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# Photochemical Production of Ionic and Particulate Aluminum and Iron in Lakes

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Photochemical liberation of allochthonous organically bound aluminum (Al) and iron (Fe) and in-lake hydroxide precipitation are important sources of these metals to lake sediments. Mass budgets of ionic Al and Fe ($Al_i$, $Fe_i$), organically bound Al and Fe ($Al_o$, $Fe_o$), and particulate Al and Fe ($Al_p$, $Fe_p$) were measured for two western Czech Republic forest lakes (Plešné and Čertovo) in the 2000−2003 hydrological years. The lakes were net sinks of $Al_i$, $Al_o$, and $Fe_o$ and net sources of $Al_p$ and $Fe_p$. The average $Al_o$ and $Fe_o$ inputs from terrestrial sources (66−110 and 12−17 mmol $m^{-2}$ $yr^{-1}$, respectively, on a lake area basis) were reduced 45% and 25% in the lakes. Mass budgets of dissolved organic carbon, particulate organic C, and Al species indicated that only a minor part of the observed in-lake retention of $Al_o$ could be explained by coagulation and sedimentation of organic matter, or from $Al_i$ hydrolysis and formation of $Al_p$. Laboratory experiments with a short-time irradiation (∼300 nm, ∼800 W $m^{-2}$) of water from inlets to Plešné Lake showed the importance of photochemical processes in the liberation of Al and Fe from $Al_o$ and $Fe_o$. After 12 h of irradiation, $Al_o$ and $Fe_o$ concentrations decreased 54 ± 6% and 70 ± 16%, respectively, compared to those of the dark controls. The photoliberated $Al_o$ and $Fe_o$ increased the $Al_i$ and $Fe_i$ concentrations reciprocally, on a 1:1 mass basis. The subsequent hydrolysis of $Al_i$ and $Fe_i$ in lakes forms insoluble hydroxides, increasing the sediment concentrations of Al and Fe.

## Introduction

The biogeochemistry of aluminum (Al) is poorly understood although this element is the most abundant metal in the lithosphere (*1*). The use of Al in water treatment technologies led to early relatively detailed studies on Al hydrolysis and formation of hydroxy complexes in artificial aquatic systems (*2*, *3*). In contrast, Al chemistry in natural waters has been of less concern than that of other elements, because Al is not a plant or animal nutrient (*4*). The interest in aquatic Al chemistry has grown since the 1970s, when increased concentrations were documented in soil solutions and waters acidified by long-range transport of S and N compounds (*5*−*7*). The elevated concentrations of ionic (and other bioavailable) forms of aluminum ($Al_i$) in the biosphere were recognized to be toxic for a variety of terrestrial and aquatic organisms (*8*−*10*) and were also suspected of contributing to human chronic diseases such as Alzheimer's disease (*11*).

Detailed studies on mass fluxes of Al species consistently show that lakes in different regions retain $Al_i$ and organically bound aluminum ($Al_o$) (*1*). In-lake retention of $Al_i$ is a result of hydrolysis, formation of Al−hydroxy complexes, and precipitation of insoluble particulate Al ($Al_p$) under higher pH conditions in lakes than in their inlets. The pH gradient between lake inputs and output results from (i) degassing of $CO_2$ from soil solutions emerging to surface waters (*12*), (ii) mixing of waters of different acidities (*9*, *13*), and (iii) in-lake alkalinity production due to biochemical reduction of $SO_4^{2-}$ and $NO_3^-$, cationic exchange at the sediment water interface (*14*, *15*), and photochemical and microbial decomposition of dissolved allochthonous organic acids (*16*). Additionally, mixing of anoxic discharging groundwater with oxygenated surface water causes hydrolysis and precipitation of iron hydroxides (*17*). Despite relatively well-described mechanisms of in-lake retention of $Al_i$, the reason why lakes are such efficient sinks for $Al_o$ (up to 81%) (*1*) has not been satisfactorily explained. Here, we show that photochemical transformation of dissolved allochthonous organic matter is an important process that liberates $Al_o$ and $Fe_o$ from organic complexes, as well as supplies potentially toxic $Al_i$ species in lakes.

## Materials and Methods

**Site Description.** Plešné and Čertovo Lakes are in the Bohemian Forest of the Czech Republic (Middle Europe, 13°−14° E, 49° N, ∼150 km south of Prague) at altitudes of 1028 and 1090 m above sea level, respectively. The lakes are of glacial origin (tarns), with surface areas of 7.5 and 10.5 ha, maximum depths of 18 and 36 m, and water residence times of 0.7 and 1.6 yr, respectively. Their watershed areas are 67 and 88 ha, with maximum local relief of 288 and 313 m, respectively. Soils developed from till are thin and acidic. Both watersheds are fully forested by ∼150 yr old Norway spruce (*Picea abies*) (*19*, *20*). Plešné Lake is mesotrophic with Secchi transparency of 1−1.5 m, and Čertovo Lake is oligotrophic with transparency of 3−5 m. The thermocline depth is 4−5 m in both lakes. The lakes were acidified by atmospheric deposition to pH < 5 before the 1970s (*18*).

