

Ammonium uptake in alpine streams in the High Tatra Mountains (Slovakia)

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Abstract

Uptake of NH_4^+ -N by streambed biota of mountain brooks was studied in the alpine zone of the High Tatra Mountains. Experiments were performed involving *in situ* dosing of ammonium directly to the acidified stream and incubations of ammonium and streambed bryophytes in enclosures within a range of pH from 4.45 to 8.10.

NH_4^+ -N uptake length decreased with decreasing stream discharge, while comparable values of discharge-normalized uptake lengths were found during two *in situ* experiments.

Maximum uptake rates of NH_4^+ -N obtained during the incubation of bryophytes (6 to $11 \text{ mg m}^{-2} \text{ h}^{-1}$) were comparable with results of two *in situ* experiments (8 and $12 \text{ mg m}^{-2} \text{ h}^{-1}$). The average NH_4^+ -N uptake rates observed during incubations lasting 3 to 5 hours ($4.3 \text{ mg m}^{-2} \text{ h}^{-1}$) were not related to the pH of stream water. Nitrification of about 50% of the NH_4^+ -N added was observed in non-acidified streams, but was negligible in acidified streams. Significant photoinhibition of nitrification was observed in non-acidified streams during enclosure experiments.

Introduction

The chemistry of lakes and streams in small alpine watersheds, with sparse vegetation and a bedrock characterized by low rates of chemical weathering and ion exchange processes, is largely determined by the composition of precipitation (Wright & Gjessing, 1976; Wright & Johannessen, 1980; Catalan *et al.*, 1992). A remarkable exception to other ions is ammonium, which is retained in the watershed, and whose concentrations are considerably lower in lakes than in precipitation. Dillon & Molot (1990) reported 81% to 99% retention of ammonium in stream and lake watersheds in Europe and North America. Similarly, Wathne *et al.* (1989) and Mosello *et al.* (1991) showed that 20% and 50% of inorganic nitrogen from atmospheric deposition reaches the lakes in Norway and in the Alps, respectively.

Concentrations of NH_4^+ -N in lake water of the High Tatra Mountains follow the same trend, and are usually lower (except during thaw periods) than $30 \mu\text{g l}^{-1}$ (Fott *et al.*, 1992; Kopáček & Stuchlík, 1994),

despite high concentrations of ammonium in precipitation. The mean concentration of NH_4^+ -N was $340 \mu\text{g l}^{-1}$ in snow cores (Gazda & Lopašovský, 1983) and $640 \mu\text{g l}^{-1}$ in summer precipitation (May to October 1991) (Grodzinska-Jurczak & Krywult, 1992).

The retention of ammonium is related to vegetation uptake, and its oxidation to nitrate, which accelerates the acidification of alpine regions, is assumed to have an important role (Schuurkes & Mosello, 1988; Henriksen & Brakke, 1988; Dillon & Molot, 1990). It is difficult to measure directly the intensity of these processes in the entire watershed, but small mountain streams or lakes, being simpler systems, are better suited for studying transformations of nitrogen and evaluating the role of nitrification in the retention of NH_4^+ -N (Richey *et al.*, 1985; Rudd *et al.*, 1988; Howard-Williams *et al.*, 1989).

The role of streambed biota in nitrogen transformations during passage downstream has been reported to be considerable in Antarctica (Howard-Williams *et al.*, 1989) and a forested mountain area (Richey *et al.*, 1985). Remarkable changes in NH_4^+ -N concen-

trations were also observed during our earlier studies in the alpine zone of the High Tatra Mountains. High concentrations of $\text{NH}_4^+\text{-N}$ (usually above $300\ \mu\text{g l}^{-1}$) in streams originating in melting snow fields decreased drastically, with levels at nearly zero only 100 to 200 m downstream (Sraškrabová & Blažka, 1990). The aim of this study was to quantify this process.

We measured the uptake rate of $\text{NH}_4^+\text{-N}$ by incubating the streambed biota of different brooks in the alpine zone of the High Tatra Mountains, and compared it to the retention of ammonium in a section of stream during *in situ* enrichment experiments. The role of nitrification in this process was assessed in relation to the pH and to light conditions.

Description of sites studied

The High Tatra Mountains (HTM; $20^\circ 10' \text{ E}$, $49^\circ 10' \text{ N}$; maximum altitude 2655 m a.s.l.) belong to the Carpathian chain. The bedrock consists mainly of acidic granites with sparse calcareous inclusions in the west and central part of the HTM, while the Belanské Tatry Mts., the eastern part of the HTM, are formed of limestone. The area is loaded by acid deposits, with sulphate and nitrate as dominant anions and an annual weighted mean pH of 4.3 (Cerovský, 1983; Moldan *et al.*, 1987). The acid neutralizing capacity of the stream and lake water in these mountains ranges from 0 to $2800\ \mu\text{eq l}^{-1}$ and its pH from 4.0 to 8.3 (Stuchlík *et al.*, 1985).

