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Proton production by transformations of aluminium and iron in lakes.
Jiří Kopáček, Josef Hejzlar, and Stephen A. Norton
Proton production by transformations of aluminium and iron in lakes

Jiří Kopaček, Josef Hejzlar, Stephen A. Norton

Abstract

The effect of in-lake transformations of Al and Fe species on H⁺ production was studied in strongly atmospherically acidified Plesné Lake, Czech Republic, in 2005. We developed a model that quantifies the impact of individual processes (changes in metal concentration and charge, precipitation, and liberation from organic complexes). The net H⁺ production associated with Al and Fe transformations was 252 and 1 meq m⁻² yr⁻¹ (on the lake area basis), respectively, reflecting fluxes of ionic, organic, and particulate forms into and out of the lake and the pH gradient between the inlet and outlet. The greater importance of Al was due to two orders of magnitude higher Al than Fe fluxes. The most important H⁺-producing processes were precipitation of Al(OH)₃ from ionic Al (Ali) (producing 166 meq H⁺ m⁻² yr⁻¹), and hydrolysis of inlet Ali (130 meq H⁺ m⁻² yr⁻¹) that decreased the average charge of Ali due to pH increase from 4.3 in the inlets to 4.7 at the outlet. The liberation of organically bound Al (Alo) was the most important H⁺ sink among the metal transforming processes (44 meq H⁺ m⁻² yr⁻¹). The H⁺ production in the lake associated with the change in Ali storage and its charge due to pH change between the end and start of the mass budget periods were quantitatively unimportant (4 and 4 meq H⁺ m⁻² yr⁻¹, respectively).

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1. Introduction

The acid-neutralizing capacity (ANC) of the oceans and most freshwaters is predominately associated with the carbonate buffering system and is commonly defined as a carbonate alkalinity (ALK) by (e.g., Norton and Veselý, 2004)

\[ \text{ANC} = \text{ALK} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- - \text{H}^+, \]  

where all concentrations are in eq l⁻¹ (eq = equivalent = mole of charge). A more general definition of ANC is based on a charge balance Eq. (2), assuming the equivalence between the total positive and negative electric charges of the water constituents (Reuss and Johnson, 1986), or in other words, the equivalence between the sum of the cations and the sum of the anions, expressed in eq l⁻¹:

\[ \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{NH}_4^+ + \text{H}^+ + \text{Al}^{m+} + \text{Fe}^{m+} = \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + \text{F}^- + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- + A^{k-}. \]  

In Eq. (2), Al²⁺ and Fe³⁺ represent the sum of the charged species of aluminium and iron, respectively, and A⁻ is the equivalent concentration of the dissociated organic acid anions. The concentrations of other weak acid anions (such as phosphate, nitrite, or silicic acid) are neglected. This definition includes the carbonate buffering system and buffering by Al and Fe hydroxy complexes and organic acids that become important in acidified and coloured waters.
respectively. For waters sensitive to acidification, the concentrations of \( \text{CO}_3^{2-} \) and \( \text{OH}^- \) are trivial and can be neglected. ANC can be defined, rearranging Eqs. (1) and (2), as

\[
\text{ANC} = \text{HCO}_3^- - \text{H}^+ \\
= (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^- + \text{NH}_4^+ + \text{Al}^{n^+} + \text{Fe}^{m^+}) \\
- (\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^- + \text{F}^- + \text{A}^-).
\]  

(3)

According to this definition, a change in ANC may be caused by any independent change in any of the terms in the equation. Thus, ANC increases when some process (i) removes strong acid anions (and \( \text{H}^+ \)) from water, e.g., \( \text{SO}_4^{2-} \) adsorption in soils and sediments, accompanied by \( \text{OH}^- \) desorption and \( \text{H}^+ \) neutralization, or microbial reduction of \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \), (ii) increases the concentrations of metals together with \( \text{HCO}_3^- \) concentration or reciprocally to a decrease in \( \text{H}^+ \) concentration (e.g., weathering, desorption of cations from soils and sediments, decay of dead biomass, acid dissolution of \( \text{Al} \) and \( \text{Fe} \) oxyhydroxides, or reductive dissolution of \( \text{Al} \) and \( \text{Fe} \) oxyhydroxides), or (iii) increases NH\(_4^+) \) concentration during dissimilation of organic matter (e.g., Reuss and Johnson, 1986; Rudd et al., 1986; Psenner, 1988; Psenner and Catalan, 1994). In contrast, ANC decreases when some process (i) increases concentrations of \( \text{H}^+ \) and strong acid anions (e.g., acidic precipitation, nitrification, or oxidation of sulphide minerals or aqueous species), (ii) decreases concentrations of cations, releasing the equivalent amount of \( \text{H}^+ \) (e.g., assimilation of base cations and \( \text{NH}_4^+) \) by biomass, adsorption of cations in soils and sediments, \( \text{Fe}^{2+} \) oxidation and precipitation of \( \text{Fe}(\text{OH})_3 \), or (iii) hydrolyses \( \text{Al}^{n^+} \) and \( \text{Fe}^{m^+} \) (Reuss and Johnson, 1986; Psenner and Catalan, 1994; Stumm and Morgan, 1981).

The ANC of circum-neutral freshwaters is mostly generated by weathering in their catchments and the associated increase in concentrations of \( \text{HCO}_3^- \) and base cations (Psenner and Catalan, 1994). However, in strongly acidified areas, in-lake ANC production may be dominated by biogeochemical reduction of \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) (Schindler et al., 1986) and photochemical and microbial oxidation of DOC (Kopáček et al., 2003) and may be quantitatively more important than the terrestrial sources. The ANC-generating processes are of great interest in acidified waters, because they strongly influence water pH, concentrations and speciation of metals, and toxicity to aquatic organisms (Psenner and Catalan, 1994). The pH-dependent changes in concentration and charge of \( \text{Al} \) and \( \text{Fe} \) can further affect the water ANC concentration (Eq. (3)). As an ecosystem acidifies, the effects of reactions involving \( \text{Al} \) and \( \text{Fe} \) on proton budgets increase and can play (besides N transformations) a substantial role in strongly acidified systems that have depleted carbonate buffering systems and reduced soil pools of exchangeable base cations (e.g., Kopáček et al., 2006a). Here we evaluate the quantitative role of individual \( \text{Al} \) and \( \text{Fe} \) transformations on ANC production through an acidified catchment-lake ecosystem.

