

## Photochemical, chemical, and biological transformations of dissolved organic carbon and its effect on alkalinity production in acidified lakes

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### Abstract

We evaluated the significance of photochemical and biological degradation of allochthonous dissolved organic carbon (DOC) on in-lake  $H^+$  budgets by laboratory experiments and with a mass budget study for major ions in three atmospherically acidified forest lakes in the Bohemian Forest. In the experiments, photodegradation of DOC from a lake tributary resulted in (1) a liberation of organically bound Al and Fe, which consumed an equivalent amount of  $H^+$ , (2) a minor decrease in concentrations of organic acid anions ( $A^-$ ) despite a major decrease in DOC concentrations, and (3) the production of biologically available DOC. Biological degradation of the photochemically transformed DOC resulted in a lesser decrease in DOC concentrations than during photodegradation (28–45% of the total decline) but in a pronounced decrease in  $A^-$  concentrations (64–85% of the total decline), leading to a significant pH increase. Hydrolysis of photoliberated metals under increasing pH partly reduced net  $H^+$  consumption within the whole process. Watersheds of the lakes studied exported more  $SO_4^{2-}$ ,  $NO_3^-$ , and  $H^+$  than they received by throughfall, and the lakes were the dominant acidity-consuming parts of the whole ecosystems, neutralizing 50–58% of  $H^+$  input. In-lake photochemical, biological, and chemical changes in  $A^-$  fluxes consumed 56–190  $meq\ m^{-2}\ yr^{-1}$  of  $H^+$  and were the third major internal alkalinity-producing mechanism after the biochemical reduction of  $NO_3^-$  and  $SO_4^{2-}$  (333–396 and 143–214  $meq\ m^{-2}\ yr^{-1}$ , respectively). In contrast, the hydrolysis of inorganic Al was the dominant in-lake  $H^+$ -producing process (144–340  $meq\ m^{-2}\ yr^{-1}$ ). The in-lake  $A^-$  removal was positively related to the DOC loading. Consequently, changes in DOC and  $A^-$  fluxes should not be omitted in alkalinity budgets in lakes with low or no bicarbonate concentration and elevated DOC input.

Mass balance studies for watershed–lake ecosystems in areas sensitive to acidification show a wide variability in the relative importance of terrestrial and in-lake processes in the acid-neutralizing capacity of the ecosystem (e.g., Schindler 1986). The dominant terrestrial alkalinity-producing processes—like ionic exchange, weathering, and the biological assimilation of nitrate and other anions—depends mostly on the watershed geology, morphology, soil characteristics, and hydrological conditions (van Breemen et al. 1984; Psenner and Catalan 1994). Although terrestrial alkalinity generation prevails in nonacidified areas, in-lake processes become more important as an ecosystem acidifies and the concentrations of  $NO_3^-$  and  $SO_4^{2-}$  increase (Schindler 1986). Internal alkalinity production in acid-sensitive lakes is usually dominated by the biochemical reduction of  $NO_3^-$  and  $SO_4^{2-}$  (Cook et al. 1986; Rudd et al. 1986) and  $H^+$ –base cation exchange in sediment (Schiff and Anderson 1986, 1987; Psenner 1988). Schindler et al. (1986), Schindler (1986), and Cook et al. (1986) have mentioned that the in-lake removal of

organic acids can consume some amount of  $H^+$ . However, in their studies, this process was negligible in alkalinity production and was not included in the mass budgets. In contrast, the in-lake removal of allochthonous organic matter was found to be a significant internal alkalinity-producing process in the acidified Adirondack and Bohemian Forest lakes (Driscoll and Postek 1996; Kopáček et al. 2001a,b,c).

Sunlight has been shown to effectively reduce concentrations of dissolved aquatic humic matter, decrease its average molecular weight, and change its optical properties (Allard et al. 1994; Lean 1998). The photochemical degradation of allochthonous recalcitrant organic matter can have important consequences for the microbial productivity of both marine and freshwater ecosystems (e.g., Kieber et al. 1989; Lindell et al. 1995). The partial photochemical degradation of allochthonous DOC produces numerous biologically available compounds (like acetic, formic, citric, malonic, and oxalic acids; Bertilsson and Tranvik 2000) and results in enhanced bacterial growth. Consequently, either the total photochemical oxidation of humic matter to inorganic carbon (mono- and dioxide) or the partial photochemical degradation of recalcitrant organic matter followed by the microbial uptake of low-molecular weight organic acids influence in-lake concentrations of organic acids and  $H^+$ .

The purpose of our study was to evaluate the effect of photochemical and biological degradation of allochthonous organic matter on lake water chemistry. We provide here mass budgets for major ions in three atmospherically acidi-

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Table 1. Major morphological characteristics of the Bohemian Forest lakes and their water balance in hydrological year 2000.  $Q^{\text{IN}}$ , water input into the lake from its watershed;  $Q^{\text{DAD}}$ , direct atmospheric deposition on the lake surface;  $Q^{\text{OUT}}$ , water output from the lake.

Parameter	Černé	Čertovo	Plešné
Lake area ( $10^5 \text{ m}^2$ )	1.84	1.03	0.75
Lake volume ( $10^6 \text{ m}^3$ )	2.88	1.85	0.62
Maximum depth (m)	40	36	18
Mean depth (m)	16	18	8
Watershed area ( $10^6 \text{ m}^2$ )	1.29	0.86	0.67
$Q^{\text{IN}}$ ( $10^6 \text{ m}^3 \text{ yr}^{-1}$ )	1.71	1.23	0.81
$Q^{\text{DAD}}$ ( $10^6 \text{ m}^3 \text{ yr}^{-1}$ )	0.30	0.17	0.12
$Q^{\text{OUT}}$ ( $10^6 \text{ m}^3 \text{ yr}^{-1}$ )	1.76	1.17	0.84
Water residence time (yr)	1.6	1.6	0.7

fied lakes in the Bohemian Forest and experimental data showing that photo- and biodegradation of allochthonous organic matter can significantly affect in-lake  $\text{H}^+$  budgets and fractionation of metal species in lakes with elevated DOC inputs.

## Materials and methods

*Description of study sites*—Černé, Čertovo, and Plešné Lakes are situated in the Bohemian Forest (Middle Europe,  $13\text{--}14^\circ\text{E}$ ,  $49^\circ\text{N}$ ) at altitudes of between 1,008 and 1,090 m above sea level. The lakes are of glacial origin, with surface areas of 7.5–18.4 ha. Their major morphological characteristics are given in Table 1. The watershed areas of the lakes are steep, with a maximum local relief of 288–335 m. Bedrock is made up of granite in the Plešné watershed and from mica-schists (muscovitic gneiss) in the Černé and Čertovo watersheds. The watersheds are covered with a thin layer of forest humus. Soils are mostly spodo-dystric cambisol and iron-containing acidic podzol in different stages of development (average depth  $\sim 0.5$  m) with average values of cation exchange capacity and base saturation ranging from 12 to 23  $\text{eq m}^{-2}$  and from 9 to 15%, respectively, (Kopáček unpubl. data). Vegetation is dominated by secondary ( $\sim 150\text{--}200$  yr old) Norway spruce forest with sparse white fir and beech. The forest covers 70–90% of the lake watersheds. Černé, Čertovo, and Plešné Lakes have nine, seven, and two surface tributaries, respectively, some of which are temporal. Moreover, Plešné Lakes has two subsurface tributaries accessible in a small cave and well.

*Water sampling and analyses*—The study was performed in hydrological year 2000 (from November 1999 to October 2000). Atmospheric deposition was collected at five sites. Two sites (precipitation and throughfall) were situated in the watershed of Plešné Lake and three sites (precipitation and two throughfalls) were between geographically adjacent Černé and Čertovo Lakes. Rain was sampled biweekly and snow from 2- to 4-week intervals. Samples from the tributaries and water column (five depths between the lake surface and the maximum depth) were taken monthly and from the outlets biweekly. The discharges of tributaries were estimated using a method of stopwatch and bucket. These discharge

data of tributaries were underestimated, representing only water in the stream but not in its hyporheic zone. Hence, these values were only used to calculate the annual volume-weighted mean composition of terrestrial inputs for the lakes, whereas the total water output from the watershed was estimated from the budget for  $\text{Cl}^-$  (see below). The discharges of outlets were measured with recording gauges at Čertovo and Plešné Lakes and estimated from the data on electricity production in the hydroelectric power station at Černé Lake.

