

## Response of alpine lakes and soils to changes in acid deposition: the MAGIC model applied to the Tatra Mountain region, Slovakia-Poland

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### ABSTRACT

A dynamic process-based model of surface water acidification, MAGIC, was applied to 31 representative alpine lakes in the Tatra Mountains (~50% of all alpine lakes >0.3 ha in the lake-district). The model was calibrated to observed lake chemistry for the period 1980-2002. Surface water and soil chemistry were reconstructed from 1860 to 2002, given estimates of historical acid deposition, and forecast to 2020 based on the reduction in sulphur and nitrogen emissions presupposed by the Gothenburg Protocol. In the 1860s, all lakes were buffered by the carbonate system and only ~6% of lakes had acid neutralising capacity (ANC) <20 µeq l<sup>-1</sup>. Lake acidification progressed until 1980s, at which time 23% of lakes had a depleted carbonate buffering system and 33% of lakes had ANC <20 µeq l<sup>-1</sup>. Reversal of water chemistry from acidification started in the late 1980s as a response to decreasing acid deposition. ANC has increased such that only ~16% of the lake population currently has ANC <20 µeq l<sup>-1</sup>. The number of low ANC lakes is predicted to decrease to 10% by 2020, but the original carbonate buffering system of these lakes will not be re-established. The patterns in long-term changes of sulphate and chloride primarily reflected trends in atmospheric deposition and were similar for all lakes. Base cations (BC), ANC, nitrate, and pH, however, were significantly influenced by catchment characteristics. The water chemistry response to changes in strong acid anion (SAA) inputs varied among the lakes. The changes in SAA were compensated for (1) by parallel changes in BC concentrations (~75% of the SAA change) in non-sensitive lakes (high weathering rates and abundant soils with high base saturation), (2) by inverse changes in bicarbonate concentrations (>50% of the SAA change) in sensitive lakes with intermediate weathering rates and little soils (low BC exchangeable capacity and elevated terrestrial export of nitrate) and (3) by parallel changes in concentrations of protons and aluminium (each ~20% of the SAA change) in extremely sensitive lakes, with the lowest weathering rates and soil base saturation. The full implementation of the Gothenburg Protocol will not be sufficient to allow recovery of the latter group of lakes, which will remain acidified after 2020.

Key words: atmospheric deposition, water chemistry, acidification, recovery

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### 1. INTRODUCTION

Surface water acidification due to atmospherically-deposited sulphur (S) and nitrogen (N) compounds became a major ecosystem stress in acid sensitive regions over Europe during the 1900s. The adoption of four international protocols to reduce S and N emissions during the 1980s and 1990s (Jenkins 1999) led to a significant decrease in acid deposition and a widespread reversal of European surface waters from acidification (e.g., Evans *et al.* 2001; Jenkins *et al.* 2003). The last (Gothenburg) Protocol was signed in 1999, and when fully implemented by 2010 will significantly reduce emissions of S and both oxidised and reduced N compound across Europe (UN-ECE 1999).

In this study we apply a dynamic process-based model - MAGIC (Model of Acidification of Groundwater in Catchments; Cosby *et al.* 2001) - to reconstruct past acidification and predict recovery of lake water chemistry in the Tatra Mountains, one of the most severely acidified European alpine ecosystems. Such results should be relevant for decision-makers, in that they

give an estimate of surface water recovery after full implementation of the Gothenburg Protocol.

The Tatra Mountain lakes have exhibited a pronounced long-term dynamic in nitrate concentrations and great differences in water chemistry due to their catchment characteristics (Kopáček *et al.* 2000). Thus, the MAGIC calibration of the lakes was site-specific and was first tested at four selected lakes (Kopáček *et al.* 2003). The successful approach was then applied to another 27 representative Tatra Mountain lakes. This study evaluates the modelled long-term trends in water chemistry of the Tatra Mountain lakes on a regional scale, compares the modelled and measured data, and simulates the future water response in the lake district given reductions in S and N deposition under the Gothenburg Protocol (UN-ECE 1999).

### 2. METHODS

#### 2.1. Data sources

The Tatra Mountains belong to the Carpathian chain and are situated at the Slovak-Polish border (20° E,

**Tab. 1.** Major morphological and hydrological characteristics for the Tatra Mountain catchment-lake ecosystems. Numbers at lake names represent lake sensitivity to acidification: <sup>1)</sup> non-sensitive; <sup>2)</sup> sensitive; <sup>3)</sup> extremely sensitive.

Lake code	Lake name	Altitude (m a.s.l.)	Lake volume (10 <sup>3</sup> m <sup>3</sup> )	Max depth (m)	Lake area (ha)	Seepage	Residence time (y)	Precipitation (m y <sup>-1</sup> )	Catchment area (ha)	Max relief (m)	Bare rocks (%)	Moraine (%)	Meadow (%)
TA0001	Horné Roháčske <sup>1)</sup>	1718	49	8	1.5	no	0.29	1.44	14	302	40	20	40
TA0003	Nižné Jamnícke <sup>1)</sup>	1728	18	9	1.1	no	0.03	1.35	49	335	20	20	60
TA0004	Vyšné Račkove <sup>1)</sup>	1697	35	13	0.7	no	0.05	1.36	56	440	20	20	60
TA0006	Veľké Bystré <sup>1)</sup>	1876	43	13	0.9	yes	0.10	1.53	32	372	20	30	50
TA0007	Zielony Staw Gašienicowy <sup>1)</sup>	1672	261	15	3.8	no	0.65	1.43	33	419	40	10	50
TA0008	Zelené krivánske <sup>1)</sup>	2017	305	23	4.3	yes	0.38	1.61	59	478	60	20	20
TA0009	Długi Staw Gašienicowy <sup>2)</sup>	1784	81	11	1.6	no	0.09	1.59	65	517	44	27	29
TA0010	Zadni Staw Gašienicowy <sup>2)</sup>	1852	15	8	0.5	no	0.04	1.64	25	449	60	30	10
TA0011	Nižné Terianske <sup>1)</sup>	1941	879	43	4.9	no	0.57	1.64	110	487	40	32	28
TA0013	Czarny Staw Gašienicowy <sup>1)</sup>	1620	3798	51	17.9	no	1.5	1.47	205	671	40	25	35
TA0014	Vyšné Terianske <sup>3)</sup>	2109	8.9	4	0.5	yes	0.03	1.76	19	319	40	45	15
TA0017	Vyšné Wahlenbergovo <sup>2)</sup>	2145	421	21	5.0	yes	0.93	1.67	32	259	37	51	12
TA0018	Czarny Staw Polski <sup>1)</sup>	1722	2826	50	12.7	no	3.8	1.45	60	333	40	15	45
TA0019	Nižné Temnosmrečinské <sup>1)</sup>	1674	2161	41	13.2	no	0.83	1.43	215	704	35	15	50
TA0022	Vyšné Temnosmrečinské <sup>1)</sup>	1716	460	20	4.5	no	0.33	1.46	112	662	40	34	26
TA0023	Wielki Staw Polski <sup>1)</sup>	1655	12967	79	34.4	no	2.1	1.50	491	646	30	15	55
TA0026	Malé Hincovo <sup>1)</sup>	1923	74	6	2.2	yes	0.29	1.43	21	277	20	30	50
TA0027	Veľké Hincovo <sup>1)</sup>	1946	4139	53	18.2	no	2.5	1.54	127	486	35	40	25
TA0029	Czarny Staw pod Rysami <sup>1)</sup>	1580	7762	76	20.6	no	3.4	1.51	179	920	50	20	30
TA0030	Veľké Žabie <sup>2)</sup>	1919	63	7	2.3	yes	0.06	1.54	87	581	40	20	40
TA0031	Dračie <sup>1)</sup>	1998	120	16	1.7	yes	0.16	1.62	56	549	40	30	30
TA0032	Vyšné Žabie bielovodské <sup>1)</sup>	1699	736	24	8.1	no	0.56	1.51	101	564	30	20	50
TA0036	Litvorové <sup>1)</sup>	1863	130	19	1.7	no	0.14	1.69	63	566	30	45	25
TA0037	Batizovské <sup>2)</sup>	1879	160	11	2.8	no	0.05	1.57	234	775	40	30	30
TA0042	Pusté <sup>1)</sup>	2055	40	7	1.2	no	0.14	1.60	20	328	20	30	50
TA0045	Ladové pleso <sup>1)</sup>	2057	114	18	1.7	yes	0.66	1.59	13	293	32	53	15
TA0047	Starolesnianske <sup>3)</sup>	1986	11	4	0.7	no	0.41	1.42	2.3	44	30	10	60
TA0049	Žabie javorové <sup>1)</sup>	1886	47	16	0.8	no	0.05	1.78	67	717	30	35	35
TA0054	Veľké spišské <sup>2)</sup>	2014	138	10	2.4	no	0.08	1.66	123	613	20	40	40
TA0107	Satanie <sup>3)</sup>	1900	1.3	2	0.2	no	0.05	1.34	2.1	80	30	15	55
TA0108	Morskie Oko <sup>1)</sup>	1395	9935	51	34.9	no	1.3	1.38	630	1105	40	20	40