The effect of \( \text{Al} \) and \( \text{Fe} \) dynamics on proton budgets in the terrestrial part of catchment-lake ecosystems depends on the types of chemical reactions and final reaction products. Secondary \( \text{Fe} \) mineral phases (oxyhydroxides) originate from weathering of \( \text{Fe} \) (typically \( \text{Fe}^{2+} \)) silicate and sulphide minerals (Garrels and Christ, 1965). For example, the weathering of the Fe component of pyroxene can be represented as

\[
\text{FeSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Fe}^{2+} + \text{H}_4\text{SiO}_4. 
\]  

(4)

Liberated \( \text{Fe}^{2+} \) oxidizes in oxic conditions, forming \( \text{Fe} \) hydroxide:

\[
4\text{Fe}^{2+} + \text{O}_2 + 10\text{H}_2\text{O} = 4\text{Fe(OH)}_3 + 8\text{H}^+. 
\]  

(5)

Two equivalents of \( \text{H}^+ \) are consumed per one mole of \( \text{Fe} \) by reaction (4), at pH <8, where \( \text{H}_2\text{SiO}_4 \) is dissociated in trivial amounts, while two equivalents of \( \text{H}^+ \) are produced per one mole of \( \text{Fe} \) by reaction (5), resulting in zero net ANC production associated with the transformation of the primary ferrous minerals to \( \text{Fe(OH)}_3 \). Reaction (5) is, however, slow in acidic waters (Stumm and Morgan, 1981), and the potential net \( \text{Fe}^{2+} \) export would result in an equivalent \( \text{H}^+ \) consumption and ANC generation in the terrestrial ecosystem.

Oxidation of \( \text{FeS} \) and subsequent hydrolysis of liberated \( \text{Fe}^{3+} \) to \( \text{Fe(OH)}_3 \) (Eqs. (6a) and (6b), respectively) result in the net production of one mole of \( \text{Fe(OH)}_3 \) and \( \text{H}_2\text{SO}_4 \) per mole of \( \text{FeS} \) (Eq. (7)):

\[
4\text{FeS} + 9\text{O}_2 + 4\text{H}^+ = 4\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 2\text{H}_2\text{O}, 
\]  

(6a)

\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{H}^+, 
\]  

(6b)

\[
4\text{FeS} + 9\text{O}_2 + 10\text{H}_2\text{O} = 4\text{SO}_4^{2-} + 8\text{H}^+ + 4\text{Fe(OH)}_3. 
\]  

(7)

This process consumes ANC in the terrestrial ecosystem, producing two equivalents of \( \text{H}^+ \) per one mole of \( \text{Fe} \) due to the full dissociation of the \( \text{H}_2\text{SO}_4 \).

The incongruent weathering of primary \( \text{alumino-silicate} \) minerals to secondary minerals such as kaolinite (\( \text{AI}_2\text{Si}_2\text{O}(\text{OH})_4 \)) and gibbsite (\( \text{Al(OH)}_3 \)) is illustrated with potassium feldspar (Eqs. (8a) and (8b)), but other silicates dissolve following analogous reactions (Psenner and Catalan, 1994):

\[
2\text{KAlSi}_3\text{O}_8 + 9\text{H}_2\text{O} + 2\text{H}^+ = \text{Al}_4\text{Si}_3\text{O}_9(\text{OH})_4 + 2\text{K}^+ + 4\text{H}_2\text{SiO}_4, 
\]  

(8a)

\[
\text{KAI}_3\text{Si}_3\text{O}_8 + 7\text{H}_2\text{O} + \text{H}^+ = \text{Al(OH)}_3 + \text{K}^+ + 3\text{H}_2\text{SiO}_4. 
\]  

(8b)

These reactions produce ANC according to Eq. (3), but the \( \text{H}^+ \) retention is associated with \( \text{K}^+ \) liberation. The net ANC production per mole of \( \text{Al} \) transformed from the primary minerals to \( \text{Al}_4\text{Si}_3\text{O}_9(\text{OH})_4 \) or \( \text{Al(OH)}_3 \) is zero.

The dissolution of \( \text{Fe} \) and \( \text{Al} \) oxyhydroxides under acidic conditions consumes \( \text{H}^+ \), producing ionic \( \text{Fe} \) and \( \text{Al} \) forms according to Eqs. (9) and (10):

\[
\text{Fe(OH)}_3 + m\text{H}^+ = \text{Fe(OH)}_{3-m} + m\text{H}_2\text{O}, 
\]  

(9)

\[
\text{Al(OH)}_3 + n\text{H}^+ = \text{Al(OH)}_{3-n} + n\text{H}_2\text{O}. 
\]  

(10)

where \( m \) and \( n \) values represent the \( \text{Fe} \) and \( \text{Al} \) charge, respectively, varying between \(-1 \) and \( 3 \), according to the water pH (Stumm and Morgan, 1981). The maximum net ANC production associated with the dissolution of \( \text{Fe} \) and \( \text{Al} \) oxyhydroxides in acidic soils is 3 equivalents per mole of metal. The release of \( \text{Al} \) and \( \text{Fe} \) from their hydroxides thus increases ANC for the terrestrial ecosystem. Some ANC is consumed after groundwater emerges to streams, because \( \text{Al} \) and \( \text{Fe} \) hydrolyse if pH of soil water increases due to CO\(_2\) degassing (Norton and Henriksen, 1983) or mixing with higher pH surface water (Rosseland et al., 1992). In that case, water
ANC decreases, but any precipitated and settling Al and Fe hydroxides increase the ANC of the stream sediments.

