

**Supporting Information to**  
***Effects of acidic deposition on in-lake phosphorus availability: A lesson from lakes recovering from acidification.***

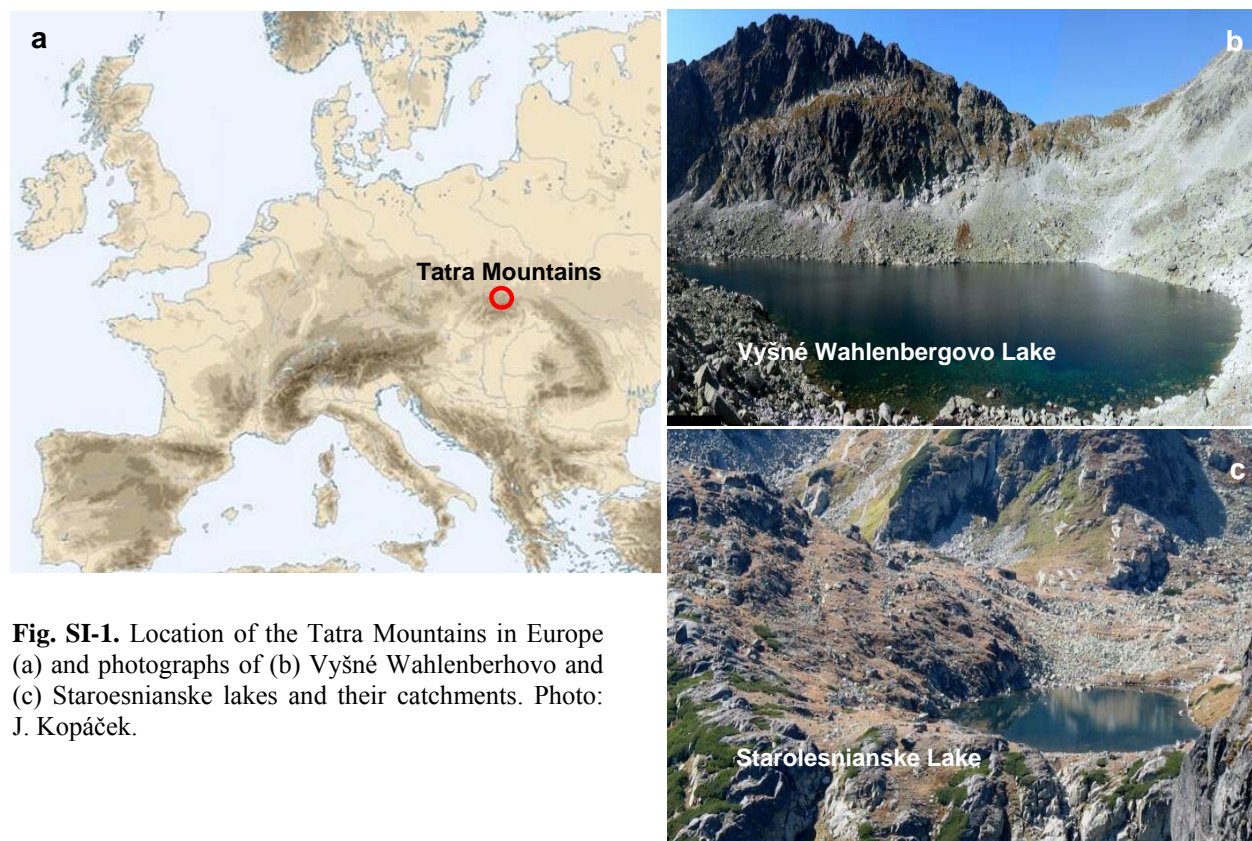
**Jiří Kopáček, Josef Hejzlar, Jiří Kaňa, Stephen A. Norton, Evžen Stuchlík**

(Supporting Information includes 7 pages, 4 figures and 3 tables)

**Part SI-1: Details to section: Methods**

***Site description***

The Tatra Mountains belong to the Carpathian chain and are situated at the Slovak-Polish border (20° E, 49° 15' N) in central Europe (Fig. SI-1). There are 138 lakes with surface areas 0.01–35 ha and 123 small lakes (seasonal or <0.01 ha). The Tatra lakes are of glacial origin and are mostly (~70%) situated in the alpine zone. Grazing, logging, or any other kinds of land uses have been prohibited in the lake district since the 1950s when the Tatra Mountains became a national park.



**Fig. SI-1.** Location of the Tatra Mountains in Europe (a) and photographs of (b) Vyšné Wahlenbergovo and (c) Starolesnianske lakes and their catchments. Photo: J. Kopáček.

In this study we use 20 alpine lakes selected for long-term monitoring along the Tatra Mountain range on the basis of previous studies.<sup>35,36</sup> These lakes have been annually sampled since 1990–1993 and are representative for local topography of the Tatra alpine zone regional (geographic position; elevation), morphology (dominant land cover in the catchment), and chemistry (from acidic and calcium-poor lakes to circum-neutral lakes). Nineteen lakes are situated in the alpine zone at elevations of 1580–2145 m; one lake (Morskie Oko) is at 1395 m, i.e. below the local tree line, but most of its catchment lies in the alpine zone. Five lakes are (mostly artificially) populated with brook and brown trout, one lake with bullhead, and 14 lakes are fishless (Table SI-1).