**Sample Collection and Analyses.** Al and Fe inputs (terrestrial export via lake inlets plus atmospheric deposition) and surface outputs were based on mass balances of water and concentrations of inorganic, organic, and particulate species during the 2000−2003 hydrological years, from November 1999 to October 2003 (*19*, *20*) (Figure 1). Terrestrial export was measured for all tributaries (four for Plešné Lake and seven for Čertovo Lake). Atmospheric deposition of water and elements was measured in two forested areas and one area without trees in each watershed. The latter deposition was assumed to represent atmospheric inputs of elements to the lake surfaces. The water balance was based on the atmospheric deposition to the watershed plus lake surface, and outflow from the lake (a gauge recorder at a weir). The Al and Fe fluxes were obtained by linking discharge with the corresponding concentration by the method of period-weighted mean (*21*). Atmospheric deposition, inlets, and outlets were sampled for each lake at 2−4 week intervals throughout the year and more frequently (1−3 week intervals) during spring. The annual change in the storage of metals

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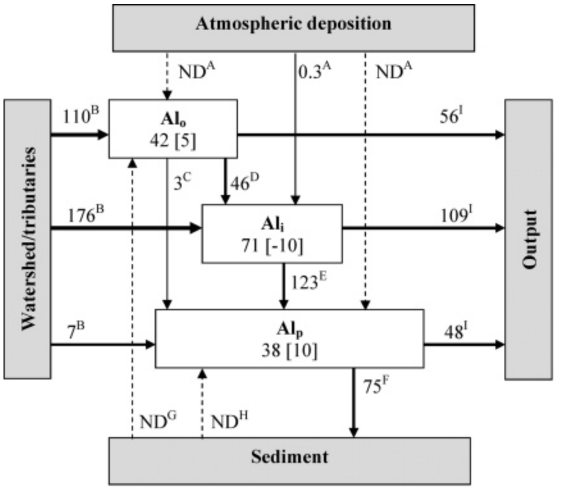

A Direct atmospheric input of $Al_T$ was set equal to $Al_i$.
B Input by tributaries.
C Coagulation of $Al_o$ containing DOC.
D Photochemical liberation of $Al_o$.
E $Al_i$ hydrolysis and formation of Al hydroxides.
F Sedimentation of $Al_p$ (measured accumulation rate of Al in sediment is 81 mmol $m^{-2}$ $yr^{-1}$) (*25*).
G Liberation of $Al_o$ from sediments (not measured; neglected)
H Sediment re-suspension (not measured; neglected – most sediments are below the thermocline).
I Output from the lake by outflow.

**FIGURE 1. Average values of major fluxes and pools of organically bound, ionic, and particulate Al ($Al_o$, $Al_i$, and $Al_p$, respectively) in Plešné Lake in the 2001−2003 hydrological years. Arrows represent Al fluxes (mmol $m^{-2}$ $yr^{-1}$, on a lake area basis). Boxes represent pools of Al forms (mmol $m^{-2}$) with annual changes in their storage in the lake (mmol $m^{-2}$ $yr^{-1}$) given in brackets. Total Al concentration is given by $[Al_T] = [Al_o] + [Al_i] + [Al_p]$.**

in lakes was calculated using the lake volumes and water column composition (five depths along the vertical profile) at the end and beginning of the hydrological years. Details on mass budget studies are given in refs *16*, *19*, and *20*.

Fractionation of Al according to Driscoll (*22*), i.e., total Al ($Al_T$), dissolved Al ($Al_D$), and $Al_o$, was determined at 20−25 °C from unfiltered samples, filtered samples (glass-fiber filter of 0.4 $\mu$m pore size), and cation-exchanged filtered samples, respectively; Al in all fractions was measured following Dougan and Wilson (*23*). The concentration of $Al_i$ is defined as the difference between the $Al_D$ and $Al_o$ concentrations. The concentration of $Al_p$ is defined as the difference between the $Al_T$ and $Al_D$ concentrations. The Fe species ($Fe_T$, $Fe_i$, $Fe_o$, and $Fe_p$) were isolated analogously to Al species, and measured by a thiocyanate colorimetric method after sample digestion with perchloric acid (*16*). Dissolved organic carbon (DOC) was analyzed with a TOC 5000A analyzer (Shimadzu). Concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$, and $F^-$ were analyzed by ion chromatography (Dionex IC25).

The accuracy and precision of analytical methods were checked by means of standard samples, which were assayed with each series of field and laboratory samples (including all experiments). For example, in 2003, the coefficients of variation of the means for pH (4.3), [DOC] (0.33 mmol $L^{-1}$), $[Al_D]$ (19.5 $\mu$mol $L^{-1}$), and $[Fe_D]$ (1.5 $\mu$mol $L^{-1}$) were 1%, 7%, 4%, and 5%, respectively (average values given in parentheses). The accuracy of the analyses was also checked using ion balance calculations for each sample (*24*). The differences between the sum of the cations and the sum of the anions were $<\pm5\%$ of the ionic concentration for all fluxes used in this study (*16*, *19*, *20*). Changes in speciation between $Al_o$ and $Al_i$ and between $Fe_o$ and $Fe_i$ were checked by mass balance.