The net ANC production associated with the formation of organic–metal complexes (Al₅⁺ and Fe₆⁺) depends on the type and protonation of organic ligands (Vance et al., 1996). For example, Al₅⁺ complexation with fully dissociated ligands (e.g., chelation with the carboxylic groups) can be shown as

\[ n\text{Al}^{n+} \rightarrow n\text{Al}^{n+} \times n\text{H}^+ \]

(11)

In such a case, formation of organic–metal chelates consumes equivalent amounts of ironic metals and dissociated organic anions, and has no net impact on ANC (Eq. (3)). However, completely deprotonized ligands occur only at high pH, whereas in acidic waters, H⁺ competes with Al₅⁺ for ligand complexation sites (Vance et al., 1996). Consequently, Al complexation with organic functional groups (such as –COOH and phenolic/alcoholic) results in the release of H⁺:

\[ n\text{Al}^{n+} + n\text{H}_2\text{A} = n\text{Al} \times \text{A}^- + n\text{H}^+ \]

(12)

The amount of H⁺ release depends on pH. In acidic soil solutions (pH<4), the value of \( n \) is 3 and organic ligands are mostly protonated. For simplicity, we assume that Al₅⁺ binding produces three equivalents of H⁺ per mole of the complexed Al₅⁺ (Kopáček et al., 2003). Eq. (12) has an analogy for Fe complexation, but the value of \( m \) is 2 in anoxic conditions where Fe²⁺ ions dominate. The net terrestrial ANC production associated with the Al₅⁺ and Fe₆⁺ release to surface waters is zero because protons consumed during mobilisation from a solid phase are released back during metal complexation.

Another source of ANC changes is the biochemical reduction of Fe at low redox (Eh) conditions in soils, waters, or sediments. Biochemical reduction of Fe²⁺ to Fe²⁺ ions associated with oxidation of organic matter (CH₂O) consumes two equivalents of H⁺ per mole of Fe (Eq. (13)):

\[ 4\text{Fe(OH)}_3 + \text{CH}_2 \text{O} + 8\text{H}^+ = 4\text{Fe}^{2+} + \text{CO}_2 + 11\text{H}_2\text{O} \]

(13)

But, Fe²⁺ re-oxidation back to Fe³⁺ at higher Eh conditions produces two H⁺ (Eq. (5)), resulting in no net effect on the ecosystem ANC. The net impact of Fe⁰ to Fe²⁺ reduction on the ANC balance thus depends on the proportion of Fe²⁺ that is re-oxidised back to Fe³⁺. In the presence of S²⁻, however, the produced Fe²⁺ precipitates as FeS removing two eq H⁺ mol⁻¹ of Fe from the ecosystem (Eq. (14)):

\[ 4\text{Fe(OH)}_3 + \text{CH}_2 \text{O} + 8\text{H}^+ + 4\text{S}^{2-} = 4\text{FeS} + \text{CO}_2 + 11\text{H}_2\text{O} \]

(14)

The oxidation and reduction transformation of the Fe in FeS through Fe(OH)₃ and back to FeS (Eqs. (7) and (14)) thus have no net effect on the ecosystem ANC balance.

The Al and Fe dynamics in soils and streams lead to net ANC generation in the terrestrial part of the catchment-lake ecosystem, if the terrestrial exports of metals are in ionic form; the export of particulate hydroxides and Al₅⁺ and Fe₆⁺ species has no net effect (except for Fe(OH)₃ produced by FeS oxidation).

Our study focuses on lakes, the final part of the ecosystem, and quantifies the importance of individual internal Al and Fe transformations (changes in metal concentration and charge, precipitation, and liberation from organic complexes) on the in-lake H⁺ and ANC budgets, using the strongly acidified Plešné Lake, Czech Republic, as an example.

2. Materials and methods

2.1. Site description

Plešné Lake is situated in the Bohemian Forest of the Czech Republic (13°52'E, 48°47'N; ~150 km south of Prague) at an elevation of 1090 m. The lake is of glacial origin (a tarn), with surface area 7.5 ha, volume 620,000 m³, maximum depth 18 m, and mean water residence time 0.8 yr. Plešné Lake is mesotrophic, with Secchi transparency of ~1 m, and the thermocline depth is 4–5 m. The lake has been acidified by atmospheric deposition to pH <5 since the 1960s and has a depleted carbonate buffering system (Majer et al., 2003). The Plešné Lake catchment is 67 ha (including the lake), has a maximum local relief of 288 m, and is almost fully forested by ~150-yr-old Norway spruce (Picea Abies). Soils are sandy (~75%), low in clay (~2%), thin (~0.45 m), and acidic, with catchment-weighted mean base saturation of 15% and soil pHCaCl₂ of 2.5–3.1 in the A-horizon and 3.2–4.4 in the deep mineral horizons.

2.2. Sampling and analyses

The Al and Fe input (terrestrial export via lake inlets plus atmospheric deposition) and output from the lake were based on mass balances of water and concentrations of inorganic, organic, and particulate species during the 2005 hydrological year, from November 1, 2004 to October 31, 2005. Terrestrial export was measured for all four tributaries of the lake. Atmospheric deposition of water and its chemical constituents was determined at two forested sites (throughfall) and one area without trees (bulk deposition). Bulk deposition was assumed to represent the direct atmospheric input of elements to the lake surface. The lake water balance was based on the atmospheric deposition to the catchment (via throughfall) plus lake surface (from bulk deposition), and outflow from the lake (a gauge-recorder at the weir). The Al and Fe fluxes were obtained by linking discharge with the corresponding concentration by the method of period-weighted mean (Likens et al., 1977). Atmospheric deposition, inlets, and outlets were sampled at 2–4-week intervals throughout the year. The outlet was sampled weekly during spring, the period of highest discharge. The annual change in the storage of metals in the lake was calculated using the lake volume and water column composition (concentration data for five water layers along the vertical profile were linked with their corresponding volumes) at the end and beginning of the hydrological year.

Total Al (Al₅⁺), total dissolved (~0.4 μm) Al, and organically bound Al (Al₆⁺) were analysed in unfiltered samples, filtered samples, and cation exchanged samples after their filtration, respectively, using the catechol violet colorimetric method (Driscoll, 1984; Dougan and Wilson, 1974). The strongly acidic cation exchanger (Amberlite) was used in a mixture of Na⁺ (98%) and H⁺ (2%) forms, so as to reduce effects on sample pH from ionic exchange. The first 25 ml of the filtrate (50% of the...
exchanger volume) was discharged to prevent contamination from the previous sample. Ionic Al (Al\textsubscript{I}) was calculated as the difference between total dissolved Al and Al\textsubscript{o} concentrations. Particulate Al (Al\textsubscript{p}) was the difference between Al\textsubscript{T} and total dissolved Al concentrations. The respective Fe fractions (Fe\textsubscript{o}, Fe\textsubscript{o}, and Fe\textsubscript{o}) were obtained analogously; their concentrations and the average charges of Al were calculated from pH of samples and the equilibrium constants of Al\textsuperscript{3+} hydrolysis to Al(OH)\textsubscript{2}\textsuperscript{+}, Al(OH)\textsubscript{3}\textsuperscript{+}, and Al(OH)\textsubscript{4}\textsuperscript{−}:

\[
n = 3x_0 + 2x_1 + x_2 - x_4. \quad (15)
\]