All observations in this study were made above the timberline in the alpine zone, at altitudes of 1600 to 2100 m a.s.l. *In situ* enrichment experiments were conducted in an upper part of the acidified brook, at an altitude of about 2000 m a.s.l. The brook begins between the Huncovský and V. Svišť'ovka peaks, and cascades down a broad gorge toward east-north-east, with a gradient of 40%. The streambed is largely bedrock and gravel, about 50% covered with mixed epiphyte, predominantly bryophytes. During the experiments the stream discharge varied from 1.1 to $2.9\ \text{l s}^{-1}$; pH was 4.65 in 1990 and between 4.50 and 4.65 in 1991; temperature varied from 3°C to 6°C in 1990 and from 13°C to 15°C in 1991. The slopes of the gorge are covered with sparse alpine meadows and bare granitic rocks with patches of lichens. Samples of bryophytes and water, used in enclosure experiments, were also collected in the V. Studená and Žabia Bielovodská valleys (granitic part of the HTM, pH from 4.65 to 6.40)

and in the Tristárská valley (the Belanské Tatry Mts.; pH = 8.10).

Materials and methods

In this study two different types of experiments were performed: *in situ* enrichment experiments, in which the retention of $\text{NH}_4^+\text{-N}$ by an acidified stream was measured, and enclosure incubations of streambed bryophytes in $\text{NH}_4^+\text{-N}$ enriched water at different pH. All the experiments were conducted in early summer, when the role of vegetation in ammonium uptake and resulting acidification is assumed to be considerable (Schuurkes & Mosello, 1988).

In situ enrichment experiments

The relationship between the concentration of $\text{NH}_4^+\text{-N}$ in stream water and its retention by a section of stream was measured on June 26 and 27, 1990 (Exp. Ia). The time relationship and rate of the $\text{NH}_4^+\text{-N}$ retention was studied on July 14 and 16, 1991 (Exp. Ib).

A stock solution of NH_4Cl and/or $\text{NH}_4\text{Cl} + \text{NaCl}$ (chloride was applied as a conservative tracer) was continuously introduced by a 5 l dropping-bottle into a small waterfall about 3 m upstream from a little pool, the outflow of which we considered as the starting point of the experimental section during the experiments Ia and Ib. The rate of addition of the spike solution was constant ($55\ \text{ml min}^{-1}$), but its concentration was different in every experiment according to the actual stream discharge and the desired initial concentration of ammonium. The background concentration of Cl^- (0.34 to $0.38\ \text{mg l}^{-1}$) was thus increased by about 0.5 to $1.0\ \text{mg l}^{-1}$ at the starting point. The end points of the section were in other small pools 71 m (Exp. Ia), and 60 m or 102 m (Exp. Ib) downstream of the starting point. Between the start and end points there was neither a visible inflow nor a snow field, which could be an additional source of $\text{NH}_4^+\text{-N}$.

Water samples at the start and end points were taken before the experiment and 60 min. after its beginning in Exp. Ia. During Exp. Ib, samples were taken at the starting point at 10- to 15-minute intervals. Samples at the downstream sites were taken at 2- to 5-minute intervals until the concentration of ammonium became stable (plateau was found photometrically by a direct nesslerization method (Golterman & Clymo, 1969) immediately in the field) and then at 5- to 20-minute intervals during the steady-state period.

The streambed area overgrown with biota, which was submerged and/or sprayed during the experiments, and the mean water width was estimated for each 2-metre subsection by each of the authors separately, and then calculated for the whole section, as described by Howard-Williams *et al.* (1989).

The stream discharges at the start and end points were calculated using the known concentration of Cl^- in the introduced stock solution, its dosing rate, and concentrations of Cl^- in the stream water at the start and end points before and during the experiment (Triska *et al.*, 1989a, b). The difference between downstream and upstream discharges represents subsurface water infiltration into the section.

Volume (V) of the section was calculated as:

$$V = \frac{M_{In} - M_{Out}}{C_E - C_B},$$

where M_{In} and M_{Out} are amounts of Cl^- (g) which passed into and out of, respectively, the section during the time period between the beginning of the experiment and reaching the plateau concentration of Cl^- . M_{In} was calculated as the sum of mass-balances of Cl^- in subsurface water infiltration and in the stream water at the starting point of the section. M_{Out} was obtained by integrating the relationship of Cl^- flux vs time at the downstream site. C_E is plateau and C_B is background concentration of Cl^- (g m^{-3}) at the end point of the section.

Mean water depth and stream velocity were calculated from the discharge, volume, length, and mean width of the stream.