The accuracy of in-lake mass budgets of ions (including organic acid anions and $Al_i$ and $Fe_i$) was checked by a comparison of the measured and calculated in-lake retention of $H^+$. The measured $H^+$ retention was based on pH measurements in terrestrial and atmospheric inputs and outputs. The calculated $H^+$ retention was the difference between the net in-lake retention of all anions and all cations (except for $H^+$). The 2000−2003 averages for the measured and calculated in-lake $H^+$ retention were both 0.27 mol $m^{-2}$ $yr^{-1}$ in Plešné Lake and 0.23 and 0.26 mol $m^{-2}$ $yr^{-1}$, respectively, in Čertovo Lake. The differences between measured and calculated element fluxes were tested at Plešné Lake for the storage of aluminum, carbon, nitrogen, and phosphorus in sediments (*25*). The average difference between the measured and calculated fluxes was ±9%.

**Saturation Index.** The conservative/nonconservative nature of $Al_i$ in the lakes was evaluated using the mineral-saturation index (SI) (*1*). SI is defined 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 ($\log K_r = 8.11$ at 25 °C). The temperature dependence for $K_r$ was estimated from the van't Hoff equation $[d \ln(K_r)/dT = \Delta_r H°/RT^2]$, where $R$ is the gas constant (8.314 J $K^{-1}$ $mol^{-1}$), $T$ is the absolute temperature (K), and $\Delta_r H°$ is enthalpy change of the reaction. A $\Delta_r H°$ of −95.4 kJ $mol^{-1}$ was used (25 °C), and its small change with temperature was neglected (*26*). An SI value $< 0$ represents undersaturation with respect to the solubility of $Al(OH)_3$, SI $= 0$ indicates saturation, and SI $> 0$ indicates supersaturation. We assumed that all $Al_i$ could be hydrolyzed (i.e., $Q_P$ was based on measured $Al_i$ and assumed equal to $Al_i$ activity; i.e., activity coefficients were close to 1). Additionally, other inorganic Al complexes (*27*) were ignored. These assumptions produced maximum SI values.

**Irradiation.** Photochemical experiments were carried out with water from the major surface inlet of Plešné Lake taken five times with different chemistries and hydrologies. Water samples were filtered through membrane filters (pore size 0.2 $\mu$m) before irradiation. One subsample was a dark control. A second subsample was irradiated for 0.5, 1, 2, 4, 10, and 12 h in a Rayonet reactor RPR 100 equipped with RPR 3000 A lamps (Branford, CT). The lamps provide UV light in the region 254−350 nm; wavelengths under 300 nm were filtered out by a glass filter. The quanta flux incident upon the reaction vessel was $1.24 \times 10^{-5}$ einstein $cm^{-2}$ $min^{-1}$ (∼800 W $m^{-2}$), as determined at 297−313 nm by ferrioxalate actinometry (*28*). The spectrophotometric method with 1,10-phenanthroline (molar adsorption coefficient at 510 nm of $1.1 \times 10^4$ $mol^{-1}$ L $cm^{-1}$) was used for determination of $Fe^{2+}$ in samples before and during irradiation. The temperature of the samples was 38−41 °C during irradiation. Temperature effects on sample composition were evaluated for two samples and had about an order of magnitude lower effect than the irradiation (e.g., 12 h heating of sample E at 40 °C caused 6−15% changes in $Al_i$, $Al_o$, $Fe_i$, and $Fe_o$ concentrations compared to those after 12 h of irradiation). However, higher temperature probably led to more rapid kinetics than would occur under environmental conditions.

## Results and Discussion

**Mass Budget Studies.** Watersheds of both lakes received acidic precipitation, with a volume-weighted mean pH of 4.9. Lake inputs were even more acidic (pH 4.3) due to high terrestrial export of strong acid anions ($SO_4^{2-}$ and $NO_3^-$) and organic acids (DOC) (Table 1). This anion export to the lakes was compensated by leaching of $Al_i$ (17 $\mu$mol $L^{-1}$), which dominated (60−70%) the $Al_T$ pool. $Al_o$ formed from 30% to 40% of $Al_T$, and $Al_p$ was negligible in the lake inlets. Higher pH in the lakes caused $Al_i$ hydrolysis (*2*) and an increase in $Al_p$ concentrations ($[Al_p] = [Al_T] - [Al_i] - [Al_o]$) and its

**TABLE 1. Volume-Weighted Mean Composition of Precipitation (PREC), Terrestrial Input (IN; all tributaries), and output (OUT) of Plešné and Čertovo Lakes in the 2000−2003 Period[a]**