Bedrock of the selected lakes is predominantly granodiorite (biotite granodiorites to tonalites), gneiss, and mica schist.<sup>S1</sup> Meadow soils in the alpine meadow areas are poorly developed, with negligible carbonate content. Soil depth and amount of the dry weight <2-mm soil fraction range from 0.1 to 0.84 m and from 38 to 255 kg m<sup>-2</sup>, respectively. Soils are acidic, with pH (H<sub>2</sub>O extracts) of 4.4 ± 0.3 (average ± standard deviation) and 4.6 ± 0.3 in the



organic and mineral horizons, respectively. Their cation exchangeable capacity varies between 20 and 207 meq kg<sup>-1</sup> (one equivalent is 1 mol of charge) and is dominated by exchangeable Al<sup>3+</sup> (70% on average).<sup>37,S2</sup> Till soils have formed thin (<3 cm deep) layers or lenses of finer-grained material between boulders in the skree areas below a 20–80 cm thick layer of surface stones (Fig. SI-2). Mass of the till soils (<2 mm; dried weight) range between 4–33 kg m<sup>-2</sup>; their chemical composition is similar to mineral layers of soils in the alpine meadows, but have ~2-times higher concentrations of all phosphorus forms.<sup>37,S2</sup>

Vegetation of the alpine Tatra zone is dominated by alpine meadows (dry tundra with mostly *Festuca picturata*, *Luzula alpino-pilosa*, *Calamagrostis villosa*, and *Juncus trifidus*), 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*, Fig.SI-2) at elevations >1800 m.<sup>S3</sup>



**Fig. SI-2.** A detail of (a) skree in the catchment of Vyšné Wahlenbergovo Lake and (b) till soil ~50 cm below the surface stones. Photo: J. Kopáček.

The annual average air temperature decreases with elevation by 0.6 °C per 100 m, being 1.6 and –3.8 °C at elevations of 1778 and 2635 m, respectively.<sup>S4</sup> The amount of precipitation increases with increasing elevation, ranging from ~1.0 to ~1.6 m yr<sup>-1</sup> between 1330 and 2635 m, but reaches >2 m yr<sup>-1</sup> in some valleys.<sup>S5</sup> Snow cover usually lasts from October to June at elevations >2000 m.

**Table SI-1.** Major morphological and hydrological characteristics for the Tatra Mountain catchment-lake systems.<sup>35,S6,S7</sup>

Lake name	Lake code	Latitude (°N, WGS)	Longitude (°E, WGS)	Altitude (m)	Volume (10 <sup>3</sup> m <sup>3</sup> )	Maximum depth (m)	Lake area (ha)	Retention time (yr)	Catchment area (ha)	Maximum relief (m)	Exposed rock (%)	Till/skree cover (%)	Meadow <sup>1)</sup> cover (%)	Fish <sup>2)</sup>
Vyšné Wahlenbergovo	VW	49.164	20.027	2145	421	21	5.0	0.93	32	259	37	51	12	No
Starolesnianské	ST	49.180	20.168	1986	11	4	0.7	0.41	2.3	44	30	10	60	No
Batizovské	BA-1	49.152	20.132	1879	160	11	2.8	0.05	234	775	40	30	30	No
Długi Staw Gąsienicowy	GA-4	49.227	20.011	1784	81	11	1.6	0.09	65	517	44	27	29	No
Zielony Staw Gąsienicowy	GA-7	49.229	20.001	1672	261	15	3.8	0.65	33	419	40	10	50	T.
Veľké Hincovo	ME-1	49.180	20.061	1946	4139	53	18.2	2.5	127	486	35	40	25	T.
Malé Hincovo	ME-2	49.174	20.059	1923	74	6	2.2	0.29	21	277	20	30	50	No
Vyšné Satanie	ME-4	49.170	20.063	1900	1.3	2	0.2	0.05	2.1	80	30	15	55	No
Czarny Staw pod Rysami	MO-1	49.189	20.078	1580	7762	76	20.6	3.4	179	920	50	20	30	T.
Morskie Oko	MO-2	49.198	20.072	1395	9935	51	34.9	1.3	630	1105	40	20	40	T.
Wyżni Mnich. Staw IX	MO-6	49.195	20.055	1870	0.5	2.3	0.1	0.02	1.7	50	20	40	40	No
Vyšné Terianske	NE-1	49.168	20.022	2109	8.9	4	0.5	0.03	19	319	40	45	15	No
Nižné Terianske	NE-3	49.170	20.014	1941	879	43	4.9	0.57	110	487	40	32	28	No
Wielki Staw Polski	PS-3	49.213	20.040	1655	12967	79	34.4	2.1	491	646	30	15	55	T.
Vyšné Račkové	RA-1	49.200	19.807	1697	35	13	0.7	0.05	56	440	20	20	60	B.
Štvrté Roháčske	RO-1	49.206	19.627	1718	49	8	1.5	0.29	14	302	40	20	40	No
Vyšné Temnosmrečinské	TE-1	49.189	20.040	1716	460	20	4.5	0.33	112	662	40	34	26	No
Ľadové	VS-4	49.184	20.163	2057	114	18	1.7	0.66	13	293	32	53	15	No
Slavkovské	SL-2	49.153	20.183	1676	1.1	3	0.1	0.02	5.1	34	0	0	100	No
Vyšné Furkotské	FU-7	49.144	20.030	1698	3.3	2.4	0.4	0.05	13.7	182	10	10	80	No