49°15' N). The total number of alpine Tatra Mountain lakes with an area >0.3 ha is 56 (other 28 lakes have an area 0.1-0.3 ha). All are perennial, of glacial origin, and situated in the western (the West Tatra Mountains) and central (the High Tatra Mountains) regions. For the purpose of this study we selected 31 lakes (~50% of all major alpine lakes >0.3 ha) along the Tatra Mountains on the basis of previous studies (e.g., Kopáček *et al.* 2000), so that the selected lakes were representative for the alpine zone both regionally (geographic position; altitude) and morphologically (dominant land cover in the catchment). Thirty lakes are situated between 1580 and 2145 m above sea level (a.s.l.) and the highest points of their catchments range from 1980 to 2654 m a.s.l. Among them, only lake TA0107 has an area <0.3 ha. One lake (Morskie Oko, TA0108) is situated below the local tree line at an altitude of 1395 m a.s.l., but most of its catchment lies in the alpine zone. Consequently, its chemistry is comparable with the other alpine Tatra Mountain lakes and differs significantly from the forest lakes in the region. The lake was included in this study due to its extensive historical record of water chemistry. Major morphological characteristics and numerical codes of selected lakes are given in table 1.

Vegetation of the alpine zone of the Tatra Mountains is dominated by alpine meadows (dry tundra with mostly *Calamagrostis villosa*, *Festuca picta*, and *Luzula luzuloides*), with patches of dwarf pine (*Pinus mugo*), and an increasing percentage of rocks (bare or covered with lichens - commonly *Rhizocarpon*, *Acarospora oxytona*, and *Dermatocarpon luridum*) above the upper tree line of 1800 m a.s.l. (Vološčuk 1994).

Geological characteristics were estimated by using a 1:50,000 map (Nemčok *et al.* 1993). The bedrock geology of the High Tatra Mountains is composed almost exclusively of granitoids (mostly biotite granodiorites to tonalites), while the West Tatra Mountains also contain a significant amount of metamorphics (gneiss and mica schist) in addition to granodiorite.

Data on soil come from a 1998-2001 survey (Stuchlík *et al.* 2002; Kopáček *et al.* 2004). Alpine soils (in meadows) are mostly regosols, leptosols, podsoles, and cambisols, with negligible carbonate content. Soil depth and amount of dry weight <2 mm soil vary from 0.1 to 0.84 m and from 38 to 255 kg m<sup>-2</sup>, with averages of 0.45 m and 121 kg m<sup>-2</sup>, respectively. Soil pH is generally low, with pH<sub>CaCl2</sub> within the 3.2-4.2 range in organic and 3.6-4.8 range in mineral horizons. The cation ex-

**Tab. 2.** Major soil (dry, <2 mm) and water characteristics for the Tatra Mountain catchment-lake ecosystems. For lake names see table 1. Measured soil data (\*). Soil pool, dry weight <2 mm soil fraction; CEC, cation exchangeable capacity (1M NH<sub>4</sub>Cl extractable Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> plus 1M KCl extractable Al<sup>3+</sup> and H<sup>+</sup>); BS, base saturation; C-org, organic carbon.

Lake code	Soil characteristics					Water characteristics (1997-2000 average)											
	Soil pool (kg m <sup>-2</sup> )	Depth (m)	C org. (mol m <sup>-2</sup> )	CEC (meq kg <sup>-1</sup> )	BS (%)	Ca <sup>2+</sup> (μeq l <sup>-1</sup> )	Mg <sup>2+</sup> (μeq l <sup>-1</sup> )	Na <sup>+</sup> (μeq l <sup>-1</sup> )	K <sup>+</sup> (μeq l <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (μeq l <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (μeq l <sup>-1</sup> )	Cl <sup>-</sup> (μeq l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (μeq l <sup>-1</sup> )	ANC (μeq l <sup>-1</sup> )	pH	Al (μeq l <sup>-1</sup> )	DOC (μmol l <sup>-1</sup> )
TA0001*	44	0.20	332	123	9	102	11	15	3.0	0.9	58	4.2	25	39	6.33	0.19	46
TA0003*	64	0.41	228	107	7	155	101	22	2.6	0.5	73	5.2	18	188	7.07	<0.01	33
TA0004*	77	0.24	137	53	15	163	145	22	2.7	0.6	67	4.8	19	235	7.07	0.01	29
TA0006*	46	0.18	389	116	14	299	79	21	3.3	4.3	55	6.0	26	314	7.13	<0.01	83
TA0007	62	0.23	352	98	12	134	16	22	3.4	0.9	51	4.5	17	98	6.76	<0.01	67
TA0008	27	0.09	147	95	12	133	7	23	2.7	2.9	49	4.2	29	80	6.71	<0.01	25
TA0009*	33	0.11	136	91	11	90	8	15	2.8	1.5	52	3.8	35	21	6.11	0.07	16
TA0010*	15	0.05	63	79	13	103	8	18	2.0	1.9	48	3.8	44	37	6.38	0.00	20
TA0011*	51	0.13	296	86	8	139	7	14	2.4	0.8	45	4.1	28	82	6.69	<0.01	25
TA0013	45	0.16	253	96	12	113	11	15	3.1	1.1	58	5.7	36	34	6.24	<0.01	43
TA0014*	52	0.14	280	94	7	41	5	8	2.2	0.8	35	3.1	25	-4	5.13	2.67	56
TA0017*	22	0.08	79	72	11	83	8	9	1.7	0.8	37	4.4	29	26	6.20	0.03	14
TA0018	56	0.20	319	98	12	114	10	16	2.6	0.8	50	5.0	19	61	6.47	<0.01	62
TA0019	62	0.23	354	98	12	274	24	17	2.6	2.0	54	4.9	22	216	7.01	<0.01	30
TA0022*	28	0.10	283	126	9	294	28	17	2.7	3.0	52	4.5	20	252	7.05	<0.01	17
TA0023	68	0.25	389	98	12	122	10	16	2.5	0.9	48	4.2	21	71	6.63	<0.01	38
TA0026*	44	0.24	160	95	16	306	85	15	2.3	1.1	110	3.8	17	276	7.18	<0.01	55
TA0027*	50	0.15	377	114	12	165	15	14	2.3	0.3	58	4.3	29	102	6.76	0.01	29
TA0029	39	0.14	216	96	12	212	14	16	2.6	0.7	69	4.7	32	133	6.91	<0.01	31
TA0030	51	0.18	286	97	12	104	7	11	2.2	1.5	49	4.3	32	35	6.22	<0.01	13
TA0031	40	0.14	220	95	12	176	11	15	2.0	1.4	55	3.9	33	111	6.70	<0.01	4
TA0032*	51	0.25	344	139	10	109	8	15	2.2	1.5	54	3.5	22	46	6.31	<0.01	36
TA0036	36	0.11	191	92	12	165	13	16	2.0	1.0	50	2.9	31	109	6.86	<0.01	12
TA0037	40	0.14	220	95	12	99	8	16	2.4	0.7	54	4.2	30	29	6.21	0.04	12
TA0042	64	0.23	359	97	12	169	12	14	2.8	1.6	46	2.6	21	130	6.88	<0.01	23
TA0045*	29	0.06	109	74	20	110	7	11	1.7	1.6	35	3.8	23	67	6.57	0.03	12
TA0047*	100	0.29	489	99	8	29	6	9	3.9	1.8	43	3.5	4	-2	5.27	0.95	103
TA0049	47	0.16	257	95	12	209	13	16	2.0	1.9	68	3.2	40	131	6.99	0.00	8
TA0054	53	0.18	294	95	12	76	6	8	1.1	0.1	36	3.7	29	20	6.08	<0.01	14
TA0107	68	0.25	389	97	12	28	7	11	3.4	1.5	50	4.4	10	-8	4.96	6.33	91
TA0108	51	0.18	286	97	12	189	14	19	3.2	1.2	64	4.9	26	128	6.82	0.01	41

changeable capacity (1M NH<sub>4</sub>Cl extractable Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> plus 1M KCl extractable Al<sup>3+</sup> and H<sup>+</sup>) of alpine soils varies between 20 and 207 meq kg<sup>-1</sup> (all horizons) and is dominated by exchangeable Al<sup>3+</sup> (70% on average). The base saturation of soils is 4-45% (12% on average) of the cation exchangeable capacity, and is primarily based on Ca<sup>2+</sup> (~40%). The till soils in moraine areas form thin (<3 cm deep) layers covered by a 20-60 cm thick layer of surface stones, or lenses between stones. Pools of the till soils vary between 4-33 kg m<sup>-2</sup>, with an average of 13 kg m<sup>-2</sup> (<2 mm; dried weight), and their chemical composition is similar to mineral layers of alpine soils.

