

Seasonal patterns in chemistry of tributaries to Plešné and Čertovo Lakes in the 1998 hydrological year

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Abstract

Ionic and nutrient compositions of tributaries to Plešné Lake (3 inlets, granite bedrock) and Čertovo Lake (7 inlets, mica schist bedrock) were analyzed monthly from October 1997 to November 1998 to describe water chemistry during the seasonal cycle. Annual average discharges of the tributaries varied from 0.4 to 9.6 l s⁻¹. All tributaries were strongly acidic with the annual volume weighted mean (VWM) pH between 4.0 and 4.5. The annual VWM concentrations of ions in tributaries varied from 350 to 460 µeq l⁻¹ with the following average equivalent composition: base cations (BC), 26%; H⁺, 14%; ionic Al species (Al^{III}), 10%; SO₄²⁻, 29%; NO₃⁻, 10%; Cl⁻, 4%; and organic anions (R⁻), 7%. Concentrations of BC were positively correlated to silica (Si, P<0.01-0.001) and negatively to R⁻ (P<0.05-0.001) in all tributaries. In the Plešné tributaries, BC were correlated to SO₄²⁻ (P<0.001) and NO₃⁻ (P<0.01). In the Čertovo tributaries, BC was correlated to NO₃⁻ (P<0.001) but not to SO₄²⁻. Concentrations of Al^{III} were positively correlated to NO₃⁻ (P<0.05-0.001) in all tributaries. In contrast, no consistent correlation was found between H⁺ and any anion throughout the year. Concentrations of dissolved P and organically bound Al and Fe were related to DOC concentrations (P<0.05-0.001). Most of chemical constituents followed similar seasonal trends in all tributaries. Winter (November-April) VWM concentrations of Al^{III}, K⁺, NO₃⁻, SO₄²⁻, and Cl⁻ were higher than their summer (May-October) VWM values, while R⁻ was higher in summer due to elevated DOC concentrations. Winter and summer VWM concentrations of H⁺, Ca²⁺, Mg²⁺, and Na⁺ were nearly comparable. The most pronounced seasonal trends were found for NO₃⁻, Al^{III}, and K⁺, which were 2–3 fold higher from December to May than during vegetation period.

Key words: Acidification, nitrogen, sulfur, aluminum, base cations, pH, dissolved organic carbon.

Introduction

Whereas numerous data on water composition of the Bohemian Forest lakes within last two decades are available in the literature, chemistry of tributaries to these lakes has been studied exceptionally (SCHMIDT & al. 1993, Hejzlar & al. 1998). The first more detailed study on chemistry of tributaries has come from 1997, when water inputs to Černé, Čertovo, Prášílské, and Plešné lakes were analyzed in spring, summer, and autumn (KOPÁČEK & HEJZLAR 1998). A study on chemical composition of the tributaries to Prášílské Lake, focussed on the period of summer temperature stratification of the lake, was performed in 1998 (KOPÁČEK & al., 1999). In the above two studies, chemistry of tributaries was evaluated with respect to bedrock composition and terrestrial characteristics of the individual sub-watersheds and the research was carried out to explain differences in the lake water composition. Major results of these studies were as follows: (1) Tributaries to Plešné Lake had higher concentrations of Ca²⁺, Na⁺, and dissolved reactive P, while lower Mg²⁺ than tributaries to the other lakes due to a different bedrock composition. (2) Concentrations of ionic Al forms were primarily cor-

related with SO_4^{2-} , while base cations with NO_3^- . (3) The tributaries draining sub-watersheds with damaged forest had increased concentrations of NO_3^- and base cations.

The aim of this study was to evaluate chemistry of tributaries to Čertovo and Plešné Lakes in the 1998 hydrological year to find, which chemical constituents follow similar seasonal patterns in all tributaries and if some of these patterns differ between the watersheds due to their different bedrock composition.

Materials and methods

Description of study sites

Čertovo Lake and Plešné Lake are situated in Bohemian Forest (13° to 14° E, 49° N) at altitudes of 1030 and 1090 m a. s. l., respectively. Steep and rocky watersheds of Čertovo and Plešné lakes (85.7 and 66.6 ha, respectively) are forested (~90% and ~70%, respectively) by spruce with sparse fir and beech and their bedrocks consist predominately of mica-schist (muscovite gneiss) with quartzite intrusions and coarse-grain granites, respectively (VESELÝ 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. Soils are iron containing acidic podzols; soil profiles consist of an upper organic horizon (~10 cm), eluvial gray horizon, and enriched rusty-brown B-horizon (PELIŠEK 1966, KOPÁČEK & al. 1998). More details on the physical characteristics, geology, vegetation, and history of land use of the watershed areas are given in VESELÝ (1994).

Tributaries of the lakes are small and short (from ~50 m to ~1 km), mostly first order brooks. There are seven tributaries to Čertovo Lake and three to Plešné Lake. The tributaries have no names and are designated by abbreviations (CT for Čertovo Lake and PL for Plešné Lake) and Roman numerals in order starting from the outlet and moving in a counterclockwise direction. Their locations are given in the previous study (KOPÁČEK & HEJZLAR 1998).