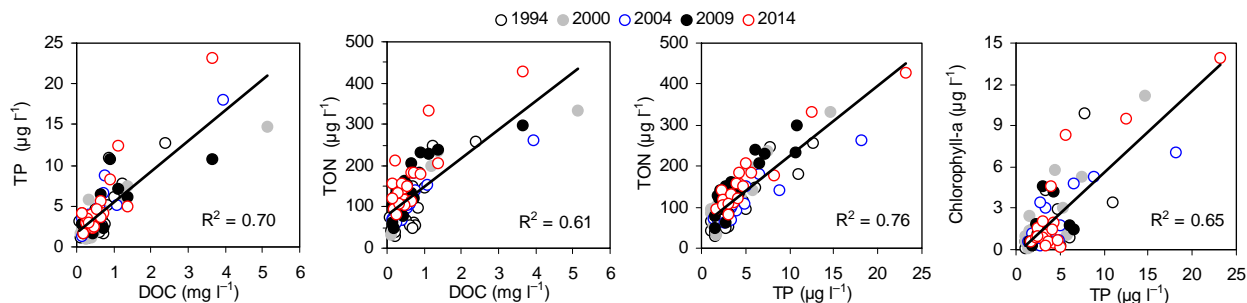
<sup>1)</sup> Alpine meadows or areas covered with dwarf pine (*Pinus mugo*).

<sup>2)</sup> Abbreviation No = no fish; T. = trout; B. = bullhead.



## Part SI-2: Details to section: Results

### Water chemistry



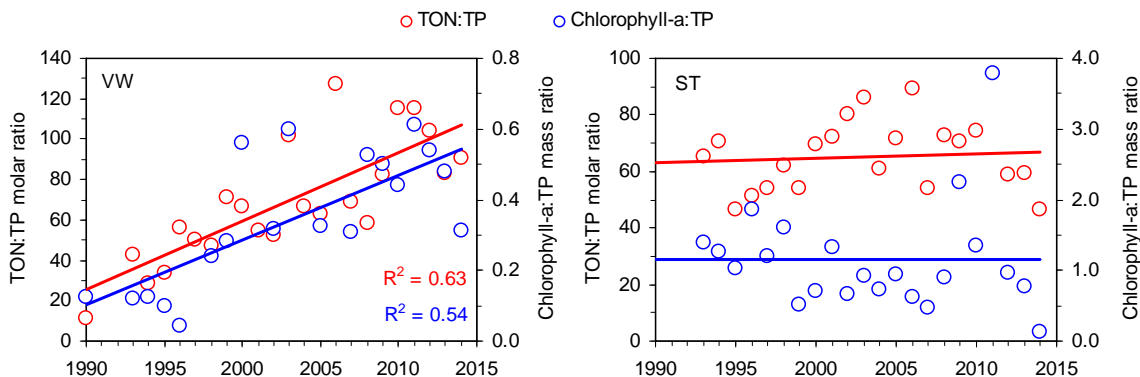
**Fig. SI-3.** Relationships between concentrations of dissolved organic carbon (DOC), total phosphorus (TP), total organic nitrogen (TON), and chlorophyll-a in the Tatra Mountain lakes from Table 1 in the years 1994, 2000, 2004, 2009, and 2014. All linear regressions (solid lines) are significant at  $p < 0.001$ .

**Table SI-2.** Ranges (minimum to maximum) of concentrations and slopes of linear regressions between concentrations and time for 20 Tatra Mountain lakes from 1990–1993 to 2014. Number of observations for individual lakes and water constituents is 15–25. Significance: \*\*\*,  $p < 0.001$ ; \*\*,  $p < 0.01$ ; and \*,  $p < 0.05$ . For full lake names and characteristics see Table SI-1.