The soil data used in this study were measured in 15 catchments (lakes with asterisks in table 2). The mean physical-chemical composition of the meadow soil profile was calculated for each catchment, but that for the moraine class was averaged across all catchments. These soil characteristics were then used to calculate a catchment-weighted mean soil amount (and composition) using the proportion of alpine meadows and moraine areas in the catchment area. The areas of land

cover classes (Tab. 1) were estimated by using a 1:25,000 map, planimetry of photographs, and field observations. The soil data for 16 other catchments were derived from their land cover characteristics and the average pools and mean composition of the meadow and till Tatra Mountain soils (Tab. 2).

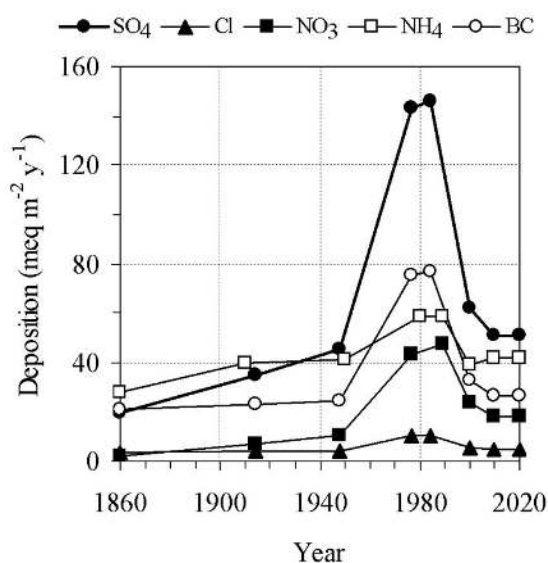
Data on lake water chemistry come from: (i) Stanzenberg (1938) for 1937 (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>), (ii) Bombówna (1965) and Procházková (unpubl. data) for 1963 and 1961, respectively (pH, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>), (iii) Stuchlík *et al.* (1985; unpubl. data) and Bombówna & Wojtan (1996) for 1980-1984 and 1985, respectively, (iv) Henriksen *et al.* (1992), Kopáček & Stuchlík (1994), Kopáček *et al.* (2002) and Stuchlík (unpubl. data) for the 1986-2002 period. No reliable historical data are available for acid neutralising capacity (ANC) and base cations (BC; sum of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) before the 1980s or for pH before the 1960s. Since the 1980s, the lakes have been sampled once a year in September-October. In the 1980-1992 period, anions were determined colorimetrically and/or by capillary isotachopheresis, and BC and Al by atomic absorption spectrophotometry and/or inductively

coupled plasma atomic emission spectrometry. Since 1992, concentrations of major ions have been analysed by ion chromatography and Al colorimetrically according to Driscoll (1984). ANC has been determined by Gran titration since 1980. Positive ANC is given as  $\text{HCO}_3^-$  concentration. Dissolved organic carbon (DOC) was analysed using a TOC 5000A analyser (Shimadzu). More details on analytical methods used for analyses before and after 1992 are given by Kopáček & Stuchlík (1994) and Kopáček *et al.* (2000), respectively.

The long-term average annual precipitation amount was derived for individual catchments from the following sources: (i) the 1941–2001 average precipitation at Skalnaté Pleso (1.34 m at 1778 m a.s.l.; southern part of the central massif; data of the Geophysical Institute of the Slovak Academy of Sciences), and (ii) the elevation gradient of catchment, assuming increasing precipitation proportionally to altitude by 40 and 70 mm per 100 m of elevation in the southern and northern part of the mountain range, respectively (Chomitz & Šamaj 1974). The resulting data (Tab. 1) were used as constants for the whole study period. The specific outflow in the alpine zone of the Tatra Mountains was estimated at 85% of the deposition (Lajczak 1996).

The 1860–2000 trends in bulk deposition of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  in the Tatra Mountains come from Kopáček *et al.* (2001) and were based on the following data sources: (i) the measured current deposition at Starolesnianske Lake (southern part; 2000 m a.s.l.) in 1997–2000 (Stuchlík *et al.* 2002; unpubl. data) and at Hala Gasienicowa (northern part; 1520 m a.s.l.) in 1993–1998 (Lydersen *et al.* 1997; The MOLAR Chemistry Group 1999), (ii) the long-term trend (1978–2000) in bulk deposition in northern Slovakia (Chopok station, situated ~40 km south west of the Tatra Mountains at an elevation of 2008 m; data of the Slovak Hydrometeorological Institute), and (iii) S and N emission rates in central Europe (Kopáček *et al.* 2001). The deposition scenario used for the future (2000–2020) predictions, has a decreasing trend until 2010 and then is constant until 2020. The changes in deposition of S and N compounds within the 2000–2010 period were assumed to be proportional to the changes in their respective emission levels in central Europe as required by the Gothenburg Protocol (UN-ECE 1999). Trends in deposition of Cl<sup>-</sup> and BC were the sums of their background values (3.6 and 21  $\text{meq m}^{-2} \text{y}^{-1}$ , respectively) and contributions from industrial sources, which were assumed to be proportional to S emissions in the region (Kopáček *et al.* 2003). The respective dry deposition of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  in the Tatra Mountains (13.2, 7.1, and 11.6  $\text{meq m}^{-2} \text{y}^{-1}$ ; Lydersen *et al.* 1997) represented 19%, 16%, and 36% of their bulk deposition in 1995–1996. These values were used to estimate trends in dry deposition factors, which varied between 1.0 and 1.2 for  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , Cl<sup>-</sup> and BC, and between 1.0 and 1.35 for  $\text{NO}_3^-$ . The highest dry deposition factors were applied

for the 1970s and 1980s, and lower values (proportional to the bulk deposition levels) before 1970 and after 2000 (Kopáček *et al.* 2003). Then, the total deposition was the product of bulk deposition and dry deposition factor (Fig. 1).



**Fig. 1.** Long-term trends in total deposition of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , Cl<sup>-</sup>, base cations (BC), and  $\text{NH}_4^+$  in the Tatra Mountains used for MAGIC modelling. Data were derived from Kopáček *et al.* (2003).

The deposition sequences used in this study were successfully applied for MAGIC modelling of four lakes in the Tatra Mountains (Kopáček *et al.* 2003). In general, they have similar shapes to the deposition sequences derived for the region from the EMEP Lagrangian acid deposition model by Schöpp *et al.* (2003), but they are lower and have a broader peak of maximum N deposition in the 1970s and 1990s (consistent with the measured data at the nearby Chopok station; Kopáček *et al.* 2001).

## 2.2. Model calibration

The MAGIC (version 7) model by Cosby *et al.* (2001) was calibrated individually to each lake using the average atmospheric deposition for the 1997–2000 period, lake water chemistry for the 1997–2002 period, and soil chemistry for the 1998–2001 period (Tab. 2). The calibrations at each site proceeded by the following sequential steps:

- 1) Trends in the total deposition of  $\text{SO}_4^{2-}$ , Cl<sup>-</sup>,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and BC into the catchments were applied as shown in figure 1.
- 2) Fixed parameters (Tab. 3): Dissociation constants of tri-protic organic acids, the  $\text{Al}(\text{OH})_3$  solubility, and stability constants of organic-Al complexes ( $K(\text{AlA})$  and  $K(\text{AlHA}^+)$ ) were set according to Majer *et al.* (2003), where the modelled concentrations reasonably

**Tab. 3.** Fixed parameters (measured\* or estimated) for the Tatra Mountain lakes and catchment soils used in calibration of MAGIC. <sup>1)</sup>Estimated and tested by Majer *et al.* (2003) and Kopáček *et al.* (2003).