Sampling and analyses

Tributaries were sampled roughly monthly from October 1997 to November 1998 near their inlets to the lake, except for tributary PL-III that is subsurface and was sampled in a small cave. The water discharge was estimated by means of a bucket and stop-watch. In subwatersheds containing several tributaries in close proximity (CT-V, PL-I and PL-II), an integrated sample was taken with sample volumes proportional to the discharge of the individual streams. Samples were immediately filtered through a 40- μm polyamide sieve to remove coarse particles. Each sample was analyzed separately and chemical inputs to Čertovo and Plešné Lake were calculated from volume-weighted mean (VWM) concentrations for all CT and PL tributaries, respectively.

Atmospheric deposition was collected in bulk samplers protected against light and bird perching, and fitted with a 100- μm polyamide sieve to remove coarse particles. Samplers were situated in the forest (throughfall, 9 samplers). One site was situated at Plešné Lake at 1130 m a.s.l. (PL-TF) and two sites were situated at Čertovo Lake at 1045 m a.s.l. (CT-TF-1) and 1330 m a.s.l. (CT-TF-2). Samples were taken from 3 November 1997 to 4 November 1998. Rain was sampled in two-week intervals, and snow in two to four-week intervals. All samples from each site were combined to obtain an integrated sample.

In the laboratory, samples were filtered through membrane filters (pore size of 0.45 μm) for determination of ions and through glass-fibre filters (MN-5; pore size of 0.4 μm ; Macherey Nagel) for the analyses of P, organic matter, and dissolved Al and Fe. The samples for pH, acid neutralizing capacity (ANC), and total P and Al were not filtered. Dissolved or-

ganic carbon (DOC) was analyzed with the LiquiTOC analyser (Foss/Heraeus). ANC (Gran titration), pH, dissolved reactive P (DRP, molybdate method), dissolved P (DP, perchloric acid digestion), and dissolved reactive silica (DR-Si, molybdate method) were analyzed within 24 hours of sampling. Dissolved organic P (DOP) was the difference between DP and DRP. Dissolved organic N (DON) was determined by Kjeldahl digestion and distillation. Samples for ion determination (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , and F^-) were frozen at $-20\text{ }^\circ\text{C}$ and analyzed by ion chromatography (Thermo Separation Products) within a month.

Fractionation of aluminum, i.e. dissolved monomeric Al (Al_D) and organic-monomeric Al (Al_O , representing Al complexed with organic matter) were determined according to DRISCOLL (1984) with the colorimetric method by DOUGAN & WILSON (1974); inorganic-monomeric Al (Al_I , ionic Al forms) was obtained as the difference between Al_D and Al_O . Ionic Fe (Fe_I) and organically bound Fe (Fe_O) were determined analogously to Al fractions. Concentrations of dissolved Fe (Fe_D) and Fe_O were analyzed by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid (HEJZLAR & KOPÁČEK 1998). Samples for Fe_O were analyzed after the ion-exchange procedure used for the Al_O determination. Concentration of Fe_I was obtained as the difference between Fe_D and Fe_O . Equivalent concentrations of Al_I^{n+} and Fe_I^{2+} ($\mu\text{eq l}^{-1}$) were calculated by multiplying the molar Al_I and Fe_I concentrations ($\mu\text{mol l}^{-1}$) by average charges of Al hydroxocomplexes (n) and 2, respectively. The n value was estimated from the theoretical distribution of ionization fractions of aqueous Al hydroxocomplexes (KOPÁČEK & HEJZLAR 1998). Concentrations of organic acid anions (R^- , $\mu\text{eq l}^{-1}$) in tributaries were estimated according to the model by OLIVER & al. (1983) as described by KOPÁČEK & HEJZLAR (1998). In the throughfall samples, R^- concentrations were obtained by multiplying DOC concentration with a coefficient of 4 (4 μeq per mg DOC), which best fitted the charge balance control within the pH range observed in this study (KOPÁČEK, unpublished data). More details on the analytical methods are given in KOPÁČEK & HEJZLAR (1998) or KOPÁČEK & al. (1999, 2000).

Results and discussion

Chemical composition of tributaries and throughfall

Annual VWM concentrations of the major chemical constituents of throughfall and tributaries are given in Table 1. The annual amount of throughfall varied widely from 982 mm at PL-TF to 1599 mm at CT-TF-2. In contrast, composition of throughfall samples at the three sites differed only slightly with the annual VWM concentrations of ions and pH of 319–384 $\mu\text{eq l}^{-1}$ and 4.32–4.53, respectively. The relative average equivalent composition of throughfall was as follows: base cations ($\text{BC} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$), 28%; H^+ , 12%; NH_4^+ , 10%; SO_4^{2-} , 19%; NO_3^- , 13.5%; Cl^- , 5.5%; and R^- , 12%.

The annual average discharge of tributaries varied from 0.4 to 9.6 l s^{-1} . All tributaries were strongly acidic with the annual VWM pH between 4.0 and 4.5. The annual VWM concentrations of ions in tributaries varied from 350 to 460 $\mu\text{eq l}^{-1}$ with the following average equivalent composition: BC, 26%; H^+ , 14%; Al_I^{n+} , 10%; SO_4^{2-} , 29%; NO_3^- , 10%; Cl^- , 4%; and R^- , 7%.