| | Plešné Lake | | | Čertovo Lake | | |
|---|---|---|---|---|---|---|
| | PREC | IN | OUT | PREC | IN | OUT |
| $H^+$ | 12 | 41 | 17 | 15 | 55 | 34 |
| $Ca^{2+}$ | 5 | 19 | 19 | 7 | 12 | 12 |
| $Mg^{2+}$ | 1 | 7 | 7 | 2 | 13 | 13 |
| $Na^+$ | 8 | 45 | 38 | 10 | 31 | 29 |
| $K^+$ | 3 | 9 | 8 | 5 | 8 | 8 |
| $NH_4{}^+$ | 26 | 1 | 5 | 31 | 1 | 4 |
| $NO_3{}^-$ | 24 | 57 | 27 | 31 | 64 | 45 |
| $SO_4{}^{2-}$ | 11 | 41 | 39 | 13 | 43 | 44 |
| $Cl^-$ | 8 | 13 | 12 | 9 | 15 | 15 |
| $F^-$ | 0.3 | 3.9 | 4.0 | 0.8 | 2.1 | 2.0 |
| DOC | 86 | 695 | 368 | 102 | 475 | 281 |
| $Al_T$ | 0.2 | 28 | 19 | 0.2 | 22 | 19 |
| $Al_i$ | ND | 17 | 10 | ND | 16 | 15 |
| $Al_o$ | ND | 10.6 | 5.0 | ND | 6.2 | 2.9 |
| $Fe_T$ | 0.4 | 1.6 | 1.7 | 0.4 | 2.5 | 3.5 |
| $Fe_i$ | ND | 0.4 | 0.4 | ND | 0.9 | 0.9 |
| $Fe_o$ | ND | 1.1 | 0.7 | ND | 1.5 | 0.6 |
| water | 114 | 778 | 832 | 158 | 1093 | 1170 |

[a] Units $\mu$mol $L^{-1}$, except for water ($10^3$ $m^3$ $yr^{-1}$). ND = not determined.

**TABLE 2. Average Mass Fluxes of Major Aluminum and Iron Species in Plešné and Čertovo Lakes for 2000−2003**

| | $Al_i$ | $Al_o$ | $Al_p$ | $Al_T$ | $Fe_i$ | $Fe_o$ | $Fe_p$ | $Fe_T$ |
|---|---|---|---|---|---|---|---|---|
| **Plešné Lake** | | | | | | | | |
| input | 176 | 110 | 7 | 293 | 4 | 12 | 1 | 17 |
| change in storage | −10 | 5 | 10 | 5 | 0.5 | 0.5 | 3 | 4 |
| output | 109 | 56 | 48 | 213 | 4 | 8 | 7 | 19 |
| net production | −77 | −49 | 51 | −75 | 0 | −3 | 9 | 6 |
| **Čertovo Lake** | | | | | | | | |
| input | 167 | 66 | 3 | 235 | 9 | 17 | 1 | 28 |
| change in storage | −25 | 2 | 6 | −18 | 2 | 2 | 7 | 11 |
| output | 169 | 32 | 13 | 214 | 10 | 6 | 23 | 39 |
| net production | −23 | −32 | 16 | −39 | 3 | −9 | 29 | 23 |

[a] Units mmol $m^{-2}$ $yr^{-1}$, on a lake area basis. Total Al and Fe ($Al_T$, $Fe_T$) concentrations are sums of the concentrations of their inorganic ($Al_i$, $Fe_i$), organic ($Al_o$, $Fe_o$), and particulate ($Al_p$, $Fe_p$) forms. Net production = (output + change in storage) − input. Negative values of production indicate net removal.

proportion in $Al_T$ to 23% and 6% in the outflows from Plešné and Čertovo Lakes, respectively (Table 1).

The average input of $Al_T$ into Plešné Lake via inlets was 293 mmol $m^{-2}$ $yr^{-1}$, on a lake area basis ($Al_T$ concentration multiplied by the water flux (Table 1) and divided by the lake surface area), in the 2001−2003 period (Table 2). $Al_T$ input by direct atmospheric deposition was ~0.1% of the terrestrial load (Figure 1). Of this amount, $Al_i$, $Al_o$, and $Al_p$ represented 176, 110, and 7 mmol $m^{-2}$ $yr^{-1}$, respectively. The lake was an average net sink for 75 mmol of $Al_T$ $m^{-2}$ $yr^{-1}$ that was assumed to have been deposited in the sediments as $Al_p$. This result corresponds well with the average accumulation rate of Al in Plešné Lake sediment (81 mmol $m^{-2}$ $yr^{-1}$), estimated from the average concentration of Al in surface sediment and average mass accumulation rate of the sediment (*25*). Additionally, the lake was a net source of 51 mmol of $Al_p$ $m^{-2}$ $yr^{-1}$ that left the lake via outflow or increased its concentration in the water column (change in storage). The sum of these two fluxes represented a net in-lake production of $Al_p$ (126 mmol $m^{-2}$ $yr^{-1}$), originating from changes in the proportions of species within the lake, and decreased fluxes of $Al_i$ and $Al_o$ (38% and 49%, respectively, compared to influxes) from the lake (Table 2).