Parameter	For water or soil	Units	All lakes
Temperature*	soil and water	°C	2-3
Organic acid anions	water	mmol m <sup>-3</sup>	0.2-4.9
	soil <sup>1)</sup>	mmol m <sup>-3</sup>	85
CO <sub>2</sub> partial pressure	water	%	0.04-0.08
	soil	%	0.4
pK <sub>1</sub> (organic acids)	soil and water	-Log	2.6
pK <sub>2</sub> (organic acids)	soil (water)	-Log	5.66 (5.8)
pK <sub>3</sub> (organic acids)	soil (water)	-Log	5.94 (7.0)
Solubility Al(OH) <sub>3</sub>	soil and water	Log	9.0
SO <sub>4</sub> <sup>2-</sup> ads. maximum-capacity	soil	meq kg <sup>-1</sup>	12
SO <sub>4</sub> <sup>2-</sup> ads. half-saturation	soil	meq m <sup>-3</sup>	100
K(AIA)	water	Log	8.5
K(AlHA <sup>+</sup> )	water	Log	10

**Tab. 4.** Median values and ranges of calibrated parameters for the Tatra Mountain lakes obtained from MAGIC. Number of observations, 31.

	Units	Minimum	25%	Median	75%	Maximum
Cation exchange selectivity coefficients						
Al-Ca	Log	-1.7	1.1	2.7	6.8	10.7
Al-Mg	Log	-2.0	-1.0	0.4	4.6	10.1
Al-Na	Log	-6.1	-5.1	-3.7	-2.5	0.2
Al-K	Log	-7.6	-7.2	-6.2	-4.7	-2.8
Weathering rates						
Ca <sup>2+</sup>	meq m <sup>-2</sup> y <sup>-1</sup>	12	100	122	194	363
Mg <sup>2+</sup>	meq m <sup>-2</sup> y <sup>-1</sup>	3	5	8	15	126
Na <sup>+</sup>	meq m <sup>-2</sup> y <sup>-1</sup>	2	7	10	12	19
K <sup>+</sup>	meq m <sup>-2</sup> y <sup>-1</sup>	0.1	0.2	0.3	0.6	1.4
Initial base saturation (1860)						
Ca	%	2.3	6.0	8.2	9.8	21.2
Mg	%	1.0	2.3	2.9	3.3	4.1
Na	%	0.6	2.6	3.1	3.5	4.4
K	%	1.3	1.9	2.2	2.4	2.7

equalled the observed lake water concentrations of ionic and organic Al forms and organic acid anions.

- 3) Net annual removal of NO<sub>3</sub><sup>-</sup> in the lakes was estimated according to Kelly *et al.* (1987), with the mass transfer coefficient (5.0 m y<sup>-1</sup>) set at a lower range of values given by Kaste & Dillon (2002). Because the bottoms of some lakes are partly covered with rocks and big boulders, the above results were reduced proportionally to the per cent cover of bottom with sediment. The area of sediment was estimated at the lakes, and varied between 10% and 100% of the lake area. For lakes with no information on sediment cover a value of 50% was used. Estimated values of in-lake removal of NO<sub>3</sub><sup>-</sup> (1-65% of the loading) were held constant for the whole period. Net annual removal of SO<sub>4</sub><sup>2-</sup> in the lakes (1-14% of its loading), estimated according to Kelly *et al.* (1987) was too low for seepage lakes to satisfactorily model maxima in SO<sub>4</sub><sup>2-</sup> concentrations in the 1980s or the current lowered concentrations (Kopáček *et al.* 2003). Consequently, the values of in-lake SO<sub>4</sub><sup>2-</sup> removal were fitted during the calibration process and were used in the range of 1-30%.

Moreover, the fitted values represented a correction for uncertainties associated with S dynamics within the whole catchment-lake ecosystems. We assumed that the fitted percent in-lake removal of SO<sub>4</sub><sup>2-</sup> was stable throughout the study period. Net annual retention of BC in the lakes was neglected.

- 4) The soil sulphate chemistry was fitted in the calibration procedure such that modelled concentration equalled the measured in-lake concentrations of SO<sub>4</sub><sup>2-</sup> in the 1980s and 1990s, because the measured adsorption data (1.6 to 4.6 meq kg<sup>-1</sup>) were too low (Kopáček *et al.* 2003). The fitted SO<sub>4</sub><sup>2-</sup> maximum adsorption capacity, which reasonably simulated the observed trends in water chemistry, was 12 meq kg<sup>-1</sup>, and was used for all catchments. The used SO<sub>4</sub><sup>2-</sup> adsorption half saturation was 100 meq m<sup>-3</sup>.
- 5) In the model, net catchment retention of N was roughly set as a function of time and catchment characteristics as follows: (i) For the 1860-1945 period, 100% uptake of NO<sub>3</sub><sup>-</sup> was assumed only in the part of catchment covered with meadows and 100% uptake of NH<sub>4</sub><sup>+</sup> was assumed in the whole catchment. (ii) For the 1955-2020 period, 100% uptake of

$\text{NH}_4^+$  and  $\text{NO}_3^-$  was assumed only in the part of catchment covered with meadows. (iii) For the 1945-1955 period, linear interpolation was used between the previous and following periods. The  $\text{NO}_3^-$  entering the lake originated from  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition on the rocky and moraine areas. We assumed that all  $\text{NH}_4^+$  deposited to these parts of the catchment was nitrified but not retained in the soils (Kopáček *et al.* 2003). These adjustments to the N parameters were needed in order to adequately calibrate the model to observed changes in  $\text{NO}_3^-$  concentrations.

- 6) 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 concentrations equalled the measured soil exchange pools and lake chemistry concentrations of each base cation for the 1998-2001 period (Tab. 4). The obtained rates and coefficients were applied as constants for the whole study period. The vegetation net uptake of BC and long-term net BC storage in biomass was set equal to zero as there is no removal of biomass from the catchments.

