 4a, b). Hruška and Krám (1994), Krám *et al.* (1995, 1999) and Driscoll and Postek (1996) detailed extremely elevated concentrations of Al in stream water at Lysina and similarly high values of Al were observed at Grosse Pyra catchment, Germany, underlain by exactly the same bedrock (Lorz *et al.*, 2003). High organic acid concentrations produced fairly low stream water pH (5.5) prior to the onset of acidic deposition at Lysina. As a result of atmospheric deposition of S and soil base cation depletion, stream water pH declined to a

minimum annual average of 3.87 during the 1980s. After the period of declining S deposition, the measured and modelled pH was 4.07 in 2000 and 4.08 in 2001. In 2002, an extremely wet year, pH again dropped to 4.01 (Fig. 4a). If current deposition (scenario 'Deposition 2001', Fig. 6a) is projected until 2030, modelled pH rises to 4.25 in 2010 and then more slowly to 4.3 in 2030. Application of the Gothenburg Protocol leads to slightly higher pH (4.3 in 2010 and 4.35 in 2030). A theoretical decrease in deposition to the 1850 level (Deposition 1850, Fig. 6a) increases pH to 4.7 in 2030, still much lower than the preindustrial estimate of pH 5.5 and similar to values estimated for the 1930s. Contrary to the previous scenarios, the 'Deposition 1991' scenario decreases pH between 2002 and 2030 to 3.8 which is similar to values modelled for the 1980s (Fig. 6a).

At Pluhuv Bor, measured discharge-weighted annual pH values did not show any trend during the 1990s and variations (6.6–7.3) were caused mainly by hydrology (Fig. 4a). During wet years, discharge-weighted pH values were low compared to other years. The lowest simulated pH of 6.9, which was modelled for the entire 1980s, was only 0.3 pH unit lower than the pre-industrial estimate of pH 7.2, despite enormous changes in SO_4 deposition (Fig. 2) and stream water SO_4 concentrations (Figs.4a, 6b). All future scenarios of deposition will have only a very small effect on pH which will remain near pH 7.1 between 2003–2030. Only the worst-case scenario 'Deposition 1991' will keep pH at the level of 6.9. However, the stream water at Pluhuv Bor catchment experiences episodic stream water acidification during high flows in spite of the above mentioned acidification resistance in annual time step, with temporal pH depressions down to 5.9 (Krám *et al*, 2003).

Total Al concentrations in the MAGIC model are controlled by $Al(OH)_3$ solubility. The $Al(OH)_3$ solubility constant for Lysina was optimised using stream water measurements between 1990 and 2000. Using calibrated $-pK_{Al(OH)3} = 7.1$ (Table 2), the MAGIC model reproduced the measured Al and pH satisfactorily. The simulated forecast estimated only a small decline of total Al until 2010, from 24 μmol L^{-1} in 2002 (Fig. 4b) to 23 μmol L^{-1} in 2010 under the 'Deposition 1991' scenario. Thereafter, Al remains near 20 μmol L^{-1} for the additional two modelled decades. Gothenburg Protocol application leads to an additional small reduction to a modelled Al concentration of 15 μmol L^{-1} in 2030 (Fig. 6a). Application of 'Deposition 1850' scenario results in a further decline to 10 μmol L^{-1} in 2010 and < 10 μmol L^{-1} at Lysina in 2030. It is questionable whether these predictions are realistic, because stream waters with pH around 4.7 in the Czech Republic usually have about 25 μmol L^{-1} of total Al (Veselý and Majer, 1996). Application of 'Deposition 1991' scenario will raise Al concentrations in 2030 to the level estimated for the acidification peak of the 1980s (Fig. 6a).