The predicted concentration of NH_4^+ -N in stream water at the end of the section (assuming no retention of ammonium within the stream) was calculated as described by Richey *et al.* (1985), using initial concentrations of NH_4^+ -N and their dilution by infiltrating water.

In all these calculations, we supposed that the background concentration of Cl^- in stream water did not change by infiltration, and we neglected the concentration of NH_4^+ -N in the infiltrating water (the background concentrations of NH_4^+ -N varied from 14 to 34 $\mu\text{g l}^{-1}$ at the upstream site and from 3 to 14 $\mu\text{g l}^{-1}$ at the downstream sites before the experiments).

Enclosure experiments

Uptake of NH_4^+ -N by streambed bryophytes and its nitrification were determined from changes in ammonium and nitrate concentrations during the incubation

of the sample (Exp. II). These experiments were performed in July 1991 and June–July 1992. Samples of bryophytes were carefully taken from the streambed of the brook, so as not to damage their bottom part (rhizoids with retained organic detritus and inorganic sediments). Each sample was divided into 2 parts of approx. equal area (15 to 50 cm^2), and each was placed in one of two 500-ml polyethylene bottles, one wrapped in aluminium foil to keep the sample in darkness. Then the sample was covered with 200 to 400 ml of 40 μm filtered stream water enriched by ammonium. The final concentrations of NH_4^+ -N ranged from 120 to 515 $\mu\text{g l}^{-1}$ at the start of incubation, in order to simulate high ammonium loads during snowmelt. Both the light and dark bottles were submerged in the stream. Subsamples of 50 ml of water for chemical analysis were taken immediately after adding the spike and after termination of the experiment, which lasted 3 to 5 hours. Alternatively, the entire experiment was performed at 15 °C in the laboratory on the day after sampling.

Samples were incubated at pH of original stream water. In one of the incubations, when the response of NH_4^+ -N uptake and nitrification to the drop in pH was studied, samples of bryophytes from nonacidified stream (pH = 6.10) were also incubated in water from the acidified stream (pH = 4.65).

Chemical analyses and error estimates

Samples for ammonium, nitrate, nitrite, and chloride determination were filtered immediately after collection through Whatmann GF/C filters (prewashed with original stream water), transported to a field laboratory in polyethylene bottles, and assayed within 5 hours after termination of the experiment.

Ammonium was determined by the rubazoic acid method (Procházková, 1964), as modified by Kopáček & Procházková (1993), nitrate by reduction to nitrite using alkaline hydrazine (Procházková, 1959), nitrite following Bendschneider & Robinson (1952), and chloride according to Zall *et al.* (1956). Alkalinity was determined by Gran titration (Mackereth *et al.* 1978); pH was measured in the field with a pH meter (Radiometer PHM 29b) after standardization of glass electrodes (Radiometer) with 10^{-4} M HClO_4 . The samples of bryophytes (Exp. II) were dried at 105 °C, and organic and inorganic matter were determined at 550 °C as, respectively the loss of weight on ignition (LI) and total residue (TR).

Table 1. Experimental conditions and load calculations for Exp. Ib.

	Units	Date of experiment (1991)	
		July 14	July 16
<i>Background concentration:</i>			
Upstream site:			
NH ₄ ⁺ -N	10 ⁻³ g m ⁻³	15	14
Cl ⁻	g m ⁻³	0.38	0.38
<i>Downstream site:</i>			
NH ₄ ⁺ -N	10 ⁻³ g m ⁻³	5	8
Cl ⁻	g m ⁻³	0.38	0.38
<i>Initial concentration:</i>			
NH ₄ ⁺ -N	10 ⁻³ g m ⁻³	302	296
Cl ⁻	g m ⁻³	1.11	1.07
<i>Plateau downstream concentration:</i>			
NH ₄ ⁺ -N	10 ⁻³ g m ⁻³	54	172
Cl ⁻	g m ⁻³	0.84	0.905
<i>Experimental section:</i>			
Length	m	102	60
Mean water depth	10 ⁻² m	3.1	2.4
Mean water width	m	0.71	1.20
Volume	m ³	2.24	1.77
Overgrown and sprayed area	m ²	70	72
Discharge (starting point)	10 ⁻³ m ³ s ⁻¹	1.1	2.2
Discharge (end point)	10 ⁻³ m ³ s ⁻¹	1.74	2.89
Stream velocity	m s ⁻¹	0.050	0.076
Residence time	min	34	13
<i>Mass-balance:</i>			
Input of NH ₄ ⁺ -N ⁽¹⁾	g	4.38	6.83
Output of NH ₄ ⁺ -N DI ⁽²⁾ + AI ⁽³⁾	g	1.21	5.20
Net retention of of NH ₄ ⁺ -N ⁽⁴⁾	g	3.17	1.63

(1) Sum of background plus added amount of NH₄⁺-N at the starting point.