All tributaries had higher concentrations of H^+ , Al_I^{n+} , Mg^{2+} , Na^+ , SO_4^{2-} , and F^- , while lower concentrations of K^+ , and NH_4^+ than throughfall. Concentrations of Ca^{2+} , NO_3^- and R^- in tributaries were mostly lower than in throughfall except for the subsurface tributary PL-III (higher Ca^{2+} and NO_3^-), tributary CT-II with the highest discharge (higher NO_3^-), and the most colored tributary PL-I (higher R^-). The most pronounced differences in the chemical compo-

Table 1. – Annual volume weighted mean composition (VWMC) of throughfall (3 Nov. 1997 to 4 Nov. 1998) in the Čertovo watershed (2 sites; CT-TF-1, amount of 1020 mm; and CT-TF-2, amount of 1599 mm) and in the Plešné watershed (PL-TF, amount of 982 mm) and of the tributaries to Černé Lake (CT, 13 Oct. 1997 to 17 Nov. 1998) and Plešné Lake (PL, 14 Oct. 1997 to 4 Nov. 1998). Number of observations, n.

Parameter	VWMC of throughfall			VWMC of CT-tributaries							VWMC of PL-tributaries			
	CT-TF-1	CT-TF-2	PL-TF	CT-I	CT-II	CT-III	CT-IV	CT-V	CT-VI	CT-VII	PL-I	PL-II	PL-III	
n	17	17	22	13	14	9	13	8	14	14	14	10	12	
Discharge l s ⁻¹				0.4	9.6	1.2	1.7	0.4	2.2	1.7	2.0	1.2	1.3	
H ⁺ µeq l ⁻¹	29	42	48	61	64	92	86	80	39	40	72	58	35	
Al ³⁺ µeq l ⁻¹	ND	ND	ND	20	49	46	45	45	42	26	55	54	56	
Ca ²⁺ µeq l ⁻¹	33	28	42	18	23	18	19	16	33	30	32	37	56	
Mg ²⁺ µeq l ⁻¹	11	8	10	29	32	26	26	27	41	35	12	13	20	
Na ⁺ µeq l ⁻¹	15	16	17	39	34	31	30	30	41	41	53	53	50	
K ⁺ µeq l ⁻¹	35	29	43	7	7	5	5	4	9	11	8	9	10	
NH ₄ ⁺ µeq l ⁻¹	38	41	30	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Fe ²⁺ µeq l ⁻¹	ND	ND	ND	1.1	1.2	1.2	1.2	1.2	1.1	1.1	0.8	0.7	0.2	
NO ₃ ⁻ µeq l ⁻¹	36	49	55	24	60	36	30	18	40	45	40	47	67	
SO ₄ ²⁻ µeq l ⁻¹	62	69	71	112	106	132	130	136	137	102	117	112	124	
Cl ⁻ µeq l ⁻¹	20	19	19	18	19	16	17	17	19	20	18	15	15	
F ⁻ µeq l ⁻¹	1.2	0.9	1.2	2.8	2.4	2.8	2.3	2.4	2.7	2.1	3.9	3.9	5.4	
R ⁻ µeq l ⁻¹	4.3	31	46	20	24	35	33	27	10	13	50	38	21	
pH	4.53	4.37	4.32	4.22	4.19	4.04	4.07	4.09	4.41	4.40	4.14	4.24	4.46	
DOC mg l ⁻¹	10.7	7.7	11.5	5.8	6.9	10.9	10.0	8.0	2.8	3.6	14.8	10.9	5.4	
DON µg l ⁻¹	451	469	484	235	286	325	255	261	178	199	420	354	347	
DP µg l ⁻¹	14.0	9.3	6.5	2.7	3.5	4.0	4.1	2.6	2.1	2.4	29.1	29.3	17.7	
DRP µg l ⁻¹	9.1	5.5	1.5	<1	<1	<1	<1	<1	<1	<1	23.3	25.2	15.1	
Al _d µg l ⁻¹	10	12	10	340	679	720	703	665	555	426	984	905	848	
Al _n µg l ⁻¹	ND	ND	ND	133	186	278	265	226	81	132	434	353	190	
Fe _d µg l ⁻¹	ND	ND	ND	146	150	181	197	134	33	54	137	97	40	
Fe _n µg l ⁻¹	ND	ND	ND	109	103	126	143	89	18	33	99	63	31	
DR-Si mg l ⁻¹	ND	ND	ND	2.3	2.1	2.1	2.0	1.9	2.5	2.6	4.5	4.3	4.0	

sition of throughfall and tributaries were apparently due to a retention of K^+ and inorganic N in soils and leaching of SO_4^{2-} , Al_1^{n+} , and Na^+ from the terrestrial sources.