In the laboratory, samples were filtered with membrane filters (A45/25; pore size  $0.45 \mu\text{m}$ ; Macherey Nagel) for the determination of ions or with glass fiber filters (MN-5; pore size  $0.4 \mu\text{m}$ ; Macherey Nagel) for the analyses of organic matter and dissolved Al and Fe. Absorbance at 254 nm ( $A_{254}$ ), alkalinity (Gran titration), and pH were analyzed within 8 h of sampling. Dissolved organic carbon (DOC) and particulate organic carbon ( $C_{\text{part}}$ ) were analyzed using a TOC 5000A analyzer (Shimadzu) by combustion of the filtrate and glass fiber filter with the retained particulate organic matter, respectively, within 24 h of sampling. Molar absorptivity of DOC at 254 nm ( $A_{254}:\text{DOC}$ ,  $\text{m}^2 \text{ mol}^{-1}$ ) was obtained as a ratio of  $A_{254}$  (absorbance at 254 nm recalculated per 1 m absorption path) to DOC concentration ( $\text{mol m}^{-3}$ ). Samples for ion determination ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{F}^-$ ) were frozen at  $-20^\circ\text{C}$  and analyzed by ion chromatography (Dionex IC25) within a month. Fractionation of aluminum according to Driscoll (1984) (i.e., total Al [ $\text{Al}_t$ ], dissolved Al [ $\text{Al}_d$ ], and organically bound Al [ $\text{Al}_o$ ]) was analyzed in nonfiltered samples, filtered samples, and cation exchange-treated samples after their filtration, respectively, using the Dougan and Wilson (1974) method within 24 h of sampling. The concentration of ionic Al ( $\text{Al}_i$ ) was the difference between  $\text{Al}_d$  and  $\text{Al}_o$ . Particulate Al ( $\text{Al}_{\text{part}}$ ) was the difference between  $\text{Al}_t$  and  $\text{Al}_d$  concentrations. The concentrations of total Fe ( $\text{Fe}_t$ ), dissolved Fe ( $\text{Fe}_d$ ), and organically bound Fe ( $\text{Fe}_o$ ) were analyzed by the thiocyanate colorimetric method after sample evaporation and digestion with perchloric acid.  $\text{Fe}_o$  was analyzed after the ion exchange procedure in the subsamples used for  $\text{Al}_o$  determination. The concentration of ionic Fe ( $\text{Fe}_i$ ) and particulate Fe ( $\text{Fe}_{\text{part}}$ ) were obtained analogously to  $\text{Al}_i$  and  $\text{Al}_{\text{part}}$ . Equivalent concentrations of  $\text{Al}_i$  and  $\text{Fe}_i$  ( $\text{Al}_i^{n+}$  and  $\text{Fe}_i^{m+}$ ) were obtained from their molar concentrations by multiplying by the average charges of Al hydroxocomplexes ( $n$ ) and Fe hydroxocomplexes ( $m$ ), respectively. The  $n$  and  $m$  values were estimated from the theoretical distribution of ionization fractions of aqueous Al and Fe hydroxocomplexes, respectively, at the sample pH (Stumm and Morgan 1981). Ignoring Al–F and Al– $\text{SO}_4$  complexes in the estimation of the average Al charge resulted in only a negligible error (Kopáček et al. 2000b).

The concentrations of organic acid anions ( $\text{A}^-$ ,  $\mu\text{eq L}^{-1}$ ) were obtained as follows: The  $\text{A}^-$  concentrations in tributaries were estimated from DOC,  $\text{Al}_o$ ,  $\text{Fe}_o$ , and  $\text{H}^+$  concentrations according to Kopáček et al. (2000b), assuming that the average total concentration of carboxylic groups per mass of DOC is  $120 \text{ meq mol}^{-1}$  (Oliver et al. 1983) and the concentration of carboxyl groups complexed with metals is, on an equivalent bases, equal to the concentrations of  $\text{Al}_o$  and  $\text{Fe}_o$ . An empirical coefficient of  $48 \text{ meq (mol DOC)}^{-1}$

was used to estimate  $A^-$  concentrations in precipitation (Kopáček unpubl. data). This calculation provided an estimate of  $A^-$ , which did not depend on analyses of other ions (except for  $H^+$ ); therefore, the  $A^-$  values could have been used for the ionic balance control of the correctness of all analytical results. The calculated  $A^-$  data well corresponded with a commonly used direct measurement (discrepancy in charge balance). For example, we obtained the following tight relationship for 260 samples of tributaries with ionic concentration between 215 and 625  $\mu\text{eq L}^{-1}$ :  $A^-_{\text{discrepancy}} = 0.99 \times A^-_{\text{calculated}}$  ( $r = 0.86$ ,  $p < 0.001$ ).

The reliability of analytical methods was checked by means of a standard sample, which was assayed with each series of samples. Coefficients of variation of the mean were 1–5% for pH,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , DOC, and  $\text{Al}_d$  and <10% for base cations (Kopáček et al. 2001a). The accuracy of analyses was checked using ionic balance control of each sample. The differences between the sum of the cations and the sum of the anions were  $< \pm 4\%$  of the ionic concentration for all fluxes used in this study.

*Mass balances*—In-lake mass balance of chemical constituents was calculated according to Eq. 1.

$$Q^{\text{IN}}C^{\text{IN}} + Q^{\text{DAD}}C^{\text{DAD}} + P = Q^{\text{OUT}}C^{\text{OUT}} + \Delta M \quad (1)$$

$Q^{\text{IN}}$ ,  $Q^{\text{DAD}}$ , and  $Q^{\text{OUT}}$  (all in  $\text{m}^3 \text{yr}^{-1}$ ) are water input into the lake from its watershed, direct atmospheric deposition on the lake surface, and total water output from the lake, respectively.  $C^{\text{IN}}$ ,  $C^{\text{DAD}}$ , and  $C^{\text{OUT}}$  (all in  $\text{mol m}^{-3}$ ) are annual volume-weighted mean concentrations of a constituent in tributaries, direct atmospheric deposition on the lake surface, and total output from the lake, respectively. The  $Q^{\text{IN}}$  value was determined from the annual amounts of precipitation, throughfall, measured outflow from the lakes, and the budget for  $\text{Cl}^-$ , assuming that  $\text{Cl}^-$  behaved conservatively with no net retention or production within the whole ecosystem. Major results and details on the water balance are given in Table 1 and in Kopáček et al. (2001a,b,c), respectively.  $\Delta M$  ( $\text{mol yr}^{-1}$ ) is change in storage of a constituent in the lake and was obtained as the difference between element amounts in the lake (based on changes in concentrations and water levels) at the end and start of the mass budget period. Finally,  $P$  ( $\text{mol yr}^{-1}$ ) is net mass production (when positive) or retention (when negative) of a constituent in the lake.

Net production (or consumption) of protons and the contributions of individual constituents to this process were estimated from budgets for ions using the equation of electro-neutrality (Eq. 2).

$$\begin{aligned} [\text{H}^+] &= [\text{SO}_4]^{2-} + [\text{NO}_3]^- + [\text{Cl}]^- + [\text{F}]^- + [\text{A}]^- \\ &\quad - [\text{NH}_4]^+ - [\text{Na}]^+ - [\text{K}]^+ - [\text{Ca}]^{2+} \\ &\quad - [\text{Mg}]^{2+} - [\text{Al}]^{n+} - [\text{Fe}]^{m+} \end{aligned} \quad (2)$$

Brackets represent equivalent concentrations of components and concentrations of  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  are neglected because Gran titration was negative in all fluxes (see below). According to this approach, any increase in concentration of cations or decrease in concentration of anions are taken as proton-consuming processes. In contrast, any decrease in

concentration of cations or increase in concentration of anions are taken as proton-producing reactions.

