

Water chemistry of surface tributaries to the acidified mountain lakes in the Bohemian Forest

Chemismus povrchových přítoků okyselených Šumavských jezer

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Abstract

Water chemistry of the surface tributaries to four Czech lakes in the Šumava Mountains (Bohemian Forest) was analyzed in spring, summer, and autumn 1997 to explain differences in lake water composition. All tributaries were strongly acidified with pH values between 3.7 and 4.8. On an equivalence basis, H^+ and Al^{3+} ions were the dominant cations (31 % and 20 % on average, respectively); SO_4^{2-} and NO_3^- ; the most common anions (53 % and 25 %, respectively). Average contribution of organic acids was 14 %. The pH values and concentrations of aluminum were tightly correlated with both sulfate and organic acids, while concentrations of base cations were more closely related to nitrate and silica concentrations. NO_3^- levels were negatively correlated with organic carbon. Plešné Lake received the highest inflow concentrations of phosphorus, dissolved organic carbon, and silica, explaining its higher productivity and lower NO_3^- concentrations (due to assimilation and denitrification) among the Šumava lakes. Inputs of aluminum to Prášílské lake were low corresponding to the low SO_4^{2-} concentrations in its tributaries. Highest concentrations of H^+ and NO_3^- were observed in the inputs to Čertovo Lake and Černé Lake, respectively, as well as in the lakes themselves.

Key words: Šumava Mountains, nitrogen, sulfur, aluminum, organic carbon, phosphorus.

Introduction

The limnology of lakes in the Šumava Mountains has been more or less intensively studied since the late 19th century. VESELÝ (1994), FOTT & al. (1994), and VRBA & al. (1996) summarized historical, as well as recent data on the chemistry and biota of the lakes with particular emphasis on changes due to acidification. The rate of anthropogenic acidification of lake waters reached a maximum in the late 1980s (VESELÝ 1996). Since 1989 water chemistry in the Šumava lakes has been recovering from acidification (KOPÁČEK & al. 1998), due to political and economic changes in the post-communist Central European countries, resulting in a substantial reduction in atmospheric emissions of sulfur and nitrogen (KOPÁČEK & al. 1997).

Whereas a good deal of data comparing water composition of the Šumava lakes are currently available in the literature showing important differences between the lakes, there are with the exception of SCHMIDT & al. (1993) no data on the composition of tributaries to the lakes. To understand differences in composition of the Šumava lakes, a more detailed study of the chemical composition of all tributaries to the lakes was needed. The purpose of our study was i) to evaluate the chemistry of surface tributaries to Černé, Čertovo, Prášílské and Plešné

Lakes, ii) to describe differences in their acidity, nutrients, organic matter, and aluminum concentrations, and iii) to compare the composition of water in the tributaries to that in the lakes.

Materials and methods

Description of study sites

The four lakes studied were: Černé (CN, Schwarzsee), Čertovo (CT, Teufelsee), Prášilské (PR, Stubenbachsee), and Plešné (PL, Plöckensteiner See) (abbreviations and German names in brackets), all situated in the Šumava Mts. (13° to 14° E, 49° N) at altitudes between 1008 and 1090 m a. s. l. All lakes are of glacial origin; they are small (3.7 to 18.4 ha) and are surrounded by steep, rocky, forested slopes of their corries and moraines. Their watershed to lake surface ratios range from 7 to 14.

The bedrock of CN, CT, and PR watersheds consists predominately of mica-schist (muscovite gneiss) with quartzite intrusions, while the bedrock of PL lake is composed of coarse-grain granites (VESELY 1994). Most of the watersheds are covered with a thin layer of forest humus. Soils are iron-containing acidic podzols with low levels of Ca and K and unsaturated sorption complexes. Soil profiles deeper than 10 cm are rare and consist of an upper gray E-horizon and lower enriched rusty-brown B-horizon (PELIŠEK 1966).

Vegetation is dominated by spruce forest (with sparse fir and beech) which nearly completely covers the lake watersheds. The history of land-use differs from lake to lake. The forest surrounding CN and CT lakes was undisturbed until 1600; then it was used for charcoal and potash production for local iron smelters and glassworks, respectively, in the 17th century, and for fuel and timber in the 18th and 19th centuries (VESELY & al. 1993). Between 1754 and 1859, the area was used for grazing approximately 100 cows after which time grazing was prohibited; marshy soils were drained and the watersheds revegetated with forest (VESELY 1994). The area has been protected as a nature park since 1911 and at present the forest is 80–140 years old. The history of the PR lake watershed is in contrast to those of CN and CT lakes. For example, there are no records of mining activities (VESELY 1994). The forest surrounding PR lake was not intensively exploited in the Middle Ages and was 200–300 years old in 1812; however, it was seriously damaged by gales in the second half of the 19th century (VESELY 1994). Within the last decade the approximately 150 year-old forest has been drastically reduced (from ~80 % to <30 % coverage of the watershed) by gales and insects (VESELY 1996), and only a part of the damaged forest area has recovered. There are few available data in the literature on the history of land-use in the PL lake watershed. Prospecting for gold occurred there in the second half of the 16th century (VESELY 1994). At present, more than 70 % of the PL lake watershed is covered with secondary spruce forest which is ~150 years old. During the 20th century there was a tourist cottage (from 1911 to 1947) and barracks (from 1952 to 1989) in the close vicinity of the outlet from PL lake. Since World War II access to the CN, CT, PR, and PL watersheds and most kinds of land-use have been restricted there due to frontier protection (up to 1989). In 1963, the Šumava Mountains were designated as a protected area. More details on the physical characteristics, geology, vegetation, and history of land use of the watershed areas are given in VESELY (1994).

Tributaries of the lakes are small forested first order brooks, except for tributary PL-III which is subsurface. Most are short (from ~50 m to ~1 km), steep, and run only seasonally. Their locations are given in Fig. 1. The brooks have no names and are designated by abbreviations and Roman numerals in order starting from the outlet and moving in a counterclockwise direction. In subwatersheds containing several tributaries in close proximity (few meters distance), the tributaries are further identified by a single lower letter if they were sampled

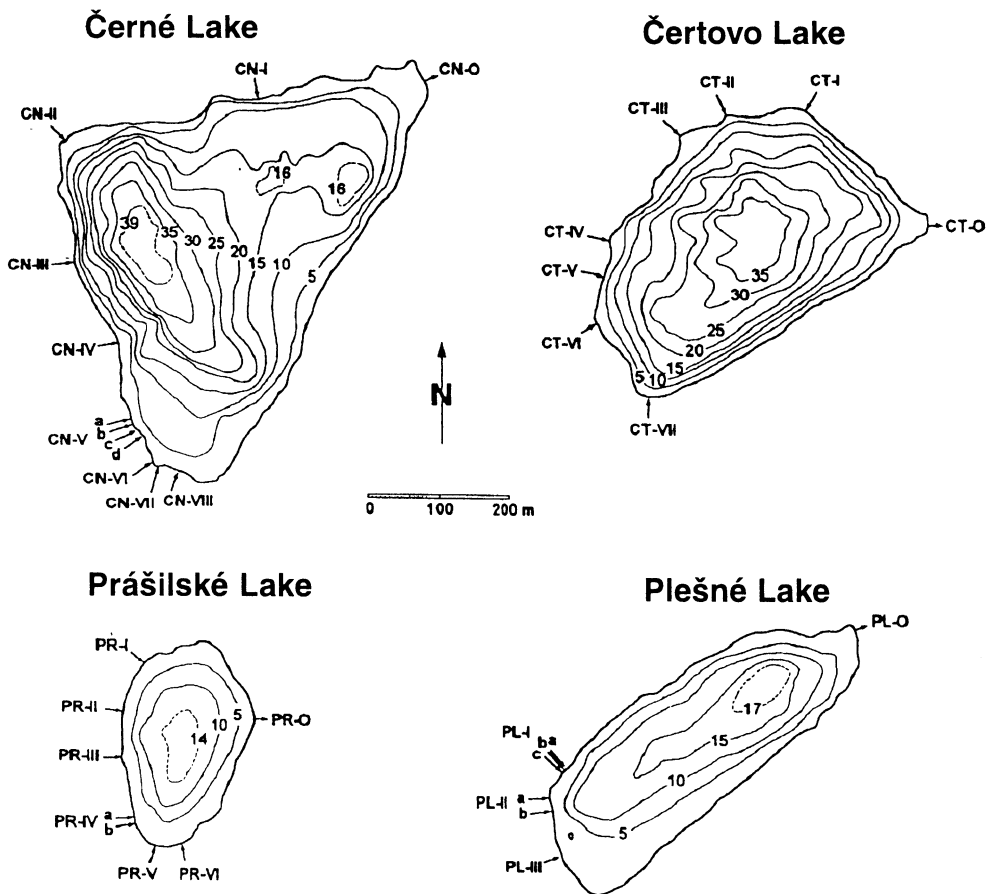


Fig. 1. – Bathymetric maps of the Šumava lakes redrawn from Švambers (1939) with arrows showing locations of tributaries (for abbreviations see „Materials and methods“) and outflows (CN-O, CT-O, PR-O, and PL-O).

individually (e.g. PL-II-a, PL-II-b) and/or with a group of lower letters, when samples were combined (e.g. PL-I-ab). If samples from all brooks in the cluster were combined to obtain one sample, no lower letters were added to the main abbreviation (e.g. CT-V, PR-IV).

Sampling and analyses

Samples from the CN, CT, and PR lakes and their tributaries were taken on May 19, July 22, and October 13, 1997; PL lake was always sampled one day later. Tributaries were sampled near their outfalls, usually from small natural waterfalls, where the water discharge rate could be estimated by means of bucket and watch; tributary PL-III was sampled in a small cave. When tributaries were in clusters and their temperatures comparable, an integrated sample was taken with sample volumes proportional to the discharges of the individual streams. However, tributaries were sampled separately when their temperatures differed $>\pm 0.5$ °C. Samples were immediately prefiltered through a 40 μ m polyamide sieve to remove coarse parti-

cles. Samples of lake water were taken from the surface (10–50 cm depth) above the deepest point of the lake and were prefiltered through a 200 µm polyamide sieve. In the laboratory samples were filtered with membrane filters (0,45 µm, Sartorius) for determination of ions and silica, and with glass-fibre filters (0,4 µm; Macherey Nagel MN–5) for analyses of phosphorus, organic matter, absorbances, and dissolved reactive aluminum. Samples for determinations of pH, alkalinity, conductivity, total phosphorus, total aluminum, and total iron were not filtered.