Lake	Range Slope	pH	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	ANC	Ca <sup>2+</sup> +Mg <sup>2+</sup>	H <sup>+</sup>	DOC	TON	TP	Chl-a
			µeq L <sup>-1</sup>				mg L <sup>-1</sup>		mg L <sup>-1</sup>	µg L <sup>-1</sup>		
			µeq L <sup>-1</sup> yr <sup>-1</sup>				mg L <sup>-1</sup> yr <sup>-1</sup>		mg L <sup>-1</sup> yr <sup>-1</sup>	µg L <sup>-1</sup> yr <sup>-1</sup>		
VW	Range	5.22–6.84	21–60	20–46	3–9	1–86	64–120	0.1–6.0	0.04–0.51	31–188	1.6–4.2	0.1–2.2
	Slope		-1.51***	-0.73***	-0.13**	3.49***	1.02*	-0.13***	0.007*	5.7***	0.05**	0.06***
ST	Range	4.53–5.84	8–106	0–26	2–8	-20 to 11	26–74	1.5–30	0.6–2.7	117–512	3.4–19	1.6–28
	Slope		-2.81***	-0.32*	-0.11*	0.85***	-1.1***	-0.77***	0.004	3.17	0.02	-0.10
BA-1	Range	5.36–6.73	31–94	23–59	3–7	16–63	88–153	0.2–4.4	0.10–0.50	10–125	0.5–2.1	0.03–1.4
	Slope		-1.85***	-1.05***	-0.04	1.79***	-0.62	-0.06**	0.005	3.28***	0.00	0.04***
GA-4	Range	5.24–6.62	27–85	17–62	2–11	3–51	72–147	0.2–5.8	0.15–0.71	30–152	1.0–3.4	0.01–1.9
	Slope		-2.04***	-1.26***	-0.12*	1.82***	-1.42**	-0.14***	0.014**	3.82***	0.06**	0.06***
GA-7	Range	6.26–7.06	28–75	6–25	3–11	74–130	116–193	0.1–0.6	0.21–1.11	77–208	3.0–5.6	3.1–18.0
	Slope		-2.02***	-0.59***	-0.11*	1.49***	-1.74**	-0.01**	0.01	2.65*	0.02	0.11
ME-1	Range	6.27–7.05	35–98	16–46	3–10	91–150	138–217	0.1–0.5	0.21–0.68	61–160	1.3–3.2	0.6–5.0
	Slope		-2.17***	-0.82***	-0.13**	2.27***	-0.67	-0.01**	-0.002	1.27	-0.01	0.0
ME-2	Range	6.59–7.51	80–156	10–36	3–7	250–383	357–447	0.03–0.3	0.24–0.93	90–251	1.6–4.2	0.3–2.2
	Slope		-2.26***	-0.67***	-0.05	4.87***	1.18	-0.003*	0.008*	1.66	0.05*	-0.01
ME-4	Range	4.74–5.47	22–87	2–18	2–8	-13 to 6	22–47	3.4–18.1	0.77–1.69	93–244	2.9–6.2	0.1–10.6
	Slope		-2.28***	-0.31*	0.03	0.58***	-0.62**	-0.62***	0.020*	3.24*	0.02	0.14
MO-1	Range	6.30–7.18	39–88	18–44	4–10	111–175	178–256	0.1–0.5	0.21–0.50	45–147	0.7–3.0	0.5–1.6
	Slope		-2.16***	-1.07***	-0.10*	1.85***	-1.77**	-0.01**	-0.004	2.00*	-0.01	-0.02
MO-2	Range	6.25–7.13	36–96	15–29	3–8	115–169	172–276	0.1–0.6	0.31–0.75	65–162	1.0–7.3	0.6–3.2
	Slope		-2.25***	-0.61***	-0.06	1.94***	-2.04**	-0.01**	0.008*	3.28**	0.05	0.05**
MO-6	Range	4.59–5.54	19–82	8–49	2–9	-20 to 6	26–67	2.9–25.6	0.37–1.02	90–251	2.4–8.9	0.4–12.2
	Slope		-2.16***	-1.16**	-0.04	0.67***	-0.93**	-0.77***	0.022**	4.46*	0.09	0.23*
NE-1	Range	4.76–5.93	13–67	9–40	2–11	-15 to 14	16–80	1.2–17.4	0.41–1.71	79–519	2.9–22.3	1.7–59.6
	Slope		-1.80***	-1.11***	-0.11	0.74**	-1.41***	-0.67***	0.026*	7.53*	0.30	1.29*
NE-3	Range	6.33–7.07	26–70	20–38	3–8	65–140	121–194	0.1–0.5	0.16–0.52	45–206	1.6–4.3	0.4–9.5
	Slope		-1.79***	-0.62***	-0.05	3.00**	-0.25	-0.01***	0.009	4.61**	0.02*	0.17***
PS-3	Range	6.23–7.03	29–73	12–29	4–8	59–100	105–173	0.1–0.6	0.39–0.82	48–152	0.8–3.5	0.2–1.0
	Slope		-1.78***	-0.47***	-0.13***	1.72***	-1.53**	-0.01**	0.006	2.27*	0.04	0.02*
RA-1	Range	6.61–7.49	47–85	9–26	3–11	176–334	245–365	0.03–0.2	0.13–1.70	65–193	1.4–5.7	0.3–5.0
	Slope		-1.35***	-0.45**	-0.19***	3.48***	-0.55	-0.005*	0.008	2.67*	0.02	0.09*
RO-1	Range	6.04–6.84	34–93	9–42	2–10	20–75	61–169	0.1–0.9	0.31–0.82	57–201	1.8–5.3	0.3–3.2
	Slope		-1.99***	-1.11**	0.04	2.19***	-0.93	-0.03***	0.014***	4.55***	0.08**	0.07**
TE-1	Range	6.81–7.42	24–69	12–35	2–5	217–309	241–360	0.04–0.2	0.18–0.46	50–208	1.7–3.1	0.5–2.5
	Slope		-1.56***	-0.83***	-0.06	3.09***	0.03	-0.004*	0.012*	2.74	0.02	0.04
VS-4	Range	6.29–6.93	20–73	16–45	2–9	12–105	87–171	0.1–0.5	0.02–0.65	33–138	1.4–5.9	0.4–3.9
	Slope		-1.85***	-0.90***	-0.13**	1.91***	-0.98	-0.01***	-0.001	1.68*	-0.06	-0.02
SL-2	Range	4.70–5.54	18–94	0–5	3–12	-16 to 14	19–61	2.9–20.0	2.38–5.54	160–454	6.0–23.1	1.3–16.0
	Slope		-2.96***	-0.10**	0.07	0.76***	-0.93***	-0.62***	0.074**	5.58*	0.15	0.21
FU-7	Range	6.00–6.71	35–81	16–33	4–6	34–69	77–160	0.2–1.0	0.23–0.95	69–280	1.9–11.3	0.1–1.6
	Slope		-1.93***	-0.54**	-0.05*	0.79*	-2.20***	-0.03***	0.009	4.30*	-0.07	0.01
Average slope <sup>1)</sup>			-2.0±0.4	-0.7±0.3	-0.07±0.07	2.0±1.1	-0.9±0.9	-0.2±0.3	0.012±0.016	3.5±1.6	0.04±0.08	0.12±0.29

<sup>1)</sup> Average slope for all 20 lakes ± standard deviation





**Fig. SI-4.** Molar total organic nitrogen to total phosphorus (TON:TP) ratios and mass chlorophyll-a to TP ratios in the Tatra Mountain lakes Vyšné Wahlenbergovo (VW) and Starolesnianske (ST) during their recovery from atmospheric acidification (1990–2014). Both linear regressions (solid lines) are significant at  $p < 0.001$  for VW and not significant ( $p > 0.05$ ) for ST.