In concordance with the previous study (KOPÁČEK & HEJZLAR 1998), tributaries to Plešné Lake had higher concentrations of Ca^{2+} , Na^+ , F, DR-Si, DOC, and DRP while lower Mg^{2+} than tributaries to Čertovo Lake. These differences could be attributed to different bedrock compositions. Higher concentrations of organic matter in Plešné tributaries resulted there in higher R: concentrations compared to Čertovo tributaries (20–50 and 10–35 $\mu eq\ l^{-1}$, respectively). There were no other consistent differences in the ionic composition of tributaries in both watersheds.

Seasonal patterns

Comparison of the winter (November–April) and summer (May–October) ionic composition of throughfall and tributaries is given in Fig. 1. The winter VWM concentrations of all ions were generally higher than the summer values at all throughfall sites. Seasonal changes in the chemistry of tributaries were not as pronounced or followed inverse patterns than in throughfall. The winter VWM concentrations of Al_1^{n+} , K^+ , NO_3^- , SO_4^{2-} , and Cl^- in tributaries were higher than their summer VWM values, while R: was higher in summer. Differences between winter and summer VWM concentrations of H^+ , Ca^{2+} , and Mg^{2+} were lower than that of the above ions. However, H^+ was slightly higher in summer while Ca^{2+} , and Mg^{2+} were slightly elevated in winter (Fig. 1). Winter VWM concentrations of DR-Si were higher than summer ones in Čertovo tributaries, but lower in Plešné tributaries.

Seasonal changes in the relative contribution of individual ions to the total ionic pool were evaluated for the average throughfall composition (arithmetical mean of the 3 annual VWM concentrations from Table 1) and the total annual chemical inputs to Čertovo and Plešné lakes. In contrast to the pronounced differences between winter and summer concentrations of ions (Fig. 1), the relative ionic composition of throughfall was relatively stable (Fig. 2). Similar pattern was observed in the ionic composition of tributaries with the exception for NO_3^- and R:; their relative contributions were higher and lower in the winter, respectively (Fig. 2).

Seasonal patterns of the total discharge, VWM temperature, and VWM ionic composition of all CT- and PL-tributaries are given in Fig. 3. The most pronounced seasonal trends were found for NO_3^- , Al_1^{n+} , and K^+ , which were 2–3 fold higher from December to May than during the vegetation period. In contrast, R: concentrations reached their minima in winter and increased in summer and autumn. The SO_4^{2-} and Cl^- concentrations seemed to decrease continuously during the study period and did not follow any seasonal trend (Fig. 3). However, more than one-year data are needed to confirm this trend.

Seasonal variations in NO_3^- concentrations were consistent with higher terrestrial bio-consumption of inorganic N in summer. However, high NO_3^- concentrations even in the growing season (Fig. 3) displayed a progressive stage of N-saturation (according to STODDARD 1994) in both watersheds. The seasonality in Al_1^{n+} concentrations was tightly associated with nitrate as a carrier from soils (see later) and can be explained by seasonal changes in the water chemistry.

Among BC, K^+ followed the most pronounced seasonal variation (Fig. 3). Similarly, the retention of K^+ in soils (the difference between concentrations in throughfall and tributaries) was higher than the Ca^{2+} retention. Moreover, both watersheds were net sources of Mg^{2+} and Na^+ (Table 1, Fig. 1). Similar patterns are typical for numerous forest ecosystems, where K^+ biogeochemistry differ from other cations in that its uptake in the soils exceeds leaching (e.g. JOHNSON 1992, KRÁM & al. 1997).

Seasonal variations in R: in tributaries followed changes in DOC concentrations. Similar