(2) Output of NH₄⁺-N from the experimental section during infusion of stock solution.

(3) Output of NH₄⁺-N from the experimental section after infusion of stock solution was finished.

(4) Difference between the input and total output of NH₄⁺-N.

Results of the enclosure experiments are calculated as N uptake per unit area of bryophytes periphyton (mg m⁻² h⁻¹) to be easier comparable to the results of *in situ* enrichment experiments. Conversion to approximate values of the N uptake per unit mass of organic matter (in mg of N per g_{LI} of bryophytes) can be made by dividing mg m⁻² by 820, since the mean value of LI was 820 ± 260 g (± SD; n = 11) per 1 m² of bryophytes periphyton.

Error for uptake length (Exp. Ib) was calculated according to Hart *et al.* (1992) and is given in Table 2. The sprayed and overgrown area of the streambed was estimated with about ± 20% error (based on differences between the authors' individual estimates for each subsection). Consequently, error for N uptake by streambed biota in the *in situ* enrichment experiments is also about ± 20%. Errors associated with the data on uptake rates and net retention values (Exp. II) were

Table 2. Some basic uptake parameters of the stream (Exp. Ib), calculated according to Stream Solute Workshop (1990) and Hart *et al.* (1992) using data from Table 1.

	Units	Date of experiment (1991)	
		July 14	July 16
Uptake of NH_4^+ -N per area, $U^{(1)}$	$\text{mg m}^{-2} \text{h}^{-1}$	12.0	8.0
Estimated error in U	%	20	20
Uptake rate coefficient, $k_c^{(2)}$	10^{-4}s^{-1}	6.1	4.0
Mass transfer coefficient, $v_f^{(3)}$	10^{-5}m s^{-1}	1.9	1.0
Uptake length, $S_w^{(4)}$	m	82	190
Estimated error in S_w	%	5	10
Normalized uptake length, $S_w(n)^{(5)}$	$10^3 \text{m}^{-2}\text{s}$	75	86

(1) U is calculated as net retention of NH_4^+ -N per overgrown and sprayed area of the section.

(2) $k_c = \frac{u}{x} \cdot \ln \frac{C_0}{C_x}$, where u is stream velocity (m s^{-1}), x is length of the section, and C is background corrected concentration of NH_4^+ -N, and the subscripts are: 0, initial; x, observed plateau after dilution correction.

(3) $v_f = h k_c$, where h is water depth (m).

(4) $S_w = u/k_c$, where u is stream velocity (m s^{-1}).

(5) $S_w(n) = S_w/Q$, where Q is stream discharge ($\text{m}^3 \text{s}^{-1}$).

estimated from the differences in the results of duplicate incubations; relative errors of the averages varied from $\pm 4\%$ to $\pm 13\%$ with the mean value of $\pm 9\%$.

Results and discussion

In situ enrichment experiments

1. Exp. Ia: The five initial stream NH_4^+ -N concentrations (the first two background, the others background with added nitrogen) at the starting point during Exp. Ia were 20, 34, 57, 145, and $465 \mu\text{g l}^{-1}$. The predicted concentrations of NH_4^+ -N at the downstream site (based on the assumption that NH_4^+ -N behaves conservatively) were 13, 25, 38, 96, and $337 \mu\text{g l}^{-1}$, and those observed were 3, 14, 26, 59, and $114 \mu\text{g l}^{-1}$.

The data obtained show that actual concentrations of NH_4^+ -N at the downstream site were significantly lower than predicted. Retention of NH_4^+ -N by the stream section appeared to be constant (10 to $12 \mu\text{g l}^{-1}$) at low, initial concentrations (20 to $57 \mu\text{g l}^{-1}$), but it increased at higher concentrations.

The data do not allow a differentiation between two possible mechanisms of the increased retention of NH_4^+ -N at its higher initial concentrations ($>100 \mu\text{g l}^{-1}$): an increased ammonium uptake by bryophytes or an increased physical/chemical adsorption of ammonium (Stream Solute Workshop, 1990).

2. Exp. Ib: Experimental conditions and load calculations for Exp. Ib are shown in Table 1. Input of NH_4^+ -N was calculated as the sum of background and added amounts of NH_4^+ -N at the starting point of the experimental stream section. Total output of NH_4^+ -N from the section was obtained by integrating the area under the observed concentration of NH_4^+ -N at the end point vs. time curve, and multiplying by the respective stream discharge. The calculation was performed for the time period from the beginning of the experiment until the time when the concentration of NH_4^+ -N at the end point attained its background value again, once the infusion was stopped (see Fig. 1). The retention of NH_4^+ -N by the experimental section (the net difference between the input and the output) was 3.17 g on July 14 and 1.63 g on July 16.