*Conservative/nonconservative nature of  $\text{Al}_i^{n+}$  in the lakes*—The mineral saturation index (SI) of Al forms was estimated according to Driscoll and Postek (1996) as  $\log(Q_p/K_p)$ , where  $Q_p$  is the ion activity product of the solution and  $K_p$  is the thermodynamic solubility product of synthetic gibbsite ( $\log K_r = 8.1$  at  $25^\circ\text{C}$ , Driscoll and Postek 1996) and amorphous  $\text{Al}(\text{OH})_3$  ( $\log K_r = 9.0$  at  $25^\circ\text{C}$ , Lydersen et al. 1990). For a rough estimation of SI, we assumed that all  $\text{Al}_i^{n+}$  could be hydrolyzed (i.e.,  $Q_p$  was equal to  $\text{Al}_i^{n+}$  activity), which produced the maximum SI values because  $\text{Al}_i^{n+}$  also included other Al complexes (e.g., Driscoll and Postek 1996). The change in  $K_r$  dependent on temperature was estimated from the van't Hoff equation (Eq. 3).

$$d \ln(K_r)/dT = \Delta_r H^\circ / RT^2 \quad (3)$$

$R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  (K) is the absolute temperature, and  $\Delta_r H^\circ$  is enthalpy change of the reaction. Because  $\Delta_r H^\circ$  is assumed to be constant over small temperature intervals, we used the value  $-95 \text{ kJ mol}^{-1}$  (Lydersen et al. 1990; Driscoll and Postek 1996) for all calculations between 0.5 and  $25^\circ\text{C}$ .

*Photodegradation experiments*—Water samples were taken from the major surface tributary of Plešné Lake in winter (27 January 2000) and fall (31 October 2000) (i.e., during periods of minimum and maximum annual DOC concentrations in tributaries, respectively, Kopáček et al. 2001c). In the laboratory, samples were filtered with membrane filters (pore size  $0.2 \mu\text{m}$ ) and divided into seven 500-ml subsamples, which were irradiated inside the temperature-controlled ( $38\text{--}41^\circ\text{C}$ ) photochemical reactor (RAYONETT-RMR 100, The Southern New England Ultraviolet Company) equipped with RPR 3000 A lamps. Radiation up to 300 nm was filtered by optical glass. The amount of radiation incident upon the reaction vessel has been determined at 297–313 nm by ferrioxalate actinometry (Hatchard and Parker 1956). The number of quanta absorbed by the actinometer was  $1.24 \times 10^{-5} \text{ Einstein cm}^{-2} \text{ min}^{-1}$  (i.e.,  $\sim 800 \text{ W m}^{-2}$  [at 300–320 nm]). One subsample was a dark control and six others were irradiated for different periods until  $\sim 50\%$  of the original  $A_{254}$  were reached. Hence, the winter and fall samples were irradiated for up to 10 and 11.5 h, respectively. After irradiation, each subsample was divided into two parts: the first for chemical analyses (pH, DOC,  $A_{254}$ ,  $\text{Al}_i$ ,  $\text{Al}_o$ ,  $\text{Fe}_i$ ,  $\text{Fe}_o$ , and ions) and the second for a biodegradation experiment, which is described later. Concentrations of  $A^-$  in the subsamples were calculated as described above.

*Biodegradation experiments*—The dark control and irradiated subsamples from the previous step were inoculated with a natural bacterial inoculum from Plešné Lake ( $< 200 \mu\text{m}$ ; equivalent to 2% of sample volume) and incubated in polyethyleneterephthalate bottles in the dark at  $20^\circ\text{C}$  for 28 d (Servais et al. 1989). A blank was performed from double-distilled water without inoculum. After the incubation, pH was measured in unfiltered samples, and the other chemical parameters (the same as after the photodegradation experi-

Table 2. Volume-weighted mean composition of precipitation (PREC, average for two sites), throughfall (TF, average for three sites), and terrestrial input (IN<sub>ter</sub>, all accessible tributaries) and output (OUT) of three lakes in the Bohemian Forest in hydrological year 2000. ND, not determined.

Constituent	PREC	TF	Černé Lake		Čertovo Lake		Plešné Lake	
			IN <sub>ter</sub>	OUT	IN <sub>ter</sub>	OUT	IN <sub>ter</sub>	OUT
H <sup>+</sup> (μeq L <sup>-1</sup> )	13	23	43	17	54	38	42	20
Ca <sup>2+</sup> (μeq L <sup>-1</sup> )	12	1	35	43	26	24	42	41
Mg <sup>2+</sup> (μeq L <sup>-1</sup> )	3	29	36	36	31	27	15	15
Na <sup>+</sup> (μeq L <sup>-1</sup> )	10	11	37	37	35	33	51	41
K <sup>+</sup> (μeq L <sup>-1</sup> )	5	17	11	11	9	9	9	9
NH <sub>4</sub> <sup>+</sup> (μeq L <sup>-1</sup> )	26	29	2	8	2	4	3	6
NO <sub>3</sub> <sup>-</sup> (μeq L <sup>-1</sup> )	28	32	98	64	75	56	62	31
SO <sub>4</sub> <sup>2-</sup> (μeq L <sup>-1</sup> )	25	50	98	84	101	98	99	94
Cl <sup>-</sup> (μeq L <sup>-1</sup> )	9	45	17	18	16	16	13	13
F <sup>-</sup> (μeq L <sup>-1</sup> )	0	16	1	2	1	1	3	3
A <sup>-</sup> (μeq L <sup>-1</sup> )	4	29	8	3	10	5	27	10
Al <sub>i</sub> <sup>3+</sup> (μeq L <sup>-1</sup> )	0	0	58	20	45	47	41	19
Fe <sub>i</sub> <sup>3+</sup> (μeq L <sup>-1</sup> )	ND	ND	0.5	0.6	1.1	1.0	0.7	0.4
DOC (μmol L <sup>-1</sup> )	75	597	297	113	358	254	583	325
Al <sub>i</sub> (μmol L <sup>-1</sup> )	0.2	0.4	24	10	17	17	18	10
Al <sub>o</sub> (μmol L <sup>-1</sup> )	ND	ND	4.5	1.3	5.6	2.7	9.5	4.6
Al <sub>part</sub> (μmol L <sup>-1</sup> )	ND	ND	0.3	1.7	0.0	0.7	0.4	4.2
Fe <sub>i</sub> (μmol L <sup>-1</sup> )	ND	ND	0.4	0.6	1.0	0.9	0.5	0.4
Fe <sub>o</sub> (μmol L <sup>-1</sup> )	ND	ND	0.6	0.2	1.0	0.8	0.9	0.6
Fe <sub>part</sub> (μmol L <sup>-1</sup> )	ND	ND	0.1	0.4	0.1	0.4	0.1	0.5

ment) were determined in the filtrates (glass fiber or membrane filters for ions, pore size 0.4 or 0.45 μm, respectively).

## Results

**Mass budget study**—Water inputs into the lakes via tributaries and direct atmospheric deposition were acidic with a depleted carbonate buffering system and high SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Al<sub>i</sub><sup>3+</sup>, and H<sup>+</sup> concentrations (Table 2). All tributaries were more acidic than precipitation or throughfall in the Bohemian Forest, with pH values ranging from 4.0 to 4.9. Volume- and time-weighted mean concentration of DOC in the individual tributaries varied from 0.1 to 1.4 mmol L<sup>-1</sup>, and DOC significantly ( $p < 0.001$ ) influenced concentrations of organically bound metals and contributed to acidity of tributaries (Fig. 1). The average content of Al<sub>o</sub> and Fe<sub>o</sub> associated with organic matter ranged between 12 and 25 mmol mol<sup>-1</sup> (average of 17 mmol mol<sup>-1</sup>) of DOC. Both Al<sub>o</sub> and Fe<sub>o</sub> represented a significant part of the total contents of these metals in the tributaries, averaging 16–34% of Al<sub>i</sub> and 48–61% of Fe<sub>i</sub> in terrestrial inputs of the lakes studied. In contrast, concentrations of Al<sub>part</sub> and Fe<sub>part</sub> were usually low in tributaries (Table 2). Compared to the tributaries, the lake outputs had substantially lower concentrations of DOC, Al<sub>o</sub>, Fe<sub>o</sub>, H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, indicating their removal in the lakes (Table 2).