Changes of ANC at Lysina were driven predominantly by changes in Al, H^+ and $RCOO^-$ concentrations. Relatively high historic ANC (128 μeq L^{-1}) at Lysina was a result of high $RCOO^-$ concentration ($ANC=[RCOO^-]+[HCO_3^-]-[Al^{n+}]-[H^+]$). Since the middle of the 20th century, as Al and H^+ increased while $RCOO^-$ decreased, ANC declined markedly (Fig. 4b). The lowest ANC was simulated during the 1980s (-240 μeq L^{-1}). During the acidification recovery in the 1990s, ANC increased sharply to –14 μeq L^{-1} in 2002 (Fig. 4b). ANC will rise to 0 μeq L^{-1} in 2010 and reach positive values (+15 μeq L^{-1}) by 2030 under the 'Deposition 1991' scenario (Fig. 6a). Gothenburg Protocol scenario results in ANC of +10 μeq L^{-1} in 2010 and +30 μeq L^{-1} in 2030. Scenario 'Deposition 1850' predicts significantly higher ANC (+70 μeq L^{-1}) in 2030. Scenario 'Deposition 1991' decreased ANC in 2030 to –260 μeq L^{-1}, which is even lower than ANC during the acidification peak in 1980s. Compared to Lysina, Pluhuv Bor showed opposite patterns of measured Al concentrations. Measured total Al concentrations in streamwater increased significantly (from 3 μmol L^{-1} to 41 μmol L^{-1} between 1992–2002, Fig. 4b) despite fairly stable high pH during the period of observations. It is impossible to model this trend using MAGIC, because gibbsite equilibrium cannot reproduce the observed trend. Al speciation at Pluhuv Bor did not show any significant increase in organic or inorganic monomeric Al which together contribute less than 10% to total Al. Therefore, more than 90% of total Al at Pluhuv Bor is made up of the colloidal and particulate Al fractions. Such a tremendous increase of Al might be explained by dissolution of a secondary Al-bearing minerals containing SO_4, such as alunite or jurbanite (Nordstrom, 1982; Lükewille *et al*, 1985) or by mechanical erosion. When solute SO_4 concentration declined significantly (Fig. 4a), mineral equilibria might be shifted to enhance Al leaching to keep the solubility product constant.

Pluhuv Bor is an intensively buffered catchment, where ANC is dominated by HCO_3 ions from weathering. During the 1990s, observed ANC increased sharply from 450 μeq L^{-1} to almost 900 μeq L^{-1} but year to year variability was large depending on runoff depth (Fig. 4b). MAGIC was not able to reproduce measured ANC variability completely. Pre-industrial estimate of ANC was 910 μeq L^{-1} and simulated ANC for the 1980s was 520 μeq L^{-1}. Scenarios 'Deposition 2001' and 'Gothenburg' forecast very similar ANC values of about 710 μeq L^{-1} in 2010 and 720 μeq L^{-1} in 2030 (Fig. 6b).

BASE CATIONS AND SILICA IN STREAM WATER

The modelled sum of base cations (Ca, Mg, K, Na) in stream water increased gradually, while the major mobile anion (SO_4) increased over the hindcast period 1851–1991 at both catchments (Fig. 4a). The SBC then declined following the decrease of SO_4 (Fig. 4a). The major difference between the catchments is in base cation concentrations. At Lysina 180 μeq L^{-1} was simulated as the pre-industrial SBC concentration and model simulation of the SBC for the 1980s was nearly 500 μeq L^{-1}. During the 1990s, modelled as well as observed SBC declined to 170 μeq L^{-1} in 2002 (Fig. 4a). Under the scenario 'Deposition 1991' and 'Gothenburg', the concentration of 160–170 μeq L^{-1} will be reached between 2010–2030. Application of "Deposition 1850" will result in a further decrease to 130 μeq L^{-1} in 2030 (Fig. 6a). All above mentioned scenarios resulted in concentrations lower than the historic estimate of 180 μeq L^{-1}.

Contrary to low SBC at Lysina, Pluhuv Bor exhibited a very high historic SBC concentration of 1000 μeq L^{-1} which increased during acidification to the peak of 1800 μeq L^{-1} in 1980s and SBC release was able to neutralise atmospheric deposition of SO_4 completely. During the 1990s, SBC declined from 1590 μeq L^{-1} to 1030 μeq L^{-1} in 2002 (Fig. 4a). Under the scenarios 'Deposition 1991' and 'Gothenburg' SBC concentration of 1000 μeq L^{-1} will be reached between 2010–2030 (Fig. 6b). Application of 'Deposition 1850' results in a further decrease to 900 μeq L^{-1} in 2030. The low supply of base cations from the soil exchange complex and weathering was a major contributor to the severe acidification of soils and stream water at Lysina whereas a high weathering rate and large soil base saturation were the major reasons for resistance to acidification of stream water at Pluhuv Bor.

Weathering rates (Table 2) were estimated by the MAGIC calibration procedure synchronously with historic soil base saturation. The fitted annual weathering rate of 65 meq m^{-2} yr^{-1} for Lysina seems to be realistic given the environmental conditions. Langan *et al.* (2001) published weathering rates estimated for granitic areas in northern Europe calculated in different ways ranging between 10 meq m^{-2} yr^{-1} and 85 meq m^{-2} yr^{-1}. For Pluhuv Bor, underlain by serpentinite, magnesium-rich silicate, the SBC weathering rate was estimated at 241 meq m^{-2} yr^{-1}. Mg weathering was modelled as 230 meq m^{-2}, 95% of the SBC weathering rate.