Concentrations of NH_4^+ -N and Cl^- at the end point increased rapidly during the passage of the pulse, then reached a plateau and became constant. After some time, concentrations of NH_4^+ -N began to increase again, contrary to the tendency in concentrations of chloride (see Fig. 1). This phenomenon, observed in

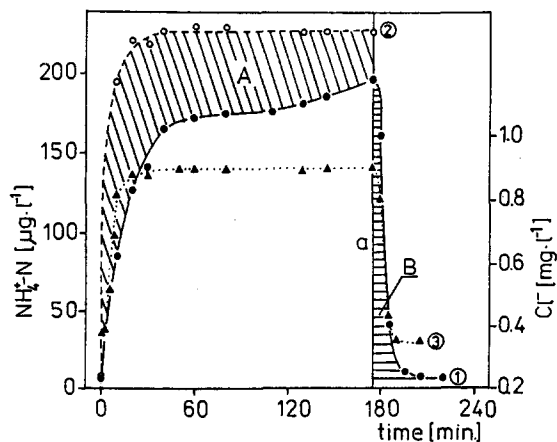


Fig. 1. Ammonium and chloride concentrations vs time for the Exp. Ib at the end point of the experimental section (July 16, 1991): (1) observed concentrations of $\text{NH}_4^+\text{-N}$; (2) predicted concentrations of $\text{NH}_4^+\text{-N}$; (3) observed concentrations of Cl^- ; (a) 175 min (the end of the infusion of $\text{NH}_4^+\text{-N}$); (A) area represents retention of $\text{NH}_4^+\text{-N}$ during infusion; (B) area represents output of $\text{NH}_4^+\text{-N}$ after infusion was finished.

all of the experiments, suggests a gradual saturation of the section by $\text{NH}_4^+\text{-N}$. Concentrations of $\text{NO}_3^-\text{-N}$ were nearly equal at either sampling site before and during the experiments, and varied from 1310 to 1340 $\mu\text{g l}^{-1}$ and from 1210 to 1250 $\mu\text{g l}^{-1}$ on July 14 and July 16, respectively. Nevertheless, they did not follow any apparent trend. Concentrations of $\text{NO}_2^-\text{-N}$ at both the sampling sites were less than 2 $\mu\text{g l}^{-1}$ either before or during experiments. Downstream alkalinity and pH increased slightly both before and during experiments. This increase was related to the length of the section in the same way as the increases in concentrations of Ca, Mg, and Mn, which suggests the release of alkalinity from the bedrock. At the applied concentrations of $\text{NH}_4^+\text{-N}$, the release of alkalinity was higher than the production of strong acid generated by the consume of ammonium.

The main basic uptake parameters of the stream were calculated according to Stream Solute Workshop (1990) and Hart *et al.* (1992) (Table 2). The uptake rates of $\text{NH}_4^+\text{-N}$, related to the overgrown and sprayed area of the experimental section, were 12 and 8 $\text{mg m}^{-2} \text{h}^{-1}$; the higher value obtained during lower stream discharge. Uptake rate coefficients (a measure of the uptake on a volumetric basis), calculated from initial and observed plateau (for dilution by infiltrating water corrected) concentrations of $\text{NH}_4^+\text{-N}$, were $6.1 \cdot 10^{-4} \text{ s}^{-1}$ on July 14 and $4.0 \cdot 10^{-4} \text{ s}^{-1}$ on July 16. Their inverses, representing the aver-

age turnover time of ammonium in the water column (Stream Solute Workshop, 1990), are 27 min. and/or 42 min. at the higher stream discharge. Mass transfer coefficients (a measure of the vertical velocity at which ammonium migrates through the bottom/water interface) were $1.9 \cdot 10^{-5} \text{ m s}^{-1}$ and $1.0 \cdot 10^{-5} \text{ m s}^{-1}$ on July 14 and 16, respectively. Considerably higher value of uptake length was obtained at increased stream discharge (the initial concentrations of $\text{NH}_4^+\text{-N}$ were the same during Exp. Ib), which confirmed strong relation between the uptake length and discharge reported by Howard-Williams *et al.* (1989) and Stream Solute Workshop (1990). More comparable are the results of discharge-normalized uptake lengths (75 000 $\text{m}^{-2} \text{ s}$ and 86 000 $\text{m}^{-2} \text{ s}$), calculated for the observed stream discharges (Hart *et al.*, 1992).