The individual ionic fluxes within the ecosystems studied have been described elsewhere (Kopáček et al. 2001a,b,c) and the major results (net retention of ions and its effect on in-lake alkalinity production) are summarized in Table 3. The total in-lake inputs of H<sup>+</sup> by tributaries and precipitation (417–657 meq m<sup>-2</sup> yr<sup>-1</sup>, given on a lake surface area basis) were from 50 to 58% neutralized by net in-lake alkalinity

production, varying between 244 and 318 meq m<sup>-2</sup> yr<sup>-1</sup> (Table 3). In-lake removal of DOC was associated with a pronounced reduction in A<sup>-</sup> concentrations (56–190 meq m<sup>-2</sup> yr<sup>-1</sup>), which significantly (9–26%) contributed to the total in-lake alkalinity production. For comparison, biochemical reduction of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in sediments and water, which are commonly the dominant proton-consuming processes in acidified lakes (Cook et al. 1986; Rudd et al. 1986), accounted for 51–58% and 19–33%, respectively, of total in-lake alkalinity production. A relatively important internal alkalinity source was the assimilation of NO<sub>3</sub><sup>-</sup> in the epilimnion of the most productive lake, Plešné (Kopáček et al. 2001c), which is similarly to observations made by Driscoll and Schafran (1984). Exchange of H<sup>+</sup> for base cations in sediment, often reported as a significant in-lake alkalinity source during the early stage of lake acidification (e.g., Schiff and Anderson 1986; Psenner 1988), was not observed (with the exception of K<sup>+</sup>) in the long-term acidified Bohemian Forest lakes. According to the mass budget, the lakes were net sinks for base cations, which consumed an equivalent amount of alkalinity (Table 3).

Surprisingly high in-lake retention of base cations (higher than the accumulation rate in sediments, Kopáček et al. 2001a,b,c) probably indicated a significant proportion of overflow and interflow not sampled (water passing through the upper soil horizons) in the total terrestrial water export during hydrologic events like snowmelt or heavy rains. This process produces water of low pH, alkalinity, and concentrations of base cations but elevates DOC concentrations (Likens et al. 1977). Although neglecting these water fluxes probably overestimated volume-weighted mean concentrations of base cations in the lake inputs, the DOC concentrations were underestimated. In accordance, the biggest dif-

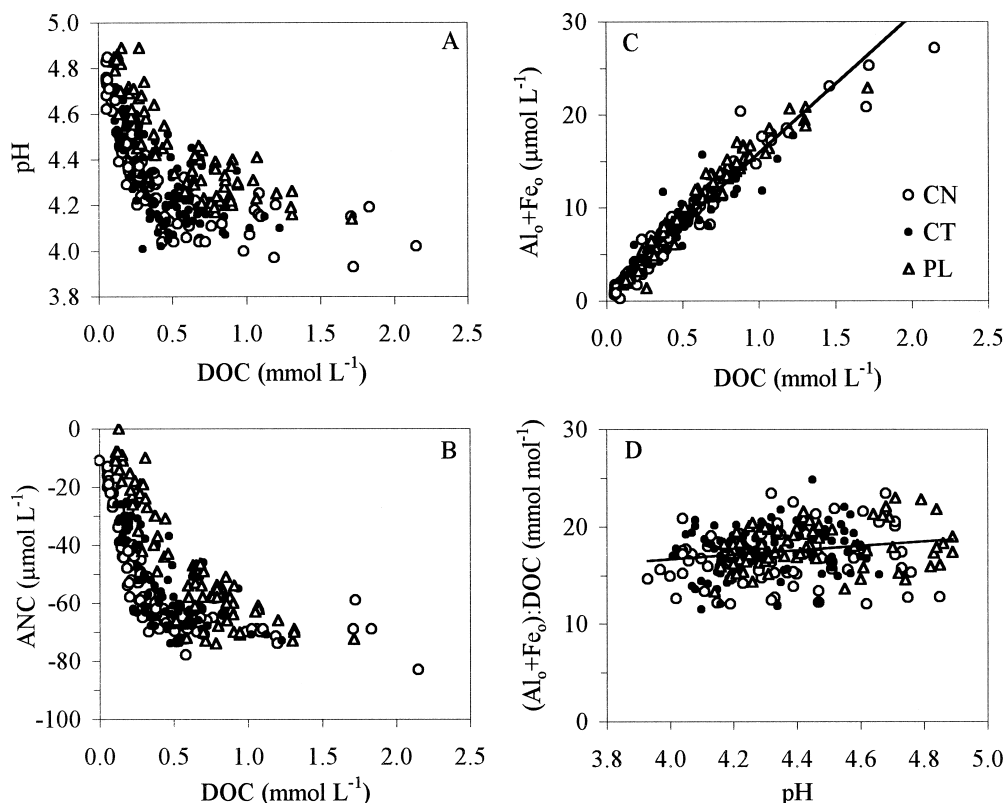


Fig. 1. The relationships of (A) DOC versus pH, (B) acid-neutralizing capacity, and (C) organically bound Al and Fe and of (D) pH versus the ratio of  $(Al_0 + Fe_0)$  to DOC in the tributaries of the Bohemian Forest lakes in hydrological year 2000. Solid line represents linear regression;  $(Al_0 + Fe_0) = 1 + 15DOC$  ( $r = 0.96$ ) and  $(Al_0 + Fe_0):DOC = 7.53 + 2.28pH$  ( $r = 0.20$ ). CN, Černé Lake; CT, Čertovo Lake; PL, Plešné Lake.

ferences between concentrations of base cations in tributaries and outflow were observed in winter (Kopáček et al. 2001a,b,c). In hydrological year 1998, when the snow cover was extremely low, the mass fluxes of base cations were roughly balanced, and higher (not underestimated) DOC loading of the lake was observed (Kopáček et al. 2000a). The real significance of in-lake DOC removal in total in-lake alkalinity production was probably even higher than the reported data in hydrological year 2000.

Table 3. Net retention (NR,  $mmol m^{-2} yr^{-1}$ ) of the major water constituents and its effect on in-lake alkalinity production (AP,  $meq m^{-2} yr^{-1}$ ) in the Bohemian Forest lakes in the hydrological year 2000. Negative values of production indicate net removal.

	Černé Lake		Čertovo Lake		Plešné Lake	
	NR	AP	NR	AP	NR	AP
H <sup>+</sup>	243		291		278	
BC	45	-71	83	-137	128	-144
NH <sub>4</sub> <sup>+</sup>	-47	47	2	-2	-8	8
NO <sub>3</sub> <sup>-</sup>	335	335	333	333	396	396
SO <sub>4</sub> <sup>2-</sup>	107	214	75	149	71	143
DOC (A <sup>-</sup> )	1828	56	1600	72	3675	190
Al <sub>i</sub> (Al <sub>i</sub> <sup>n+</sup> )	133	-340	62	-144	89	-273
Fe <sub>i</sub> (Fe <sub>i</sub> <sup>m+</sup> )	6	3	-30	25	-2	-1
Net change		244		296		318

Changes in concentrations of Al species were a major (50–80%) in-lake source of H<sup>+</sup> and an important alkalinity-consuming process. Internal alkalinity production in waters with a depleted carbonate buffering system results in the development of a pronounced pH gradient between tributaries and lake (Kopáček et al. 2001d). With the pH increasing toward neutrality, Al<sub>i</sub> hydrolyzes with an equivalent production of H<sup>+</sup> and forms colloidal oxyhydroxides (Stumm and Morgan 1981; Driscoll 1984). The Al<sub>i</sub> input from terrestrial sources ( $194\text{--}219 mmol m^{-2} yr^{-1}$ ) increased up to  $30\text{--}54 mmol m^{-2} yr^{-1}$  by liberation of Al<sub>o</sub> from organic complexes. This increase was calculated as the decrease in Al<sub>o</sub> fluxes. Although a part of this decrease could be associated with DOC coagulation (e.g., Driscoll and Postek 1996), the importance of photochemical liberation of Al<sub>o</sub> was evident from laboratory experiments (*see below*). From 32 to 63% of the total in-lake pool of Al<sub>i</sub> was completely hydrolyzed and resulted in production of Al<sub>part</sub>. A major part of Al<sub>part</sub> was removed from the water column by sedimentation. The Al<sub>part</sub> buried in the bottom represented a stable alkalinity sink in the ecosystem because Al oxyhydroxides are insensitive to redox changes and because the pH of surface sediments was relatively high ( $\sim 5.7$ ) despite strong water acidification.

A similar net alkalinity production (and/or retention) derived from changes in Fe speciation was less important and straightforward than that of Al and differed among the lakes

Table 4. Photo- and biodegradation laboratory experiments with water from a major surface tributary of Plešné Lake sampled in January (No. 1) and October (No. 2) 2000. Dark C, dark control; PD, photochemical degradation (time of irradiation is given in brackets); Dark C + BD, dark control after biological degradation; PD + BD, photochemical degradation followed with biological degradation.

