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Acidification of Northeastern USA Lakes From Rising Anthropogenic-Sourced Atmospheric Carbon Dioxide and Its Effects on Aluminum Speciation

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Key Points:

- Rising atmospheric CO₂ from anthropogenic activities will lead to acidification of lakes in the northeastern USA during the 21st century
- Acidification will alter Al speciation and lower concentrations required to cause a sub-lethal response in 20% of the resident brook trout
- Anthropogenic-sourced CO₂ could reverse gains in lake water quality realized since implementation of the Clean Air Act

Supporting Information:

Supporting Information may be found in the online version of this article.

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Acidification Of Northeastern USA Lakes From Rising Anthropogenic-Sourced Atmospheric Carbon Dioxide and Its Effects on Aluminum Speciation

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Abstract The impact of rising atmospheric CO₂ (pCO₂^{atm}) from anthropogenic activities on pH, dissolved inorganic carbon, carbonate mineral saturation, and aluminum (Al) speciation is evaluated for 18 northeastern USA lakes using polythermal, sliding activity reaction path models. pCO₂^{atm} was forced using two scenarios from the IPCC's Sixth Assessment Report in which pCO₂^{atm} attains either 600 or 1,100 ppm in 2,100. Results suggest pH will decrease 0.15 and 0.32 pH units, $\alpha_{\text{CO}_3^{2-}}$ will decrease 24% and 49%, and $\Omega_{\text{aragonite}}$ will decrease 21% and 45%, respectively. These changes are of the same magnitude as those expected for the oceans. The effects of rising pCO₂^{atm} on sub-lethal 20% effect concentrations (i.e., EC20) of Al for brook trout (*Salvelinus fontinalis*) are evaluated with the biotic ligand model, which indicates Al toxicity effects will increase as pH decreases. These changes could reverse gains in water quality and fisheries health achieved since implementation of the Clean Air Act.

Plain Language Summary Fossil fuel consumption, deforestation, and changing land use are all contributing to rising CO₂ concentrations in the atmosphere. In addition to atmospheric warming and climate impacts, rising atmospheric CO₂ will also promote acidification of ocean surface waters, which is expected to have detrimental effects on marine ecosystems. Much less is known about how rising atmospheric CO₂ will impact terrestrial freshwaters such as lakes and streams. We developed reaction path models for 18 lakes from northeastern USA to investigate possible impacts of rising atmospheric CO₂ and temperature on these systems. The models indicate that acidification of these lakes could be of similar magnitude to ocean acidification. The saturation state of these lakes with respect to the mineral aragonite, which is important for calcifying organisms, will also decrease. Finally, acidification will alter aluminum (Al) speciation, which could augment toxic effects from this metal on important sport fish like brook trout, possibly reversing gains made in water quality since implementation of the Clean Air Act decreased the input of strong acids via acid rain.

1. Introduction

Acidification of the ocean from rising atmospheric CO₂ concentrations (pCO₂^{atm}) derived from anthropogenic activities, chief among which is the combustion of fossil fuels, is of concern for several reasons including ensuring the sustainability of important shellfish fisheries and marine ecosystems (Doney et al., 2009; Orr et al., 2005; Waldbusser et al., 2015). Despite efforts to understand and predict the impacts of human-driven rises in pCO₂^{atm} on ocean acidification (Balch et al., 2022; Millero et al., 2009), less effort has focused on the likelihood these processes will also lead to acidification of terrestrial, freshwater systems (e.g., Ninokawa & Ries, 2022; Phillips et al., 2015). Acidification of lakes and streams by increasing atmospheric CO₂ could be more marked and occur more rapidly than in marine systems as most terrestrial freshwaters exhibit lower alkalinities than the ocean and hence possess lower buffering capacities.

A complicating factor in the study of lake acidification by rising pCO₂^{atm} is that most lakes appear to be supersaturated with respect to CO₂ (e.g., Cole et al., 1994; Lazzarino et al., 2009; Raymond et al., 2013). Consequently, lakes are thought to be net sources of CO₂ to the atmosphere owing to the pCO₂ gradient between their surface waters and the overlying atmosphere (Alin & Johnson, 2007; Hanson et al., 2004). At the same time, direct measurements of lake surface water pCO₂ values (i.e., pCO₂^{water}) are relatively rare. Instead, most reported pCO₂^{water}

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values are computed from coupled, in situ measurements of pH and alkalinity, pH and dissolved inorganic carbon (DIC) concentrations, or DIC and alkalinity using carbonate equilibria and geochemical software (e.g., Hunt et al., 2011). However, owing to the low accuracy and precision that commonly characterizes measurements of CO₂-system parameters of many lake data sets, the computed pCO₂^{water} values are known to be highly uncertain and thus, difficult to evaluate as shown by direct comparisons of measured and calculated pCO₂^{water} values (Abril et al., 2015; Golub et al., 2017). Nonetheless, although lakes are commonly sources of CO₂ to the atmosphere, this feature will not inevitably shield them from the effects of rising atmospheric CO₂-driven acidification (Phillips et al., 2015).