Samples were analyzed for dissolved reactive phosphorus (DRP) by the molybdate method (MURPHY & RILEY 1962), total phosphorus and total dissolved phosphorus (TP, TDP) by perchloric acid digestion, (KOPÁČEK & HEJZLAR 1993), pH, acid neutralization capacity (Gran titration) and conductivity (at 25 °C) within 24 hours after sampling. In addition, analyses for dissolved organic carbon (DOC) by LiquiTOC analyzer (Foss-Heraeus, Germany), absorbances at 254 and 400 nm (A_{254} and A_{400}), and dissolved reactive silica (DR-Si) using the molybdate technique (MACKERETH & al. 1987) were performed within 48 hours after sampling. Molar absorptivities of dissolved organic matter at 254 and/or 400 nm were calculated as ratios of A_{254} and/or A_{400} (1m absorption path) to DOC concentrations (mol m^{-3}). Dissolved organic phosphorus (DOP) was estimated as the difference between TDP and DRP. Dissolved organic nitrogen (DON) was measured as a difference between Kjeldahl nitrogen and ammonium concentrations. Kjeldahl nitrogen was determined by Kjeldahl digestion and distillation (Procházková, 1960) within one week after sampling. Fractionation of aluminum, i.e. total reactive Al (TR-Al, from non-filtered water), dissolved reactive Al (DR-Al), non-labile monomeric Al (NL-Al; complexed with organic matter) and labile monomeric Al (L-Al; ionic forms) were determined according to Driscoll (1984) within two weeks after sampling. Samples for determinations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , and F^- were frozen at -20°C until analyzed by ion chromatography (Thermo Separation Products). Samples for total aluminum (T-Al) and total iron (T-Fe) were preserved with nitric acid and analyzed by inductively coupled plasma spectrometry (ICP) (Pye Unicam 7450). All analyses were completed within one month after sampling.

Data evaluation – ionic balance

Ionic balance was calculated according to the equation (1)

$$2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+] + n [\Sigma\text{Al}^{n+}] = 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{F}^-] + [\text{R}^-] \quad (1)$$

where ΣAl^{n+} represents the sum of charged Al species, R^- is the concentration of organic acid anions, and concentrations of HCO_3^- and CO_3^{2-} are neglected for waters with depleted carbonate buffering systems. Square brackets denote molar concentrations.

The concentration of Al^{n+} ($\mu\text{eq l}^{-1}$) was calculated by multiplying the L-Al concentration ($\mu\text{mol l}^{-1}$) by an average charge (n) of Al hydroxycplexes; n was calculated from the distribution of particular ionization fractions of aqueous Al:

$$n = 3\alpha_0 + 2\alpha_1 + \alpha_2 + \alpha_4 \quad (2)$$

where α_0 , α_1 , α_2 , and α_4 are ionization fractions of Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, and $\text{Al}(\text{OH})_4^-$, respectively, which were calculated from the equilibrium constants of Al^{3+} hydrolyses given by STUMM & MORGAN (1981). A rearrangement of equation (2) yields the relationship between n and pH:

$$n = \frac{3[\text{H}^+]^4 + 2K_1[\text{H}^+]^3 + \beta_2[\text{H}^+]^2 - \beta_4}{[\text{H}^+]^4 + K_1[\text{H}^+]^3 + \beta_2[\text{H}^+]^2 + \beta_3[\text{H}^+] + \beta_4} \quad (3)$$

where $K_1 = 1.07 \times 10^{-5}$, $\beta_2 = 5.01 \times 10^{-10}$, $\beta_3 = 10^{-15}$, and $\beta_4 = 10^{-23}$ are equilibrium constants for $[Al^{3+}]$ vs. $[Al(OH)^{2+}]$, $[Al(OH)_2^+]$, $[Al(OH)_3]_{aq}$, and $[Al(OH)_4^-]$, respectively. Aluminum fluoride complexes were neglected in the estimation of the average Al charge. In our samples pH was frequently < 4.5 and the average L-Al to F^- molar ratio was ~ 7 . Under these conditions most of the fluoride was complexed to form AlF^{2+} (SCHECHER & DRISCOL 1987, PLANKEY & al. 1986). The charge of this complex was close to the n values of 2.2–3, obtained for hydroxialuminum complexes at pHs < 4.5 . SO_4 -Al complexes were also neglected since they comprise $< 10\%$ of the total soluble Al in acidified fresh waters at typical SO_4^{2-} concentrations (SCHECHER & DRISCOL 1987). Hence, our simplified approach gave only a limited error in the evaluation of the n value. However, it could lead to some overestimation of the average Al charge at elevated F^- and SO_4^{2-} concentrations and/or at low L-Al concentrations (e.g. in PR lake and its tributaries).

The concentration of ionized organic acids (R^- , $\mu eq\ l^{-1}$) was estimated according to OLIVER (1983) from the concentration of DOC ($mg\ l^{-1}$) and ionization of carboxyl groups, following equations (4), (5), and (6):

$$[R^-] = \frac{\bar{K} \cdot [C_T]}{\bar{K} + [H^+]} \quad (4)$$

where C_T ($\mu eq\ l^{-1}$) represents the concentration of total carboxyl groups and \bar{K} is a mass action quotient (an average equilibrium constant of dissociation of humic acids containing a variety of functional groups). \bar{K} was estimated by using the empirical relationship between the mass action quotient and pH:

$$p\bar{K} = 0,96 + 0,90 \cdot pH - 0,039 \cdot (pH)^2 \quad (5)$$

C_T was calculated from the concentration of DOC ($mg\ l^{-1}$) and the average carboxyl content of aquatic humic substances (X , $\mu eq\ mg^{-1}$).

$$C_T = X \cdot DOC \quad (6)$$

According to Oliver (1983), the average carboxyl content of humic and fulvic acids is generally $\sim 10\ \mu eq$ per 1 mg DOC. However, this value represents an upper limit in natural waters, where some of the humic materials may be complexed with metals. This complexation decreases the amount of ionized carboxyl groups. In our study, we did not use the average carboxyl content of humic substances given by OLIVER (1983). Instead we estimated the average carboxyl content of aquatic humic substances non-complexed with metals (X_N) as follows. First, concentrations of organic acid anions were obtained independently of DOC as the difference between the sum of cations (including ΣAl^{n+}) and sum of strong acid anions ($SAA = SO_4^{2-} + NO_3^- + Cl^-$) according to equation (1). Then, X_N value was calculated for each sample using equations (4) and (5) rearranged as follows:

$$X_N = \frac{[R^-] \cdot (K + [H^+])}{K \cdot DOC} \quad (7)$$

The average X_N value ($5.9 \pm 1.9\ \mu eq\ mg^{-1}$; mean \pm standard deviation) was then used to calculate the R^- concentration from DOC and pH according to equations (6) and (4).

Results

General

A total of 75 samples were taken from tributaries in 1997; 26 in both summer and autumn and 23 in spring when tributaries CN-III, CN-VI, and PR-IV were without water. According to our previous observations, only the following tributaries were perennial: CN-VII, CN-VIII, CT-II, CT-IV, CT-VI, and PR-V. Water discharge in the individual tributaries varied from 0.1 to $\sim 20 \text{ l s}^{-1}$. Total water input from surface tributaries to PR and PL lakes was usually $\sim 50 \%$ of the outflow, indicating that $\sim 50 \%$ of the total water input occurred via diffuse runoff and/or subsurface tributaries. Water outflows from CN and CT lakes were not possible to assess due to fluctuations in outflow due to operation of a hydroelectric-power station and seepage through the moraine at the outlet, respectively.

All samples were strongly acidic due to a depleted carbonate buffering system with pH values ranging from 3.71 to 4.83 (Table 1). Concentrations of $\text{NO}_3\text{-N}$, SO_4^{2-} , and TR-Al were higher than 0.4, 4.7, and 0.48 mg l^{-1} , respectively, in 75 % of the samples. Concentrations of

Table 1. – Variability in chemical composition of tributaries.

Total number of samples was 75

Variable	Unit	Minimum	25% Quart.	Median	75% Quart.	Maximum
pH		3.71	4.06	4.18	4.37	4.83
Gran alkalinity	mmol l^{-1}	-0.068	-0.060	-0.054	-0.044	-0.002
Conduct. (25 °C)	mS m^{-1}	2.37	3.73	4.35	5.31	9.82
Ca^{2+}	mg l^{-1}	0.18	0.48	0.62	0.78	1.55
Mg^{2+}	mg l^{-1}	0.12	0.23	0.32	0.40	0.60
Na^+	mg l^{-1}	0.26	0.64	0.76	0.92	1.42
K^+	mg l^{-1}	0.03	0.19	0.28	0.37	0.84
$\text{NH}_4\text{-N}$	$\mu\text{g l}^{-1}$	<5	<5	<5	10	50
$\text{NO}_3\text{-N}$	mg l^{-1}	0.01	0.39	0.66	1.13	2.42
SO_4^{2-}	mg l^{-1}	1.79	4.68	5.57	6.50	8.88
Cl	mg l^{-1}	0.23	0.44	0.59	0.67	0.89
F	mg l^{-1}	0.00	0.02	0.08	0.10	0.15
DOC	mg l^{-1}	1.19	4.53	8.00	11.73	33.50
A_{254}	254 nm; 1 m	3.58	15.6	29.8	45.7	140
A_{400}	400 nm; 1 m	0.27	1.32	2.92	4.50	15.3
DRP	$\mu\text{g l}^{-1}$	0.0	0.0	1.3	8.0	29.6
TDP	$\mu\text{g l}^{-1}$	1.4	2.8	4.0	13.7	36.3
DON	mg l^{-1}	0.125	0.240	0.290	0.368	0.675
DR-Si	mg l^{-1}	1.18	1.76	1.97	2.66	4.94
T-Al	mg l^{-1}	0.136	0.470	0.745	0.890	1.350
TR-Al	mg l^{-1}	0.217	0.478	0.726	0.842	1.425
DR-Al	mg l^{-1}	0.133	0.508	0.730	0.839	1.438
NL-Al	mg l^{-1}	0.017	0.133	0.208	0.309	0.521
L-Al	mg l^{-1}	0.116	0.278	0.456	0.612	1.283
T-Fe	mg l^{-1}	< 0.05	0.08	0.17	0.34	2.96

base cations (BC = $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$), nutrients, and DOC in the 4 lake systems varied by one to two orders of magnitude (Table 1), predominantly due to differences in the morphological, geochemical, and biological properties of the subwatersheds. Seasonal changes in concentrations of particular constituents were not usually pronounced, except for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, which reached their minima in summer, and DOC, which was lowest in spring.