No.	Sample treatment	pH	DOC (mmol L <sup>-1</sup> )	A <sub>254</sub> (m <sup>-1</sup> )	Al <sub>o</sub> (μmol L <sup>-1</sup> )	Fe <sub>o</sub> (μmol L <sup>-1</sup> )	H <sup>+</sup> (μeq L <sup>-1</sup> )	A <sup>-</sup> (μeq L <sup>-1</sup> )	Al <sub>i</sub> (μeq L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (μeq L <sup>-1</sup> )
1	Dark C	4.36	0.60	31	9	1.4	44	25	58	74
	PD(10 h)	4.53	0.36	17	4	0.2	30	21	66	74
	Dark C+BD	4.38	0.58	29	9	1.4	42	24	ND	73
	PD+BD	4.68	0.27	13	4	0.2	21	14	ND	69
2	Dark C	4.27	0.97	51	13	1.5	54	45	38	36
	PD(11.5 h)	4.48	0.66	26	5	0.3	33	41	55	36
	Dark C+BD	4.26	0.89	49	14	1.5	55	37	30	36
	PD+BD	4.59	0.41	20	4	0.3	26	24	33	33

studied (Table 3). The reason for this was the sensitivity of ferric oxyhydroxides to redox changes and the liberation of Fe from bottom sediments during anoxia, which was an important internal Fe source in Čertovo and Plešné Lakes with the hypolimnetic anoxia (Kopáček et al. 2001a,c). However, Fe<sub>o</sub> was the dominant Fe form in the lake tributaries (Table 2), and its liberation from organic complexes was a significant in-lake source of Fe<sub>i</sub>, especially in Černé Lake, with no Fe release from sediments.

**Laboratory experiments**—Photochemical and biological degradation experiments were performed to better understand the effect of solar radiation and the following biodegradation of partially photodegraded allochthonous DOC on lake water chemistry. Chemical changes in water from the tributary of Plešné Lake followed similar patterns during photochemical decomposition and biodegradation both in winter and fall, despite different water compositions (Table 4). Irradiation of the water resulted in a continuous decrease in DOC concentrations and organically bound Fe and Al (Fig. 2A,B,C). Although DOC concentrations decreased by 40 and 32% and A<sub>254</sub> by 45 and 49% in winter and fall samples, respectively, A<sup>-</sup> concentrations decreased by “only” 16 and 7% during irradiation of the samples (Table 4). This disproportion resulted from two parallel yet opposing processes: (1) a decrease in A<sup>-</sup> concentrations because of DOC oxidation and (2) an increase in the concentration of ionized carboxylic functional groups after liberation of organically bound metals by partial ionization of the original A<sup>-</sup> at higher pH. The ratio of organic acid anions to DOC concentrations (A<sup>-</sup>:DOC) increased by ~17 meq mol<sup>-1</sup>, whereas the ratio of organically bound metals to DOC concentrations ([Al<sub>o</sub> + Fe<sub>o</sub>]:DOC) decreased by 5 mmol mol<sup>-1</sup> during the photochemical decomposition in both experiments. This suggests that charge density (i.e., the concentration of ionizable carboxylic functional groups per mole of DOC) increased after the liberation of Al<sub>o</sub> and Fe<sub>o</sub> from organic complexes. The liberation of organically bound metals increased concentrations of Al<sub>i</sub> and Fe<sub>i</sub> (Fig. 2B,C). These changes affected the mass balance of H<sup>+</sup>. The concentration of H<sup>+</sup> decreased by 14 and 21 μeq L<sup>-1</sup> during the irradiation of winter and fall samples, respectively, and their decline was compensated for by the decrease in A<sup>-</sup> concentrations (4 and 3 μeq L<sup>-1</sup>) and increase in Al<sub>i</sub><sup>n+</sup> (8 and 16 μeq L<sup>-1</sup>) and Fe<sub>i</sub><sup>n+</sup> (~1 μeq L<sup>-1</sup>) concentrations. During irradiation, a

part of the allochthonous humic acids was photochemically oxidized to inorganic carbon, but another part was partly degraded and partly protonated (the functional groups originally bound with metals) to reach a new equilibrium with respect to pH. Consequently, the pH of samples increased during the photochemical decomposition (Table 4; Fig. 2E).

Chemical changes in water composition after biological degradation were significantly more pronounced in the irradiated samples than in the dark controls and depended on the time of irradiation (Table 4; Fig. 2). Over the 28-d incubation, DOC concentrations decreased slightly (by 0.02 and 0.08 mmol L<sup>-1</sup>) in winter and fall dark controls, respectively. However, DOC removal in the longest irradiated samples was 0.33 and 0.56 mmol L<sup>-1</sup> in winter and fall experiments, respectively, compared to the original water composition (Table 4). Photochemical oxidation accounted for a major part of this total removal of DOC (72 and 55% in winter and fall samples, respectively), and the contribution of biological degradation was less significant (Table 4). The effects of photochemical and biological degradation on changes in A<sub>254</sub> values were similar to DOC, with the prevailing effect of photodegradation. However, biological degradation was a dominant sink for A<sup>-</sup>, accounting for 64 and 85% of the total A<sup>-</sup> removal (11 and 21 μeq L<sup>-1</sup> in winter and fall samples, respectively, Table 4).

Biodegradation of A<sup>-</sup> was coupled with a pH increase (Fig. 3D,E) and was a major alkalinity-producing process during the whole experiment. The reduction of NO<sub>3</sub><sup>-</sup> by the bacterial community during incubation was another process partly contributing to the total alkalinity production but accounted for only ≤5 μeq L<sup>-1</sup> (Table 4). Concentrations of SO<sub>4</sub><sup>2-</sup> were stable, and changes in concentrations of other ions (e.g., NH<sub>4</sub><sup>+</sup>) were negligible with respect to ionic balance.

The H<sup>+</sup> mass budgets were more complicated than budgets for the previous ions. At increasing pH, Al<sub>i</sub><sup>n+</sup> ions hydrolyzed, their concentration decreased (Fig. 2F), and the equivalent amount of H<sup>+</sup> was generated. For example, Al<sub>i</sub><sup>n+</sup> hydrolysis produced 22 μeq L<sup>-1</sup> of H<sup>+</sup> in the irradiated sample after its biological decomposition during the fall experiment (the change in Al<sub>i</sub><sup>n+</sup> concentration in the irradiated sample after its biodegradation, Table 4). In parallel, the concentration of H<sup>+</sup> ions in the sample decreased by 7 μeq L<sup>-1</sup>. Consequently, biochemical changes removed 29 μeq L<sup>-1</sup> of H<sup>+</sup>. Decline in A<sup>-</sup> and NO<sub>3</sub><sup>-</sup> compensated for 20 μeq L<sup>-1</sup> of