Enclosure experiments

1. Ammonium uptake: The mean value of $\text{NH}_4^+\text{-N}$ uptake rate obtained in all 3- to 5-hour experiments (in field and laboratory) was $4.3 \pm 1.1 \text{ mg m}^{-2} \text{ h}^{-1}$ (mean \pm standard deviation (SD), $n = 20$) and $6.0 \pm 3.0 \text{ } \mu\text{g g}_{\text{LI}}^{-1} \text{ h}^{-1}$ (mean \pm SD, $n = 11$) related to the sample area of bryophytes and to the organic matter, respectively. Uptake of $\text{NH}_4^+\text{-N}$ was negligible in blanks without samples of bryophytes. The maximum velocities of $\text{NH}_4^+\text{-N}$ uptake (6 to 11 $\text{mg m}^{-2} \text{ h}^{-1}$) occurred between the 1st and 3rd hours of enclosure experiments and agree well with the *in situ* results obtained in Exp. Ib.

No significant relationship was observed between $\text{NH}_4^+\text{-N}$ uptake rates and the pH of the stream water in the range from 4.45 to 8.1. No significant differences in ammonium uptake were obtained in light or in dark bottles. The concentration of $\text{NO}_2^-\text{-N}$ and the pH did not significantly change during these experiments.

Alkalinity, however, increased within a wide range, from 0.8 to 7.0 $\mu\text{eq m}^{-2} \text{ h}^{-1}$ and/or 0.1 to 1.9 $\mu\text{eq g}_{\text{TR}}^{-1} \text{ h}^{-1}$, according to the area of the sample and/or its inorganic matter. The production of alkalinity from inorganic sediments retained in the bottom part of bryophytes exceeded acid production from the ammonium conversion in these experiments. The alkalinity produced by weathering processes in the HTM is thus nowadays a sufficient buffer to acid production by biochemical conversion of ammonium in its common concentrations in precipitation.

The area of bryophytes used in enclosure experiments was at least 15 cm^2 , so as to reduce the release of $\text{NH}_4^+\text{-N}$ from damaged samples, which was observed

Table 3. Average NH_4^+ -N uptake rate and NO_3^- -N release obtained during 3- to 5-hour enclosure experiments. (Light bottles, and temperature of between 7 to 11 °C in field and 15 °C in laboratory experiments).

pH	Alkalinity ⁽¹⁾ ($\mu\text{eq l}^{-1}$)	NH_4^+ -N			NO_3^- -N		% of NH_4^+ -N uptake
		Initial conc: ($\mu\text{g l}^{-1}$)	Loading (mg m^{-2})	Uptake ⁽²⁾ ($\text{mg m}^{-2}\text{h}^{-1}$)	Initial conc. ($\mu\text{g l}^{-1}$)	Release ⁽²⁾ ($\text{mg m}^{-2}\text{h}^{-1}$)	
4.45 ⁽³⁾	-35	195	180	5.8	670	0.0	0
		515	105	2.6	685	0.0	0
4.65	-30	320	32	3.5	440	0.0	0
		415	54	5.6	440	0.5	9
6.30	27	120	55	4.9	455	2.3	47
		315	51	2.3	455	1.2	52
6.40	18	210	34	4.5	655	1.8	40
		410	34	4.9	640	2.3	47
8.10	880	275	33	5.2	420	-4.2 ⁽⁴⁾	—

(1) Gran titration.

(2) Estimated error in NH_4^+ -N uptake and NO_3^- -N release is $\pm 9\%$.

(3) These two experiments were done in laboratory.

(4) Uptake occurred instead of production.

Table 4. Average NH_4^+ -N uptake rate and NO_3^- -N release obtained during 5-hour incubation of bryophytes, taken from 2 different sites of a non-acidified stream, in their original water (pH = 6.1) and in water taken from an acidified stream (pH = 4.65). Samples (area of 25 cm²) were incubated at 15 °C in light bottles (laboratory).

	Unit	Sample 1		Sample 2	
pH of water		6.10	4.65	6.10	4.65
Initial concentration:					
NH_4^+ -N	$\mu\text{g l}^{-1}$	310	320	310	320
NO_3^- -N	$\mu\text{g l}^{-1}$	645	440	645	440
Final concentration:					
NH_4^+ -N	$\mu\text{g l}^{-1}$	94	41	145	140
NO_3^- -N	$\mu\text{g l}^{-1}$	680	515	705	525
Uptake ⁽¹⁾ :					
NH_4^+ -N	$\text{mg m}^{-2} \text{h}^{-1}$	4.1	5.3	3.0	3.4
Production ⁽¹⁾ :					
NO_3^- -N	$\text{mg m}^{-2} \text{h}^{-1}$	1.4	1.4	1.1	1.6
Nitrification					
of NH_4^+ -N	%	34	26	37	47

(1) Estimated error in NH_4^+ -N uptake and NO_3^- -N production is $\pm 9\%$.

(2) *Scapania undulata*

(3) *Bryum weigelii*

at the beginning of the enclosure experiments. This release was dependent on the area of the bryophytes as samples with smaller area show comparatively more damage than the larger ones. The release of ammonium from damaged samples probably arose from its desorption from the bottom part of the bryophytes, since streambed sediments are a significant pool of adsorbed ammonium (Rithey *et al.*, 1985).