The average relative ionic composition of water samples indicated strong acidification of watershed soils. On an equivalence basis, H^+ and Al^{3+} ions dominated the cation pool comprising 7–65 % (31 % on average) and 3–46 % (20 % on average), respectively, whereas BC were quantitatively less important with average contributions as follows: Ca^{2+} , 16 %; Na^+ , 16 %; Mg^{2+} , 13 %; and K^+ , 4 %. In the anion pool, SO_4^{2-} was most prominent (17–79 %, 53 % on average) with NO_3^- and R^- contributing between 1–71 % and 1–57 % (averages of 25 % and 14 %), respectively. Cl^- was less variable ranging from 1–17 % (7 % on average).

Results of linear regression analysis of relationships between concentrations of major cations and anions are given in Table 2. These regressions were calculated for all tributaries except for PR-I and PR-II, whose subwatersheds were severely affected by a decline in forest health due to storm and insect damage (see later). In the other tributaries, concentrations of BC were positively correlated with NO_3^- concentrations. Surprisingly BC were not correlated with SO_4^{2-} concentrations and the correlation between BC and R^- concentrations was negative. In contrast H^+ concentrations were tightly correlated with R^- concentrations with the highest correlation between H^+ and the sum of SO_4^{2-} and R^- . L-Al concentrations were primarily correlated with SO_4^{2-} and significantly less with NO_3^- concentrations.

Variability in chemistry of tributaries

Table 3 shows the chemical compositions of all tributaries in 1997. From these data, we calculated per-cent contributions by the major tributaries (CN-VII, CT-II, PR-V, and PL-I-ab) to the total mass inputs into the lakes. While tributaries PR-V and CT-II were the dominant sources (~80 % and ~50–60 %) to PR and CT lakes, respectively, tributaries CN-VII and PL-Iab contributed < 40% of the total input to CN and PL lakes, respectively.

In the watershed of CN lake, the pH of surface tributaries varied from 3.79 to 4.60. The

Table 2. – Intercepts (a), slopes (b) and correlation coefficients (r) of linear regressions between the concentrations of major ions ($\mu\text{eq l}^{-1}$) in the tributaries of CN, CT, PR, and PL lakes except PR-I and PR-II tributaries (number of observations was 69).

Y	X	a	b	r
BC	NO_3^-	71±15	0.47±0.06	0.72***
BC	SO_4^{2-}	106±21	-0.10±0.09	0.13
BC	R^-	100±18	-0.46±0.09	0.52***
H^+	NO_3^-	80±35	-0.15±0.14	0.13
H^+	SO_4^{2-}	20±33	0.45±0.15	0.35**
H^+	R^-	42±27	0.98±0.14	0.66***
H^+	$\text{SO}_4^{2-} + \text{R}^-$	-62±21	0.91±0.08	0.81***
L-Al	NO_3^-	32±19	0.30±0.07	0.45***
L-Al	SO_4^{2-}	-19±15	0.56±0.07	0.72***
L-Al	R^-	55±20	-0.27±0.10	0.31*

Levels of significance: * 5%, ** 1%, *** 0.1%.

Table 3. - Chemical composition of tributaries to the Bohemian Forest lakes in 1997. Part I – Černé Lake.

Tributary	CN-I			CN-II			CN-III			CN-IV			CN-V			CN-VI			CN-VII			CN-VIII			
	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	
Q	1 s ⁻¹	0.3	1.0	1.0	1.5	4.5	4.0	4.0	0.2	0.2	1.5	2.0	3.5	5.0	5.5	7.0	4.0	7.0	20.0	13.0	18.0	7.0	9.0	7.0	7.0
pH		3.89	3.79	3.80	4.08	3.97	3.90	4.06	4.11	4.02	4.03	3.97	4.15	4.12	4.12	4.13	4.28	4.18	4.37	4.33	4.32	4.63	4.57	4.60	4.60
Ca ²⁺	mg l ⁻¹	0.43	0.38	0.53	0.61	0.38	0.48	0.33	0.40	0.65	0.37	0.43	0.68	0.60	0.60	0.60	0.53	0.57	0.72	0.58	0.81	0.93	0.80	0.88	0.88
Mg ²⁺	mg l ⁻¹	0.21	0.19	0.28	0.30	0.25	0.31	0.28	0.33	0.36	0.28	0.35	0.41	0.39	0.48	0.33	0.35	0.40	0.34	0.42	0.52	0.48	0.48	0.47	0.47
Na ⁺	mg l ⁻¹	0.49	0.41	0.58	0.53	0.46	0.58	0.43	0.52	0.78	0.66	0.88	0.70	0.63	0.86	0.57	0.76	0.64	0.51	0.72	0.91	0.88	0.93	0.93	0.93
K ⁺	mg l ⁻¹	0.19	0.19	0.19	0.32	0.17	0.20	0.21	0.28	0.30	0.15	0.23	0.36	0.19	0.28	0.28	0.28	0.28	0.44	0.29	0.38	0.56	0.50	0.52	0.52
NH ₄ -N	µg l ⁻¹	10	<5	10	20	<5	<5	9	50	<5	12	30	<5	2	<5	20	<5	20	<5	20	<5	20	<5	5	5
NO ₃ -N	mg l ⁻¹	0.52	0.09	0.64	0.82	0.16	0.50	0.50	0.95	1.14	0.34	0.69	1.27	0.59	0.83	0.61	1.05	1.34	0.66	1.15	1.87	1.55	1.60	1.60	1.60
SO ₄ ²⁻	mg l ⁻¹	5.28	5.35	5.51	5.81	6.43	5.59	8.88	8.47	6.37	6.68	6.61	6.43	6.88	6.67	6.25	6.12	5.38	6.02	5.50	4.4	4.8	4.45	4.45	4.45
Cl ⁻	mg l ⁻¹	0.59	0.43	0.88	0.61	0.49	0.88	0.42	0.66	0.64	0.37	0.71	0.6	0.4	0.68	0.41	0.80	0.65	0.41	0.77	0.76	0.66	0.79	0.79	0.79
F	mg l ⁻¹	ND	0.02	0.09	ND	0.00	0.09	0.02	0.10	ND	0.03	0.11	ND	0.02	0.11	0.03	0.11	ND	0.03	0.12	ND	0.05	0.11	0.11	0.11
DOC	mg l ⁻¹	23.0	32.8	32.3	14.4	16.4	22.6	7.0	5.9	8.4	9.3	10.1	5.1	6.1	6.4	4.2	5.2	3.0	3.9	3.3	1.7	1.7	2.5	2.5	2.5
DRP	µg l ⁻¹	9.6	7.6	13.8	8.3	2.5	8.3	<1	<1	2.5	3.9	2.0	2.3	2.2	<1	1.6	1.6	<1	1.5	<1	<1	<1	<1	<1	<1
TDP	µg l ⁻¹	22	19	23.2	15.7	9.4	13.3	3.4	3.3	3.5	5.2	6.5	3.4	3.4	2.5	3.5	3.9	2	3.1	2.6	1.7	1.7	2.9	2.9	2.9
DON	mg l ⁻¹	ND	0.59	0.68	ND	0.38	0.48	0.34	0.30	ND	0.37	0.38	ND	0.29	0.26	0.25	0.27	ND	0.27	0.19	ND	0.17	0.21	0.21	0.21
DR-Si	mg l ⁻¹	1.82	1.87	2.80	1.62	1.59	2.00	1.40	1.79	1.93	1.80	2.30	1.94	1.81	2.34	1.66	2.11	1.74	1.52	1.98	2.20	2.23	2.30	2.30	2.30
DR-Al	mg l ⁻¹	0.70	0.83	0.90	1.12	0.76	0.92	1.22	1.44	0.71	0.59	0.68	0.80	0.62	0.70	0.77	0.90	0.84	0.73	0.83	0.87	0.84	0.85	0.85	0.85
NL-Al	mg l ⁻¹	0.46	0.52	0.43	0.43	0.38	0.39	0.20	0.16	0.27	0.25	0.22	0.19	0.17	0.16	ND	0.13	0.14	0.10	0.08	0.10	0.06	0.09	0.09	0.09
L-Al	mg l ⁻¹	0.24	0.31	0.47	0.69	0.38	0.53	1.02	1.28	0.45	0.34	0.46	0.61	0.45	0.54	ND	0.77	0.71	0.63	0.75	0.77	0.78	0.77	0.77	0.77
T-Fe	mg l ⁻¹	0.52	0.64	0.65	0.04	0.05	0.33	ND	0.07	<0.01	<0.01	0.17	ND	<0.01	0.08	ND	0.06	<0.01	<0.01	0.01	0.06	<0.01	<0.01	<0.01	<0.01

ND - Not determined

Table 3. – Chemical composition of tributaries to the Bohemian Forest lakes in 1997. Part II – Čertovo Lake.