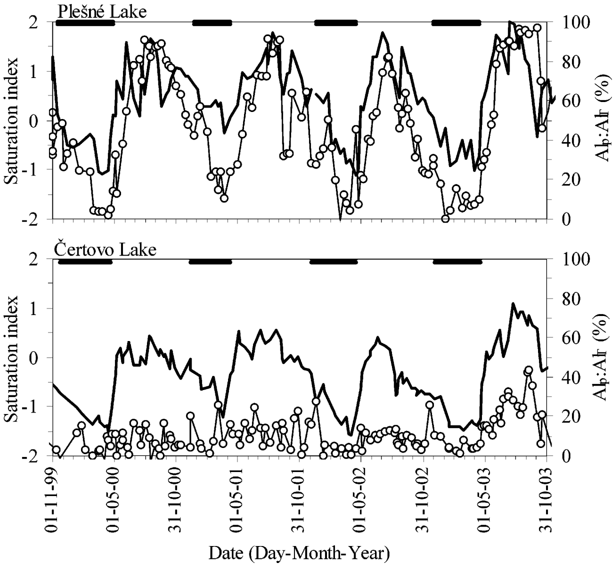

**FIGURE 2. Seasonal variations in the ratio of particulate to total aluminum ($Al_p$:$Al_T$; circles) and the saturation index (adjusted for ambient temperature) with respect to the solubility of synthetic gibbsite (solid line) for Plešné and Čertovo Lakes. Horizontal solid lines represent periods of ice cover.**

Plešné Lake was a net sink of 43−56 mmol of $Al_o$ $m^{-2}$ $yr^{-1}$ during the study period. This in-lake reduction in the $Al_o$ flux is similar to that of other lakes (*1*). Previous studies (*1*, *29*) suggested that coagulation of DOC by positively charged Al−hydroxide complexes could cause decreasing concentrations of DOC and $Al_o$ in the water column. Similar processes occur during DOC removal from drinking waters treated with aluminum salts (*3*).

The outflow from Plešné Lake was significantly oversaturated with respect to $Al(OH)_3$ as suggested by the SI values (Figure 2). Under conditions of SI > 0, formation of Al−hydroxy complexes and $Al_p$ is thermodynamically favored (*1*). $Al_p$ was the dominant form of $Al_T$ in the Plešné Lake outflow during the summer stratification periods (Figure 2), when the water pH increased to ~5 and temperature increased to ~20 °C. Such results suggest that conditions in Plešné Lake were thermodynamically favorable for $Al_i$ hydrolysis and possibly for coagulation of allochthonous organic matter, including organically bound Al. However, the detailed mass budget study for Al species and DOC for Plešné Lake in the 2001 hydrological year (*20*, *25*) showed that coagulation was not an important sink for $Al_o$. The annual discharge-weighted mean $Al_o$:DOC ratio in the inlets of Plešné Lake was 0.016 mol $mol^{-1}$. The sedimentation rate of particulate organic carbon ($C_p$) from sedimentation traps was 2211 mmol $m^{-2}$ $yr^{-1}$ (*25*). If all this sedimenting $C_p$ had originated from coagulation of allochthonous DOC, the amount of $Al_o$ converted to $Al_p$ would have been (0.016 mol $mol^{-1}$)(2211 mmol $m^{-2}$ $yr^{-1}$) = 36 mmol $m^{-2}$ $yr^{-1}$, i.e., only 64% of the measured in-lake sink of $Al_o$ (56 mmol $m^{-2}$ $yr^{-1}$ in 2001 (*20*)). However, the flux of sedimenting $C_p$ in Plešné Lake was 66% and 31% from algal and bacterial production, respectively, and coagulation of allochthonous DOC represented only ~3% (*25*). Consequently, the amount of $Al_o$ converted to $Al_p$ by direct coagulation of allochthonous DOC was probably negligible (~3 mmol $m^{-2}$ $yr^{-1}$). Assuming that the average net in-lake retention of $Al_o$ in Plešné Lake was 49 mmol $m^{-2}$ $yr^{-1}$, the dominant portion of in-lake $Al_o$ retention (49 − 3 = 46 mmol $m^{-2}$ $yr^{-1}$) was associated with different processes. From the evidence provided later, we conclude that photochemical liberation of $Al_o$ dominates this flux (Figure 1).

Čertovo Lake received water with a comparable volume-weighted mean $Al_o$:DOC ratio (0.015 mol $mol^{-1}$), but had

**TABLE 3. Discharge (*Q*) and Chemical Characteristics of the Major Inlet to Plešné Lake in the 2000−2003 Period (Upper Part), Initial Chemical Composition of Samples from This Inlet Used for Photochemical Experiments (Dark Controls A−E) (Middle Part), and Chemical Changes in Their Composition after Irradiation (Time in Parentheses) (Lower Part)**