According to Reuss (1994), weathering is accelerated by an elevated input of H^+ from the atmosphere and this hypothesis is supported by laboratory experiments (Sverdrup, 1990). Assuming that the Si concentration in the stream is an indicator of silicate mineral weathering rate, no support for this hypothesis was found at the two experimental catchments. Despite huge reductions in H^+ inputs to the catchments, dissolved Si did not decline; rather, it increased significantly between 1990 and 2002 by 2.3 μmol L^{-1} yr^{-1} ($p < 0.00045$) at Lysina and by 7.8 μmol L^{-1} yr^{-1} ($p < 0.001$) at Pluhuv Bor. This represents an increase of 15% relative to the long-term discharge-weighted average of 170 μmol L^{-1} at Lysina and an increase of 18% at Pluhuv Bor (long-term average 413 μmol L^{-1}). In contrast to the increases in Si, the second potential weathering indicator, Na in runoff, decreased slightly (by 1.8 μeq L^{-1} yr^{-1} at Lysina and 1.9 μeq L^{-1} yr^{-1} at Pluhuv Bor but also significantly ($p < 0.001$ for both catchments). The decrease in Na may indicate the expected weathering decrease in the period of recovery from acidification, or a decrease in soil cation exchange of Na. Due to the contradictory signals from these two major weathering indicators, constant weathering rates were used in MAGIC for the whole modelled period 1851–2030 at Lysina and Pluhuv Bor.

MODELLING OF SOIL BASE SATURATION

The simulated soil base saturation at Lysina declined from 24.7% in 1851 to the 6.8% measured in 1993. Depletion of base cations from cation-exchange sites was the crucial mechanism for neutralising incoming acidic deposition. During the peak of acidification, soil cation exchange was the dominant source of base cations in the streams. Base saturation of 6.0% was simulated for 2030, an increase from the minimum of 5.6% simulated for 2002 under the scenarios 'Deposition 2001' and 'Gothenburg' (Fig. 6a). Also 'Deposition 1850' produced a negligible difference from the above-mentioned scenarios. 'Deposition 1991' results in a further decline of soil base saturation to values of about 3.5% in 2030 (Fig. 6a). While the modelled increase in soil base saturation marks the beginning of soil recovery from acidification, the modelled value of 6.0% by the year 2030 is still very low compared to the 24.7% in the preindustrial era. The two major reasons for the soil depletion of base cations at Lysine were deposition of strong acids and forest growth. These two processes are different in long-term dynamics with the tree uptake much less variable (Hruska *et al.*, 2002).

At Pluhuv Bor, the measured soil base saturation (89% in 1993) declined slightly compared to the historical pre-industrial estimate of 95%. Three scenarios of atmospheric deposition ('Deposition 1991', 'Deposition 2001' and 'Deposition 1850') resulted in almost identical base saturations (88%) predicted for 2030.

TARGET LOADS

Multiple target load functions for stream water were calculated using MAGIC model, version 7, distributed in 2002 (Cosby *et al.*, 2001). They were calculated for both catchments in 2030 using deposition scenarios of SO_4 and NO_3 displayed in Fig. 2. The values of ANC=0 μeq L^{-1} and ANC=40 μeq L^{-1} for stream water were chosen as criteria for target load calculations (Fig. 7).

Critical loads were not exceeded for any of the deposition scenarios mentioned at Pluhuv Bor which confirmed the large resistance to acidification of stream water in that catchment (figures not shown) in the annual time step. The annual values of ANC (or pH and Gran alkalinity) are high at Pluhuv Bor; however, these parameters could be depressed significantly in stream water during short-term snow melt periods or large storms due to acidification via shallow water pathways (Krám *et al.*, 2003; Shanley *et al.*, 2004).

For Lysina, the continuation of deposition measured in 1991 will result in significant exceedence of the target load under both criteria. The target loads will not be exceeded