Tributary	CT-I			CT-II			CT-III			CT-IV			CT-V			CT-VI			CT-VII			
	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.	
Q	1 s ^l	0.4	0.6	0.5	12.0	25.0	20.0	2.0	4.0	5.0	3.0	8.7	4.0	0.8	1.0	1.0	1.5	7.0	5.0	2.0	7.0	3.0
pH		4.17	4.19	4.26	4.13	4.13	4.10	4.00	3.98	3.98	4.00	3.99	4.02	4.03	4.04	4.06	4.39	4.31	4.37	4.38	4.33	4.36
Ca ²⁺	mg l ⁻¹	0.38	0.18	0.29	0.54	0.47	0.39	0.53	0.35	0.28	0.64	0.35	0.33	0.55	0.33	0.24	0.77	0.62	0.62	0.78	0.69	0.53
Mg ²⁺	mg l ⁻¹	0.28	0.23	0.28	0.37	0.36	0.33	0.38	0.29	0.30	0.38	0.27	0.31	0.39	0.28	0.32	0.55	0.40	0.46	0.45	0.36	0.39
Na ⁺	mg l ⁻¹	0.84	0.74	0.81	0.82	0.63	0.71	0.70	0.59	0.70	0.84	0.58	0.67	0.69	0.57	0.74	1.00	0.68	0.93	0.94	0.79	1.02
K ⁺	mg l ⁻¹	0.15	0.08	0.12	0.36	0.18	0.18	0.22	0.10	0.12	0.34	0.17	0.16	0.24	0.11	0.08	0.37	0.22	0.30	0.36	0.19	0.32
NH ₄ -N	µg l ⁻¹	20	<5	20	<5	20	<5	10	<5	<5	20	<5	10	<5	10	<5	20	<5	10	<5	10	<5
NO ₃ -N	mg l ⁻¹	0.26	0.04	0.01	1.26	0.72	0.45	1.23	0.46	0.42	1.25	0.29	0.31	1.19	0.11	0.10	1.10	0.39	0.52	0.88	0.46	0.60
SO ₄ ²⁻	mg l ⁻¹	5.52	4.56	3.97	5.36	5.57	5.46	6.81	7.03	6.74	6.82	7.05	7.08	7.11	7.23	7.51	6.77	7.42	6.74	5.16	5.41	4.92
Cl ⁻	mg l ⁻¹	0.56	0.57	0.89	0.63	0.45	0.65	0.58	0.35	0.60	0.59	0.33	0.61	0.56	0.31	0.64	0.66	0.47	0.68	0.61	0.47	0.84
F ⁻	mg l ⁻¹	ND	0.02	0.10	ND	0.02	0.09	ND	0.03	0.10	ND	0.02	0.10	ND	0.02	0.10	ND	0.03	0.10	ND	0.02	0.09
DOC	mg l ⁻¹	6.5	9.1	8.8	6.1	8.0	10.6	7.4	10.2	11.6	7.1	10.0	10.5	5.6	8.3	8.2	2.5	3.1	3.2	3.3	3.9	4.6
DRP	µg l ⁻¹	<1	1.0	<1	2.5	<1	<1	<1	2.1	<1	<1	3.0	<1	<1	<1	<1	<1	1.9	<1	<1	<1	<1
TDP	µg l ⁻¹	3.5	3.9	3.9	2.1	3.2	4.0	2.5	3.9	4	3.6	4.4	4.2	2.7	4.0	2.7	2.5	2.6	2.2	2.7	2.7	2.9
DON	mg l ⁻¹	ND	0.28	0.19	ND	0.34	0.29	ND	0.37	0.30	ND	0.31	ND	ND	0.26	0.23	ND	0.24	0.17	ND	0.20	0.19
DR-Si	mg l ⁻¹	1.57	1.65	1.95	1.83	1.66	1.96	1.91	1.77	2.13	1.87	1.52	1.90	1.73	1.42	1.80	2.51	1.89	2.29	2.38	1.96	2.52
DR-Al	mg l ⁻¹	0.32	0.42	0.37	0.70	0.71	0.62	0.82	0.70	0.76	0.83	0.69	0.74	0.89	0.62	0.74	0.68	0.65	0.56	0.40	0.40	0.48
NL-Al	mg l ⁻¹	0.17	0.21	0.16	0.20	0.24	0.23	0.21	0.26	0.26	0.20	0.27	0.24	0.24	0.21	0.23	0.03	0.08	0.09	0.13	0.11	0.13
L-Al	mg l ⁻¹	0.15	0.21	0.21	0.50	0.47	0.39	0.62	0.44	0.50	0.63	0.42	0.50	0.65	0.41	0.52	0.65	0.56	0.47	0.27	0.29	0.36
T-Fe	mg l ⁻¹	ND	<0.01	0.24	0.03	<0.01	0.26	ND	<0.01	0.21	0.15	0.53	0.18	ND	ND	0.11	ND	1.56	<0.01	ND	0.28	0.05

ND - Not determined

Table 3. – Chemical composition of tributaries to the Bohemian Forest lakes in 1997.
Part III - Prášílské Lake.

Tributary Date	PR-I			PR-II			PR-III			PR-IV			PR-V			PR-VI		
	May	July	Oct.	May	July	Oct.	May	July	Oct.	July	Oct.	May	July	Oct.	May	July	Oct.	
Q	1 s ⁻¹	1.0	0.4	0.2	1.0	1.0	2.0	2.0	2.0	1.6	0.8	0.4	15.0	15.0	18.0	0.2	0.4	0.3
pH		4.75	4.80	4.83	4.59	4.69	4.66	4.28	4.32	4.31	3.76	3.71	4.50	4.45	4.47	4.45	4.37	4.31
Cd ²⁺	mg l ⁻¹	1.55	1.51	1.45	1.37	1.42	1.39	0.93	0.69	0.91	0.41	0.50	0.66	0.56	0.57	0.57	0.62	0.79
Mg ²⁺	mg l ⁻¹	0.60	0.55	0.59	0.53	0.51	0.60	0.40	0.32	0.42	0.23	0.31	0.37	0.34	0.38	0.23	0.26	0.32
Na ⁺	mg l ⁻¹	1.34	1.28	1.42	0.98	0.92	1.05	0.73	0.65	0.81	0.53	0.69	0.74	0.66	0.74	0.43	0.26	0.37
K ⁺	mg l ⁻¹	0.65	0.53	0.61	0.77	0.62	0.84	0.56	0.28	0.45	0.26	0.35	0.23	0.10	0.17	0.22	0.03	0.10
NH ₃ -N	µg l ⁻¹	20	<5	<5	40	<5	<5	20	<5	<5	<5	<5	10	<5	10	<5	10	<5
NH ₄ -N	mg l ⁻¹	2.42	2.07	2.13	1.88	1.49	1.59	1.50	0.55	1.09	0.46	1.56	0.63	0.25	0.27	0.01	0.01	0.01
SO ₄ ²⁻	mg l ⁻¹	2.14	2.14	1.79	3.49	3.68	3.48	3.10	3.28	3.31	5.50	5.40	3.25	3.36	3.36	2.68	2.30	3.64
Cl ⁻	mg l ⁻¹	0.77	0.73	0.83	0.70	0.60	0.76	0.66	0.43	0.68	0.40	0.85	0.52	0.47	0.73	0.37	0.23	0.36
F ⁻	mg l ⁻¹	ND	0.02	0.09	ND	0.01	0.09	ND	0.01	0.09	0.01	0.10	ND	0.01	0.09	ND	0.01	0.09
DOC	mg l ⁻¹	1.2	1.5	1.5	2.6	2.1	2.5	6.0	9.1	7.7	33.5	23.9	4.8	8.1	7.7	11.9	16.9	12.8
DRP	µg l ⁻¹	<1	<1	1.2	<1	1.0	1.6	<1	1.0	2.5	2.0	1.3	1.0	<1	<1	<1	<1	1.8
TDP	µg l ⁻¹	2.0	1.9	1.4	3.4	2.2	1.8	4.3	4.2	3.3	8.4	9.0	4.2	4.3	4.9	6.2	8.5	7.1
DON	mg l ⁻¹	ND	0.13	0.15	ND	0.17	0.18	ND	0.26	0.34	0.58	0.65	ND	0.25	0.24	ND	0.28	0.33
DR-Si	mg l ⁻¹	2.91	2.88	3.00	2.24	2.34	2.52	1.58	1.46	1.83	1.97	2.67	1.67	1.66	2.06	1.22	1.18	1.67
DR-Al	mg l ⁻¹	0.34	0.23	0.13	0.47	0.33	0.27	0.50	0.43	0.46	0.73	0.75	0.24	0.28	0.25	0.38	0.52	0.34
NL-Al	mg l ⁻¹	0.09	0.03	0.02	0.11	0.04	0.07	0.23	0.24	0.19	0.51	0.32	0.12	0.15	0.10	0.25	0.37	0.18
L-Al	mg l ⁻¹	0.25	0.20	0.12	0.36	0.29	0.21	0.28	0.19	0.28	0.22	0.43	0.12	0.13	0.16	0.13	0.14	0.15
T-Fe	mg l ⁻¹	<0.01	<0.01	<0.01	ND	0.70	<0.01	<0.01	<0.01	0.07	0.41	0.31	0.28	0.11	0.20	0.28	0.38	0.26

ND - Not determined

lowest pHs as well as concentrations of BC and NO₃-N were in tributaries CN-I and CN-II. Concentrations of DOC in these two brooks were the highest of all the tributaries sampled in this study and were accompanied by high levels of NL-Al and T-Fe. Moreover, CN-I and CN-II were the only tributaries in the CN watershed with elevated phosphorus content (Table 3) and represented a significant source of DRP to CN lake. Tributaries CN-I and CN-II drained relatively flat subwatersheds with small marshes and deeper forest soils than observed in the other CN subwatersheds, which were steeper.

Table 3. - Chemical composition of tributaries to the Bohemian Forest lakes in 1997.
Part IV - Plešné Lake.

Tributary Date	PL-I-ab		PL-I-c		PL-II-a		PL-II-b		PL-III							
	May	July	May	July	May	July	May	July	May	July						
Q	1 s ⁻¹	4.0	4.5	3.0	1.5	1.5	1.0	1.5	1.5	1.5	2.0	1.0	3.0	3.5	2.5	
pH		4.13	4.08	4.07	4.13	4.10	4.08	4.25	4.13	4.18	4.25	4.21	4.19	4.50	4.44	4.43
Ca ²⁺	mg l ⁻¹	0.70	0.58	0.64	0.68	0.58	0.67	0.79	0.70	0.74	0.76	0.74	0.80	1.06	1.10	1.26
Mg ²⁺	mg l ⁻¹	0.13	0.12	0.14	0.15	0.12	0.14	0.15	0.13	0.16	0.13	0.14	0.15	0.22	0.23	0.24
Na ⁺	mg l ⁻¹	1.02	0.92	1.19	0.90	0.91	1.20	0.88	1.01	1.29	0.88	0.97	1.30	0.89	0.98	1.20
K ⁺	mg l ⁻¹	0.43	0.30	0.29	0.40	0.23	0.30	0.36	0.31	0.28	0.38	0.30	0.33	0.39	0.36	0.42
NH ₄ -N	µg l ⁻¹	30	<5	<5	30	<5	<5	10	<5	<5	10	<5	<5	10	<5	<5
NH ₃ -N	mg l ⁻¹	0.74	0.24	0.64	0.75	0.24	0.66	0.84	0.35	0.84	0.83	0.39	0.93	0.91	0.67	1.11
SO ₄ ²⁻	mg l ⁻¹	5.48	5.68	6.05	5.48	5.62	6.06	5.14	5.76	5.97	5.19	5.76	5.88	5.96	6.56	6.35
Cl ⁻	mg l ⁻¹	0.60	0.33	0.61	0.55	0.32	0.61	0.59	0.35	0.51	0.55	0.32	0.50	0.53	0.39	0.55
F ⁻	mg l ⁻¹	ND	0.03	0.13	ND	0.03	0.14	ND	0.03	0.13	ND	0.04	0.13	ND	0.07	0.15
DOC	mg l ⁻¹	12.3	17.3	16.5	12.4	17.5	15.9	8.7	12.3	11.5	8.4	12.1	10.1	4.4	5.3	4.6
DRP	µg l ⁻¹	25.0	23.7	23.3	26.7	28.4	27.5	24.6	28.7	25.4	24.6	29.6	25.4	12.9	14.2	13.8
TDP	µg l ⁻¹	29.2	33.4	29.6	33.0	34.9	32.3	28.7	34.1	28.3	29.1	36.3	29.3	14.0	16.6	15.7
DON	mg l ⁻¹	ND	0.36	0.54	ND	0.39	0.45	ND	0.36	0.37	ND	0.33	0.37	ND	0.26	0.33
DR-Si	mg l ⁻¹	2.64	3.38	4.63	2.69	3.41	4.77	2.68	3.58	4.92	2.71	3.56	4.94	2.75	3.62	4.34
DR-Al	mg l ⁻¹	0.89	0.93	1.03	0.89	0.92	0.82	0.82	0.84	0.96	0.83	0.81	0.95	0.83	0.77	0.88
NL-Al	mg l ⁻¹	0.49	0.51	0.36	0.39	0.48	0.29	0.32	0.35	0.29	0.32	0.37	0.34	0.18	0.18	0.14
L-Al	mg l ⁻¹	0.40	0.43	0.67	0.50	0.45	0.53	0.51	0.50	0.67	0.52	0.44	0.61	0.65	0.59	0.73
T-Fe	mg l ⁻¹	0.07	0.09	0.10	ND	ND	0.10	0.44	ND	0.10	ND	ND	0.10	0.09	ND	0.02

ND - Not determined

In the watershed of CT lake, pH varied from 3.98 to 4.38. The minor tributaries, CT-VI and CT-VII, had lower DOC, higher pH, BC, and NO₃-N concentrations than the major tributary CT-II. Concentrations of NO₃-N and SO₄²⁻ were lower in CT-I than in the other CT tributaries.