| | *Q*, L s$^{-1}$ | pH | [DOC], mmol L$^{-1}$ | [$Al_i$], $\mu$mol L$^{-1}$ | [$Al_o$], $\mu$mol L$^{-1}$ | [$Fe_i$], $\mu$mol L$^{-1}$ | [$Fe_o$], $\mu$mol L$^{-1}$ | ($Al_o + Fe_o$):DOC ratio, mol mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| **Plešné Lake Inlet** | | | | | | | | |
| minimum | 0.1 | 4.18 | 0.60 | 7.6 | 6.3 | 0.2 | 0.7 | 0.012 |
| median | 0.7 | 4.28 | 0.90 | 13.1 | 14.0 | 0.6 | 1.8 | 0.018 |
| maximum | 5.5 | 4.41 | 1.38 | 28.2 | 17.9 | 1.6 | 2.8 | 0.023 |
| **Dark Controls** | | | | | | | | |
| A (January 2000) | 0.1 | 4.25 | 0.60 | 23.6 | 9.1 | 0.27 | 1.41 | 0.018 |
| B (October 2000) | 0.8 | 4.31 | 1.05 | 14.8 | 12.6 | 1.15 | 1.49 | 0.015 |
| C (September 2002) | 4.0 | 4.21 | 1.25 | 13.8 | 17.3 | 0.61 | 3.31 | 0.017 |
| D (March 2003) | 0.8 | 4.25 | 0.67 | 16.3 | 11.2 | 1.27 | 2.47 | 0.020 |
| E (August 2003) | 0.3 | 4.27 | 0.84 | 18.9 | 17.1 | 1.13 | 1.15 | 0.024 |
| **Chemical Changes after Irradiation** | | | | | | | | |
| A (10 h) | | 0.17 | −0.24 | 6.0 | −5.3 | 1.2 | −1.2 | −0.006 |
| B (12 h) | | 0.21 | −0.31 | 8.6 | −7.8 | 1.1 | −1.1 | −0.007 |
| C (12 h) | | 0.25 | −0.26 | 9.1 | −8.4 | 3.1 | −2.7 | −0.007 |
| D (12 h) | | 0.01 | −0.09 | 5.6 | −5.6 | 1.5 | −1.3 | −0.007 |
| E (12 h) | | 0.09 | −0.14 | 8.1 | −8.9 | 0.6 | −0.6 | −0.007 |

lower $Al_o$ loading than Plešné Lake due to lower terrestrial export of DOC (*16*, *19*, *20*). Terrestrial exports of $Al_i$ were comparable for both lakes (Table 2), because their inlets had similar pH. In contrast, the lake water pH was lower in Čertovo Lake, reaching summer maxima between 4.6 and 4.8. This difference resulted in significantly lower SI values (less favorable conditions for $Al_i$ hydrolysis), $Al_p$ formation, and DOC coagulation in Čertovo Lake (Figure 2). The loss of $Al_o$ from the input flux was 51% in Čertovo Lake over the 2000−2003 period, i.e., a percentage comparable to that in Plešné Lake (Table 2) with substantially higher SI values and $Al_p$ formation (Figure 2). In addition to the mass budget study for Plešné Lake (Figure 1), these results for Čertovo Lake provide additional evidence that indicates another process for in-lake $Al_o$ retention, other than coagulation.

Similarly to Al, the lakes were net sinks for $Fe_o$ and net sources of $Fe_p$ (Table 2). The mass budget of Fe was, however, more complicated due to the Fe liberation from sediments during periods of hypolimnetic anoxia (*19*, *20*).

**Photochemical Experiments.** Water samples used for photochemical experiments represented seasonal variability in the chemistry and hydrology of the major inlet of Plešné Lake (Table 3). All photochemical experiments demonstrated that decomposition of allochthonous DOC under irradiation was accompanied by significant changes in metal speciation. After 12 h of irradiation, DOC, $Al_o$, and $Fe_o$ concentrations decreased 24 ± 11%, 54 ± 6%, and 70 ± 16% (average ± standard deviation for samples A−E), respectively, compared to those of the dark controls. In each experiment, irradiation of the water resulted in increases in $Al_i$ and $Fe_i$ concentrations, which were reciprocal to the decreases in $Al_o$ and $Fe_o$ concentrations (Table 3). The photoliberation of $Al_o$ and $Fe_o$ from organic complexes proceeded most rapidly during the first 2 h of irradiation (Figure 3a,b), while decomposition of DOC occurred at constant rates during irradiation (Figure 3c). As a result, the ($Al_o + Fe_o$):DOC ratio of water exposed to irradiation rapidly decreased at the beginning of the experiment (Figure 3d), suggesting that the capacity of DOC to complex Al and Fe declined disproportionately rapidly compared to the loss in DOC. The changes in $Al_o + Fe_o$ concentrations (compared to that of the dark control) were more rapid than those of DOC at the beginning of irradiation (Figure 4).

An impact of solar radiation on seasonal variability in lake water ($Al_o + Fe_o$):DOC ratios occurred in the lakes. It was more pronounced in the more transparent Čertovo Lake. The average ($Al_o + Fe_o$):DOC ratio in terrestrial input to Čertovo Lake was 0.016 mol mol$^{-1}$ (Table 1). This value was reduced 13% to ~0.014 mol mol$^{-1}$ on an annual basis by dilution of terrestrial input by direct atmospheric deposition to the lake surface (see water fluxes in Table 1). The annual average ($Al_o + Fe_o$):DOC ratio in the lake outflow was 0.012 mol mol$^{-1}$ (Table 1), with maxima (0.014 ± 0.003 mol mol$^{-1}$) during the full ice cover period (January to March) and minima (0.010 ± 0.003 mol mol$^{-1}$) in summer (July to September).

The light intensity of solar radiation in the UV region between 290 and 320 nm is 0.2% (measured in Germany at the same latitude as the study lakes) (*30*) of the light intensity used in the laboratory irradiation experiments. However, short-wavelength radiation is effectively absorbed in the surface water layer of lakes. Thus, in the whole water column 23−44% of the photochemical DOC mineralization is due to higher wavelengths of photosynthetically active radiation (*31*), which was absent in the experiment. The most rapid changes in water chemistry occurred during the first 2 h of irradiation (Figure 4). Assuming the above proportions of effective radiation, the time in the reactor can be equated to approximately 500−1000 h (1−2 months) of natural sunlight conditions.