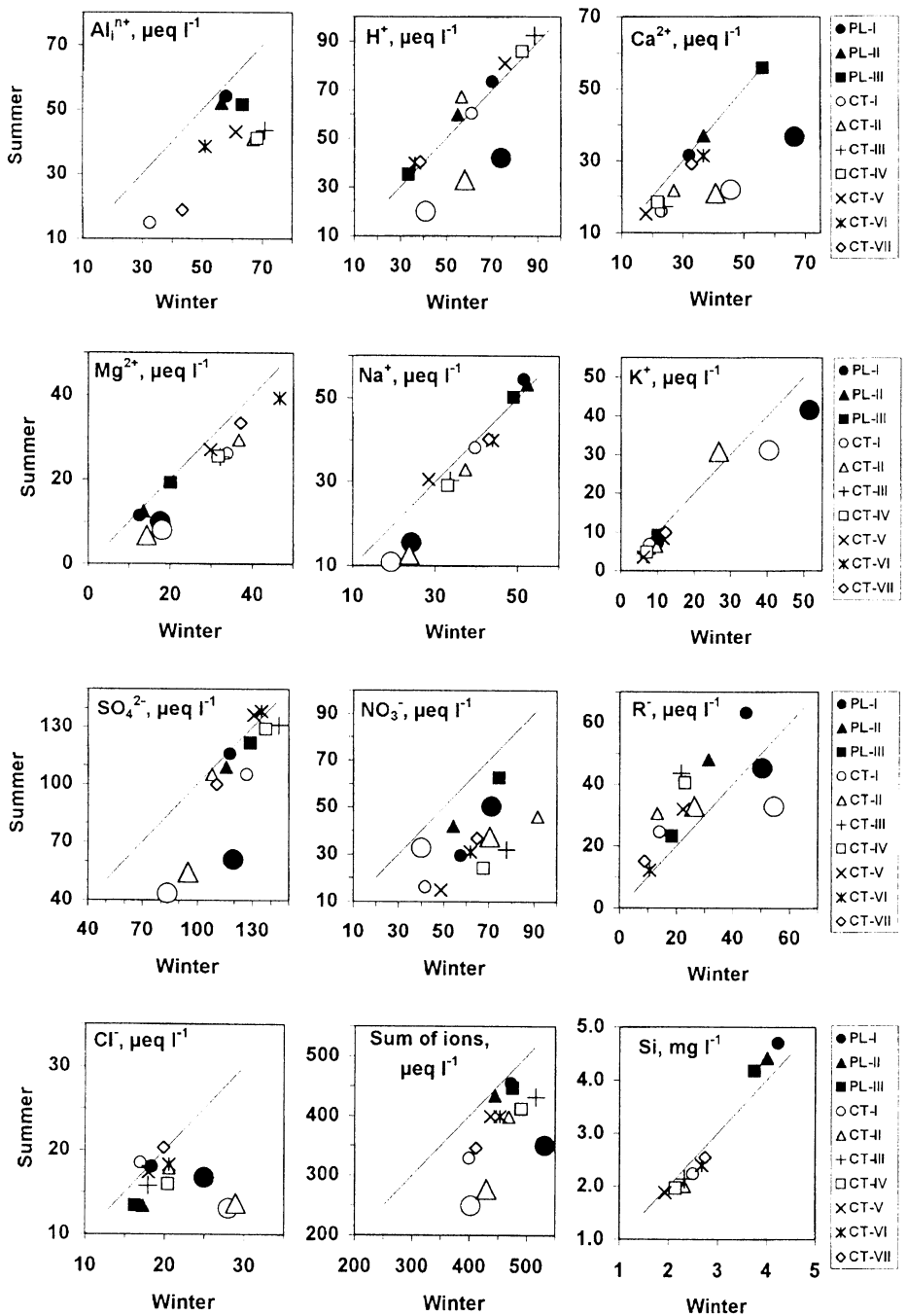


Fig. 1. - Comparison of winter (November-April) and summer (May-October) VWM concentrations of major ions and dissolved reactive silica in Plešné and Čertovo tributaries (small points) and in throughfall (large points: TF-PL, full circle; TF-CT-1, open circle; TF-CT-2, open triangle) in the 1998 hydrological year. Solid line, 1:1 relationship.

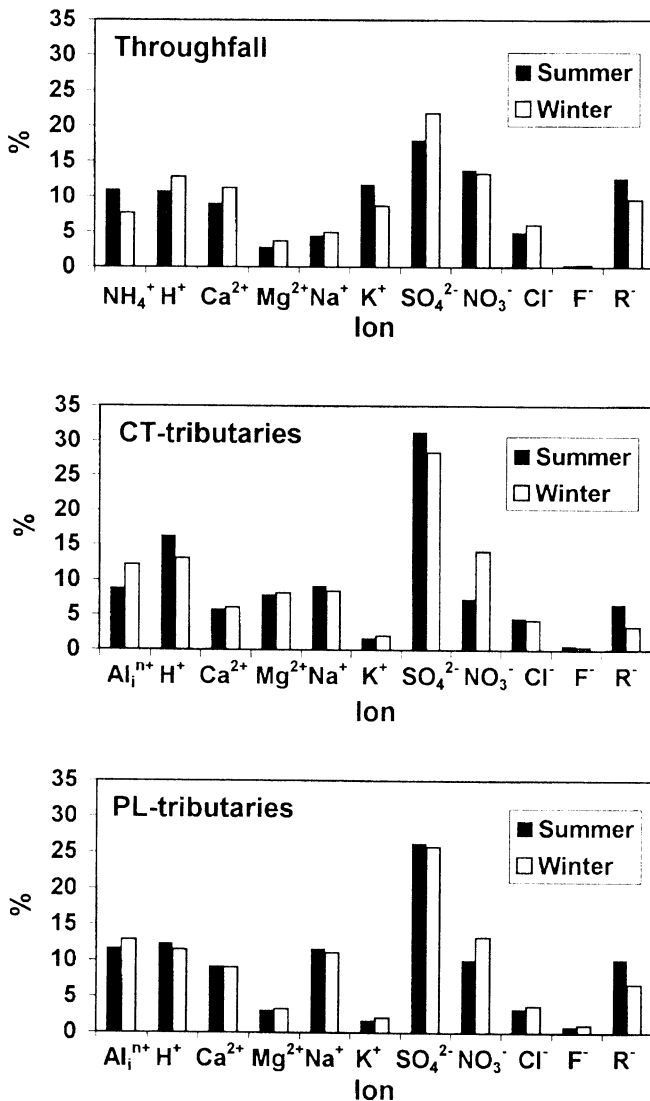


Fig. 2. - Relative contribution of individual ions to the total ionic pool of the average throughfall composition (arithmetical mean of TF-PL, TF-CT-1, and TF-CT-2) and the total annual chemical inputs to Čertovo and Plešné Lakes by their tributaries in the 1998 hydrological year. Winter and summer represents November to April and May to October period, respectively.

seasonal variation in the aquatic DOC concentrations are well known from other sites and are associated with the elevated decomposition of soil organic matter during warmer period and with differing hydrological conditions, like more pronounced water infiltration and longer water residence time in soils in summer (e.g. HRUŠKA & al. 1996).