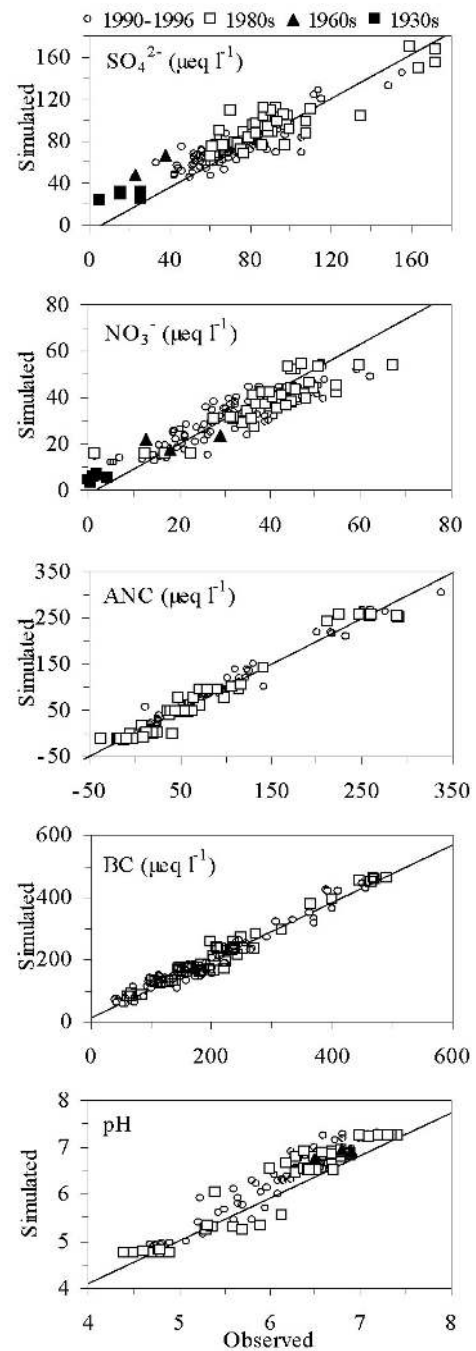
### 3. RESULTS AND DISCUSSION

#### 3.1. Simulated and observed trends in water composition

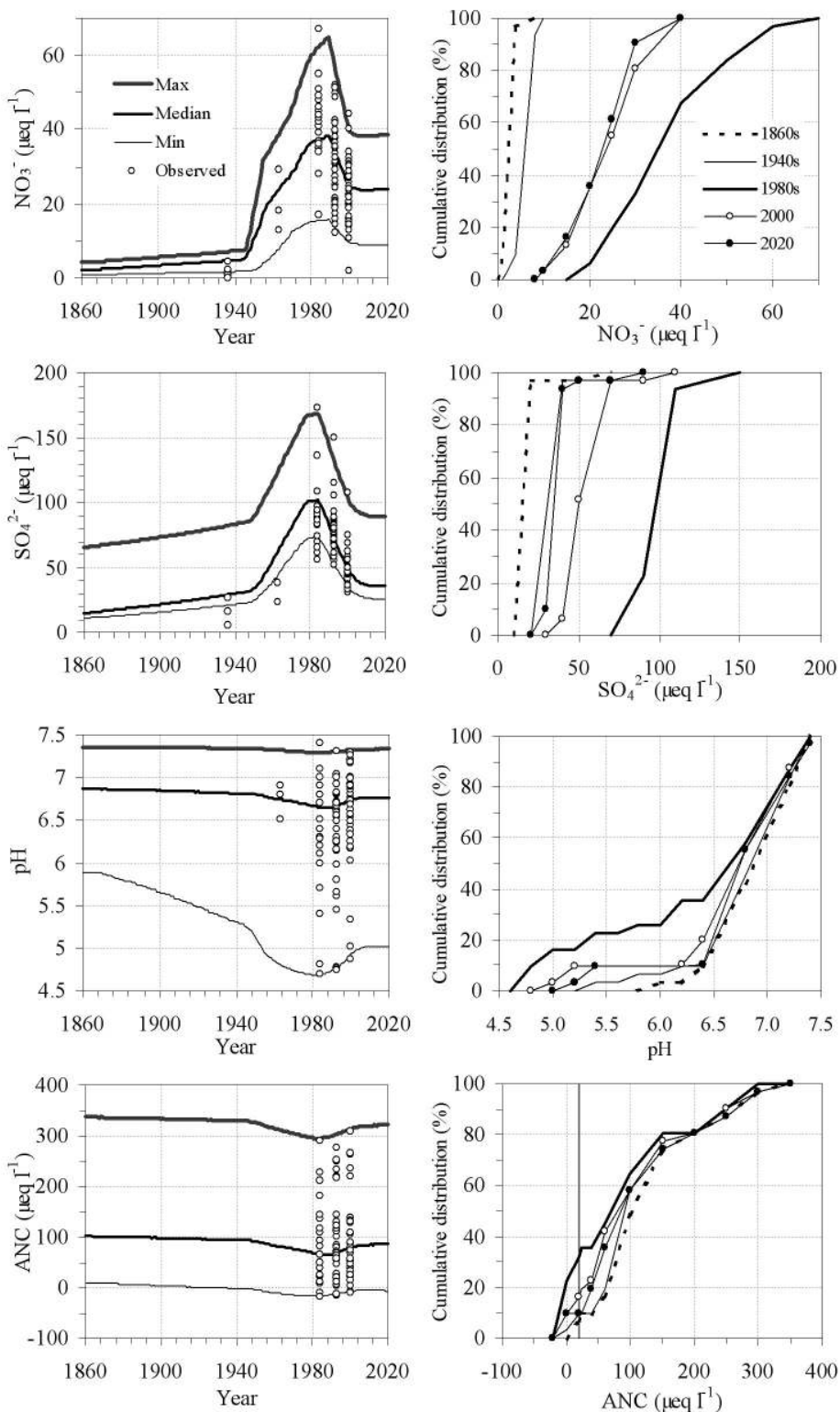
The model was successfully calibrated for all 31 lakes and the simulated concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , ANC, BC, and pH reasonably fitted the available observed data on lakes not only for the calibration years (1997-2002) but also for the 1937-1996 period, explaining 83-97% of their observed variability (Fig. 2). The simulated median composition of the alpine Tatra Mountain lakes was 21, 101, and 124  $\mu\text{eq l}^{-1}$  for strong acid anions ( $\text{SAA} = \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-$ ),  $\text{HCO}_3^-$ , and BC, respectively, in the 1860s (Tab. 5). The background SAA concentrations varied within relatively low ranges (Fig. 3), with the exception of  $\text{SO}_4^{2-}$  in lake TA0026 which also has high current  $\text{SO}_4^{2-}$  concentrations (Tab. 2). This lake has high background  $\text{SO}_4^{2-}$  concentrations (66  $\mu\text{eq l}^{-1}$ ) due probably to the weathering of S-bearing minerals in the bedrock; the soil S concentrations and pools are comparable to those in other catchments (Kopáček *et al.* 2004). The background values of pH and ANC varied within wider ranges than those of SAA (Fig. 3) and were tightly related to the BC concentrations. The simulated background relationship between ANC and BC was:  $\text{ANC} = 0.95 \times \text{BC} - 17$  (all units are  $\mu\text{eq l}^{-1}$ ;  $R = 0.99$ ). In the 1860s, all lakes still had a carbonate buffering system, and only 6% of the lake population had  $\text{ANC} < 20 \mu\text{eq l}^{-1}$  and  $\text{pH} < 6.0$  (Fig. 3).

The chemical composition of the lakes changed relatively little before the onset of major acidification in the 1950s, with the exception of pH in lakes with low

background ANC (see below). SAA concentrations then increased rapidly to their maxima in the 1980s (Tab. 5), at which time 80% of lakes had concentrations of  $\text{SO}_4^{2-} > 90 \mu\text{eq l}^{-1}$  and  $\text{NO}_3^- > 25 \mu\text{eq l}^{-1}$  (Fig. 3).



**Fig. 2.** Relationships between observed and simulated (MAGIC) concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , ANC (Gran-alkalinity), base cations (BC), and pH in the Tatra Mountain lakes (Tab. 1) during the 1937-1996 period (data for calibration years 1997-2002 not shown). Solid lines: linear regressions; numbers of observations, 130-148; all  $P < 0.001$ ;  $R^2$  values of 0.83, 0.84, 0.97, 0.96, and 0.92 for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , ANC, BC, and pH, respectively.



**Fig. 3.** Concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , pH, and ANC (Gran-alkalinity) in the Tatra Mountain lakes (Tab. 1) as simulated by MAGIC (Cosby *et al.* 2001). Left column: minimum (Min), median, and maximum (Max) simulated values (lines) and available observed data on the lakes under this study from 1937, 1963, middle 1980s, 1993-1994, and 2000 (open circles). Right column: Cumulative distribution of simulated values for the 1860s, 1940s, 1980s, 2000 and 2020. Solid line in the bottom figure represents ANC of  $20 \mu\text{eq l}^{-1}$ .

**Tab. 5.** Simulated (MAGIC) and measured (\*) median composition of the 31 selected Tatra Mountain lakes (Tab. 1). ANC, Gran-alkalinity; BC, base cations. Units,  $\mu\text{eq l}^{-1}$ .

	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$	ANC	BC
1860s	16	3	2	101	124
1940s	31	3	6	94	136
1980s	100	8	37	68	208
2000	50	4	24	79	161
2000*	52	4	26	80	161
2020	35	4	24	85	149

The observations showed that all the alpine Tatra Mountain lakes were seriously affected by acid deposition in the 1980s (Stuchlík *et al.* 1985; Kopáček & Stuchlík 1994), with concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  higher on average by  $66 \mu\text{eq l}^{-1}$  and  $30 \mu\text{eq l}^{-1}$ , respectively, compared to 1937 (Stangenberg 1938). The simulated average increases in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations during the same period agreed with those observed. This increase in SAA concentrations was accompanied by a widespread decline in lake water ANC and pH. One third of the lake population had ANC  $<20 \mu\text{eq l}^{-1}$  and 23% of the lakes had a depleted carbonate buffering system and pH  $<5.5$  in the 1980s (Fig. 3).

The deposition scenario used in this study was derived from emission trends of S and N compounds in central Europe (Kopáček *et al.* 2001) and was checked using long term data on water composition of the Bohemian Forest lakes (Majer *et al.* 2003), situated  $\sim 500$  km west of the Tatra Mountains. The simulated  $\text{SO}_4^{2-}$  concentrations, however, are higher than those observed in the early 1960s (Fig. 3). An even greater disproportion would result from the S deposition sequence provided by EMEP model (Schöpp *et al.* 2003). If the observed concentrations are correct, they indicate that the onset of strong acidification of the Tatra Mountain lakes was somewhat delayed but steeper than suggested by our modelling. The Tatra Mountain lakes are situated at a higher elevation and at a greater distance from the area of the maximum acid emissions than the Bohemian Forest and were thus probably exposed to increased depositions of pollutants later, after construction of taller smokestacks which released air pollution to higher layers of the atmosphere. The delay in acidification of the Tatra Mountain lakes (compared to the Bohemian Forest) was also suggested by the later extinction of zooplankton (Fott *et al.* 1994). The maximum acidification occurred similarly in both areas in 1977-1987.