Previous studies (*1*, *29*) suggested that in-lake $Al_o$ removal (decomplexation) is caused by increased pH and decreased $Al_i$ concentrations in the lakes during the summer stratification period, i.e., a redistribution of species. An increase in pH was not responsible for the changes in metal speciation in our experiments because the pH increased by ≤0.25 pH unit during irradiation (Table 3). Moreover, Figure 3 shows that $Al_o$ concentrations decreased as $Al_i$ concentrations increased. This implies that the ability of DOC to bind metals is more affected by the photochemical transformations of DOC than by a creation of new equilibria between $Al_i$ and $Al_o$ and the remaining organic ligands. A probable explanation for this effect is a disproportional reduction of binding sites on organic matter compared to declining DOC concentrations during irradiation, suggested by Figure 4.

The binding of Al by organic ligands can occur by chelation, coordinate linkage with a single donor group, electrostatic attraction, and water bridging (*32*). The first two bond types are stronger and likely are the predominant form of Al−organic complexes. The latter weaker bonds may become important as organic binding sites become saturated with Al (*32*). This situation occurs when soil water acidifies and Al concentration increases. Consistently, the elevated $Al_o$:DOC ratios (0.01−0.02 mol mol$^{-1}$) occur in surface waters

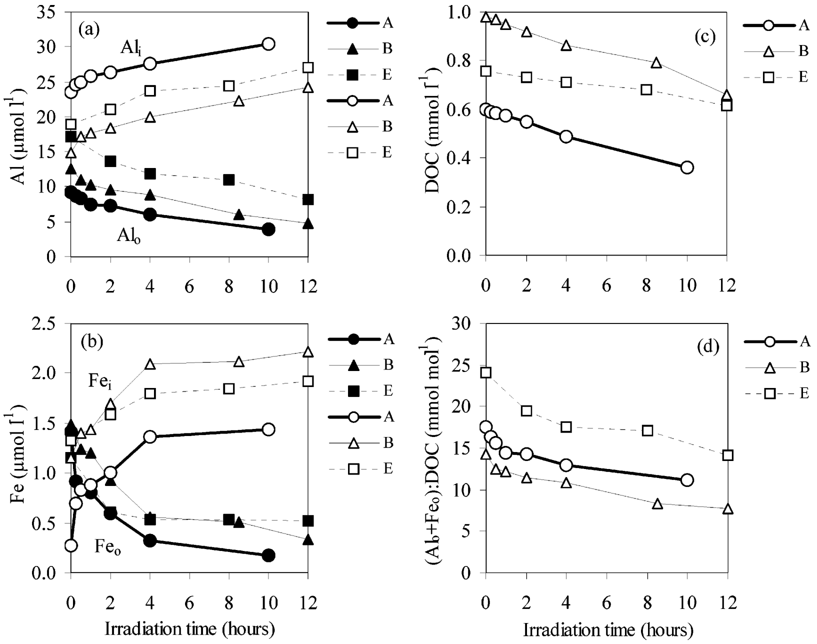

**FIGURE 3. Chemical changes in water chemistry during photochemical degradation of samples from an inlet to Plešné Lake (irradiation time 0 is for the dark control): (a) organically bound aluminum (Al$_o$; full points) and ionic aluminum (Al$_i$; open points); (b) organically bound iron (Fe$_o$; full points) and ionic iron (Fe$_i$; open points); (c) dissolved organic carbon (DOC); (d) (Al$_o$ + Fe$_o$):DOC ratios. Samples: A, January 2000; B, October 2000; E, August 2003.**

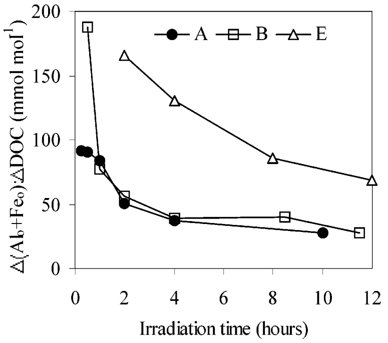

**FIGURE 4. Changes in (Al$_o$ + Fe$_o$):DOC ratios during irradiation of samples A, B, and E compared to those of their dark controls: A, January 2000; B, October 2000; E, August 2003.**

with pH < 5, whereas values of <0.01 mol mol$^{-1}$ are typical for circumneutral waters (*1*, *33*). Laboratory experiments showed that the effective complexing capacity of organic matter is approximately 0.015 ± 0.003 mol mol$^{-1}$ for Al and Fe in lakes with pH < 5 (*29*). Surface waters entering Plešné and Čertovo Lakes had a similar relationship between molar concentrations of organically bound Al plus Fe and DOC of $[\mathrm{Al_o}] + [\mathrm{Fe_o}] = 0.001 + 0.015[\mathrm{DOC}]$ ($r = 0.96$) (*16*), suggesting a high level of saturation of the available organic ligands. This relationship is dominated by [Al$_o$], which is about 10[Fe$_o$]. At this high saturation level, some Al$_o$ was probably bound to organic matter also by the weaker bonds.