Here, \(x_0, x_1, x_2, \) and \(x_4\) are fractions of Al\textsuperscript{3+}, AlOH\textsuperscript{2+}, Al(OH)\textsubscript{2}\textsuperscript{+}, and Al(OH)\textsubscript{4}\textsuperscript{−}, respectively (\(x_3\) is not included due to a charge of Al(OH)\textsubscript{3}−), which were calculated from pH of samples and the equilibrium constants of Al\textsuperscript{3+} hydrolysis to Al(OH)\textsubscript{2}\textsuperscript{+}, Al(OH)\textsubscript{3}\textsuperscript{+}, and Al(OH)\textsubscript{4}\textsuperscript{−} of \(K_1 = 10^{-4.97}, K_2 = 10^{-9.3}, K_3 = 10^{-15},\) and \(K_4 = 10^{-23}\), respectively (Stumm and Morgan, 1981). We assumed that molar concentrations were similar to dissolved Al concentrations. The respective Fe fractions (Fe\textsubscript{T}, Fe\textsubscript{o}, Fe\textsubscript{p}, and Fe\textsubscript{p}) were obtained analogously; their concentrations and the average charges of Al were calculated from pH of samples and the equilibrium constants of Fe\textsuperscript{3+} hydrolysis to FeOH\textsuperscript{2+}, Fe(OH)\textsubscript{2}\textsuperscript{+}, Fe(OH)\textsubscript{3}\textsuperscript{+}, and Fe(OH)\textsubscript{4}\textsuperscript{−} of \(K_1 = 10^{-2.19}, K_2 = 10^{-5.67}, K_3 = 10^{-12},\) and \(K_4 = 10^{-21.6}\) (Stumm and Morgan, 1981).

Dissolved organic carbon (DOC) was analysed with a TOC 5000A analyser (Shimadzu). Concentrations of ionised organic acid anions (A\textsuperscript{−}, \(\mu\text{eq} l\textsuperscript{-1}\)) were obtained independently of ion balance considerations, from concentrations of DOC, Al\textsubscript{I}, Fe\textsubscript{o}, and pH (Kopáček et al., 2000). Briefly, the A\textsuperscript{−} concentration was estimated from the concentration of DOC and ionisation of carboxylic groups at the sample pH (Oliver et al., 1983).

The accuracy and precision of analytical methods were checked by means of standard samples, which were assayed with each series of samples. The coefficients of variation of the means for pH (4.2), DOC (0.42 mmol l\textsuperscript{-1}), Al\textsubscript{T} (18 mmol l\textsuperscript{-1}), and Fe\textsubscript{T} (2.0 mmol l\textsuperscript{-1}) were 1%, 6%, 5%, and 8%, respectively. The accuracy of analyses was also checked using ion balance calculations for each sample (Kopáček et al., 2000). Concentrations of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, F\textsuperscript{−}, and A\textsuperscript{−} were analysed by ion chromatography (Dionex IC25, USA) and ANC by Gran titration. The differences between the sum of the cations and the sum of the anions were <±5% of the ion concentration for all calculations of fluxes used in this study. The accuracy of in-lake mass budgets of ions (including A\textsuperscript{−}, Al\textsuperscript{3+}, and Fe\textsuperscript{3+}) was checked by a comparison of the measured and calculated in-lake retention of H\textsuperscript{+}. The measured H\textsuperscript{+} retention, based on pH measurements in inlets (precipitation) and output, was 284 mmol m\textsuperscript{-2} yr\textsuperscript{-1}. The calculated H\textsuperscript{+} retention was the difference between the net in-lake retention of all anions and all cations (except for H\textsuperscript{+}) and was 283 mmol m\textsuperscript{-2} yr\textsuperscript{-1}. The average difference between the measured and calculated storage of Al, carbon, and nitrogen in the Plešné Lake sediments was evaluated by a similar study in 2001 and was ±9% (Kopáček et al., 2004). For more details on site characteristics, sampling, methods, mass

| Table 1 – Annual volume-weighted mean composition of precipitation (Precip. = atmospheric input on lake surface), and annual discharge-weighted mean composition of input and output waters in Plešné Lake in the 2005 hydrological year |
|-----------------|-----------------|-----------------|
| Precip.         | Input           | Output          |
| pH              | 4.8             | 4.3             | 4.7             |
| ANC (\(\mu\text{eq} l\textsuperscript{-1}\)) | −20              | −48              | 0               |
| H\textsuperscript{+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 16               | 54              | 19              |
| Ca\textsuperscript{2+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 8                | 47              | 40              |
| Mg\textsuperscript{2+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 2                | 18              | 15              |
| Na\textsuperscript{+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 7                | 48              | 39              |
| K\textsuperscript{+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 2                | 14              | 9               |
| NH\textsubscript{4}\textsuperscript{+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 21               | 0               | 6               |
| Al\textsuperscript{3+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | ND               | 51              | 17              |
| Fe\textsuperscript{3+} (\(\mu\text{eq} l\textsuperscript{-1}\)) | ND               | 0.2             | 0.3             |
| NO\textsubscript{3} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 24               | 116             | 48              |
| NO\textsubscript{2} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 21               | 72              | 66              |
| Cl\textsuperscript{−} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 7                | 16              | 15              |
| F\textsuperscript{−} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 0.4              | 5.3             | 4.3             |
| A\textsuperscript{−} (\(\mu\text{eq} l\textsuperscript{-1}\)) | 4                | 21              | 10              |
| Al\textsubscript{i} (\(\mu\text{mol} l\textsuperscript{-1}\)) | <0.2             | 20              | 9               |
| Al\textsubscript{p} (\(\mu\text{mol} l\textsuperscript{-1}\)) | ND               | 10              | 5               |
| Al\textsubscript{p} (\(\mu\text{mol} l\textsuperscript{-1}\)) | ND               | 0.5             | 4.5             |
| Fe\textsubscript{o} (\(\mu\text{mol} l\textsuperscript{-1}\)) | <0.4             | 0.2             | 0.3             |
| Fe\textsubscript{o} (\(\mu\text{mol} l\textsuperscript{-1}\)) | ND               | 1.1             | 0.8             |
| Fe\textsubscript{o} (\(\mu\text{mol} l\textsuperscript{-1}\)) | ND               | 0.1             | 0.5             |
| H\textsubscript{2}O (\(10^3 \text{mm}^2\text{yr}^{-1}\)) | 105              | 613             | 678             |

Mean pH = −log(mean H\textsuperscript{+} activity); ANC = acid neutralizing capacity (Gran titration); H\textsubscript{2}O = major water fluxes, ND = not determined.
budget calculations, and discussion of possible errors associated with the major fluxes, see Kopáček et al. (2004, 2006a).