### Part SI-3: Details to section: Results

#### Soil chemistry

Air dried soils were analyzed for: (1) the pH in distilled water and 0.01M CaCl<sub>2</sub> solution (pH<sub>H2O</sub>, pH<sub>CaCl2</sub>), (2) exchangeable base cations (sum of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) and exchangeable acidity (sum of Al<sup>3+</sup> and H<sup>+</sup>) at unbuffered soil pH by extraction with a 1M NH<sub>4</sub>Cl and a 1M KCl solution, respectively, (3) oxalate-extractable phosphorus (P<sub>ox</sub>), soluble reactive P (SRP<sub>ox</sub>), Al (Al<sub>ox</sub>) and iron (Fe<sub>ox</sub>) by extraction with acid ammonium oxalate solution (0.2 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.2 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at pH 3), (4) total P (after HNO<sub>3</sub> and HClO<sub>4</sub> acid digest using a phosphomolybdate blue method), and (5) total organic carbon (C) and nitrogen (N) using a CN analyser (NC 2100, ThermoQuest, Italy). For details on methods see ref. 37.

**Table SI-3.** Average ( $\pm$  standard deviation) composition of dominant till soils (Fig. SI-2) and dry alpine meadow soils in the catchments of Vyšné Wahlenbergovo (VW) and Starolesnianske (ST) lakes during 2012–2014.

Variable <sup>1)</sup>	Unit	VW-till soil	VW-meadow	ST-meadow
Number of samples		3	5	10
Pool	kg m <sup>-2</sup>	12 $\pm$ 6	30 $\pm$ 21	58 $\pm$ 43
LOI	%	6.1 $\pm$ 1.2	15 $\pm$ 5	20 $\pm$ 18
pH <sub>H2O</sub>		4.10 $\pm$ 0.10	4.51 $\pm$ 0.20	4.30 $\pm$ 0.14
pH <sub>CaCl2</sub>		3.83 $\pm$ 0.06	3.80 $\pm$ 0.19	3.69 $\pm$ 0.12
C	$\mu$ mol g <sup>-1</sup>	2.7 $\pm$ 0.4	6.6 $\pm$ 2.6	9.1 $\pm$ 6.5
N	$\mu$ mol g <sup>-1</sup>	0.16 $\pm$ 0.01	0.39 $\pm$ 0.15	0.53 $\pm$ 0.41
P	$\mu$ mol g <sup>-1</sup>	23.7 $\pm$ 2.7	25.9 $\pm$ 4.0	29.6 $\pm$ 20.8
P <sub>ox</sub>	$\mu$ mol g <sup>-1</sup>	13.0 $\pm$ 3.6	14.6 $\pm$ 1.5	15.9 $\pm$ 10.4
SRP <sub>ox</sub>	$\mu$ mol g <sup>-1</sup>	9.1 $\pm$ 3.5	3.4 $\pm$ 0.2	2.6 $\pm$ 1.3
Al <sub>ox</sub>	$\mu$ mol g <sup>-1</sup>	52 $\pm$ 16	157 $\pm$ 56	231 $\pm$ 140
Fe <sub>ox</sub>	$\mu$ mol g <sup>-1</sup>	37 $\pm$ 5	52 $\pm$ 4	63 $\pm$ 52
CEC	$\mu$ eq g <sup>-1</sup>	49 $\pm$ 10	68 $\pm$ 40	127 $\pm$ 54
Al <sup>3+</sup>	$\mu$ eq g <sup>-1</sup>	38 $\pm$ 8	59 $\pm$ 6	108 $\pm$ 26
H <sup>+</sup>	$\mu$ eq g <sup>-1</sup>	8.4 $\pm$ 3.0	19 $\pm$ 13	26 $\pm$ 10
BC	$\mu$ eq g <sup>-1</sup>	2.8 $\pm$ 1.8	8.3 $\pm$ 5.8	9.7 $\pm$ 7.8

<sup>1)</sup>Variable abbreviations: Pool = amount of dry (105 °C) weight soil fraction < 2 mm; LOI = loss on ignition at 550 °C; C, N, P = concentrations of organic carbon, total nitrogen and total phosphorus, respectively; P<sub>ox</sub>, SRP<sub>ox</sub>, Al<sub>ox</sub>, and Fe<sub>ox</sub> = concentrations of oxalate extractable total phosphorus, soluble reactive phosphorus, aluminium and iron, respectively; CEC = cation exchangeable capacity; Al<sup>3+</sup> and H<sup>+</sup> exchangeable aluminium and protons, respectively; BC = exchangeable base cations (sum of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>). One eq (equivalent) = one mol of charge. All concentrations are given on a basis of dry weight < 2 mm soil fraction.



#### Part SI-4: Details to section: Discussion

##### *Changes in biological composition of Vyšné Wahlenbergovo and Starolesnianske lakes during their acidification and recovery*

Model MAGIC (Modelling the Acidification of Groundwater in Catchments)<sup>S8</sup>, version 7 (ref. S9), was applied for modelling lake water chemistry of the VW and ST lakes prior to the 1980s, i.e. for a period preceding our measurements.<sup>60,S10</sup> Historical records of zooplankton and benthos composition in the lakes were based on a literature review<sup>16,59,S10–S18</sup> and palaeolimnological investigations of lake sediments.<sup>15,60,S19–S21</sup> A synthesis of chemical and biological data shows the following trends in acidification derived oligotrophication and eutrophication of the VW and ST lakes:

(1) *Vyšné Wahlenbergovo Lake*: According to historical record (Minkiewicz, 1914, 1917), *Arctodiaptomus alpinus* was the dominant zooplankton species prior to the 1970s, when water pH was > 6. After the pH decrease to < 6 in the 1970s, this species was recorded last time in 1975 (ref. S14) while no zooplankton was found in 1977 due to the lack of food.<sup>S15</sup> During 1977–1996, there were no zooplankton species present in the VW Lake, except for very low numbers of ubiquitous littoral species (*Chydorus sphaericus*, *Acanthocyclops vernalis*, and *Eucyclops serrulatus*).<sup>S15,S16</sup> Maximum acidification of lake water occurred in the 1980s, when carbonate buffering system was depleted, pH varied between 5.2 and 5.9 and Al concentrations reached ~80 µg L<sup>-1</sup> (Fig. 2a). Water transparency was higher than the maximum lake depth of 21 m, TP and TON concentrations were < 2 and < 30 µg L<sup>-1</sup>, respectively, and phytoplankton concentrations were extremely low, with concentrations of chlorophyll-*a* mostly < 0.5 µg L<sup>-1</sup> (Fig. 2b). This acidification induced oligotrophication persisted until the early 1990s.<sup>16</sup> Then, the VW chemistry started to recover: pH increased toward ~6 and ANC to ~20 µeq L<sup>-1</sup> in the middle 1990s, and water transparency decreased to 5–10 m as the TP and chlorophyll-*a* concentrations increased (Fig. 2b). In 1996, the presence of zooplankton (*Cyclops abyssorum*) was for the first time recorded in the VW pelagic zone. In 2000, calanoid *Arctodiaptomus alpinus* reappeared in the lake<sup>S22</sup> and soon became the dominant zooplankton species again, as pH increased to > 6.2 and TP and phytoplankton biomass doubled compared to the 1980s (Fig. 2b). The lake water recovery from acidification and its parallel eutrophication continued until the end of study, when TP, TON, and chlorophyll-*a* concentrations reached ~4, >100, and ~2 µg L<sup>-1</sup>, respectively, and Al concentrations decreased to < 10 µg L<sup>-1</sup>. The reappearance of cladocera *Daphnia pulex*, which was recorded in deep layers (~1700) of the VW sediment (Stuchlik, unpubl. data), has not, however, occurred until the end of study, even though the water pH has already increased to 6.8, i.e. to the modelled pre-acidification value.<sup>S10</sup> The absence of *Daphnia pulex* thus rather indicates that the present lake productivity is still lower than that at ~1700.

Subfossil chironomid record from the VW Lake showed that acidification phase was accompanied by a pronounced decline in chironomid numbers, while chironomid fauna composition remained unchanged and none of the pre-acidification chironomid taxa (including acid sensitive *Micropsectra radialis*) disappeared. The decreasing density of subfossil remains prior to 1980s was accompanied by decreasing content of organic matter in the sediment and was typical for other acidified Tatra Mountain lakes.<sup>15,S19</sup> These changes were attributed to increasing oligotrophication and decreasing primary production of the lake during its acidification<sup>15</sup>, supporting the previous observations that changes in chironomids reflect rather changes in trophic status of lakes than their acidity, provided water pH does not decrease to < 5.<sup>14,S23</sup> The increase in relative abundance of *Micropsectra radialis* together with decreasing *Heterotrissocladius marcidus* during the recovery phase in the 1990s were then interpreted as a result of increasing pH and increasing productivity of the VW Lake.<sup>15</sup> This conclusion corresponds with the observed increase in TP, TON, and chlorophyll-*a* concentrations in the lake water during the recovery phase (Fig. 2b).

(2) *Starolesnianske Lake*: Minkiewicz (1914) and Hrabě (1936) described zooplankton and benthos composition of the ST Lake as typical for dystrophic lakes. Reconstruction of the acidification history of the ST Lake by MAGIC modelling showed naturally lower pre-acidification pH of ~6.2 than in VW and other alpine Tatra Mountain lakes.<sup>35,S10</sup> This difference was caused by high DOC concentrations in the ST Lake, resulting from high proportion of meadow soils in its catchment (Table SI-1) and its low steepness.<sup>37</sup> Palaeolimnological investigations of lake sediment show that relative abundances of originally dominant zooplankton species (*Ceriodaphnia quadrangula*) declined, reflecting a gradual pH decrease, while acid-tolerant species (*Chydorus sphaericus*) increased as the lake acidified and became more eutrophic, with the major change in species composition occurring between 1970 and the early 1980s.<sup>16,60</sup> During this period, water pH declined to 4.5–4.9 and Al concentrations increased > 200 µg L<sup>-1</sup>.<sup>60,S10,S21</sup> Lake water concentrations of nutrients were high in the 1980s, with TP and TON concentrations of 9–12 and 220–300 µg L<sup>-1</sup>, respectively. The lake bottom was covered by filamentous algae (*Zygnematophyceae*) and the phytoplankton biomass reached high concentrations of chlorophyll-*a* (10–20 µg L<sup>-1</sup>) and was dominated by the dinoflagellates (*Dinophyta*) and Chlorophyta (*Koliella* sp.).<sup>S24</sup> Most of the native species of crustacean zooplankton were absent despite the high phytoplankton biomass, and the lake was inhabited by only one species of cladocerans, the ubiquitous *Chydorus sphaericus*, but in very low numbers and with biomass much lower than in oligotrophic



non-acidified lakes.<sup>16,59</sup> These unique biological conditions developed as a combination of (i) acidification induced eutrophication after the soil acidification to pH < ~3–3.5 (Fig. 5), causing high terrestrial P export, high TP, TON and chlorophyll-*a* concentrations in the lake (Fig. 2d), i.e. potentially abundant food for zooplankton, and (ii) toxicity of high Al concentrations eliminating presence of the most zooplankton species, which disabled use of the available phytoplankton.<sup>16</sup>