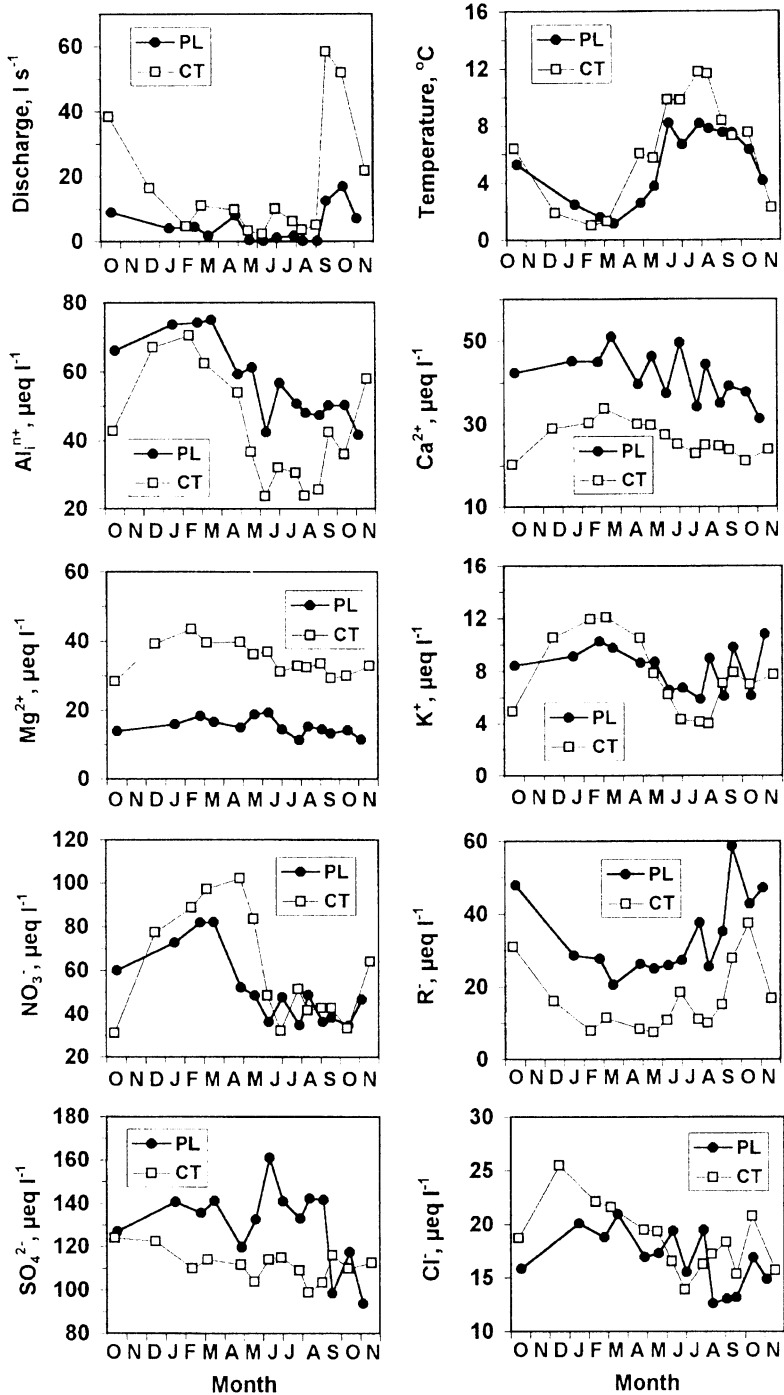


Fig. 3. - Seasonal patterns of the total discharge, VWM temperature and total VWM input of ions to Plešné Lake (PL) and Čertovo Lake (CT) in the 1998 hydrological year.

Correlations between chemical constituents

Correlation coefficients and slopes of linear regressions between chemical constituents were calculated for each tributary with at least ten observations in the 1998 hydrological year (Table 2). Significant positive or negative correlation suggested which ions followed similar or inverse seasonal trends, respectively. Concentrations of BC were positively correlated with DR-Si ($P<0.01-0.001$) and negatively with R ($P<0.05-0.001$) in all tributaries. In the Plešné tributaries, BC was correlated with SO_4^{2-} ($P<0.001$) and NO_3^- ($P<0.01$). In the Čertovo tributaries, BC was correlated with NO_3^- ($P<0.001$) but not (except for CT-I) with SO_4^{2-} . Concentrations of Al_1^{n+} were positively correlated with NO_3^- ($P<0.05-0.001$) in all tributaries. In contrast, no consistent correlation was found between H^+ and any anion throughout the year. Concentration of DOC was the most important factor explaining seasonal changes in Al_0 and Fe_0 concentrations ($P<0.05-0.001$) in all tributaries, DP and DRP ($P<0.05-0.001$) in all PL tributaries, and DP ($P<0.01$) in some CT tributaries (CT-I, CT-II, and CT-IV).