3. Results and discussion

3.1. Aluminium

Of the Al\textsubscript{p} entering Plešně Lake (246 mmol m\textsuperscript{-2} yr\textsuperscript{-1}; on the lake area basis), 98% was in the dissolved form (Al\textsubscript{d}, 65%; Al\textsubscript{o}, 33%; Al\textsubscript{p}, 2%). The Al\textsubscript{d} and Al\textsubscript{o} proportions in the Al\textsubscript{T} output (171 mmol m\textsuperscript{-2} yr\textsuperscript{-1}) decreased to 49% and 27%, respectively, while the Al\textsubscript{p} proportion increased to 24% (Table 2). The Al\textsubscript{T} pool in the lake increased by 17 mmol m\textsuperscript{-2} yr\textsuperscript{-1} during the 2005 hydrological year, and the lake was a net sink of Al\textsubscript{o} to Al\textsubscript{d}, transforming Al\textsubscript{o} to Al\textsubscript{p}.

Total H\textsuperscript{+} production (P) associated with in-lake removal (R) of Al\textsuperscript{III} [P(H\textsuperscript{+}) = R(Al\textsuperscript{III})] was calculated from the annual balance of the charged Al species (Fig. 1):

\[
P(H^+) = R(Al^{III}) = F_{IN}(Al^{III}) - F_{OUT}(Al^{III}) - \Delta M(Al^{III}).
\]

Here and henceforth in the text, symbols in front of parentheses represent fluxes, and symbols in the parentheses refer to the related chemical constituent. F\textsubscript{IN} and F\textsubscript{OUT} are annual fluxes of Al\textsuperscript{III} input (catchment export+atmospheric deposition on the lake surface) and output. \Delta M is change in storage of Al\textsuperscript{III} in the lake water column and is the difference between Al\textsuperscript{III} pools in the lake at the end and start of mass budget period (\Delta M = M\text{END} - M\text{START}). All Al\textsuperscript{III} values are meq m\textsuperscript{-2} yr\textsuperscript{-1}, on the lake area basis. Net in-lake Al\textsuperscript{III} removal was 252 meq m\textsuperscript{-2} yr\textsuperscript{-1} in Plešně Lake in the 2005 hydrological year (Table 3), resulting in the equivalent production of H\textsuperscript{+}. The Al\textsuperscript{III} pool changed due to changes in the average Al\textsubscript{i} charge (reflecting changes in water pH) and molar concentration. But, what were contributions of individual processes?

The processes that changed the molar Al\textsubscript{i} concentration were precipitation of Al(OH)\textsubscript{3} and photochemical liberation of organic complexes was the major process responsible for the decrease in Al\textsubscript{o} concentrations in Plešně Lake, transforming Al\textsubscript{o} to Al\textsubscript{p}.

### Table 2 – Fluxes of major Al species in Plešně Lake in the 2005 hydrological year and their impact on in-lake H\textsuperscript{+} production

<table>
<thead>
<tr>
<th>pH</th>
<th>Aluminium</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al\textsubscript{d}</td>
<td>Al\textsubscript{o}</td>
</tr>
<tr>
<td>M\text{START}</td>
<td>5.03</td>
<td>43</td>
</tr>
<tr>
<td>M\text{END}</td>
<td>4.97</td>
<td>51</td>
</tr>
<tr>
<td>\Delta M</td>
<td>1.3</td>
<td>2.1</td>
</tr>
<tr>
<td>F\text{IN}</td>
<td>4.26</td>
<td>160</td>
</tr>
<tr>
<td>F\text{COAG}</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>F\text{LIB}</td>
<td>25</td>
<td>\text{-----}</td>
</tr>
<tr>
<td>F\text{PREC}</td>
<td>\text{-----}</td>
<td>\text{-----}</td>
</tr>
<tr>
<td>F\text{SED}</td>
<td>58</td>
<td>\text{-----}</td>
</tr>
<tr>
<td>F\text{OUT}</td>
<td>4.72</td>
<td>84</td>
</tr>
<tr>
<td>P</td>
<td>\text{-}68</td>
<td>\text{-}25</td>
</tr>
</tbody>
</table>

Units are mmol m\textsuperscript{-2} yr\textsuperscript{-1} for F\textsubscript{P}, P, and \Delta M values; mmol m\textsuperscript{-2} for M values; pH = \text{-}\log\text{(volume-weighted mean H\textsuperscript{+} activity)} for lake and \text{-}\log\text{(discharge-weighted mean H\textsuperscript{+} activity)} for fluxes. The n and m values (mol of charge mol\textsuperscript{-1} of Al\textsubscript{i} and Fe\textsubscript{i}, respectively) were calculated from Eq. (15) for the given pH values. Change in storage of metals in the lake (\Delta M) is the difference between their in-lake pools at the end (M\text{END}) and start (M\text{START}) of the hydrological year. F\text{IN} and F\text{OUT} are input and output fluxes of metals. Liberation, precipitation, and sedimentation fluxes (F\text{LIB}, F\text{PREC}, and F\text{SED}, respectively) were calculated from Eqs. (17)–(19); F\text{COAG} (coagulation and co-precipitation with DOC) was neglected. Net in-lake productions of metal species (P) were calculated as negative values of their retentions (R) from Eq. (16). Arrows indicate changes in metal species. Changes in H\textsuperscript{+} (\Delta H\textsuperscript{+}) were calculated for individual processes using Eqs. (20)–(24), as indicated by indexes at the \Delta H\textsuperscript{+} values. Net in-lake production (P) of H\textsuperscript{+} was the sum of all individual \Delta H\textsuperscript{+} values.
the water column by coagulation ($F_{COAG}$), using

$$F_{LIB}(Al_p) = F_{IN}(Al_p) - F_{COAG}(Al_p) - F_{OUT}(Al_p) - \Delta M(Al_p).$$  

(18)

The $F_{COAG}$ was not estimated in 2005 and we neglected this flux on the basis of the previous data (Kopaček et al., 2004, 2006b), setting $F_{COAG}$ to zero in Eqs. (18) and (19). This simplification provides maximum estimates of the $F_{PREC}$ and $F_{LIB}$ values, that were 93 ($= 160+25−84−8$) and 25 ($= 82−0−46−11$) mmol m$^{-2}$ yr$^{-1}$, respectively, in 2005 (Table 2).