Subfossil chironomid record from the ST Lake showed the most apparent change during 1960–1980.<sup>15,60</sup> During this period, the original taxa *Tanytarsus lugens* group, *Zavrelimyia* sp., and *Micropsectra* sp. disappeared and were replaced by the acidotolerant and aluminium tolerant species *Tanytarsus gregarius* group, *Zalutschia tatraica*, and *Chironomus* sp. The acidotolerant *Tanytarsus gregarius* group dominated the chironomid assemblage during the acidification peak, probably benefiting from (i) the increasing lake eutrophication and higher food availability and (ii) reduced competition for food resources due to increased lake acidity.<sup>15</sup> In contrast to zooplankton, benthic communities thus was able to use advantage of the elevated lake productivity in the 1980s.<sup>15,S21</sup>

Since the 1990s, the ST Lake water chemistry has been rapidly recovering from acidification (Fig. 2c). Chemical conditions for zooplankton recovery occurred after 1996, when water pH increased above 5.0 and Al concentrations decreased to < 70 µg L<sup>-1</sup>. Cladocera *Ceriodaphnia quadrangula* (the dominant pre-acidification zooplankton species) re-appeared in 2000. At this time, however, TP and phytoplankton biomass represented only ~50% of their concentrations in the 1980s (Fig. 2d). In contrast to the VW Lake where food supply was the dominant reason for the disappearance of zooplankton during acidification (and oligotrophication) phase and their reappearance during the recovery (and eutrophication) phase, the zooplankton presence in the more strongly acidified ST Lake was primarily driven by water chemistry (i.e., water pH and Al concentrations). The phytoplankton biomass, however, closely reflected P availability in both lakes during their oligotrophication and eutrophication phases (Figs. 2b,d). The oligotrophication of ST Lake continued until 2007 when water pH ranged between 5.0 and 5.5 and ANC concentrations were close to zero. During this period, concentrations of TP, TON, and chlorophyll-*a* decreased to their minimum values during the whole study, i.e. to 3.4, 117, and 2.1 µg L<sup>-1</sup>, respectively (Fig. 2d). The Al concentrations still varied between 25 and 63 µg L<sup>-1</sup> (Fig. 2c) and zooplankton composition did not apparently change (Stuchlík, unpubl. data). Since 2008, the ST water pH has increased to 5.5–5.8, carbonate buffering system re-established, and concentrations of Al decreased to 6–25 µg L<sup>-1</sup>. In parallel, soil water pH exceeded 3.5 (Table SI-3), the critical value of the maximum phosphate adsorption ability of soils (Fig. 4) and the terrestrial P export and in-lake TP concentrations increased. Consequently, concentrations of TP, TON, and chlorophyll-*a* sharply increased in the ST Lake (Fig. 2d). The increased phytoplankton biomass (food availability) under the conditions of low Al toxicity enabled increasing zooplankton numbers, dominated by *Ceriodaphnia quadrangula* (Stuchlík, unpubl. data). In 2013, the cyclopoida *Cyclops abyssorum* (a typical zooplankton species of alpine lakes) was for the first time recorded in the ST Lake most likely as a result of continuing decrease in Al concentrations (Stuchlík, unpubl. data). In contrast, the calanoid *Mixodiatomus tatricus*, which was documented from the lake in the beginning of 20<sup>th</sup> century and which was absent in the 1980s, has not reappeared yet. This species inhabits small, shallow (often periodic) and eutrophic Tatra Mountain lakes, with water pH frequently decreasing to < 6.<sup>16</sup> *Mixodiatomus tatricus* disappeared from the ST Lake despite increasing productivity during lake acidification between 1976 and 1980 due probably to high Al toxicity.<sup>60,S21</sup> The absence of this species in the ST Lake under the improved chemical conditions is surprising, because it commonly occurs in the same valley, and dispersal limitation (often preventing re-colonizing of the recovering lakes<sup>S25</sup>, is not probable. More likely, the food resources under the present stage of lake eutrophication are still limited for this species (Stuchlík, unpubl. data).

#### Additional References (S1–S25)

- (S1) Nemček, J.; Bezák, V.; Janák, M.; Kahan, Š.; Ryja, W.; Kohút, M.; Lehotský, I.; Wiczeorek, J.; Zelman, J.; Mello, J.; Halouzka, R.; Raczkowski, W.; Reichwalder, P. *Explanation of the Geological Map of the Tatra Mountains*; Geologický ústav Dionýza Štúra: Bratislava, 1993.
- (S2) Kopáček, J.; Kaňa, J.; Šantrůčková, H. Pools and composition of soils in the alpine zone of the Tatra Mountains. *Biologia Bratislava* **2006**, 61 (Suppl. 18), S35–S49.
- (S3) Vološčuk, I. et al. *Tatra National Park*; Gradus: Bratislava, 1994. (in Slovak)
- (S4) Konček, M. & Orlicz, M. Temperature characteristics In *Climate of the Tatra Mountains*; Konček, M., Ed.; Veda: Bratislava, 1974; pp 89–179. (in Slovak)
- (S5) Chomitz, K.; Šamaj, F. Precipitation characteristics. In *Climate of the Tatra Mountains*; Konček, M., Ed.; Veda: Bratislava, 1974; pp 443–536. (in Slovak)
- (S6) Kopáček, J.; Stuchlík, E.; Wright, R. F. Long-term trends and spatial variability in nitrate leaching from alpine catchment-lake ecosystems in the Tatra Mountains (Slovakia-Poland). *Environm. Pollut.* **2005**, 136, 89–101.