The highest variability in the composition of surface waters was found in the PR watershed. The pH ranged from 3.71 to 4.83 with values of 4.45–4.50 in the major tributary, PR-V. Of all the PR tributaries PR-IV had the highest concentrations of DOC, SO₄²⁻, Al-forms, and T-Fe and lowest pH and BC levels. In contrast, brook PR-I was the least acidic, with the lowest SO₄²⁻ concentrations (1.79–2.14 mg l⁻¹) and the highest NO₃-N levels (~2.1 mg l⁻¹) among all tributaries in this study.

Variability in surface water pH was low (4.07–4.43) in the PL watershed. Differences in

water composition of the surface tributaries PL-I and PL-II were small (Table 3). In contrast, the composition of subsurface tributary PL-III was substantially different than PL-I and PL-II with higher pH, BC and $\text{NO}_3\text{-N}$ concentrations and lower DOC, DRP, DR-Al, and T-Fe concentrations. These differences may be due to decreased water contact with soils.

Comparison of water chemistry in tributaries and lakes

Concentrations and volume-weighted mean (VWM) concentrations of chemical constituents in lakes and their tributaries, respectively, are compared in Table 4.

The VWM concentrations of H^+ ions were highest in the tributaries to CT lake and decreased from PL to CN to PR lake. The VWM concentrations of base cations showed the following pattern of decreases among lake watersheds: Ca, PL>PR>CN>CT; Mg, CN>PR>CT>PL; Na, PL>PR>CT>CN. Opposite sequences for the Ca and Mg series were caused by differences in the Ca to Mg molar ratios, which were ~ 1 in the CN, CT, and PR watersheds and ~ 3 in the PL watershed. The VWM $\text{NO}_3\text{-N}$ concentrations varied among watersheds as follows: CN>CT>PR>PL in spring and summer; however, in autumn VWM concentrations of $\text{NO}_3\text{-N}$ in the inputs to PL lake were the second highest among the lakes (Table 4). Pronounced differences in VWM concentrations of SO_4^{2-} and TR-Al were observed among the watersheds with substantially lower levels in the PR tributaries compared with tributaries to the other lakes. Concentrations of SO_4^{2-} and TR-Al varied according to the following pattern: CT>PL>CN>>PR and PL>CN>CT>>PR, respectively. Elevated levels of phosphorus and silica were found in the PL watershed, where TDP concentrations were an order of magnitude higher than in the other watersheds, predominantly due to high inputs of DRP (Table 4). Concentrations of DR-Si were roughly twofold higher in PL than in the CN, CT, and PR tributaries. Despite extremely high concentrations of DOC in tributaries CN-I and CN-II (Table 3), the VWM concentrations of DOC in the total inputs of CN lake were lower than in other lakes. Highest VWM DOC concentrations were in the PL tributaries (PL>CT>PR>CN).

The chemistry of the lakes themselves reflected the chemical composition of their tributaries; however, water in the tributaries was more acidic, with higher contents of nutrients, DOC, Al-forms, and T-Fe than in the lakes (Table 4). Variations in water chemistry among lakes, such as the high $\text{NO}_3\text{-N}$ concentration and acidity in CN lake, low Al and SO_4^{2-} levels in PR lake, and high DOC and P contents in PL lake, could all be explained by differences in the compositions of their tributaries.

Discussion

The large variability in concentrations of BC, Al-forms, nutrients, and DOC within tributaries in watersheds, as well as among watersheds resulted from differences in bedrock composition, soil and forest status, and morphology of terrain in the particular subwatersheds, and was also influenced seasonally by biochemical processes as discussed later.

Base cations

There are two major sources of BC in undisturbed sites: weathering of rocks and atmospheric deposition (e. g. Psenner & Catalan 1994). The contribution of atmospheric deposition to the total pool of BC in the watershed soils was probably comparable for all lakes. The watersheds were situated relatively far from major Central European emission centers and there were no important local dust sources. Consequently, variations in BC concentrations and the Ca:Mg molar ratios observed in PL watershed compared to other watersheds were determined primarily by the differences in the bedrock composition (granite and mica-schist, respective-

Table 4. – Comparison of volume-weighted mean concentrations of water constituents in the total surface inputs to the Bohemian Forest lakes vs. lake water compositions in May 19–20, July 22–23, and October 13–14, 1997.

		Černé			Čertovo			Prášílské			Plešné		
		May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.
Tributaries ¹⁾													
Q ²⁾	l s ⁻¹	35.3	39.2	47.7	21.7	53.3	38.5	18.4	20.2	21.7	11.5	13.0	9.0
pH		4.32	4.23	4.19	4.12	4.13	4.12	4.48	4.39	4.43	4.23	4.18	4.18
Ca ²⁺	mg l ⁻¹	0.75	0.59	0.69	0.59	0.48	0.41	0.74	0.66	0.65	0.81	0.76	0.85
Mg ²⁺	mg l ⁻¹	0.42	0.36	0.41	0.39	0.34	0.34	0.39	0.35	0.39	0.16	0.15	0.17
Na ⁺	mg l ⁻¹	0.70	0.62	0.77	0.83	0.65	0.76	0.77	0.69	0.77	0.93	0.95	1.22
K ⁺	mg l ⁻¹	0.44	0.30	0.34	0.34	0.18	0.19	0.29	0.17	0.23	0.40	0.31	0.33
NH ₄ -N	μg l ⁻¹	23	<5	4	18	<5	<5	12	<5	<5	20	<5	<5
NO ₃ -N	mg l ⁻¹	1.40	0.76	1.05	1.19	0.53	0.44	0.83	0.43	0.44	0.81	0.39	0.84
SO ₄ ²⁻	mg l ⁻¹	5.39	5.96	5.71	5.84	6.16	5.95	3.17	3.37	3.38	5.52	5.93	6.10
Cl ⁻	mg l ⁻¹	0.66	0.47	0.77	0.62	0.43	0.66	0.55	0.48	0.73	0.57	0.35	0.56
F ⁻	mg l ⁻¹	ND	0.03	0.11	ND	0.02	0.10	ND	0.01	0.09	ND	0.04	0.14
DOC	mg l ⁻¹	3.90	6.19	6.67	5.85	7.33	9.21	4.80	8.78	7.74	9.29	12.72	11.58
DRP	μg l ⁻¹	1.3	1.6	1.4	<1	2.1	<1	0.8	<1	<1	22.0	23.2	21.7
TDP	μg l ⁻¹	3.0	4.1	4.4	2.5	3.3	3.7	4.1	4.3	4.7	25.7	29.6	25.8
DON	mg l ⁻¹	ND	0.27	0.26	ND	0.30	0.23	ND	0.25	0.25	ND	0.33	0.42
DR-Si	mg l ⁻¹	1.86	1.77	2.14	1.93	1.71	2.06	1.73	1.74	2.09	2.69	3.50	4.65
TR-Al	mg l ⁻¹	0.85	0.67	0.82	0.70	0.64	0.63	0.28	0.33	0.28	0.86	0.90	0.94
NL-Al	mg l ⁻¹	0.16	0.14	0.14	0.19	0.21	0.21	0.13	0.17	0.10	0.35	0.37	0.28
L-Al	mg l ⁻¹	0.69	0.52	0.68	0.52	0.45	0.42	0.15	0.15	0.17	0.51	0.48	0.66
T-Fe	mg l ⁻¹	0.02	0.02	0.08	ND	0.33	0.19	0.23	0.14	0.18	0.16	ND	0.08
Lake water ³⁾													
pH		4.78	4.66	4.79	4.45	4.36	4.43	4.73	4.69	4.78	4.71	4.68	4.74
Ca ²⁺	mg l ⁻¹	0.91	0.85	1.23	0.56	0.49	0.52	0.73	0.68	0.71	1.06	0.93	1.11
Mg ²⁺	mg l ⁻¹	0.48	0.47	0.51	0.39	0.37	0.35	0.41	0.34	0.41	0.21	0.22	0.21
Na ⁺	mg l ⁻¹	1.04	0.80	0.88	0.68	0.65	0.66	1.06	0.70	0.71	0.98	0.95	0.97
K ⁺	mg l ⁻¹	0.53	0.44	0.44	0.39	0.38	0.27	0.54	0.35	0.35	0.41	0.35	0.41
NH ₄ -N	μg l ⁻¹	80	20	19	80	24	11	60	<5	21	10	<5	35
NO ₃ -N	mg l ⁻¹	1.00	0.92	0.93	0.74	0.60	0.58	0.73	0.49	0.46	0.51	0.30	0.31
SO ₄ ²⁻	mg l ⁻¹	4.90	4.89	4.89	5.95	5.85	5.85	3.24	3.08	2.98	6.31	6.13	6.24
Cl ⁻	mg l ⁻¹	0.92	0.71	0.73	0.65	0.63	0.58	0.84	0.59	0.59	0.52	0.53	0.52
F ⁻	mg l ⁻¹	ND	0.05	0.11	ND	0.02	0.10	ND	0.01	0.09	ND	0.07	0.15
DOC	mg l ⁻¹	1.18	1.56	1.24	2.54	3.08	2.21	3.51	4.40	3.82	3.53	3.52	2.77
DRP	μg l ⁻¹	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
TDP	μg l ⁻¹	0.9	1.2	1.1	0.7	1.5	2.2	2.6	2.5	3.0	1.8	2.1	1.7
TP	μg l ⁻¹	3.1	4.8	2.4	3.3	4.2	4.5	5.8	4.3	4.9	11.1	11.6	9.4
DON	mg l ⁻¹	0.15	0.17	0.15	0.18	0.21	0.17	0.21	0.27	0.23	0.21	0.24	0.19
DR-Si	mg l ⁻¹	1.67	1.51	1.66	1.64	1.47	1.47	1.55	1.39	1.40	2.68	2.73	2.77
TR-Al	mg l ⁻¹	0.46	0.45	0.42	0.62	0.58	0.56	0.29	0.22	0.22	0.71	0.64	0.53