The produced $Al_p$ caused higher output than input of $Al_p$ and a significant portion was deposited in the sediments (Table 2). Besides the in-lake retention of $Al_p$ [246–171–17 = 58 mmol m$^{-2}$ yr$^{-1}$; Eq. (16) used for $Al_i$], the sedimentation flux of $Al_p$ ($F_{SED}$) can be calculated from the $Al_p$ mass budget (Fig. 1), using

$$F_{SED}(Al_p) = F_{IN}(Al_p) + F_{PREC}(Al_p) + F_{COAG}(Al_p) - F_{OUT}(Al_p) - \Delta M(Al_p).$$  

(19)

Thus, $F_{SED}(Al_p) = 4+93+0−41−(−2) = 58$ mmol m$^{-2}$ yr$^{-1}$ (Table 2).

The net in-lake $H^+$ production associated with $Al^{III}$ removal (Table 3) was affected by five combinations of changes in $Al$ concentration and charge:

1. The change in average charge of $Al$ entering the lake: The outflow from Plešné Lake had higher discharge-weighted pH (4.72) than the inlet water (4.26) due to the internal ANC production, associated predominantly with the in-lake reduction of $NO_3^−$, $SO_4^{2−}$, and $A^−$ fluxes (Kopaček et al., 2006a). The $Al$ entering the lake by acidic inlets hydrolysed at higher lake-water pH, changing its charge from the inlet $n_{IN} = 2.60$ to $n_{OUT} = 1.78$ in the outlet. The associated $H^+$ production was calculated from

$$H^+ = [n_{IN} − n_{OUT}] F_{IN}(Al_i)$$  

(20)

and was the second most important $H^+$ source for the lake among the $Al^{III}$ transformations, producing 130 meq H$^+$ m$^{-2}$ yr$^{-1}$ (Table 2).

2. The change in $Al_i$ charge in the lake between the start and end of the mass budget period: The pool of $Al_i$ present in the lake at the beginning of mass budget period ($M_{START}$ mmol m$^{-2}$), increased its charge from the original $n$ value ($n_{START} = 1.21$) to a new value ($n_{END} = 1.30$) at the end of the period, corresponding to the decrease in the volume-weighted lake water pH from 5.03 to 4.97. The associated

Fig. 1 – Major in-lake fluxes ($F$; mmol m$^{-2}$ yr$^{-1}$) and annual changes in the internal pools ($\Delta M$; mmol m$^{-2}$ yr$^{-1}$) of aluminium and their impact on $H^+$ production. $T$ = total, $o$ = organic, $i$ = ionic, $p$ = particulate, $Al_T = Al_o+Al_i+Al_p$, IN = into lake, OUT = out of lake, LIB = liberation ($Al_o$ transformation to $Al_i$), COAG = coagulation ($Al_i$ transformation to $Al_p$), PREC = $Al_i$ hydrolysis and precipitation of $Al(OH)_3$ ($Al_p$ transformation to $Al_p$), SED = sedimentation of $Al_p$ and $P(H^+) = H^+$ production, defined as in-lake retention of $Al^{III}$ (meq m$^{-2}$ yr$^{-1}$) by Eq. (16). In-lake changes in pools of the individual $Al$ forms are defined by Eqs. (17)–(19) as follows: $\Delta M(Al_o) = F_{IN}(Al_o)−F_{LIB}(Al_o)−F_{COAG}(Al_o)−F_{OUT}(Al_o)$; $\Delta M(Al_i) = F_{IN}(Al_i)−F_{LIB}(Al_i)−F_{COAG}(Al_i)−F_{OUT}(Al_i)$; $\Delta M(Al_p) = F_{IN}(Al_p)−F_{PREC}(Al_p)−F_{COAG}(Al_p)−F_{OUT}(Al_p)$–$F_{SED}(Al_p)$.

### Table 3 – Mass budgets of $Al^{III}$ and $Fe^{III}$ in Plešné Lake in the 2005 hydrological year

<table>
<thead>
<tr>
<th></th>
<th>$Al^{III}$</th>
<th>$Fe^{III}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{START}$</td>
<td>52</td>
<td>23</td>
</tr>
<tr>
<td>$M_{END}$</td>
<td>67</td>
<td>0.7</td>
</tr>
<tr>
<td>$F_{IN}$</td>
<td>416</td>
<td>1.9</td>
</tr>
<tr>
<td>$F_{OUT}$</td>
<td>149</td>
<td>2.4</td>
</tr>
<tr>
<td>$R$</td>
<td>252</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Units are meq m$^{-2}$ yr$^{-1}$ for $F$ (fluxes) and $R$ (net retention) values and meq m$^{-2}$ for $M$ values. $M_{START}$ and $M_{END}$ are pools of metals in the lake at the beginning and end of the hydrological year, respectively. $F_{IN}$ and $F_{OUT}$ are input and output fluxes of metals, respectively. Net retention of metal species was calculated from Eq. (16); e.g., for $Al^{III}$: 416–149–(67−52) = 252.
H⁺ production was calculated from
\[ H⁺ = \left\{ \begin{array}{l} p_{\text{start}} - p_{\text{end}} \right\} M_{\text{start}}(Al) \] (21)
and was \(-4\) meq m⁻² yr⁻¹ (Table 2). Thus, 4 meq H⁺ m⁻² yr⁻¹ was removed from the system due to the Al buffering system.