Organically bound Fe may play a role in the reduction of binding sites for both Al and Fe. Under oxic conditions, Fe may occur in organic complexes as Fe$^{III}$. After absorption of light, organically bound Fe$^{III}$ may be easily reduced to Fe$^{II}$ by ligand-to-metal electron transfer (*34*), which may result in photoreductive changes in Fe forms (*35*, *36*) and/or in photochemical oxidative reactions of organic matter (*37*). Fe$^{II}$ is a powerful catalytic species which, in the presence of dissolved oxygen, causes the decomposition of organic matter. The photochemical formation of catalytic Fe$^{II}$ (i.e., photoreduction of Fe$^{III}$ to Fe$^{II}$) and deactivation of catalytic Fe$^{II}$ (i.e., reoxidation of Fe$^{II}$ by dissolved molecular oxygen) both depend on the ligand characteristics. With some substrates, only traces of Fe may cause the catalytic effect, provided that the photogeneration of Fe$^{II}$ is fast enough (*38*). In photochemical experiments, Fe$^{2+}$ concentrations were ~10$^{-7}$ mol L$^{-1}$, i.e., near the detection limit of the method. We feel that trace Fe$^{II}$ catalysis may explain the observed photochemical changes in the experiments.

The decomposition may lead either to lower molecular weight molecules with fewer electron-pair donor groups or even to DOC mineralization. Combination of these processes results in reduction of binding sites for metals and liberation of their ionic forms. Similarly to the irradiation experiments, natural sunlight decreases the concentration of dissolved organic matter by either partial photochemical degradation to low molecular weight organic compounds or the total photochemical oxidation to CO and CO$_2$ (*39*–*41*). These processes are more pronounced in acidic water, because photoreactivity of DOC increases as water pH declines (*42*).

Our field observations and laboratory experiments suggest that photodegradation of allochthonous DOC to lower molecular weight organic compounds is responsible for rapid decomplexation of Al$_o$ and Fe$_o$. Xie et al. (*43*) showed that the absolute concentration of carboxyl groups on DOC changes little during irradiation. The carboxyl groups are responsible for strong metal binding sites in natural humic substances (*32*) or in the products of their photochemical decomposition (e.g., citric or oxalic acids) (*41*). The small changes in the numbers of carboxyl groups during photooxidation (*43*) can explain that the liberation of Al$_o$ and Fe$_o$ was not complete and a portion remained in the water after irradiation (Figure 3a,b) or left the lakes under natural conditions (Table 1). Consequently, we speculate that the liberated metals originated predominantly from the weak bonds or from those that may serve as a linkage between humic molecules (*32*), rather than from the stronger bond types.

**Implications for Surface Waters.** Our results suggest that photochemical degradation has an important role in metal chemistry in surface waters that contain organically bound Al and Fe derived from terrestrial sources. Such waters originate in many tundra, boreal forest, and temperate coniferous forest systems, with runoffs typically rich in DOC, $Al_o$, and $Fe_o$ (*44*). There are several consequences of the metal photoliberation for water ecosystems: (1) The potential photochemical changes in metal speciation should be considered in processing of samples prior to analyses, similarly to the effect of degassing of $CO_2$ on $Al_i$ precipitation. (2) Organically bound Al can be rapidly liberated from the inlet water by solar radiation and thus is an additional pool of potentially toxic $Al_i$. (3) In contrast, photoliberated Fe from allochthonous DOC may contribute to the productivity of lakes and coastal waters due to increased Fe bioavailability for phytoplankton (*45*), if hydroxide precipitates do not form. (4) Both $Al_i$ and $Fe_i$ hydrolyze under higher in-lake pH and form hydroxide precipitate (*2*). These fresh aluminum and iron hydroxides have large surface areas and bind orthophosphate ($PO_4$) (*13*, *17*), thereby decreasing the availability of $PO_4$ to phytoplankton (*46*). The photoliberation of $Al_o$ and $Fe_o$ may further contribute to the low availability of $PO_4$ in the epilimnion. (5) Moreover, the above process contributes additional aluminum and iron hydroxides to lake sediment, changing its $PO_4$ sorption characteristics and, in the case of Al, reduces P liberation from sediments to the water column during anoxia (*13*). The hydrolysis of $Al_i$ after degassing of $CO_2$ from soil solutions emerging to surface waters (*12*) and the photoliberation of $Al_o$ were both probable sources of aluminum hydroxides for lake sediments long before the effects of atmospheric acidification.

An analogous photochemical source of metal hydroxides for lakes likely operates for other metals that form organic complexes in soil solutions. The necessary conditions for the process (organically bound metals in lake inlets and higher pH in the lake) first occurred with organic soil development in the terrestrial part of the watershed–lake ecosystem. As watershed soils acidify, naturally or as a consequence of acidic deposition, the sediment flux of metal hydroxides derived from photodegradation of organic complexes likely increases, because of the saturation of DOC with metals (*29*) and DOC's increased sensitivity to photochemical degradation (*42*).

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