		Černé			Čertovo			Prášilské			Plešné		
		May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	Oct.
NL-Al	mg l ⁻¹	0.05	0.02	0.01	0.06	0.06	0.01	0.07	0.06	0.07	0.18	0.08	0.16
L-Al	mg l ⁻¹	0.40	0.43	0.41	0.57	0.52	0.55	0.21	0.15	0.16	0.53	0.57	0.37
T-Fe	mg l ⁻¹	<0.01	<0.01	0.04	0.18	<0.01	0.094	0.04	0.15	0.05	ND	<0.01	0.04

1) Volume weighted mean concentrations

2) Total measured water input by tributaries

3) Surface water (10-50 cm depth) sampled above the maximum depth of lake

ND – Not determined

ly) of the sites. On the other hand, the different BC concentrations observed in tributaries draining particular subwatersheds of a single lake reflected predominantly the intensity of weathering and leaching of soils in their subwatersheds. Weathering of silicates was probably an important source of BC in watersheds where the bedrock was composed of mica-schist; for example, in the CN, CT, and PR watersheds concentrations of Ca²⁺, Mg²⁺, Na⁺, and K⁺ were positively correlated with DR-Si. In the PL watershed, the only tight correlation was between concentrations of Na⁺ and DR-Si, while Ca²⁺ and Mg²⁺ levels were not dependent on DR-Si (Table 5, Fig. 2).

NO₃⁻ was the other factor influencing BC concentrations in the tributaries. Most of the subwatersheds appeared to be in a progressive stage of N-saturation (according to Stoddard 1994) with high NO₃⁻ concentrations even in the growing season (Table 4). Concentrations of BC were significantly correlated to NO₃⁻ in all tributaries despite the bedrock composition (Table 5, Fig. 3A). Moreover, concentrations of DR-Si were positively correlated with NO₃⁻ in tributaries situated on mica-schist (Table 5, Fig. 3B) suggesting, that the elevated NO₃⁻ levels influenced weathering of the bedrock material. Surprisingly concentrations of BC were not depen-

Table 5. – Coefficients of linear regressions: [M] = a + b[Si] + c[NO₃⁻], where M is Ca²⁺, Mg²⁺, Na⁺, or K⁺, and [Si] = a + c[NO₃⁻]. All concentrations are in μmol l⁻¹ and r is correlation coefficient. Number of observations was 60 for CN, CT, PR and 15 for PL. Levels of significance: * 5%, ** 1%, *** 0.1%.

Y	X	CN, CT, PR				PL			
		a	b	c	r	a	b	c	r
Ca ²⁺	Si	-6±7	0.32±0.06		0.57***	19±5	0.01±0.05		0.03
Ca ²⁺	NO ₃ ⁻	7±5		0.15±0.02	0.79***	11±4		0.17±0.06	0.66**
Ca ²⁺	Si, NO ₃ ⁻	4±5	0.06±0.06	0.14±0.02	0.80***	12±4	0.00±0.04	0.17±0.06	0.66**
Mg ²⁺	Si	2±3	0.19±0.03		0.67***	6±2	0.00±0.01		0.07
Mg ²⁺	NO ₃ ⁻	10±3		0.08±0.01	0.81***	4±1		0.05±0.02	0.59*
Mg ²⁺	Si, NO ₃ ⁻	6±2	0.07±0.03	0.06±0.01	0.83***	4±1	0.00±0.01	0.05±0.02	0.59*
Na ⁺	Si	-4±6	0.52±0.05		0.79***	19±3	0.20±0.02		0.92***
Na ⁺	NO ₃ ⁻	23±7		0.16±0.02	0.71***	39±7		0.13±0.09	0.37
Na ⁺	Si, NO ₃ ⁻	1±5	0.37±0.06	0.08±0.02	0.83***	16±2	0.19±0.02	0.09±0.03	0.96***
K ⁺	Si	-5±4	0.18±0.03		0.57***	12±1	-0.02±0.01		0.48
K ⁺	NO ₃ ⁻	2±2		0.09±0.01	0.88***	6±1		0.05±0.02	0.67**
K ⁺	Si, NO ₃ ⁻	2±2	0.00±0.03	0.09±0.01	0.88***	9±1	-0.03±0.01	0.06±0.01	0.88***
Si	NO ₃ ⁻	57±11	0.22±0.03		0.64***	120±32	0.21±0.45		0.13

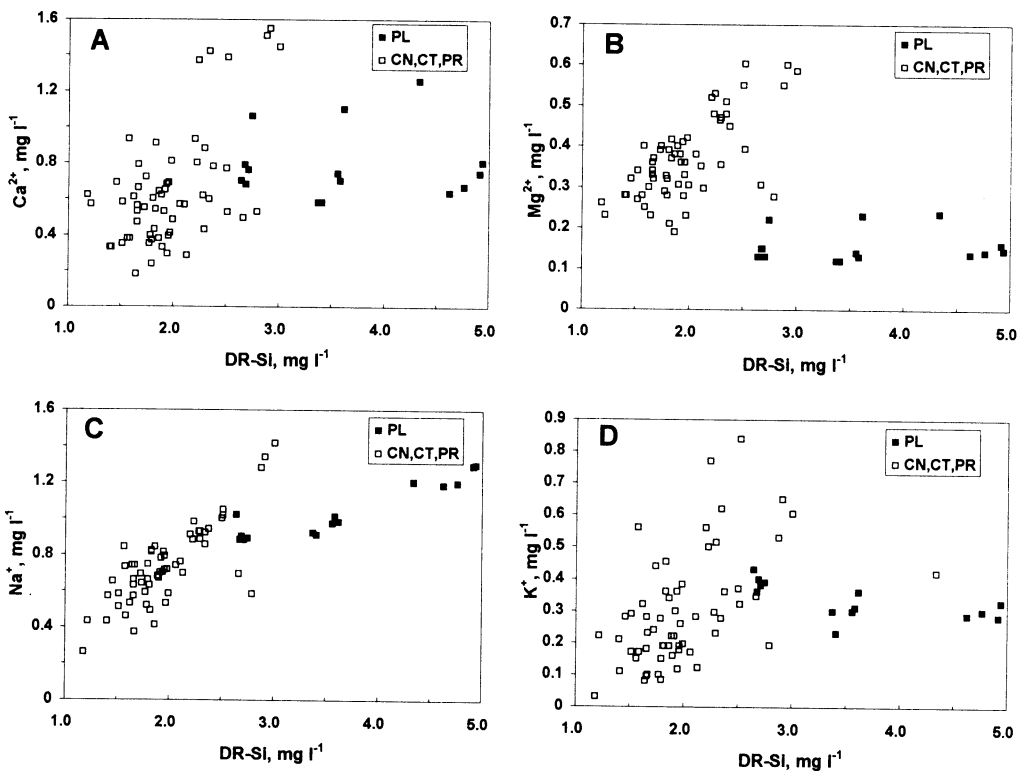


Fig. 2. – The plots of dissolved reactive Si vs. Ca^{2+} (A), Mg^{2+} (B), Na^+ (C), and K^+ (D) concentrations in the watersheds with bedrock of mica-schist (CN, CT, PR) and granite (PL). For parameters of linear regressions see Table 5.

dent on SO_4^{2-} levels (Table 2). This fact further points out the importance of nitrate in leaching of BC, particularly in subwatersheds, where the NO_3^- contribution to strong acid anions is increasing.

The equivalence ratio of $\text{NO}_3^-/(\text{NO}_3^- + \text{SO}_4^{2-})$ is often used to estimate the NO_3^- contribution to acidification (e.g. MURDOCH & STODDARD 1992). The highest published values for nitrate contributions to acidity in the Šumava lakes (particularly CN and CT), were during the late 1980s (VESELY & MAJER 1992). In the first half of the 1990s, emission rates of S and N compounds decreased substantially in Central Europe and surface water chemistry in the Šumava Mountains began to recover from acidification, reflecting development of a new equilibrium between atmospheric inputs of S and N compounds and chemistry of water and soils (Kopáček & al. 1998). Since the reduction of lake water NO_3^- concentrations was equal to or greater than that of SO_4^{2-} (relative to their levels in the late 1980s), the $\text{NO}_3^-/(\text{NO}_3^- + \text{SO}_4^{2-})$ equivalence ratios decreased in CN, CT, and PL. This situation is somewhat unique since during the last two decades the nitrate contribution to acidity has been increasing in most of the world's acidified areas due to reduced sulfur emissions and relatively constant N emis-

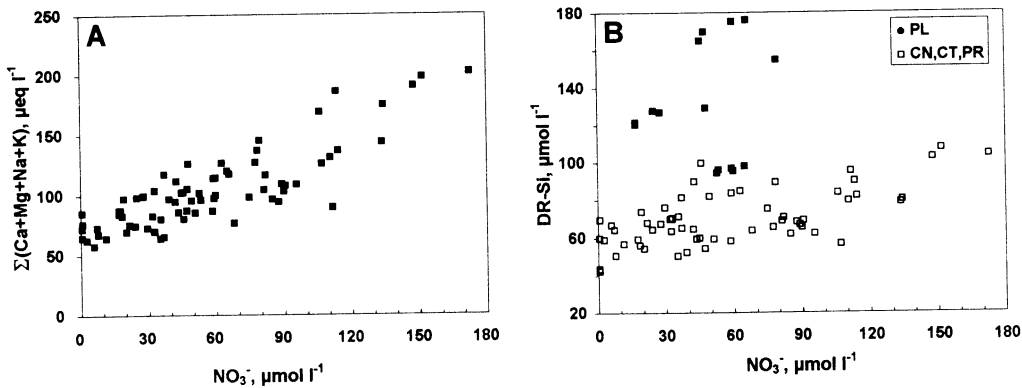


Fig. 3. – Relationship between concentrations of NO_3^- and A) base cations (all tributaries), and B) dissolved reactive Si (tributaries to PL lake are separated). For parameters of linear regressions between DR-Si and NO_3^- ; see Table 5.

sions in Northern America and Western Europe (e.g. Henriksen & Brakke 1988). Whereas improvements in water quality were observed in CN, CT, and PL lakes, PR lake experienced an increasing trend in the $\text{NO}_3^-/(\text{NO}_3^- + \text{SO}_4^{2-})$ equivalence ratio due to decreased SO_4^{2-} and increased NO_3^- inputs compared to the late 1980s (VESELY 1996). Apparently, PR lake showed a change in water quality in recent years due to forest damage in the watershed which resulted in (i) elevated nitrate output from the soils due to lower N bioconsumption (VITROUSEK & al. 1979), and (ii) decreased dry deposition of S compounds due to the lower specific adsorption surface of the deforested watershed. These changes resulted in high NO_3^- and BC concentrations and low SO_4^{2-} levels in the tributaries of PR lake, particularly in brooks PR-I and PR-II (Table 3). The $\text{NO}_3^-/(\text{NO}_3^- + \text{SO}_4^{2-})$ equivalence ratios were frequently > 0.5 in tributaries of PR lake in 1997 with maximum ~ 0.8 in PR-I.