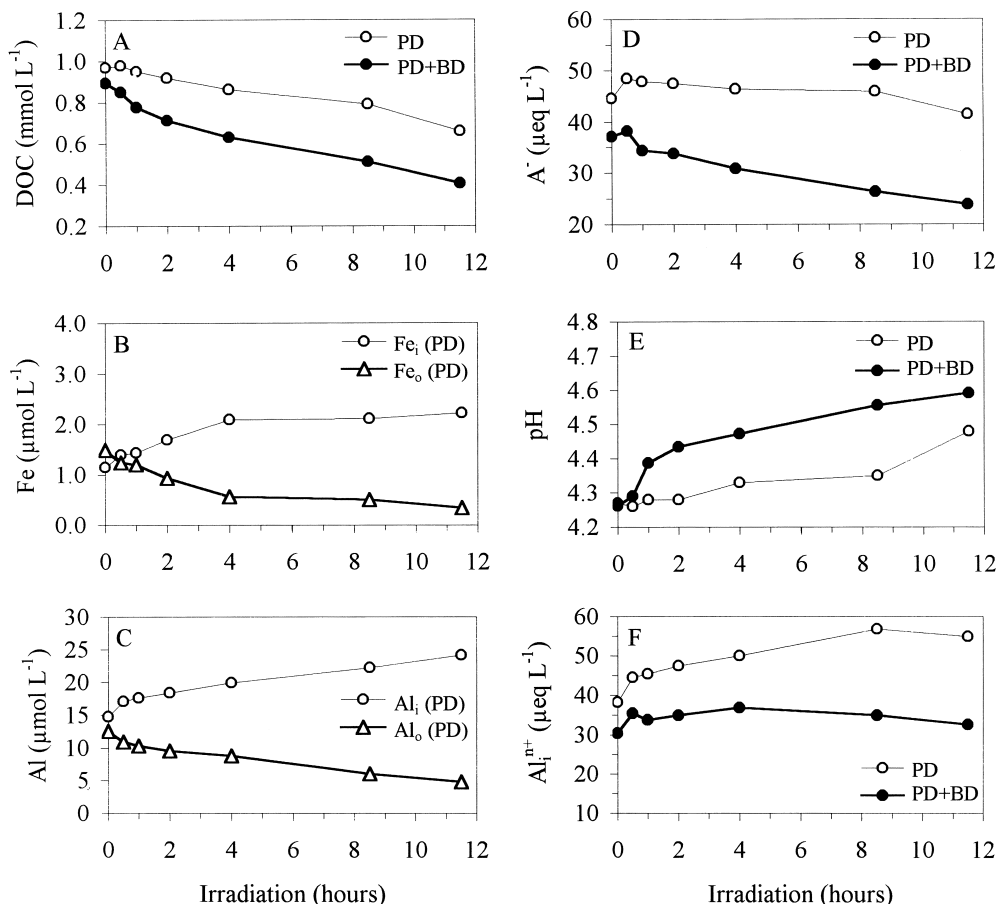


Fig. 2. Chemical changes in water composition during photochemical and biological degradation of the October 2000 sample from Plešné Lake tributary. PD, photochemical degradation; PD + BD, photochemical and biological degradation.

the  $H^+$  removal. Because the carbonate buffering system of the sample was depleted, the remaining  $9 \mu\text{eq L}^{-1}$  of  $H^+$  was probably removed by protonation of DOC. Changes similar to  $Al_i$  speciation were also observed for  $Fe_i$ , but being of less importance ( $\sim 1 \mu\text{eq L}^{-1}$ ) in the  $H^+$  budgets, they were neglected in Table 4.

## Discussion

*Allochthonous organic matter*—The most pronounced gradients between the input and output DOC concentrations occurred during the ice-free period. As an example, a 5-yr pattern of DOC concentrations and its molar absorptivity in tributaries and outlet of Čertovo Lake is given in Fig. 3. A mixing of the epilimnetic water with precipitation (14–17% of the total water input of the lakes), which had four to eight times lower DOC concentrations than the tributaries, could explain only 20–40% of the decrease in DOC concentrations between tributaries and outputs (Table 2). Consequently, the summer decreases in in-lake DOC concentrations and molar absorptivity (Fig. 3) resulted from some DOC-removing processes. Such shifts in DOC quantity and quality could be a result of either Al-mediated coagulation and flocculation or

photochemical oxidation of the aromatic portions of allochthonous organic matter (Donahue et al. 1998).

During the ice-free period, lakes were exposed to solar radiation, which suggested an important effect of photochemical processes in the development of a DOC gradient. Like the laboratory experiments (Fig. 2), the in-lake concentrations of DOC and its molar absorptivity decreased under exposure to solar radiation compared to that of tributaries, exhibiting the most pronounced differences from May to October. However, the temperature of epilimnetic waters increased up to  $20^\circ\text{C}$  during the ice-free period (Kopáček et al. 2001a,b,c), which implied more favorable conditions of oversaturation with respect to the  $Al(OH)_3$  solubility and a higher potential of DOC coagulation by particulate Al because the solubility of  $Al(OH)_3$  decreases inversely with temperature (e.g., Lydersen et al. 1990). Coagulation and coprecipitation of humic acids with positively charged colloidal Al or Fe oxyhydroxides and sedimentation of resulting particles is a well-known water treatment technique and also occurs under natural conditions in acid lakes with terrestrial transport of Al (e.g., Dickson 1978; Effler et al. 1985; Driscoll and Postek 1996). In accordance, in-lake removal of DOC ( $1.6\text{--}3.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ ) and production of  $Al_{\text{part}}$  ( $61\text{--}$

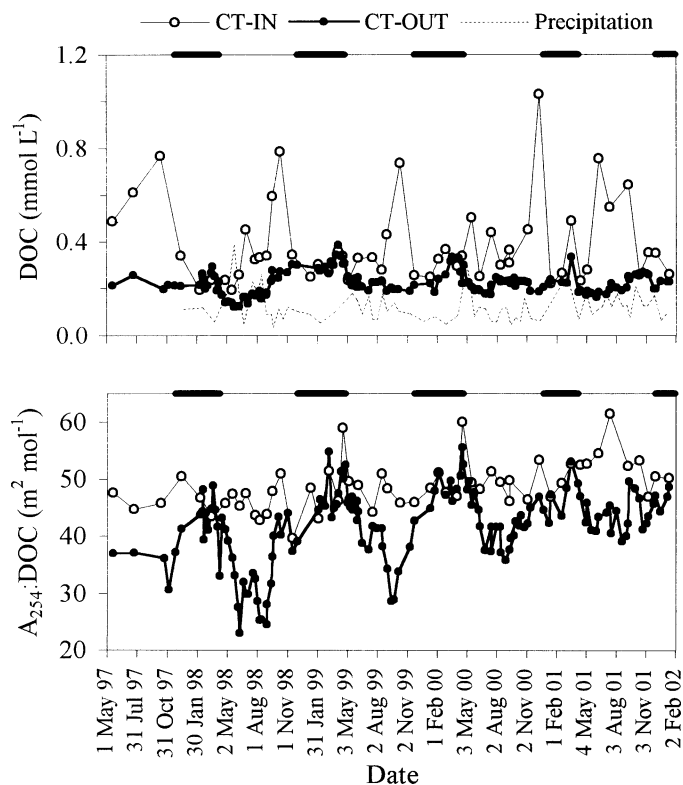


Fig. 3. Seasonal variability in DOC concentrations and its molar absorptivity at 254 nm in precipitation, tributaries (CT-IN, discharge-weighted mean of seven inlets), and output of Čertovo Lake (CT-OUT). Horizontal solid lines represent periods of ice cover. Data come from Kopáček et al. (2000a, 2001a, unpubl. data).

156 mmol m<sup>-2</sup> yr<sup>-1</sup>) were lowest in Čertovo Lake and highest in Plešné Lake, reflecting pH gradients between tributaries and lakes (Kopáček et al. 2001a,b,c). This suggested that a part of DOC could be removed from the water column as metal humates (Lydersen 1998).

The conservative/nonconservative nature of Al<sup>3+</sup> in the lakes over the annual cycle was illustrated by SI (Fig. 4). SI > 0 suggests oversaturation with respect to the solubility of the mineral phase, SI = 0 indicates equilibrium, and SI < 0 represents undersaturation (Driscoll and Postek 1996). In summer, the epilimnetic waters of all three lakes were oversaturated with respect to the solubility of synthetic gibbsite, but their oversaturation with respect to the solubility of amorphous Al(OH)<sub>3</sub> was reached only in Černé and Plešné Lakes, which had higher pH (Fig. 4A,B,C). A relationship between Al<sub>part</sub> + Fe<sub>part</sub> and C<sub>part</sub> in the lake outputs showed that the average content of metals associated with particulate organic matter was 44 mmol mol<sup>-1</sup> (Fig. 4D), with an average 80% contribution of Al<sub>part</sub>. This value was ~3-fold higher than the (Al<sub>o</sub> + Fe<sub>o</sub>):DOC ratio in tributaries (Fig. 1C) and indicated a coprecipitation of organic matter with metals. However, the thermodynamically favorable conditions of Al(OH)<sub>3</sub> formation were followed by elevated Al<sub>part</sub> and C<sub>part</sub> concentrations only in Plešné Lake (Fig. 4C), with the highest DOC concentrations (Table 2), whereas Al<sub>part</sub> and C<sub>part</sub> concentrations varied independently of the SI values within narrower ranges in the other two lakes. These results

suggested that coagulation of allochthonous organic carbon by Al and Fe hydroxides was roughly stable throughout the year in Černé and Čertovo Lakes and that the seasonal variation in in-lake DOC quantity and quality (Fig. 3) was more probably associated with photochemical processes. In contrast, DOC coagulation by Al hydroxides and coprecipitation with Al<sub>part</sub> more likely dominated over the total removal of DOC in Plešné Lake.