The same relationships among the water constituents (as given above) have been evaluated on a regional scale for a matrix of all tributaries to the Bohemian Forest lakes (KOPÁČEK & HEJZLAR 1998). A comparison of the results from both seasonal and regional approaches allowed us to distinguish spatial and temporal impacts on the water composition of tributaries from six following aspects:

(1) In the regional approach, the Al_1^{n+} concentrations were correlated mainly with SO_4^{2-} concentrations and less with NO_3^- (KOPÁČEK & HEJZLAR 1998). In contrast, the seasonal vari-

Table 2. – Correlation coefficients (r) between chemical constituents in the tributaries to Čertovo and Plešné Lakes in the 1998 hydrological year. Numbers of observations are given in Table 1. Negative r represents a negative slope of a linear regression between independent (X) and dependent (Y) variables. Significance level: *, $P<0.05$; **, $P<0.01$; and ***, $P<0.001$.

X	Y	CT-I	CT-II	CT-IV	CT-VI	CT-VII	PL-I	PL-II	PL-III
SO_4^{2-}	BC	0.86***	0.00	0.38	0.00	0.33	0.79***	0.87***	0.82***
NO_3^-	BC	0.90***	0.85***	0.89***	0.82***	0.93***	0.41	0.85**	0.81**
Cl^-	BC	0.03	0.56*	0.76**	0.73**	0.59*	0.35	0.73*	0.55
R	BC	-0.94***	-0.81***	-0.80**	-0.89***	-0.71**	-0.65*	-0.66*	-0.69*
DR-Si	BC	0.85***	0.78***	0.83***	0.79***	0.07	0.76**	0.88***	0.80**
SO_4^{2-}	H^+	0.64*	0.40	0.60*	0.52	0.37	0.21	0.69*	-0.53
NO_3^-	H^+	0.26	-0.44	0.18	-0.24	0.38	0.25	0.27	-0.02
Cl^-	H^+	-0.03	0.07	0.33	-0.05	0.55*	0.07	0.09	-0.10
R	H^+	-0.45	0.80***	-0.16	0.39	0.18	0.10	-0.30	0.61*
SO_4^{2-}	Al_1^{n+}	0.67*	0.48	0.32	-0.22	0.58*	0.28	0.69*	0.42
NO_3^-	Al_1^{n+}	0.77**	0.71**	0.83***	0.61*	0.82***	0.72**	0.96***	0.86***
Cl^-	Al_1^{n+}	-0.05	0.59*	0.71**	0.47	0.52	0.55*	0.76*	0.87***
R	Al_1^{n+}	-0.82***	-0.27	-0.72**	0.04	-0.62*	-0.36	-0.56	-0.36
DOC	DON	0.78**	0.39	0.10	0.44	0.10	0.22	0.25	0.43
DOC	DP	0.77**	0.91***	0.73**	0.18	0.20	0.88***	0.97***	0.98***
DOC	DOP	0.57*	0.85***	0.5	0.06	0.09	0.84***	0.70**	0.74**
DOC	DRP	ND ¹⁾	ND ¹⁾	ND ¹⁾	ND ¹⁾	ND ¹⁾	0.62*	0.95***	0.96***
DOC	Al_0	0.91***	0.96***	0.95***	0.73**	0.80***	0.80***	0.92***	0.96***
DOC	Fe_0	0.83***	0.94***	0.94***	0.62*	0.77**	0.82***	0.93***	0.84***

¹⁾ND, not determined due to DRP concentrations lower than a detection limit ($1\mu\text{g l}^{-1}$).

ability of Al_1^{n+} in the individual tributaries was associated primarily with NO_3^- . The later observation is in concordance with other studies, showing that elevated Al losses from forest soils are usually associated with nitrate leaching (e.g., DISE & WRIGHT 1995). The results of regional and seasonal approaches suggest a different role of SO_4^{2-} and NO_3^- in Al transport from the terrestrial sources. Spatial variability in Al_1^{n+} concentrations in the Bohemian Forest tributaries is primarily related to the variability in SO_4^{2-} concentrations probably due to a Al- SO_4 complexation in soils (NORDSTROM 1982). Thus, tributaries in subwatersheds with high SO_4^{2-} leaching display high Al_1^{n+} concentrations. However, the seasonal changes in Al_1^{n+} concentrations in the individual tributaries are driven by the seasonal variability of NO_3^- , which is more pronounced than that of SO_4^{2-} (Fig. 2). Consequently, the Al_1^{n+} concentrations in tributaries probably reflect two patterns: (1) they are high in tributaries draining subwatersheds with high terrestrial losses of SO_4^{2-} (KOPÁČEK & HEJZLAR 1998), and (2) they reach higher values in winter than in summer due to the elevated NO_3^- leaching at relatively stable SO_4^{2-} concentrations (Fig. 3).