Acidity and Al-forms

Several observations indicate that organic acids play an important role in acidification of brooks entering the Šumava lakes: i) the lowest pH values were in tributaries with elevated concentrations of organic matter (Fig. 4); ii) the relative contribution of organic acids to the total anion pool increased with DOC concentration (Fig. 5A); and iii) H^+ concentrations were better correlated with R⁻ than with SO_4^{2-} concentrations (Table 2). The high correlation coefficient for the relationship H^+ vs. $\text{R}^- + \text{SO}_4^{2-}$ suggests that most of the acidity transported from soils to tributaries was associated with SO_4^{2-} and organic acids. In contrast, H^+ concentrations did not correlate with NO_3^- levels (Table 2). This surprising fact can most likely be explained by the negative correlation between DOC and NO_3^- levels where: $[\text{NO}_3^- - \text{N}, \text{mg l}^{-1}] = 1.1 - 0.036 [\text{DOC}, \text{mg l}^{-1}]$; $P < 0.001$. Consequently, the relative contribution of NO_3^- to the anion pool decreased with increasing DOC concentration (Fig. 5B), while SO_4^{2-} and/or Cl⁻ contributions were independent of DOC. There are two possible explanations for the low nitrate concentrations in tributaries rich in organic matter: i) denitrification and/or bacterial immobilization in soils and ii) different leaching rates for NO_3^- and DOC to the tributaries.

i) Lowest NO_3^- levels were observed in DOC rich waters draining subwatersheds with low slope gradients and with more developed and wetter soils (i.e. better conditions for denitrification). We hypothesize, that denitrification is responsible for the low nitrate levels in these

Fig. 4. – Relationship between concentrations of dissolved organic carbon and pH (all tributaries).

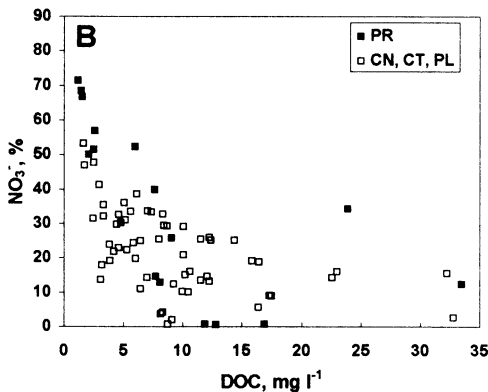
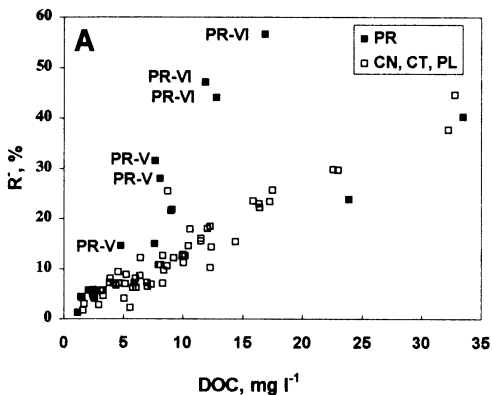
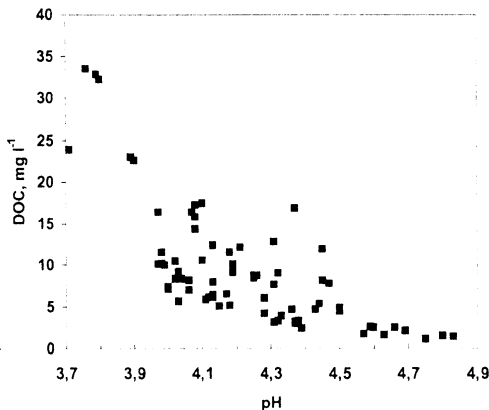


Fig. 5. – Relationship between concentrations of dissolved organic carbon and the relative contribution of A) organic acid and B) nitrate to the sum of anions. Surface waters of the PR watershed are differentiated. For location of tributaries PR-V and PR -VI see Fig. 1.

tributaries despite extremely low pH values ($\text{pH} < 4$). There is no evidence that denitrification is sensitive to acidification (KELLY 1994).

ii) On the other hand, high NO_3^- and low DOC concentrations were typically found in tributaries draining steep subwatersheds due apparently to the relatively short water residence times. The inverse situation applies to subwatersheds with more gentle slopes where low concentrations of nitrate most likely reflect high N-assimilation rate due to the longer residence time of NO_3^- -N in the soils (DISE & WRIGHT 1995). DOC losses could similarly reflect soil characteristics, which depend on the grade of slope. Hence, the tight negative relationship between nitrate and DOC could be merely coincidental reflecting their inverse relationships with grade of slope.

The high relative contributions of R^- to the total anion pool in the tributaries PR-V and PR-VI (Fig. 5A) resulted from low NO_3^- concentrations and thus, a small anion pool. In these PR subwatersheds high rates of forest regrowth may also have been responsible for the low observed NO_3^- concentrations.

As was observed for H^+ , concentrations of Al-forms were primarily correlated with R^- and

SO_4^{2-} concentrations and much less so with NO_3^- . Concentrations of NL-Al were tightly correlated to organic matter ($0.94 \pm 0.03 \mu\text{mol Al per } 1 \text{ mg DOC}$) at DOC concentrations ranging from 0 to $\sim 20 \text{ mg l}^{-1}$; however when DOC levels exceeded 20 mg l^{-1} the linear relationship between NL-Al and DOC concentration leveled off (Fig. 6). Among all major anions, concentrations of L-Al were correlated mainly with SO_4^{2-} concentrations (Table 2). These results are surprising, since elevated Al losses from forest soils are usually associated with nitrate leaching (e.g. DISE & WRIGHT 1995). Further studies should be done to explore these results.

Since tributaries of the Šumava lakes are depleted in bicarbonate buffering capacity, organic acids together with inorganic Al-forms play the dominant role in maintaining pH levels. If concentrations of humic substances were lower, pH fluctuation due to changes in deposition of strong acid anions would be higher. The average actual contribution of humic substances to the acidity calculated for all tributaries as the [R⁻] to DOC ratio is $3.5 \pm 0.3 \mu\text{eq mg}^{-1}$. This value is lower than the calculated (see equation 7) average non-complexed carboxyl content of humic substances ($X_{\text{N}} = 5.9 \pm 1.9 \mu\text{eq mg}^{-1}$) since the ionization of carboxyl groups is low at ambient pHs. This fact indicates that the potential for acidification by organic matter in these waters is high. Based on previous studies of watersheds recovering from anthropogenic acidification (WRIGHT & al. 1988) we expect further increases in R⁻ concentrations (due to increased ionization of carboxyl groups) with declining deposition of strong acid anions. Consequently, the pHs of tributaries of the Šumava lakes are likely to increase more slowly than might be expected if humic substances were absent.

Why planktonic crustacea have survived in Prášilské lake?

FOTT & al. (1994) have reported on the survival of planktonic crustacea in PR lake even during the late 1980s when these zooplankton species became extinct in other Šumava lakes with comparable pH levels. The explanation given for this survival was that the concentration of Al in PR was half that observed in the other Šumava lakes; however, it was not clear at the time why the concentration of Al in PR water was so low.

Based upon more recent data we now suggest that the low Al concentration observed in PR resulted from low SO_4^{2-} inputs. Whereas NL-Al concentrations in PR lake and its tributaries were comparable to the other lakes, L-Al concentrations were $0.25\text{--}0.42 \text{ mg l}^{-1}$ lower (Table 4). Similarly, concentrations of SO_4^{2-} were $1\text{--}3 \text{ mg l}^{-1}$ lower in PR than in the other lakes throughout 1984–1997 and even prior to the decline in forest health observed in the late 1980's (VESELY 1996, Table 4). According to the correlation between L-Al and SO_4^{2-} values

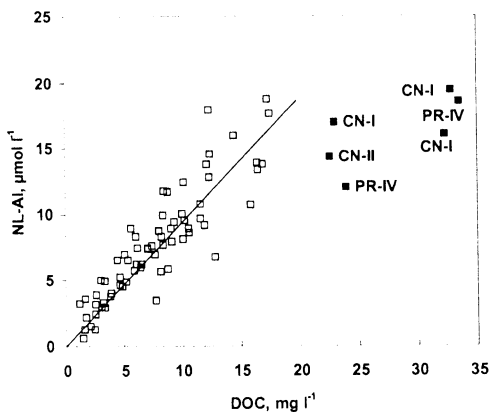


Fig. 6. – Relationship between concentrations of dissolved organic carbon and non-labile monomeric aluminum. Solid line: linear regression $[\text{NL-Al}, \mu\text{mol l}^{-1}] = (0.94 \pm 0.03) [\text{DOC}, \text{mg l}^{-1}]$; $r=0.86$; $P<0.001$; CN-I, CN-II, and PR-IV tributaries with $\text{DOC} > 20 \text{ mg l}^{-1}$ are excluded.

(Table 2), differences between Al concentrations observed in PR and the other lakes are roughly proportional to the differences in SO_4^{2-} concentrations. Concentrations of SO_4^{2-} in tributaries of PR lake thus seem to be the crucial factor governing L-Al levels in lake water.

Another possible factor affecting the potential for Al toxicity in PR is the degree of its complexation with F^- . The molar ratio of L-Al to F^- was lower in the PR lake than in other lakes. L-Al concentrations in the PR lake water were ~ 10 and $6\text{--}7 \mu\text{mol l}^{-1}$ in the late 1980s and in 1997, respectively, while concentrations of F^- ranged from $2\text{--}5 \mu\text{mol l}^{-1}$ (FOTT & al. 1994, SCHMIDT & al. 1993, Table 4). At low pHs, almost all the fluoride is complexed with Al and at Al:F molar ratios >1 , AlF_2^+ is the dominant aluminum fluoride species (SCHECHER & DRISCOLL 1987, PLANKEY & al. 1986). A substantial portion of L-Al was thus complexed with F^- in PR lake. HAVAS & ROSSELAND (1995) have reviewed the biotic impacts of aqueous aluminum species and concluded that aluminum fluoride complexation can significantly mitigate Al toxicity in natural waters. In summary, the low toxicity of PR lake water to planktonic crustacea is most likely due to low Al inputs from the watershed related to low sulfate leaching and to complexation of labile monomeric Al with fluoride in the lake itself.