- (S7) Kopáček, J.; Stuchlík, E.; Hardekopf, D. Chemical composition of the Tatra Mountain lakes: Recovery from acidification. *Biologia Bratislava* **2006**, *61* (Suppl. 18), S21–S33.
- (S8) Cosby, B. J.; Wright, R. F.; Hornberger, G. M.; Galloway, J. N. Modelling the effects of acid deposition: estimation of long term water quality responses in a small forested catchment. *Water Resour. Res.* **1985**, *21*, 1591–1601.
- (S9) Cosby, B. J.; Ferrier, R. C.; Jenkins, A.; Wright, R. F. Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrol. Earth System Sci.* **2001**, *5* (3), 499–517.
- (S10) Kopáček, J.; Cosby, B. J.; Majer, V.; Stuchlík, E.; Veselý, J. Modelling Reversibility of Central European Mountain Lakes from Acidification: Part II – The Tatra Mountains. *Hydrol. Earth System Sci.* **2003**, *7* (4), 510–524.
- (S11) Minkiewicz, S. List of fauna of the Tatra Mountain lakes. *Spraw. Kom. Fizyogr. Akad. Umietnosci, Kraków* **1914**, *48*, 114–137. (in Polish)
- (S12) Minkiewicz, S. Die Crustaceen der Tatrseen. Eine physiographisch – faunistische Skizze. *Bull. Acad. Sci. Cracov., Cl. Sci. Math. et Natur., Ser. B: Sci. Natur.* **1917**, Nov.–Dec., 262–278. (in German)
- (S13) Hrabě, S. Über die Bodenfauna der Seen in der Hohen Tatra. *Sborník klubu přírodovědného v Brně* **1939**, *22*, 1–13. (in German)
- (S14) Brtek, J. Anostraca, Notostraca, Conchostraca and Calanoida of Slovakia. Part II. *Acta Rer. Natur. Mus. Nat. Slov.* **1977**, *23*, 117–150. (in Slovak)
- (S15) Stuchlík, E.; Stuchlíková, Z.; Fott, J.; Růžčka, L.; Vrba, J. Effect of acid precipitation on waters of the TANAP territory. *Treatises Concerning the Tatra National Park* **1985**, *26*, 173–211. (in Czech)
- (S16) Fott, J.; Pražáková, M.; Stuchlík, E.; Stuchlíková, Z. Acidification of lakes in Šumava (Bohemia) and in the High Tatra Mountains (Slovakia). *Hydrobiologia* **1994**, *274*, 37–47.
- (S17) Sacherová, V.; Krsková, R.; Stuchlík, E.; Hořická, Z.; Hudec, I.; Fott, J. Long-term change of the littoral Cladocera in the Tatra Mountain lakes through a major acidification event. *Biologia Bratislava* **2006**, *61* (Suppl. 18), S109–S119.
- (S18) Catalan, J.; Barbieri, M. G.; Bartumeus, F.; Bitusik, P.; Botev, I.; Brancelj, A.; Cogalniceanu, D.; Manca, M.; Marchetto, A.; Ognjanova-Rumenova, N.; Pla, S.; Rieradevall, M.; Sorvari, S.; Stefkova, E.; Stuchlik, E.; Ventura, M. Ecological thresholds in European alpine lakes. *Freshwater Biol.* **2009**, *54*, 2494–2517.
- (S19) Bitušik, P.; Kubovčík, V.; Štefková, E.; Appleby, P. G.; Svitok, M. Subfossil diatoms and chironomids along an altitudinal gradient in the High Tatra Mountain lakes: a multi-proxy record of past environmental trends. *Hydrobiologia* **2009**, *631*, 65–85.
- (S20) Brancelj, A.; Kernan, M.; Jeppesen, E.; Rautio, M.; Manca, M.; Sisko, M.; Alonso, M.; Stuchlik, E. Cladocera remains from the sediments of remote cold lakes: a study of 294 lakes across Europe. *Adv. Limnol.* **2009**, *62*, 269–294.
- (S21) Catalan, J.; Pla-Rabés, S.; Wolfe, A. P.; Smol, J. P.; Rühland, K. M.; Anderson, N. J.; Kopáček, J.; Stuchlík, E.; Schmidt, R.; Koinig, K. A.; Camarero, L.; Flower, R. J.; Heiri, O.; Kamenik, C.; Korhola, A.; Leavitt, P. R.; Psenner, R.; Renberg, I. Global change revealed by palaeolimnological records from remote lakes: a review. *J. Paleolim.* **2013**, *49*, 513–535.
- (S22) Skála, I. *Factors Influencing Zooplankton Structure in the High Mountain Lakes*; Thesis, Charles Univ.: Prague, 2003. (in Czech)
- (S23) Olander, H.; Korhola, A.; Blom, T. Surface sediment Chironomidae (Insecta: Diptera) distributions along an ecotonal transect in subarctic Fennoscandia: developing a tool for palaeotemperature reconstructions. *J. Paleolim.* **1997**, *18*, 45–59.
- (S24) Dargocká, J.; Kneslová, P.; Stuchlík, E. Phytoplankton of several high mountain lakes in different stages of acidification. *Studies on Tatra National Park* **1997**, *2*, 41–62. (in Czech)
- (S25) Yan, N. D.; Leung, B.; Keller, W.; Arnott, S. E.; Gunn, J. M.; Raddum, G. G. Developing conceptual frameworks for the recovery of aquatic biota from acidification. *Ambio* **2003**, *32* (3), 165–169.