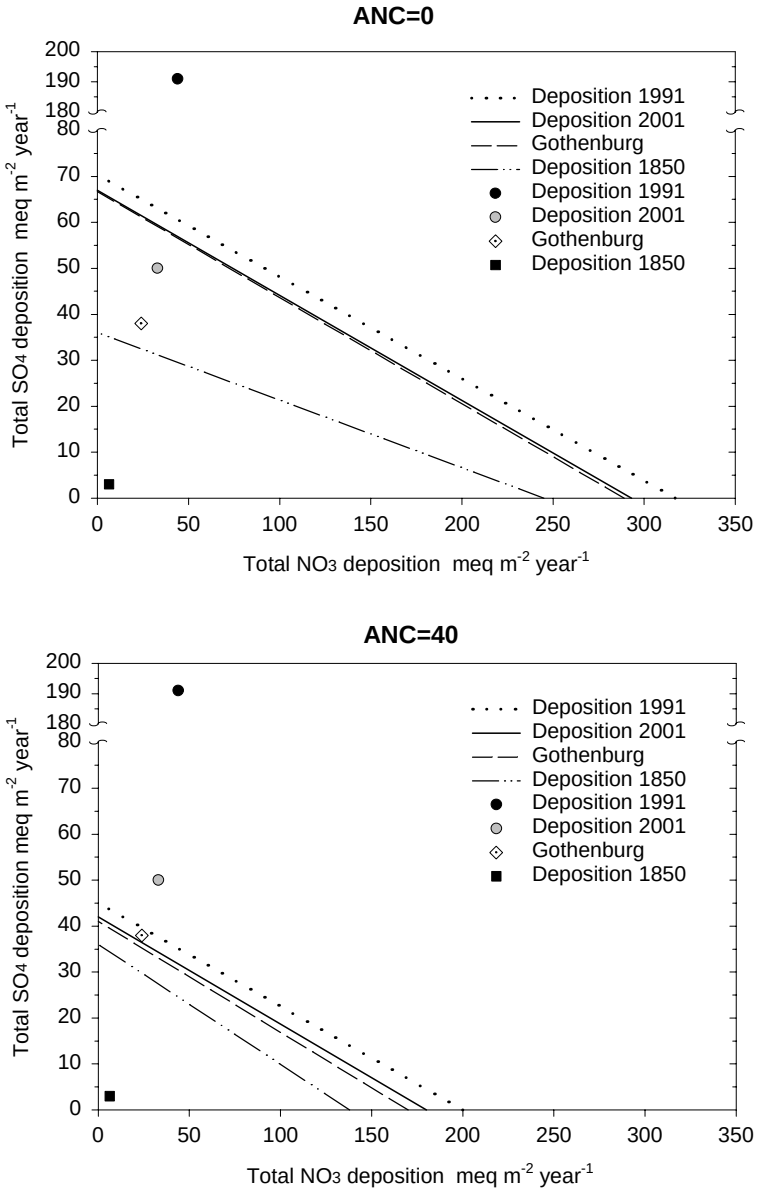

Fig. 7. *Combined critical loads for sulphate and nitrate deposition (lines) calculated for two target concentrations in stream waters (represented by the acid neutralising capacity = 0 μeq L^{-1} and 40 μeq L^{-1}) at Lysina catchment for 2030. Point symbols represent deposition projected according to appropriate scenarios (Fig. 2) for 2030. Location below the appropriate line means that the total atmospheric deposition in that scenario is below the critical load, location above the line means the deposition is higher than the corresponding critical load.*

for ANC=0 μeq L^{-1} using scenarios 'Deposition 1991' and 'Gothenburg' (Fig. 2) but will be exceeded significantly for 'Deposition 2001' and slightly for 'Gothenburg' using the criterion ANC=40 μeq L^{-1} (Fig. 7). Target loads declined significantly when scenario 'Deposition 1850' was applied, but for both ANC criteria they were not exceeded in 2030. Although ANC shows significant chemical recovery at Lysina, it is important to stress that ANC alone is not a good criterion for aquatic biota recovery in streams containing high DOC concentrations. In such waters, pH and total Al (which is present mainly in inorganic form at Lysina) remain far from the levels acceptable to fish and many other vertebrates. For example, at ANC=0 μeq L^{-1}, pH at Lysina will be only around 4.1 and total Al will be 20 μmol L^{-1} (Fig. 6a). For ANC=40 μeq L^{-1}, pH will reach only 4.4 and total Al is predicted to be 15 μmol L^{-1}. Aluminium will remain well above the potentially dangerous long-term exposure level (3.2 μmol L^{-1}) for sensitive aquatic biota (Gensemer and Playle, 1999). A reasonable ANC criterion for Lysina can be estimated at ANC=120 μeq L^{-1}, which corresponds to the modelled pre-industrial situation (Fig. 4a). This critical load (for 2030) cannot possibly be achieved under any of the deposition scenarios (even if deposition of sulphate and nitrate ceased completely in 2003).

Conclusions

Recovery from acidification of stream water (pH) and soil (base saturation) was fairly small during the period 1990–2002 compared to the estimated pre-industrial status at the acid-sensitive Lysina catchment, despite the large and rapid decline in SO_4 in stream water. In the next three decades, stream water pH is predicted to increase only slightly if atmospheric deposition does not decline much further than the current legislation (Gothenburg Protocol) requires. On the other hand, the environmental situation at Lysina will be much better than in the hypothetical scenario without implementation of the Gothenburg Protocol.

Areas with high weathering rates on acid resistant bedrock, represented by Pluhuv Bor, were able to mitigate long-term high loading of acidifying compounds successfully. Annual mean stream water chemistry experienced only negligible acidification problems in the past and no deterioration is predicted for the future. An extremely large decline in SO_4 concentrations in stream water at Pluhuv Bor was caused by a considerable reduction in dry deposition of S on this area and by shallow soils with low sulphate adsorption capacity.

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