3. The change in Al₃⁺ storage in the lake between the start and end of the mass budget period: The change in H⁺ pool associated with the change in Al₃⁺ storage in the lake between the start and end of mass budget period was calculated from:
\[ H⁺ = \left\{ \begin{array}{l} p_{\text{end}} - p_{\text{start}} \right\} M_{\text{end}}(Al) - M_{\text{start}}(Al). \] (22)

In the 2005 hydrological year, the in-lake Al₃⁺ pool increased by 8 mmol m⁻² yr⁻¹ and the \(p_{\text{end}}\) and \(p_{\text{start}}\) values were 1.78 and 1.30, respectively, resulting in a production of 4 meq H⁺ m⁻² yr⁻¹ (Table 2).

4. The change in Al₃⁺ concentration due to liberation from Al₅⁺: The liberation of Al₃⁺ from organically bound Al₅⁺ is associated with net H⁺ retention. Laboratory photochemical experiments suggested that three equivalents of H⁺ are consumed per mole of Al₅⁺ liberated from organic complexes (Kopáček et al., 2003), in accordance with the assumption that H⁺ competes with Al₅⁺ for ligand complexation sites in acidic waters (Vance et al., 1996). The liberated Al₅⁺, however, hydrolysed and decreased its charge to \(p_{\text{end}}\) producing (3-\(p_{\text{end}}\)) equivalents of H⁺ per mole of liberated Al₃⁺ (Kopáček et al., 2003). Thus, the net H⁺ production associated with the liberated Al₅⁺ was calculated by
\[ H⁺ = -p_{\text{end}}F_{\text{LIB}}(Al₃⁺). \] (23)

In the 2005 hydrological year, 25 mmol Al₅⁺ m⁻² yr⁻¹ was liberated from organic complexes in the form of Al₅⁺, which hydrolysed to \(p_{\text{end}}\) of 1.78, resulting in the net removal of 44 meq H⁺ m⁻² yr⁻¹ (Table 2). Consequently, the liberation of Al₃⁺ from Al₅⁺ was an important ANC-producing process. The associated net ANC production from photo-oxidation of Al₅⁺ varies inversely with pH. It is high in acidic waters, with high \(p_{\text{end}}\) values. In contrast, the liberated Al₃⁺ is nearly completely hydrolysed at pH > 6 and net ANC production is smaller, reflecting a level of pH-dependent deprotonation of organic ligands.

5. The change in Al₃⁺ concentration due to precipitation losses: The H⁺ production associated with the precipitation of Al(OH)₃ was calculated using Eq. (24), assuming that the charge of the precipitated Al₃⁺ decreased to zero:
\[ H⁺ = p_{\text{end}}F_{\text{REC}}(Al₃⁺). \] (24)

Al₃⁺ precipitation had the most important impact on H⁺ balance among the Al transformations in Plesné Lake, producing 166 meq H⁺ m⁻² yr⁻¹ (Table 2).

The sum of the five individual H⁺-producing and -removing processes was 252 meq H⁺ m⁻² yr⁻¹ (Table 2) and was equivalent to that calculated using Eq. (16) (Table 3). Summing Eqs. (20)–(24) and substituting \(F_{\text{REC}}\) for the right-hand side of Eq. (17) yields Eq. (16) for the major Al⁺⁺ fluxes, which provides proof that Eqs. (20)–(24) describe properly the impact of individual Al transformations on the internal H⁺ budget.

We did not include another in-lake metal transformation that may occur in lakes with less acidic inlets and higher Al₅⁺ inputs than Plesné Lake. Al(OH)₃ [and also Fe(OH)₃] precipitated in their inlets and deposited on the stream bed can be re-suspended at high discharge events and exported to downstream lakes (Norton and Henriksen, 1983; Roy et al., 1999). The hydroxides can dissolve in the lake, provided its pH is < ~6 according to Eqs. (9) and (10), removing H⁺ equivalently to the resulting Al⁺⁺ (or Fe⁺⁺) production. This process does not require a new equation, because it is included in Eq. (17); the decrease in the input flux of Al₅⁺ would be reciprocal to the increase in \(F_{\text{OUT}}(Al₃⁺)\) and \(\Delta M(Al)\) fluxes.

3.2. Iron

The 2005 mass budget for Fe species in Plesné Lake differed from that for Al in several aspects, most importantly in the higher proportion of Fe₆⁺ in the Fe₇⁺ pool in the inlet water and net in-lake production of Fe₇⁺ (Table 2). The Fe₇⁺ input flux (12.4 mmol m⁻² yr⁻¹) was dominated (75%) by Fe₆⁺, while Fe₁ and Fe₃ represented 14% and 11%, respectively. The Fe₇⁺ output flux (13.7 mmol m⁻² yr⁻¹) exceeded the input flux and the proportion of Fe₆⁺ decreased to 49%, while that of Fe₇⁺ increased to 34%. The Fe₆⁺ pool in the lake decreased from 17.2 to 16.6 mmol m⁻² yr⁻¹. The lake was a net Fe source, producing 0.7 mmol Fe₇⁺ m⁻² yr⁻¹ [i.e., retaining 12.4–13.7–(0.6) = 0.7 mmol m⁻² yr⁻¹; Eq. (16) used for Fe₇⁺]. Consequently, the sedimentation rate, calculated from Eq. (19) for Fe₆⁺, resulted in negative values (Table 2). Such a negative sedimentation flux of Fe₂⁺ and in-lake production of Fe₇⁺ was no exception during the 2001–2005 mass budgets of the Bohemian Forest lakes (Kopáček et al., 2006a) and could result from two possible sources: (i) Fe could be liberated from sediments during anoxia as Fe²⁺ (Eq. (13)), accumulated in the hypolimnion, and then, oxidised and precipitated as Fe₆⁺ underoxic conditions (Eq. (5)) during mixing periods, and partly exported from the lake. (ii) The input flux of Fe could be underestimated. The most probable source of undocumented input is groundwater, which typically is reduced and carries substantially higher concentrations of dissolved Fe than surface water. Other possible sources include deposition of needles from shoreline trees (Psencner, 1984) and overland flow directly into the lake. Because the Fe fluxes were one to two orders of magnitude lower than those of Al (Tables 2 and 3), underestimated metal inputs could have a relatively higher impact on the precision of the Fe mass budget.