2. Nitrification: Nitrification of the added ammonium strongly depended on the pH of the stream from which the bryophytes were taken from (Table 3). Nitrification was significant in streams with pH of 6.3 and 6.4. It reached levels of about 50% of the retained NH_4^+ -N in light bottles, and increased about 1.4 times in dark bottles. In acidified streams ($\text{pH} < 5$), no significant production of nitrate was detected. In the alkaline stream ($\text{pH} > 8$), where the original concentration of ammonium was zero, nitrate was utilized as the principal nitrogenous substrate, together with added ammonium. The NO_3^- -N uptake rate was considerably higher in light bottle ($4.2 \text{ mg m}^{-2} \text{ h}^{-1}$) than in dark bottle ($1.9 \text{ mg m}^{-2} \text{ h}^{-1}$).

Nearly the same values for the NH_4^+ -N uptake rate and the related percentage of nitrification were observed during the 5-hour incubation of two samples of bryophytes from the nonacidified stream ($\text{pH} = 6.1$), in both their original water and in water from the acidified stream ($\text{pH} = 4.65$) (Table 4). The data obtained suggest that short-term drops in streamwater pH, which usually happen during rain or snowmelt periods, do not influence the ability of streambed biota to oxidize ammonium. Probably, as described by Rudd *et al.* (1988) in lakes, a longer time of decrease in pH under 5.4 is needed to disrupt nitrification.

The higher intensity of nitrification observed in the dark bottles confirms the significance of the photoinhibition of nitrification in shallow, transparent waters (Vrba, 1990).

Conclusions

The retention of NH_4^+ -N by the stream was related to its initial concentration.

The mean value of the rate of NH_4^+ -N uptake by streambed biota, primarily bryophytes, in 3- to 5-hour enclosure incubations was $4.3 \text{ mg m}^{-2} \text{ h}^{-1}$, and was not related to the pH of stream water. The maximum velocities of NH_4^+ -N uptake (6 to $11 \text{ mg m}^{-2} \text{ h}^{-1}$) were obtained between the 1st and 3rd hour of incubation,

and agreed well with results obtained in 3-hour stream enrichment experiments (8 and $12 \text{ mg m}^{-2} \text{ h}^{-1}$).

Nitrification of the added NH_4^+ -N was related to stream water pH; it was significant (about 50%) at pH of 6.3 and 6.4, and negligible in acidified streams ($\text{pH} < 5$). Significant photoinhibition of nitrification was observed; the share of nitrification in ammonium uptake was about 1.4 times higher in dark than in light bottles.

A short-term decrease in stream water pH did not influence the ability of bryophytes taken from the bottom of a non-acidified stream to oxidize added ammonium.

Acid production, from biological conversion of the ammonium loads to which the High Tatra Mountains are exposed, did not exceed the production of alkalinity from weathering processes, in both the stream and the enclosure experiments.

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References

- Bendschneider, K. & R. J. Robinson, 1952. A new spectrophotometric determination of nitrite in sea water. *J. mar. Res.* 2: 87–96.
- Catalan, J., E. Ballesteros, L. Camarero, M. Felip & E. Gacia, 1992. Limnology in the Pyrenean lakes. *Limnetica* 8: 27–38.
- Cerovský, M., 1983. Measurement of air pollution at Mt. Chopok and pollution of precipitation in Bratislava. (In Slovak). Hydrochemical problems of water pollution, Geological Survey, Bratislava: 73–80.
- Dillon, P. J. & L. A. Molot, 1990. The role of ammonium and nitrate retention in the acidification of lakes and forested catchments. *Biogeochemistry* 11: 23–43.
- Fott, J., E. Stuchlík, Z. Stuchlíková, V. Straškrabová, J. Kopáček & K. Šimek, 1992. Acidification of lakes in Tatra Mountains (Czechoslovakia) and its ecological consequences. In R. Mosello, B. M. Wathne & G. Giussani (eds), *Limnology on groups of remote mountain lakes: ongoing and planned activities*. Documenta Ist. Ital. Idrobiol. No 32: 69–81.
- Gazda, S. & K. Lopašovský, 1983. Chemical composition of winter precipitation in Slovakia. (In Slovak). Hydrochemical problems of water pollution, Geological Survey, Bratislava: 63–71.
- Grodzinska-Jurczak, M. & M. Krywult, 1992. Acidification of the Waksmundzki Stream (The Polish Tatra Mountains) affected by atmospheric pollution. *Acta Hydrobiol.* 34: 19–28.