It is not yet clear why PR tributaries have low SO_4^{2-} concentrations. At present, we can hypothesize that i) PR soils have a higher retention capacity for SO_4^{2-} than soils in the other watersheds; and ii) atmospheric deposition of S compounds to the PR watershed is lower than to other watersheds due to forest decline. Generally, sulfur adsorption capacity is high in the Šumava Mountains, especially in areas with metamorphic bedrock (HRUŠKA & MAJER 1996). The lower slope gradient of the PR watershed provides better conditions for formation of more developed soils and increases water residence time in soils; thus, sulfur adsorption capacity should be higher in the PR watershed than in the steeper watersheds of CN and CT lakes. We believe, therefore, that the low SO_4^{2-} concentrations in PR tributaries are likely to be related to high sulfur adsorption capacity of soils; however, confirmation of this hypothesis awaits further study.

Organic matter

DOC concentrations in streams and rivers are generally between 1 and 30 mg l^{-1} and DOC comprises a complex mixture of organic matter, including simple low molecular weight compounds and more complex organic substances such as humic, fulvic, and hydrophylic acids (THURMAN 1985). The proportions of different types of organic substances in DOC can be roughly estimated from absorbances at various UV wavelengths. The higher the proportion of unsaturated humic acids in the total pool of organic matter the higher will be the molar absorptivity (absorbance of DOC at a concentration of 1 mol m^{-3} per 1 m absorption path). Complex organic molecules (humic acids) absorb well at both low and high UV wavelengths, while the molar absorptivity of smaller organic molecules (e.g. fulvic acids) decreases sharply with increasing wavelength. Low molecular weight and saturated compounds (e.g. saccharides and saturated fatty acids) do not absorb at $250\text{--}400 \text{ nm}$ (CHEN & al. 1977; ANONYMOUS 1960). Consequently, the lower the ratio of absorbance at 250 nm to that at 400 nm , the higher the proportion of high molecular weight and unsaturated species in the total pool of humic and fulvic acids.

DOC concentrations in tributaries of the Šumava lakes varied from 1 to 34 mg l^{-1} (Table 1). We used two parameters to characterize organic matter composition in our samples: i) molar absorptivity of organic carbon at 254 nm and 400 nm and ii) $A_{254}:A_{400}$ ratio. Molar absorptivities ranged from 35 to $60 \text{ m}^2 \text{ mol}^{-1}$ (most frequently from 40 to $50 \text{ m}^2 \text{ mol}^{-1}$) at 254 nm and from 2 to $6 \text{ m}^2 \text{ mol}^{-1}$ (most frequently from 3.5 to $5.5 \text{ m}^2 \text{ mol}^{-1}$) at 400 nm (Fig. 7). The $A_{254}:A_{400}$ ratio was ~ 11 on average; however, it ranged from 9 to 15 for $\text{DOC} < 5 \text{ mg l}^{-1}$ and from 9 to 11 at DOC levels $> 10 \text{ mg l}^{-1}$ (Fig. 8). These results imply that fulvic and hy-

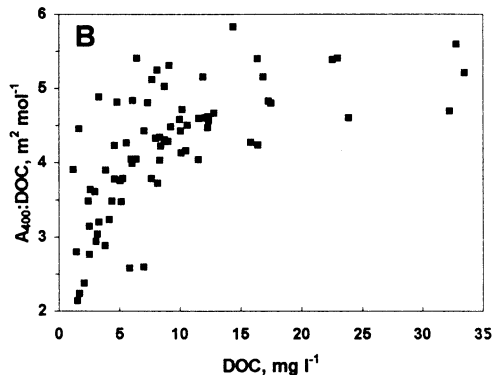
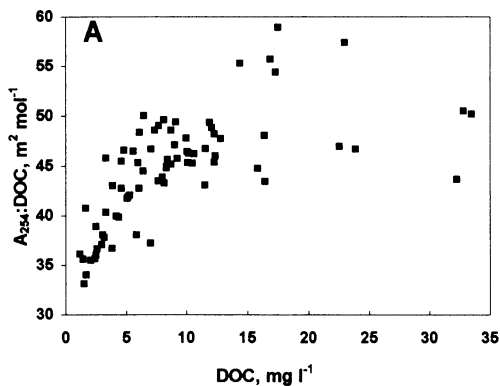


Fig. 7. – Relationship between concentration of dissolved organic carbon and molar absorptivity of DOC at A) 254 nm, and B) 400 nm.

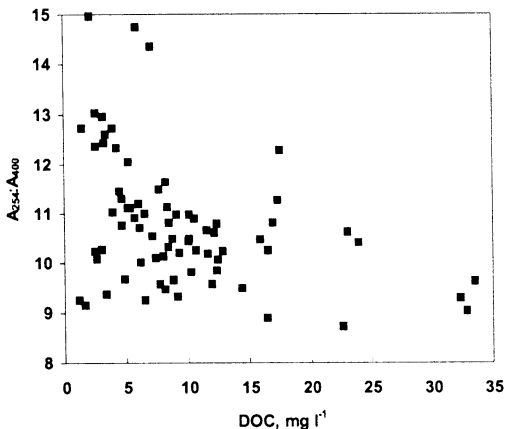


Fig. 8. – Relationship between concentration of dissolved organic carbon and $A_{254}:A_{400}$ ratio; where A_{254} and A_{400} is absorbance at 254 and 400 nm, respectively.

drophylic acids with relatively low proportions of unsaturated carbon bonds formed a substantial part of the total DOC in the tributaries.

Phosphorus and nitrogen

Concentrations of DOC, DON, and DOP for all the tributaries were tightly correlated (Table 6). The average molar DOC:DON and DOC:DOP ratios in the total surface inputs to the lakes were 30–40 and ~6000, respectively. However, concentrations of DRP were distinctly higher in the PL tributaries. Consequently, the average C:P molar ratios of water inputs (calculated as DOC:TDP) reached values of ~6000, 3000–5000, ~3500, and ~1000 in the CT, PR, CN, and PL watersheds, respectively. Among the watersheds situated on mica-schist, elevated concentrations of DRP were observed only in CN-I, CN-II, and PR-IV tributaries, i.e. in waters with the highest levels of DOC. On the other hand, high DRP concentrations were characteristic for all PL tributaries (Table 3). These differences most probably are related to the bedrock and soil composition. Granite in the PL watershed contains more P than mica-schist and this P pool is leached under acidic conditions (KOPÁČEK & al. 1998). We are currently engaged in a more detailed study of P sources to the Šumava lakes. Nevertheless, the

Table 6. – Intercepts (a), slopes (b) and correlation coefficients (r) of linear regressions between the concentrations of DOP, DON, DOC in $\mu\text{mol l}^{-1}$ calculated for all tributaries of the CN, CT, PR, and PL lakes (DON was not determined in May). Level of significance was better than 0.1% in all regressions.

Y	X	a	b	r	n
DOP	DOC	0.03±0.05	(1.13±0.09)10 ⁴	0.82	75
DON	DOC	12±4	(1.23±0.09)10 ²	0.90	51
DOP	DON	-0.02±0.06	(6.4±0.95)10 ⁻³	0.69	51

higher productivity observed in PL lake, e.g. highest concentration of TP (Table 4) and chlorophyll-a (VRBA & al. 1996), can be explained by the high phosphorus input from the watershed.

The low $\text{NO}_3\text{-N}$ levels found in PL lake compared to the other Šumava lakes (Table 4) reflects the higher biological production made possible by higher inputs of P and organic C from the watershed. VRBA & al. (1996) showed that phytoplankton growth in the Šumava lakes was P-limited; thus, higher P loads resulted in higher primary production and in higher assimilation of N. With increased sedimentation of phytoplankton and higher loads of allochthonous organic carbon, conditions were favorable for denitrification in the anoxic hypolimnion and upper layer of sediments. A similar pattern was observed in the Tatra Mountains, where lakes with high phosphorus content generally had lowered $\text{NO}_3\text{-N}$ levels (KOPÁČEK & al., submitted). After spring overturn in PL lake in 1994, the epilimnetic $\text{NO}_3\text{-N}$ pool was decreased due to assimilation and the hypolimnetic $\text{NO}_3\text{-N}$ was denitrified in the anoxic bottom layer but remained relatively unchanged between 8–12 m depth (HEJZLAR & al., this issue).

The lower $\text{NO}_3\text{-N}$ concentrations in PR lake compared to CN and CT lakes (VESELY 1996, Table 4) is due primarily to denitrification in the bottom layer (1–2 m above sediment in the deepest part of the lake), which is regularly anoxic from early summer to autumn overturn. In contrast, the high $\text{NO}_3\text{-N}$ concentrations in CN lake results from high nitrate inputs from its tributaries (Table 4), the oligotrophic status of the lake, and aerobic conditions above the bottom.

Conclusions

1) All tributaries of the Šumava lakes were strongly acidified in 1997 with a pH range of 3.71–4.83, with elevated SO_4^{2-} , NO_3^- , and Al concentrations and with low BC concentrations. BC content was tightly correlated with NO_3^- concentrations in the watersheds of all tributaries and with DR-Si concentrations in the watersheds with mica-schist bedrock. H^+ and Al concentrations correlated primarily with organic acids and sulfate concentrations.

2) Compared to the other lakes, PL lake received water inputs with higher DRP concentrations ($\sim 20 \mu\text{g l}^{-1}$), which resulted in higher primary production, higher N assimilation and pronounced denitrification, and, consequently, in the lowest NO_3^- concentrations. In contrast, high NO_3^- levels in CN lake resulted from high nitrate inputs from the tributaries and low trophic status of the lake.

3) Low Al concentrations in PR lake reflected the low SO_4^{2-} concentrations in the tributaries. Complexation of L-Al with fluoride is likely to further mitigate lake water toxicity to planktonic crustacea and explain their survival in PR lake.

4) Forest decline in the PR watershed resulted in low SO_4^{2-} concentrations and extremely high NO_3^- levels in some of the PR tributaries.

5) Concentrations of DOC in the tributaries varied from 1 to 34 mg l^{-1} . Aquatic humic sub-

stances consisted largely of fulvic and hydrophilic acids with a relatively low proportion of unsaturated carbon bonds. The average contribution of organic matter to water acidity was 3.5 ± 0.3 μeq per 1 mg of DOC. Organic acids represented 1–57 % of the total anion pool. Concentrations of DOP and DON were significantly correlated with DOC.

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