Reversal of lake acidification started in the late 1980s and progressed rapidly throughout the 1990s (Fig. 3) due to 57% and 35% declines in deposition of  $\text{SO}_4^{2-}$  and inorganic N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ), respectively, in the Tatra Mountains between the middle 1980s and 2000 (Fig. 1). Concentrations of SAA decreased by  $66 \mu\text{eq l}^{-1}$  (Tab. 5) during this period, and all lakes (except for TA0026) had  $\text{SO}_4^{2-}$  concentrations  $<70 \mu\text{eq l}^{-1}$  in 2000

(Fig. 3).  $\text{NO}_3^-$  concentrations decreased less ( $\sim 35\%$  on average) than  $\text{SO}_4^{2-}$  (50%), and  $\sim 55\%$  of the lakes had  $\text{NO}_3^-$  concentrations  $<25 \mu\text{eq l}^{-1}$  in 2000. The significant decline in  $\text{Cl}^-$  concentrations (by  $4 \mu\text{eq l}^{-1}$  on average) was similar to that observed in the nearby Czech mountain areas and was probably associated with a decline in Cl emissions (mostly as HCl) from industrial sources in the Czech Republic and Slovakia (Veselý *et al.* 2002).

As a response to decreasing SAA concentrations, ANC and pH increased significantly, and the lake population with ANC  $<20 \mu\text{eq l}^{-1}$  decreased to  $\sim 16\%$  (Fig. 3).

Model results indicate that full implementation of the Gothenburg Protocol (UN-ECE 1999) in Central Europe will produce only relatively small additional improvements of air quality in the Tatra Mountains compared to the status in 2002 (Fig. 1). Around 2010, the  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  deposition in the Tatra Mountains ( $51$ ,  $18 \text{ meq m}^{-2} \text{ y}^{-1}$ , and  $45 \text{ meq m}^{-2} \text{ y}^{-1}$  respectively) would be at levels comparable to those in the 1950s. Nevertheless, water quality will continue to recover due to decreasing release of S stored in the soils and a slow replenishment of base cation pools in the soils.

The release of all S accumulated in the Tatra Mountain soils over the last seven decades can be expected within  $\sim 20$  years at the current rates of S deposition and  $\text{SO}_4^{2-}$  leaching (Kopáček *et al.* 2001). Lake  $\text{SO}_4^{2-}$  concentrations ( $30\text{-}40 \mu\text{eq l}^{-1}$  in 80% of lakes; Fig. 3) will be comparable to that in deposition around 2020, suggesting a future steady state condition in the S input and output from the catchment-lake ecosystems. The additional decline in SAA concentrations will lead to further recovery of lakes and only 10% of lakes will have ANC  $<20 \mu\text{eq l}^{-1}$ . However, the simulated data suggest that the original carbonate buffering system of these lakes will not yet be re-established. The water quality (with the exception of higher  $\text{NO}_3^-$  concentrations) should be comparable to that in the 1940s-1950s (Fig. 3).

In our previous studies we assumed that the increase in concentrations of SAA during the acidification phase was compensated predominantly by the decrease in  $\text{HCO}_3^-$  concentrations (Kopáček & Stuchlík 1994). A potential change in concentrations of other ions was neglected due to the absence of reliable data on BC concentrations before the 1980s. However, the extent of changes in concentrations of BC,  $\text{HCO}_3^-$ ,  $\text{Al}^{3+}$  and  $\text{H}^+$  during the lake water reversal from acidification (Kopáček *et al.* 2002), as well as dynamic modelling in this study, has shown that the response of water chemistry to the elevated SAA loading was more complex. The modelled total average increase in SAA concentrations in the lakes over the 1860-1980s period ( $122 \mu\text{eq l}^{-1}$ ) was predominantly compensated for by the increase in BC (63%),  $\text{H}^+$  and  $\text{Al}^{3+}$  (2% each), while the decline in  $\text{HCO}_3^-$  concentrations was less important (34% or  $41 \mu\text{eq l}^{-1}$  on average). Similarly, the average decline in



SAA concentrations ( $80 \mu\text{eq l}^{-1}$ ) during the lake recovery period (1980s–2020) has been compensated for predominantly by the decline in concentrations of BC (68%),  $\text{H}^+$  and  $\text{Al}^{3+}$  (3% and 2%, respectively) and the increase in  $\text{HCO}_3^-$  concentrations (28% or  $23 \mu\text{eq l}^{-1}$  on average). A similar water chemistry response to acidification and recovery was also observed in other European lake-districts (e.g., Evans *et al.* 2001) and is consistent with theoretical prognoses (Reuss & Johnson 1986).

### 3.2. Lake-to-lake variations in the region

The response of chemical composition of individual lakes to the changes in acid deposition was not uniform within the lake district but differed significantly among the lakes, reflecting predominantly their catchment characteristics and acid-base status. The acid-base status of the lakes in the 1980s (Fott *et al.* 1994) was used to divide the lakes into three main categories of sensitivity to acidification (Tab. 1): non-sensitive (NS) lakes ( $\text{pH} > 6$ ,  $\text{ANC} > 25 \mu\text{eq l}^{-1}$ ); acid-sensitive (AS) lakes ( $5 < \text{pH} < 6$ ,  $\text{ANC} 0\text{--}25 \mu\text{eq l}^{-1}$ ); and extremely sensitive (ES) lakes ( $\text{pH} < 5$ ,  $\text{ANC} < 0 \mu\text{eq l}^{-1}$ ).

In contrast to  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , which exhibited similar trends in all lake categories (Fig. 5F,  $\text{Cl}^-$  not shown), the changes in atmospheric deposition of inorganic N had the greatest impact on  $\text{NO}_3^-$  concentrations in the AS lakes (Fig. 4). The increase in  $\text{NO}_3^-$  concentrations in these lakes (both observed and simulated) was higher than the increase in atmospheric deposition of  $\text{NO}_3^-$  over the period 1860–1980, indicating that part of the deposited  $\text{NH}_4^+$  (or alternatively, an equivalent amount of mineralised soil organic N) was nitrified in soils and leached from the catchments. The catchments of AS lakes have the lowest percentage of meadows (27%) and sparse soils  $36 \pm 15 \text{ kg m}^{-2}$ , while the catchments of NS and ES have significantly larger amounts of soil ( $49 \pm 13$  and  $74 \pm 24 \text{ kg m}^{-2}$ , respectively; Table 2). The ability of alpine catchments to retain N is positively related to vegetation and amount of soil (e.g., Baron *et al.* 1994; Williams *et al.* 1996; Kopáček *et al.* 2000). The sparse vegetation and low amount of soil thus explain the low terrestrial retention of N in the AS catchments, resulting in the highest  $\text{NO}_3^-$  (and, consequently, also SSA) concentration in these lakes compared to the other categories (Fig. 5E, G).