- Golterman, H. L. & R. S. Clymo, 1969. *Methods for Chemical Analysis of Fresh Waters*. IBP Handbook No 8, Blackwell Sci. Publ., Oxford, 172 pp.
- Hart, B. T., P. Freeman & I. D. McKelvie, 1992. Whole-stream phosphorus release studies: variation in uptake length with initial phosphorus concentration. *Hydrobiologia* 235/236: 573–584.
- Henriksen, A. & D. F. Brakke, 1988. Increasing contributions of nitrogen to the acidity of surface waters in Norway. *Wat. Air Soil Pollut.* 42: 183–201.
- Howard-Williams, C., J. C. Prisco & W. F. Vincent, 1989. Nitrogen dynamics in two antarctic streams. *Hydrobiologia* 172: 51–61.
- Kopáček, J. & L. Procházková, 1993. Semi-micro determination of ammonia in water by the rubazoic acid method. *Intern. J. Envir. Anal. Chem.* 53: 243–248.
- Kopáček, J. & E. Stuchlík, 1994. Chemical characteristics of lakes in the High Tatra Mountains, Czechoslovakia. *Hydrobiologia* 274: 49–56.
- Mackereth, F. J. H., J. Heron & J. F. Talling, 1978. *Water analysis: Some revised methods for limnologists*. FBA Scientific Publication No 36: 120 pp.
- Moldan, B., M. Veselý & A. Bartoňová, 1987. Chemical composition of atmospheric precipitation in Czechoslovakia, 1976–1984 – I. Monthly samples. *Atmospheric Environment* 21: 2383–2395.
- Mosello, R., A. Marchetto, G. A. Tartari, M. Bovio & P. Castello, 1991. Chemistry of alpine lakes in Aosta valley (N. Italy) in relation to watershed characteristics and acid deposition. *Ambio* 20: 7–12.
- Procházková, L., 1959. Bestimmung der Nitrate im Wasser. *Z. anal. Chem.* 167: 254–260.
- Procházková, L., 1964. Spectrophotometric determination of ammonia as rubazoic acid with bispyrazolone reagent. *Analyt. Chem.* 36: 865–871.
- Richey, J. S., W. H. McDowell, G. E. Likens, 1985. Nitrogen transformations in small mountain stream. *Hydrobiologia* 124: 129–139.
- Rudd, J. W. M., C. A. Kelly, D. W. Schindler & M. A. Turner, 1988. Disruption of the nitrogen cycle in acidified lakes. *Science* 240: 1515–1517.
- Schuurkes, J. A. A. R. & R. Mosello, 1988. The role of external ammonium inputs in freshwater acidification. *Schweiz. Z. Hydrol.* 50/1: 71–86.
- Straškrabová V. & P. Blažka, 1990. Změny dusíku a fosforu v plesích a potocích TANAPU a jejich vliv na biologické procesy. Sborník přednášek z konference k 40. výročí Tatranského národního parku, Tatranská Lomnica: 451–456. [Changes in nitrogen and phosphorus concentrations in lakes and brooks of the Tatra Mts. and their effect on biological processes].
- Stream Solute Workshop, 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. *J. N. Am. Benthol. Soc.* 9: 95–119.
- Stuchlík, E., Z. Stuchlíková, J. Fott, L. Ružička & J. Vrba, 1985. Effect of acid precipitation on waters of the TANAP territory. (In Czech, with English summary). *Treatises concerning the Tatra National Park* 26: 173–211.
- Triska, F. J., V. C. Kennedy, R. J. Avanzino, G. W. Zellveger & K. E. Bencala, 1989a. Retention and transport of nutrients in a third-order stream: Channel processes. *Ecology* 70: 1877–1892.
- Triska, F. J., V. C. Kennedy, R. J. Avanzino, G. W. Zellveger & K. E. Bencala, 1989b. Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. *Ecology* 70: 1893–1905.
- Vrba, J., 1990. Effect of periodic illumination on nitrification in the continuous cultivation. *Arch. Hydrobiol. Beih.* 34: 145–150.
- Wathne, B. M., R. Mosello, A. Henriksen & A. Marchetto, 1989. Comparison of the chemical characteristics of mountain lakes in Norway and Italy. In M. Johannessen, R. Mosello & H. Barth (eds), *Acidification processes in remote mountain lakes*. Air pollution research report 20: 41–58.
- Wright, R. F. & E. T. Gjessing, 1976. Changes in the chemical composition of lakes. *Ambio* 5: 219–223.
- Wright, R. F. & M. Johannessen, 1980. Input-output budgets of major ions at gauged catchments in Norway. *Proc., Int conf. ecol. impact acid precip. Norway, SNSF project*: 250–251.
- Zall, D. M., D. Fisher & M. Q. Garner, 1956. Photometric determination of chlorides in water. *Analyt. Chem.* 28: 1665–1668.