In contrast to the laboratory experiments, the mass budget data do not allow us to estimate the amount of DOC that was photooxidized to inorganic carbon or converted to bioavailable forms in the lakes. Bertilsson and Tranvik (2000) found that an average photoproduction of carboxylic acid carbon represented 34% of the produced inorganic carbon in 38 Scandinavian Lakes. Similarly, in our photo- and biodegradation experiments, biological degradation was a less effective DOC sink than photooxidation (Table 4). However biological degradation was a more important sink for A<sup>-</sup>. The major part of alkalinity production during the photochemical degradation of allochthonous organic matter was associated with the partial protonation of carboxylic functional groups after liberation of organically bound metals. However, partial photochemical degradation of allochthonous DOC produced biologically available low-molecular weight organic anions (e.g., Bertilsson and Tranvik 2000), the biodegradation of which represented the most significant source of alkalinity in the whole process. A comparison between the available data on measured in-lake removal of A<sup>-</sup> and DOC loading of the Bohemian Forest lakes (Fig. 5) suggests a close relationship between terrestrial DOC transport and internal alkalinity production due to its photochemical and biological degradation. Consequently, this internal alkalinity-producing process should be of great importance in forest or humic lakes, which naturally have high concentrations of allochthonous DOC, low concentrations of NO<sub>3</sub><sup>-</sup>, and low or no bicarbonate alkalinity.

However, net alkalinity production associated with the photo- and biodegradation of allochthonous DOC is lower than the sum of alkalinity production from photoliberation of Al<sub>i</sub> (or Fe<sub>i</sub>) from organic complexes and the biodegradation of A<sup>-</sup>. Three moles of H<sup>+</sup> are consumed when a mole of Al<sup>3+</sup> is liberated from organic complexes. However, Al<sup>3+</sup> hydrolyzes and decreases its charge to n<sub>OUT</sub> (a charge of Al<sub>i</sub> in the lake output), producing (3 - n<sub>OUT</sub>) moles H<sup>+</sup> mol<sup>-1</sup> photoliberated organically bound Al (Al<sub>o</sub><sup>PP</sup>). Thus, net H<sup>+</sup> production associated with the photochemical liberation of Al<sub>o</sub><sup>PD</sup> can be calculated as in Eq. 4.

$$H^+ = -n_{OUT}Al_o^{PD} \quad (4)$$

Equation 4 implies that photochemical liberation of Al<sub>i</sub> from Al<sub>o</sub> is an alkalinity-producing process, and its significance depends on lake water pH. In acid waters (e.g., forest lakes or bogs), the n<sub>OUT</sub> value is high and more alkalinity is generated. A decrease in Al<sub>o</sub> concentrations during the experimental irradiation of acid samples was accompanied by a significant H<sup>+</sup> decrease as well (Table 4). In contrast, Al<sub>o</sub><sup>PD</sup> is nearly completely hydrolyzed into oxyhydroxides at pH > 6, and net alkalinity production, associated with its photoliberation, is negligible. Driscoll and Postek (1996) summarized results on mass balances of Al for several lakes,

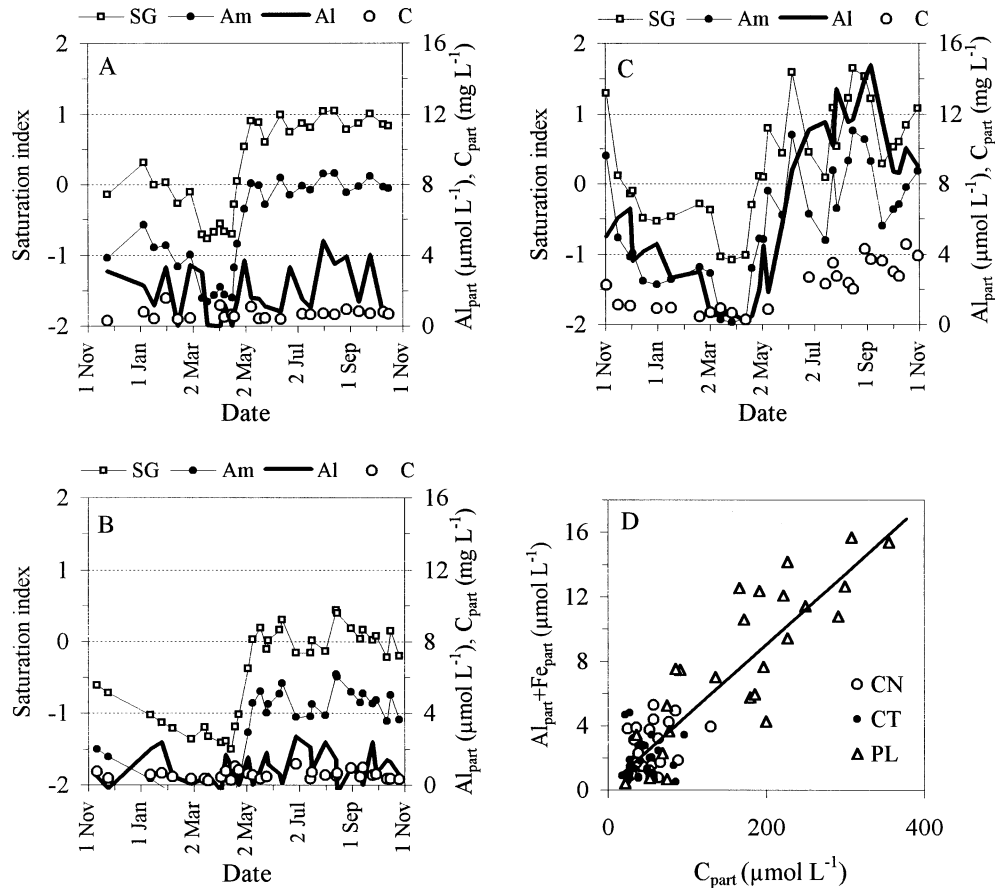


Fig. 4. Seasonal changes in concentrations of particulate Al ( $Al_{part}$ ) and particulate organic carbon ( $C_{part}$ ) and the saturation index with respect to the solubility of synthetic gibbsite (SG) and amorphous  $Al(OH)_3$  (Am) for (A) Černé Lake, (B) Čertovo Lake, and (C) Plešné Lake in hydrological year 2000. (D) The relationship of  $C_{part}$  versus  $Al_{part} + Fe_{part}$ . Solid line represents linear regression:  $(Al_{part} + Fe_{part}) = 0.2 + 0.044DOC$  ( $r = 0.88$ ). CN, Černé Lake; CT, Čertovo Lake; PL, Plešné Lake.

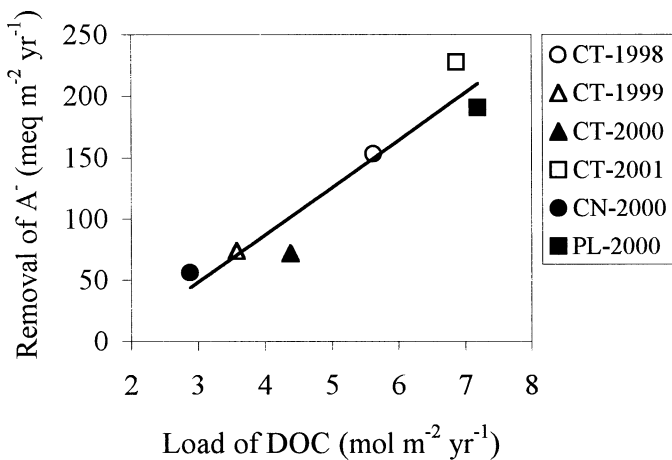


Fig. 5. The relationship between terrestrial and atmospheric loading of the Bohemian Forest lakes with DOC and in-lake removal of organic acid anions ( $A^-$ ). Solid line represents linear regression  $y = 39x - 68$ ,  $r = 0.95$ . CN, Černé Lake; CT, Čertovo Lake; PL, Plešné Lake; numbers identify hydrological years. Data come from Kopáček et al. (2000a, 2001a,b,c, unpubl. data).

showing significant retention of total Al and  $Al_o$  but little retention of  $Al_i$ . We hypothesize that a part of this disproportion could be due to photochemical liberation of  $Al_i$  from  $Al_o$ , which contributed to the  $Al_i$  pools as in the laboratory experiments (Table 4).