(2) In the regional approach, the H^+ concentrations were tightly correlated with R^- and SO_4^{2-} concentrations (KOPÁČEK & HEJZLAR 1998). The importance of organic acid anions in the acidity of the Bohemian Forest tributaries was further supported by the correlation between the annual VWM concentrations of H^+ and R^- in the individual tributaries ($P < 0.05$ and $P < 0.001$ in the Plešné and Čertovo watershed, respectively). However, no seasonal correlation was found for H^+ and any anion in the individual tributaries (except for CT-II; Table 2). The missing or poor correlations between the seasonal changes in H^+ and R^- concentrations in the tributaries are surprising, considering both the spatial H^+ to R^- relationship and the pronounced seasonality in R^- concentrations (Fig. 2). Such a discrepancy is probably explained by the opposite seasonal trends in strong acid anions and organic acids. The summer increase in R^- concentrations was probably partly compensated for the decrease in SO_4^{2-} and NO_3^- concentrations (Fig. 1), which together resulted in the mostly insignificant seasonal changes in H^+ concentrations, as well as in the insignificant correlations of H^+ with R^- , SO_4^{2-} , or NO_3^- (Table 2).

(3) Concentrations of organically bound metals were correlated with DOC both in the regional and seasonal approach. Consequently, concentrations of Al_0 followed an opposite seasonal trend than ionic forms of Al, being highest in summer (due to high DOC concentrations), when Al_1^{n+} concentrations reached their minima (Fig. 3).

(4) DOC was the primary variable explaining differences in concentrations of DP both in the regional and seasonal approach. These patterns suggest the primary role of DOC leaching in the terrestrial losses of DP. The DP pool can be divided into DOP and DRP. The annual VWM concentrations of DOP in the individual tributaries (Table 1) were correlated with the annual VWM concentrations of DOC ($P < 0.001$). However, significant seasonal correlation between DOP and DOC was obtained only for some tributaries (Table 2). This discrepancy can be probably explained by a low seasonal variability in DOC and DOP concentrations in the individual tributaries compared to their variability among tributaries (Table 1). Thus, any uncertainty in the determinations of low P concentration may affect the seasonal DOC-DOP relationship seriously due to a narrow concentration range.

Seasonal changes in DRP concentrations were also correlated with DOC (PL-tributaries; Table 2). The elevated P leaching from soils at higher DOC concentrations is probably associated with a higher content of organic acids which were shown to prevent orthophosphate precipitation by Fe or Al, and to dissolve or replace P sorbed on metal hydroxides (e.g., IYAMUREMYE & DICK 1996). To conclude, the terrestrial sources of both DOP and DRP were associated with the leaching of organic matter. Consequently, the responsible mechanism deserves a more detailed study because of its direct effect on the P export to aquatic ecosystems.

(5) Surprisingly, DON was not correlated with DOC in the seasonal approach (except for CT-I; Table 2) despite the tight spatial DON-DOC correlation (KOPÁČEK & HEJZLAR 1998). Also, the annual VWM concentrations of DON in the individual tributaries (Table 1) were correlated with the annual VWM concentrations of DOC ($P < 0.01$). The reason of this discrepancy was probably the same as in the case of DOP; i.e. narrow range of the seasonal DON variability in the tributaries compared to the precision of the analytical method ($\pm 10\%$).

(6) The positive seasonal correlations between BC and DR-Si and NO_3^- and the negative correlations between BC and R^- in the individual tributaries were in concordance with the results obtained in the regional study (KOPÁČEK & HEJZLAR 1998). The negative relationship between BC and R^- could be a reason of their inverse intercorrelations with NO_3^- . The positive correlation between BC and NO_3^- is probably associated with high mobility of nitrate in soils. The importance of NO_3^- as a cation leaching agent increases in acid soils due to a soil SO_4^{2-} adsorption, which increases with decreasing pH (JOHNSON 1992). The negative correlation between R^- and NO_3^- probably reflects an inverse impact of subwatershed slopes (i.e. water residence time in soils) on their concentrations (KOPÁČEK & HEJZLAR 1998). In that way, tributaries with high NO_3^- and BC concentrations have low DOC (and R^-) concentrations and vice versa.

Conclusions

Most of chemical constituents followed similar seasonal patterns in all tributaries to Plešné and Čertovo Lakes despite the bedrock composition. The only exception was the correlation of BC with both SO_4^{2-} and NO_3^- in the Plešné watershed, while predominantly with NO_3^- in the Čertovo watershed.

Concentrations of SO_4^{2-} were in all tributaries higher than in throughfall.

Spatial variability in Al_i^{n+} concentrations in the tributaries to Bohemian Forest lakes was primarily correlated to SO_4^{2-} leaching, while the seasonal variability in Al_i^{n+} was better explained by NO_3^- variability. Concentrations of Al_i^{n+} were highest in winter (due to highest NO_3^- concentrations), while Al_o concentrations were elevated in summer (due to higher DOC concentrations).

The inverse seasonal changes in strong acid anion concentrations (higher in winter) and organic acid anion concentrations (higher in summer) resulted in relatively stable H^+ concentrations in tributaries throughout the year.

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