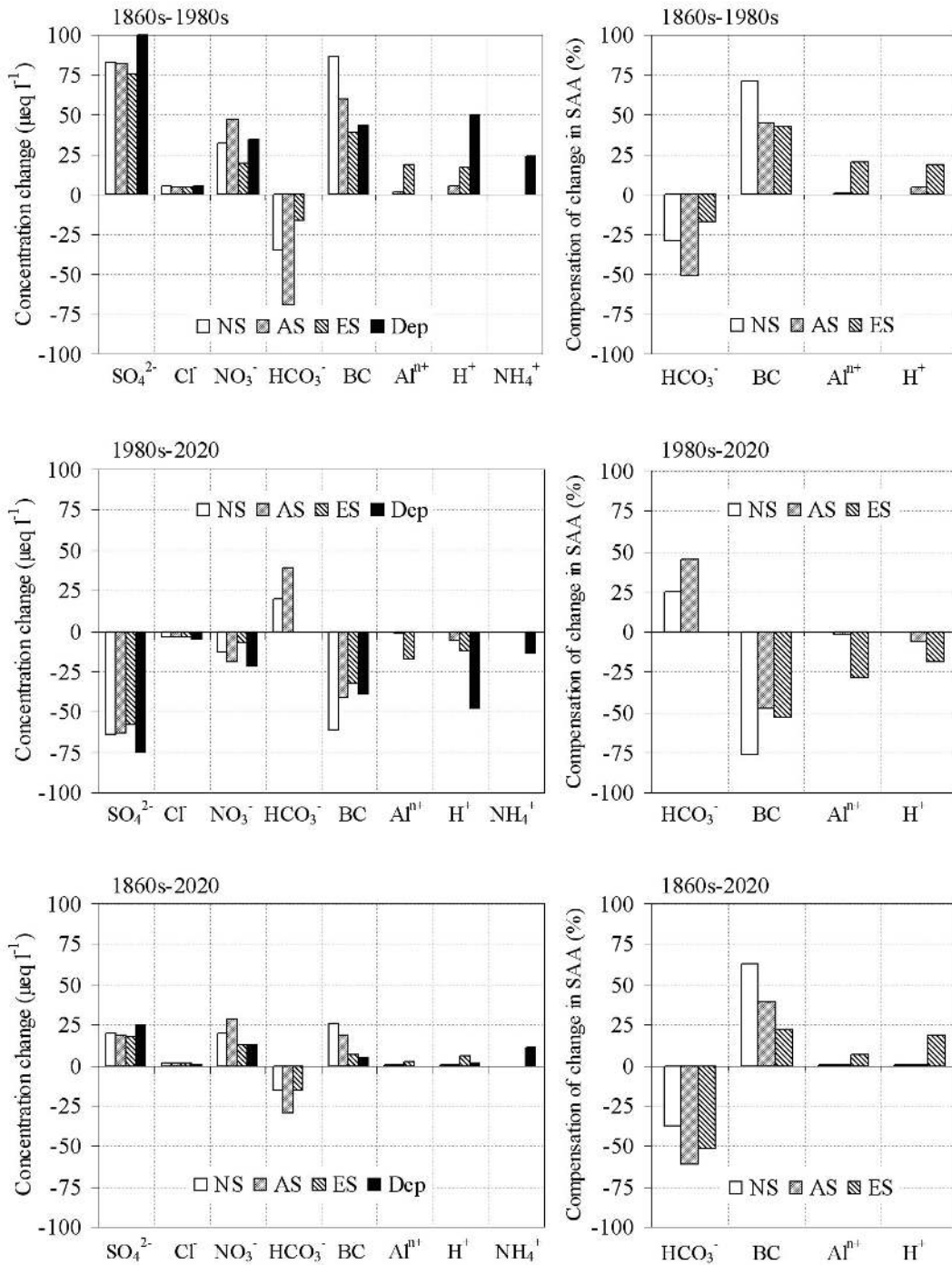
Categories of NS and AS lakes have had similar soil base saturation throughout the study period (Fig. 5D). The higher amount of soil in the NS catchments means that these catchments have a larger base cation exchange pool compared to the AS catchments. Thus, soil exchange processes in the NS catchments retain more  $\text{H}^+$  from atmospheric deposition and biological  $\text{NH}_4^+$  transformations, while more protons are leached into the AS lakes. Moreover, the simulations indicate that the NS catchments have higher weathering rates than the AS catchments ( $229$  vs  $107 \text{ meq m}^{-2} \text{ y}^{-1}$  on average),

which further contributes to the higher  $\text{H}^+$  retention by weathering within the NS catchments. The changes in acid deposition were thus predominantly compensated for by changes in BC concentrations ( $\sim 75\%$ ) in NS lakes, while mostly by the inverse changes in  $\text{HCO}_3^-$  concentrations ( $> 50\%$ ) in AS lakes (Fig. 4). Consequently, the combination of morphological (soil pool) and physical-chemical (weathering rate) characteristics predisposed the dramatic changes in pH and ANC in the AS lakes (Fig. 5A, B).

The carbonate buffering system of some of the AS lakes was depleted in the 1980s (e.g., TA0017, Kopáček *et al.* 2002, 2003) and replaced by an Al buffering system (Fig. 5H). The transparency of the TA0017 lake was substantially higher under the acid conditions compared to its current levels ( $> 17 \text{ m}$  vs  $5\text{--}6 \text{ m}$ ; unpubl. data). We can only hypothesise whether the high transparency was caused by coagulation of DOC (Steinberg 1991), increased DOC photoreactivity under more acid conditions (Anesio & Granéli 2003), or resulted mostly from lower concentrations of chlorophyll-*a* in the 1980s compared to their current levels (Stuchlík, unpubl. data). Answering this question has a crucial impact for understanding the processes of biological recovery of the Tatra Mountain lakes after their chemical reversal from acidification.

The most pronounced acidification has occurred in the ES lakes even though these lakes were exposed to lower SAA input from catchments than other lake categories due to the biggest soil pools and, consequently, lowest  $\text{NO}_3^-$  leaching (Fig. 5E, G). While the simulated pH values were stable in the NS and AS lakes before the 1950s, pH declined steadily in the ES lakes already in the 1860–1950 period, after which their carbonate buffering systems were depleted (Fig. 5B) and pH rapidly declined below 5.0 (Fig. 5A). Compared to the AS lakes, acidification of the ES lakes was mitigated to a lesser extent by  $\text{H}^+$  neutralisation with  $\text{HCO}_3^-$  anions, due to lower background ANC. In addition, the changes in SAA concentrations were compensated to a lesser extent by an increase in BC concentrations than in the NS lakes (Fig. 4) despite the bigger catchment soil pools.

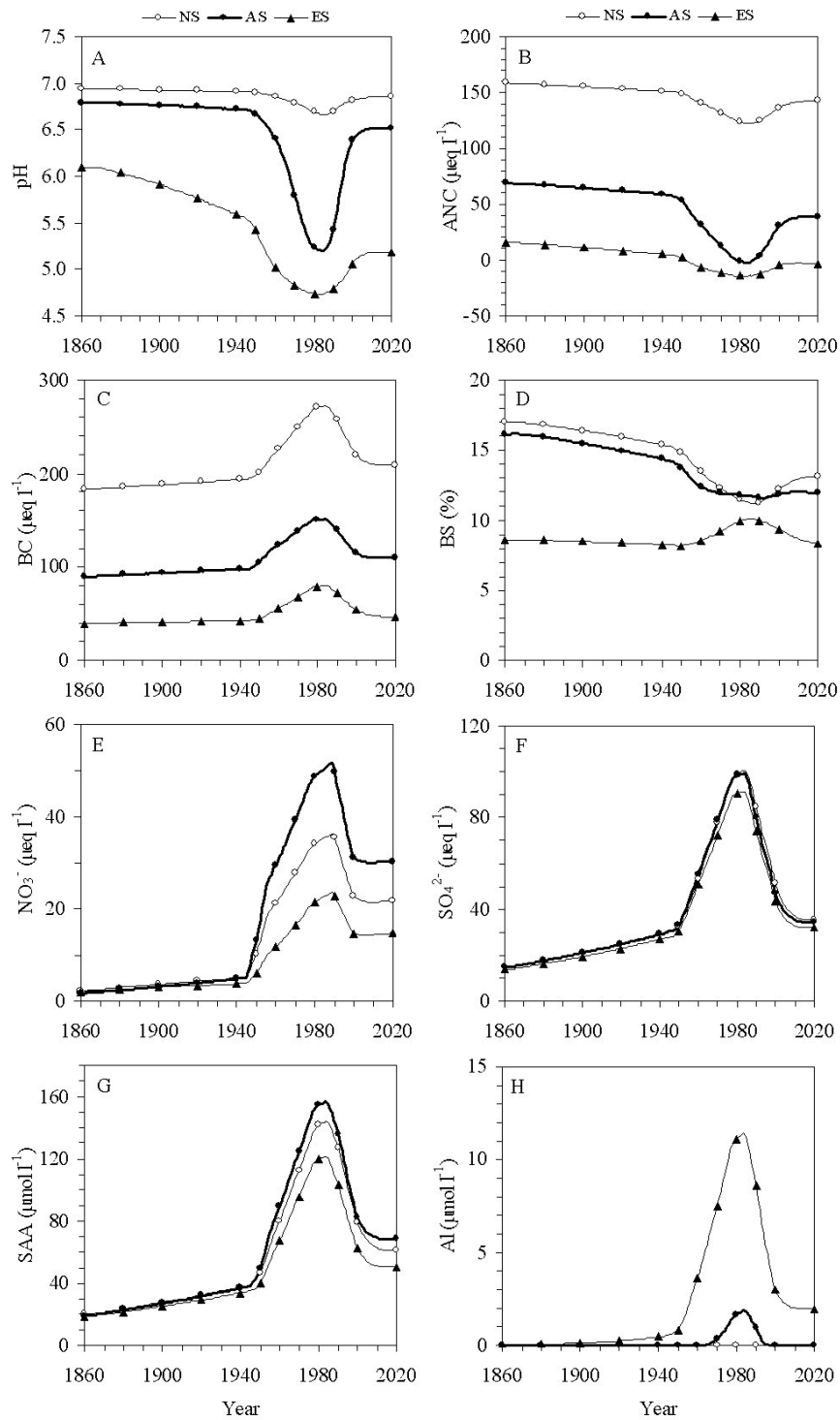
The ES catchments have lower base saturation and lower simulated weathering rates ( $37 \text{ meq m}^{-2} \text{ y}^{-1}$  on average) than the NS and AS catchments (Tab. 2; Fig. 5D). The reason behind this difference is still unclear, and may be associated with the presence of easily weatherable rocks in some catchments despite their dominant granodioritic composition; Kopáček *et al.* 2004). The ES lakes also have the lowest catchment-to-lake area ratios (Tab. 1) and, consequently, the lowest ANC input from terrestrial sources (e.g., Schindler 1986). During the acidification phase, BC export from the ES catchments was lower than the total BC input by weathering and atmospheric deposition (e.g.,  $101$  vs  $114 \text{ meq m}^{-2} \text{ y}^{-1}$  on average, in the 1980s) and BC was accumu-