An analogous mechanism to Al is also associated with the photoliberation of  $Fe_i$  from  $Fe_o$  but is more complicated because of the photochemical reduction of  $Fe^{III}$  to  $Fe^{II}$  and the redox reactions of iron within the humic-Fe complexes during the photochemical degradation of DOC (Gao and Zepp 1998; Emmenegger et al. 2001). These mechanisms, reducing  $Fe^{III}$  to  $Fe^{II}$ , are especially important at low pH and in the presence of humic acids, which both retard the  $Fe^{II}$  re-oxidation (Miles and Brezonik 1981).

*Implications for sites recovering from atmospheric acidification*—The Bohemian Forest lakes and their watersheds represent strongly acidified and nitrogen-saturated ecosystems in a pronounced stage of recovery from atmospheric acidification (Kopáček et al. 1998; Veselý et al. 1998). During the study, the watersheds of lakes exported more  $SO_4^{2-}$  and  $NO_3^-$  than they received by precipitation and throughfall.

The terrestrial release of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (given on a watershed area basis) ranged from 80 to 89  $\text{meq m}^{-2} \text{ yr}^{-1}$  and from 22 to 81  $\text{meq m}^{-2} \text{ yr}^{-1}$ , respectively (Kopáček et al. 2001a,b,c). This release of strong acid anions was substantially higher than the release of base cations (42–66  $\text{meq m}^{-2} \text{ yr}^{-1}$ ) and was predominantly compensated for by the terrestrial export of  $\text{Al}_i^{3+}$  (56–90  $\text{meq m}^{-2} \text{ yr}^{-1}$ ) and  $\text{H}^+$  (29–52  $\text{meq m}^{-2} \text{ yr}^{-1}$ ). Hence, the terrestrial part of the watershed–lake ecosystems was a pronounced net source of acidity, and in-lake alkalinity production was the dominant acid-neutralizing process within the whole of the ecosystems studied.

The biochemical reduction of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in sediments and water predictably dominated the internal alkalinity production in the lakes studied, as in other acidified regions of the world (e.g., Schindler 1986). The reduction of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in sediments can be modeled as a first-order reaction (Kelly et al. 1987), which implies that the intensity of these processes is related to the in-lake  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations. Consequently, the importance of in-lake alkalinity generation due to the biological reduction of sulfate and nitrate should decrease in parallel with reductions in emission, deposition, and terrestrial transport of sulfur and nitrogen compounds. The importance of cation exchange capacity of sediments among in-lake alkalinity-generating processes also declines when acidification lasts for a long period (Schiff and Anderson 1987; this study). Hence, the relative importance of in-lake removal of organic anions in the internal alkalinity production will probably increase during lake water recovery from acidification, along with the decrease in the above in-lake alkalinity sources. Moreover, we hypothesize that the future role of organic matter in internal alkalinity production can also increase absolutely for the following reasons.

1. We can expect an increase in concentrations of organic acid anions in the tributaries of the Bohemian Forest lakes as a result of the increased ionization of carboxyl groups due to declining concentrations of strong acid anions in soil solutions and increasing pH. The average contribution ( $\pm$ SD) of  $\text{A}^-$  (ionized carboxylic groups) to the anion pool of the Bohemian Forest streams was  $47 \pm 11$   $\text{meq mol}^{-1}$  of DOC. This value was 26  $\text{meq mol}^{-1}$  lower than the average total content of ionizable carboxylic groups there because their ionization was not complete at ambient low pH values (Kopáček et al. 2000b). This fact indicates that the acidifying potential of organic matter in the Bohemian Forest streams can increase by up to one third during the further recovery from acidification. A similar increase in  $\text{A}^-$  concentrations at stable DOC concentrations has already been observed during acid-removing “roof” experiments (Wright et al. 1988). In such cases, the in-lake photochemical and biological degradation of allochthonous organic matter will neutralize a larger negative charge per mole of DOC and will be a more significant internal alkalinity-producing process.
2. The increase in soil water pH can lead to increased dissociation of acidic organic matter and, consequently, to increased leaching of DOC. Moreover, the exclusion of strong acid anions from atmospheric deposition is fol-

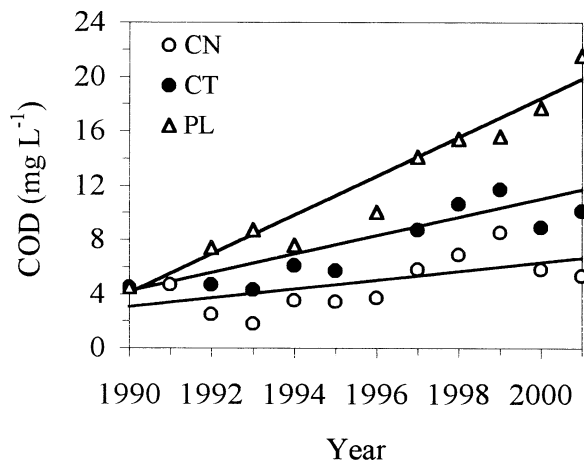


Fig. 6. The 12-yr trend in the epilimnetic concentrations of chemical oxygen demand (COD), determined according to Hejzlar and Kopáček 1990 in 200- $\mu\text{m}$  filtered waters (October samples). Solid lines represent linear regressions with slopes of 0.4, 0.7, and 1.4  $\text{mg yr}^{-1}$  and significance of  $p < 0.05$ ,  $p < 0.001$ , and  $p < 0.001$  in CN, CT, and PL, respectively. CN, Černé Lake; CT, Čertovo Lake; PL, Plešné Lake.

- lowed by decreased concentrations of aluminum and calcium in surface waters (e.g., Wright et al. 1988; Kopáček et al. 1998), which can lead to lesser precipitation of organic acids as metal humates (Lydersen 1998). If these processes were inverse to the acidification-derived loss of DOC from lake water (e.g., Davis et al. 1985; Steinberg 1991), they could lead to increased DOC concentrations during an ecosystem recovery from acidification. Such a recovery in DOC quantity (and also quality) with recovery from acidification was observed in experimentally acidified lakes at the Experimental Lakes Area (Donahue et al. 1998). Similarly, a recent increase in DOC concentrations has been reported by Evans and Monteith (2001) in surface waters in the United Kingdom. An increase in the concentration of organic matter in the Bohemian Forest lakes is also evident from long-term data on chemical oxygen demand given in Fig. 6. However, uncertainty exists at present as to whether these changes are really linked to the reduction of mineral acidity or to climatic changes (Evans and Monteith 2001). Moreover, the Bohemian Forest data are based on samples filtered through a 200- $\mu\text{m}$  polyamide sieve, so they could also partly reflect any change in phytoplankton production. Nevertheless, despite their origins, the above increasing trends in freshwater concentrations of organic matter suggest a possible further increase in terrestrial DOC input into the lakes and a consequent increase in the internal alkalinity production due to its photo- and biodegradation (Fig. 3).
3. The increasing intensity in ultraviolet (UV)-B radiation can increase the photochemical decomposition of organic matter and the penetration of UV-B radiation, which could further accelerate the decomposition of DOC (Schindler et al. 1996).

On the other hand, net alkalinity gain from photo- and biodegradation of DOC can be mitigated during the ecosys-

tem's recovery from acidification by several processes. (1) The degree of hydrolysis of the  $Al_i$  liberated from  $Al_o$  will increase at higher pH (Eq. 3). (2) The ratio of  $Al_o$ :DOC in tributaries could decrease with increasing pH (Browne and Driscoll 1993; Driscoll and Postek 1996). However, the necessary pH increase should be substantially higher than the pH range in Fig. 1D, where no decrease in  $Al_o$ :DOC was evident. According to the experience from the Hubbard Brook Experimental Forest (Likens et al. 1996), as well as the Bohemian Forest lakes (Veselý et al. 1998), the sufficient pH increase of  $>5.5$  will be unlikely to occur in the tributaries studied within the next several decades. (3) Negative relationships between the efficiency of DOC photodegradation and pH (e.g., Donahue et al. 1998; Gao and Zepp 1998, Bertilsson and Tranvik 2000) suggest that in-lake photochemically induced alkalinity production can decrease with increasing lake water pH.

Although the relative importance of in-lake alkalinity generation due to the photochemical and biological degradation of allochthonous organic matter will undoubtedly increase during the ecosystem recovery from acidification, its absolute change is difficult to predict at the present stage of knowledge. Despite the predictable increase in terrestrial DOC export and the concentration of  $A^-$ , the final extent of in-lake alkalinity production can be negatively affected by the slower pH-dependent reaction kinetics of DOC photodegradation.

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