The impact of Fe transformations on H⁺ budget, calculated from the respective Eqs. (20)–(24), was far less important that of Al transformations due to lower Fe concentrations (Table 2): (1) the hydrolysis of the inlet Fe⁺⁺⁺ resulted in a decrease of the in-lake \(m_{\text{IN}} = 1.14\) to the outlet \(m_{\text{OUT}} = 1.03\), and net production of 0.18 meq H⁺ m⁻² yr⁻¹. (2) The change in Fe⁺⁺⁺ charge from the original value of \(m_{\text{START}} = 0.98\) to the end value of \(m_{\text{END}} = 0.99\) due to lower pH removed 0.02 meq H⁺ m⁻² yr⁻¹. (3) The change in storage of Fe⁺⁺⁺ in the lake caused net removal of 0.07 meq H⁺ m⁻² yr⁻¹. (4) The liberation of Fe₁ from organically bound Fe₆⁺ and its subsequent hydrolysis removed 1.77 meq H⁺ m⁻² yr⁻¹. (5) The H⁺ production associated with the precipitation of Fe(OH)₃ was 2.79 meq H⁺ m⁻² yr⁻¹. In these calculations, coagulation of Fe₆⁺ was neglected as it was for Al₃⁺. Altogether, the Fe transformations were a net source of 1.1 meq H⁺ m⁻² yr⁻¹. The same
result was obtained from Eq. (16) calculated for Fe$^{m+}$ analogously to Al$^{m+}$ (Table 3).

Neither the analytical method used for determination of Fe concentrations nor the precision of the water budget used for calculation of Fe fluxes justifies results in two decimals. The values of Fe fluxes were not, however, rounded so as to demonstrate how they were calculated.

The possible impacts of unquantified Fe sources on the internal H$^+$ pool can be estimated as follows: (i) Fe$^{z+}$ liberation from sediments removes two H$^+$ (Eq. (13)) that are re-released during Fe$^{z+}$ re-oxidation to Fe(OH)$_3$ in the oxic water (Eq. (5)). Provided this Fe leaves the lake as Fe$_p$ in the form of Fe(OH)$_3$, there is no net change in H$^+$ budget. If this Fe leaves the lake in the form of Fe$_e$, the net H$^+$ removal (ANC production) is equivalent to the related Fe$^{m+}$ flux; Fe(OH)$_3$ changes to Fe(OH)$_{3-m}$ (Eq. (9)), where $m = m_{OUT}$ (ii) In the case of unmeasured input of Fe$^{z+}$ from groundwater, the net H$^+$ production would be by 2 mol mol$^{-1}$ of Fe greater (Eqs. (5) and (9)) than in the previous case. (iii) In the case of unmeasured input of Fe$_e$ from terrestrial sources or groundwater, there is no impact on H$^+$ budget, if Fe leaves the lake as Fe$_{og}$. In contrast, if Fe is liberated from Fe$_{og}$, the net H$^+$ removal is equivalent to the related Fe$^{m+}$ flux, where $m = m_{OUT}$. In all cases, the net impact of Fe transformations on H$^+$ pools depends on the production of Fe$_e$.

3.3. Impact of Al and Fe transformations on in-lake ANC production in Plešné Lake

The net in-lake H$^+$ retention was 284 meq m$^{-2}$ yr$^{-1}$ in Plešné Lake in the 2005 hydrological year (Kopáček et al., 2006a). The most important in-lake ANC-producing processes were NO$_3^-$ denitrification and assimilation, SO$_4^{2-}$ reduction in sediment, and photochemical and microbial Al$^{x-}$ decomposition, removing 531, 32, and 84 meq H$^+$ m$^{-2}$ yr$^{-1}$, respectively. In contrast, Al transformations dominated (65%) the total internal H$^+$ production; the remaining H$^+$ source was associated with base cations and ammonium (Kopáček et al., 2006a). Fe transformations were a significantly smaller H$^+$ source (1.1 meq H$^+$ m$^{-2}$ yr$^{-1}$), due to lower Fe fluxes (Table 2). The total net H$^+$ production associated with the in-lake Al and Fe processing was 253 meq m$^{-2}$ yr$^{-1}$. The annual average runoff was 9.04 m$^3$ m$^{-2}$ yr$^{-1}$ on the lake area basis in 2005 (Kopáček et al., 2006a). The average ANC reduction due to Al and Fe transformations thus represented 28 μeq l$^{-1}$ (253 meq m$^{-2}$ yr$^{-1}$/9.04 m$^3$ m$^{-2}$ yr$^{-1}$) and significantly reduced the net ANC production that resulted from the internal alkalinity-generating processes in a system that had virtually no carbonate system buffering capacity.

4. Conclusions

Al and Fe fluxes translocate significant amounts of ANC through acidified catchment-lake ecosystems. Terrestrial export of ionic metal species produces ANC in acidic soils, but their hydrolysis in less acidic lakes represents an important H$^+$ source that decreases the net in-lake ANC production associated with the reduction of NO$_3^-$, SO$_4^{2-}$, and Al$^{x-}$ fluxes, or even HCO$_3^-$ buffering. Terrestrial export of dissolved organically bound species and particulate hydroxides has no net effect (except for Fe(OH)$_3$ produced by FeS oxidation) on soil solution ANC. The liberation of Al$_{ig}$ and Fe$_e$ from both organic complexes and particulate metal hydroxides represents a significant H$^+$ removal, producing ANC in the lakes. The net H$^+$ production associated with transformations of the metals depends on their fluxes, the change in pH between the inlet and outlet, changes in in-lake storage, and proportion of ionic, organic, and particulate forms in the inlet water. Hydrolysis of Al$_{ig}$ and Fe$_e$ produces less H$^+$ (removes less ANC) in acidic than in circum-neutral waters due to smaller changes in their charges. In contrast, the highest H$^+$ removal (highest ANC production), associated with Al$_{ig}$ and Fe$_e$ liberation from organic complexes and metal hydroxides, occurs in strongly acidic waters (pH < 4.5) and has smaller effect in circum-neutral waters. In Plešné Lake, net H$^+$ production associated with Al$_{ig}$ and Fe$_e$ hydrolysis and precipitation exceeded H$^+$ removal associated with Al$_{og}$ and Fe$_{og}$ liberation, with a net ANC reduction of 28 μeq l$^{-1}$ in the 2005 hydrological year.

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