**Fig. 4.** Changes in chemical composition of the Tatra Mountain lakes (Tab. 1) during the acidification phase (1860s-1980s), recovery phase (1980s-2020), and over the whole study period (1860s-2020) as simulated by MAGIC (Cosby *et al.* 2001). Left column: average changes in ionic composition of the three lake categories (NS, non-sensitive; AS acid sensitive; and ES, extremely sensitive) and atmospheric deposition (Dep). Right column: average relative changes in lake water composition compensating for the changes in concentrations of strong acid anions (SAA). BC, base cations.

lated in the soils, increasing their base saturation (Fig. 5D). This phase of BC accumulation in soils was most pronounced in the catchment of lake TA0107 while only moderate for TA0047 (Kopáček *et al.* 2003), and resulted from the elevated BC deposition (Fig. 1). Be-

cause the change in SAA deposition was larger than that of BC, the net effect was a decline in ANC despite the increase in soil base saturation. Moreover, the BC removed from precipitation by cation exchange adsorption during water passage through the soil profile were re-



**Fig. 5.** Average trends in water composition of the three lake categories (NS, non-sensitive; AS acid-sensitive; and ES, extremely sensitive) in the Tatra Mountains as simulated by MAGIC (Cosby *et al.* 2001). ANC (Gran-alkalinity); BS, base saturation of soils; BC, base cations; SAA, strong acid anions.

placed by  $H^+$  and Al de-sorbed from the soils, increasing terrestrial export of acidity into the lakes (Fig. 5A, H). In the 1980s, the elevated  $H^+$  and Al concentrations compensated for ~20% each of the increase in SAA concentrations in the ES lakes (Fig. 4). We assume that

the elevated BC deposition into ES catchments with low soil base saturation had an effect on water acidification similar to that observed by Wright *et al.* (1988) after experimental addition of sea salts to acidic soils.

After the rapid decline in emissions of particulates in central Europe (>80% during the 1980-2000 period; Kopáček *et al.* 2002) the deposition of BC significantly declined (e.g., Hedin *et al.* 1994). In 2000, the ES catchments were in steady state conditions with respect to the BC, with BC output ( $69 \text{ meq m}^{-2} \text{ y}^{-1}$ ) equalling the BC supply by weathering and atmospheric deposition ( $70 \text{ meq m}^{-2} \text{ y}^{-1}$ ). The model predicts a change in these steady state conditions in the future (Fig. 5D) due to continuing decline in BC deposition and a potential increase in  $\text{NH}_4^+$  deposition (Fig. 1).

Current levels in  $\text{NH}_3$  emissions in Central Europe are already below the Gothenburg limit (UN-ECE 1999) due to the lowered agriculture production in the area of Poland, Slovakia, and Czech Republic in the 1990s (Kopáček *et al.* 2001). Under the assumption that  $\text{NH}_4^+$  emissions will increase in Central Europe, a slow increase in  $\text{NO}_3^-$  concentrations can be expected in all lake categories. At the same time deposition of BC will decline, and together these two factors will cause the soils of ES catchments to acidify. At the NS and AS catchments, on the other hand, the expected conditions should be sufficient for the slow recovery of soil base saturation (Fig. 5D) due to higher weathering rates.

Besides the uncertainty associated with future  $\text{NH}_3$  emissions, the model forecasts of lake water chemistry can be influenced by uncertainty in future change in catchment ability to retain N. In this study we assume no significant climatically- or chemically-derived changes in soil N-cycling in the 2002-2020 period which would affect the current levels of terrestrial  $\text{NO}_3^-$  leaching. Nevertheless, such changes cannot be fully excluded, because N utilisation within the Tatra Mountain catchments significantly decreased after the 1950s (Kopáček *et al.* 2001). The changes in  $\text{NO}_3^-$  leaching would significantly affect prognoses for water and soil chemistry in the ES catchment-lake ecosystems, but also in the AS lakes, where  $\text{NO}_3^-$  should represent 45% on average of the SAA pool in 2020 (Fig. 5). In contrast, the potentially altered  $\text{NO}_3^-$  leaching would have only limited impact on the overall lake chemistry in the NS lakes.

Among the 31 lakes selected for this study 22, 6, and 3 belonged to the NS, AS and ES categories, respectively. The proportion of individual categories was similar also for the total population of all 84 alpine Tatra Mountain lakes >0.1 ha (49, 28, and 7, respectively), with the exception of the AS lakes, the proportion of which was somewhat higher (30% vs 20%). Consequently, the results based on the selected 31 lakes are reasonably applicable for the whole alpine zone of the Tatra Mountains.

#### 4. CONCLUSIONS

The MAGIC model was successfully calibrated for all 31 lakes selected in this study to represent alpine zone of the Tatra Mountains. The lake water chemistry

exhibited significant changes during both the acidification (1860 to 1980s) and recovery (1980s to 2020) phases. In general, the changes in lake concentrations of SAA were compensated for by declines in  $\text{HCO}_3^-$  and increases in BC,  $\text{H}^+$ , and  $\text{Al}^{n+}$  concentrations, but the extent of these changes differed among the lakes. While concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  exhibited similar trends in all lake categories, reflecting predominantly their trends in atmospheric deposition, concentrations of other ions were determined or significantly modified by catchment characteristics such as soil pools, soil base saturation, weathering rates, and in-lake processes.

These catchment characteristics place the lakes into 3 categories of sensitivity to acidification (non-sensitive, sensitive, and extremely sensitive). Lakes in these categories became non-acidified, acidified, and strongly acidified, respectively, in the 1980s. Each category displayed a different response. Lakes with a high weathering rate and soil BC exchangeable capacity had higher ANC before the onset of acidification, and their pH was resistant to changes in atmospheric deposition chemistry. These lakes remained non-acidified even in the 1980s. Sensitive lakes showed dramatic pH changes both during the acidification and recovery phases. The sensitivity of these lakes resulted from intermediate weathering rates and sparse soils (and/or alpine meadows) in their catchments. The small soil pool (i) was a reason for low soil exchangeable BC capacity (less  $\text{H}^+$  was retained in the soils) and (ii) resulted in the lower retention of atmospherically deposited N in the catchment and, consequently, in the elevated terrestrial  $\text{NO}_3^-$  (and SAA) export. These lakes temporarily lost their carbonate buffering system in the 1980s. The sensitivity of extremely sensitive lakes resulted mostly from very low weathering rates and soil base saturation, and these lakes have been strongly acidified (with a depleted carbonate buffering system) since the 1950s.

The 2020 forecast based on the scenarios of acid deposition expected according to the Gothenburg Protocol indicates that despite the pronounced improvement in the lake water quality since the 1980s, the SAA concentrations should be still elevated by  $30\text{--}49 \mu\text{eq l}^{-1}$  (averages for individual lake categories) compared to background levels. These conditions will not be sufficient for the re-establishment of the carbonate buffering system in extremely sensitive lakes.

The full implementation of the Gothenburg Protocol should bring a stable chemical reversal from acidification for ~90% of the Tatra Mountain lakes. This situation is not unique to the Tatra Mountains, as some percentage of lakes in Central England (South Pennines), the southern Alps, southern Norway, and southern Sweden are also predicted to not return to their pre-acidification chemistry under proposed emission levels (Jenkins *et al.* 2003). A further decrease in European S or N emissions would be needed for the recovery of the most sensitive Tatra Mountain lakes.

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