During the 1970s through the early 1990s meteoric deposition of strong acids such as sulfuric and nitric acid originating from the burning of high sulfur fossil fuels and automobile exhausts, respectively, led to the acidification of lakes and streams in the northeastern USA, Ontario, Quebec, and Atlantic Canada, as well as northern Europe (Driscoll, 1991; Likens et al., 1972; Schindler, 1988). The enactment of the Clean Air Act in the USA, the Eastern Canada Acid Rain Program in Canada, and similar legislation in Europe, helped to dramatically decrease SO₂ emissions from fossil fuel fired power plants, which has since led to the recovery of many previously acidified watersheds in these regions (Skjelkvåle et al., 2005; Stoddard et al., 1999; Strock et al., 2014). Although sulfuric acid deposition decreased substantially following the implementation of these environmental laws, nitric acid deposition appears to have remained relatively constant (Driscoll et al., 2003). These legislative efforts, however, did not explicitly address the increase of atmospheric CO₂ owing to fossil fuel consumption, deforestation, and land use change, or its potential impact on poorly buffered lakes and streams. In this contribution we conduct simple numerical experiments to investigate acidification of several oligotrophic lakes in northeastern USA that could occur between now and 2100 if pCO₂^{atm} attains a concentration of 600 or 1,100 ppm (e.g., Arias et al., 2021). Our modeling includes the impacts of rising atmospheric CO₂ and temperature on lake surface water pH, DIC species, and carbonate mineral saturation states. In addition, we examine the possible impact of CO₂-induced acidification on aluminum (Al) speciation in selected lakes including expected toxic effects of changing Al speciation on the important sport fish brook trout (*Salvelinus fontinalis*).

2. Methods

Major ion chemistry (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻), alkalinity, pH, dissolved silica, dissolved oxygen, water temperature, along with sampling dates, depths, and locations were obtained from the literature and online water quality databases maintained by individual US state agencies. The partial pressure of CO₂ in the atmosphere (pCO₂^{atm}) at the time of each lake's most recent sampling was estimated from the Mauna Loa Observatory record (NOAA, 2022) for the year sampled. For compiled information used in the modeling see Tables S1 and S2 in Supporting Information S1.

To investigate possible effects of rising pCO₂^{atm} on the studied lakes, we first developed equilibrium models for each lake's surface water using the compiled geochemical data. Subsequently, we simulated changes in surface water chemistry using polythermal, sliding activity/fugacity reaction path models to raise temperature (see O'Reilly et al., 2015) and pCO₂^{atm} from levels corresponding to the global estimate for the year when each lake was last sampled, up to a value of 1,100 ppm for 2100 as per scenario SSP5-8.5 of the IPCC's Sixth Assessment Report (Arias et al., 2021). Thus, in contrast to other investigations that present changes in surface water pH and carbonate chemistry relative to time (e.g., specific years, Phillips et al., 2015), our approach shows how the lakes could respond as a function of increasing temperature and pCO₂^{atm} up to a maximum of 1,100 ppm (scenario SSP5-8.5). If, however, rising pCO₂^{atm} more closely follows scenario SSP2-4.5 of the IPCC's Sixth Assessment Report where pCO₂^{atm} attains 600 ppm in 2100, then the model predicted changes in pH and carbonate chemistry can be estimated by inspection of the model plots assuming a final pCO₂^{atm} of 600 ppm (Figure 1). Although some studies indicate that pCO₂^{atm} may rise as high as 2,000 ppm by 2,300 (e.g., Caldeira & Wickett, 2003; Millero et al., 2009), we confine our assessments to changes during the 21st century. The modeling approach follows that of Phillips et al. (2015), which assumes that as pCO₂^{atm} increases, pCO₂^{water} will also increase proportionally to keep the lake-to-air CO₂ flux constant and maintain steady-state conditions in the lakes.

3. Results and Discussion

Equilibrium modeling indicates that most of the studied lakes are supersaturated with respect to atmospheric CO₂ (Figure S1 in Supporting Information S1). The only exceptions are Lake George, Nubanusit Lake, and Mendums

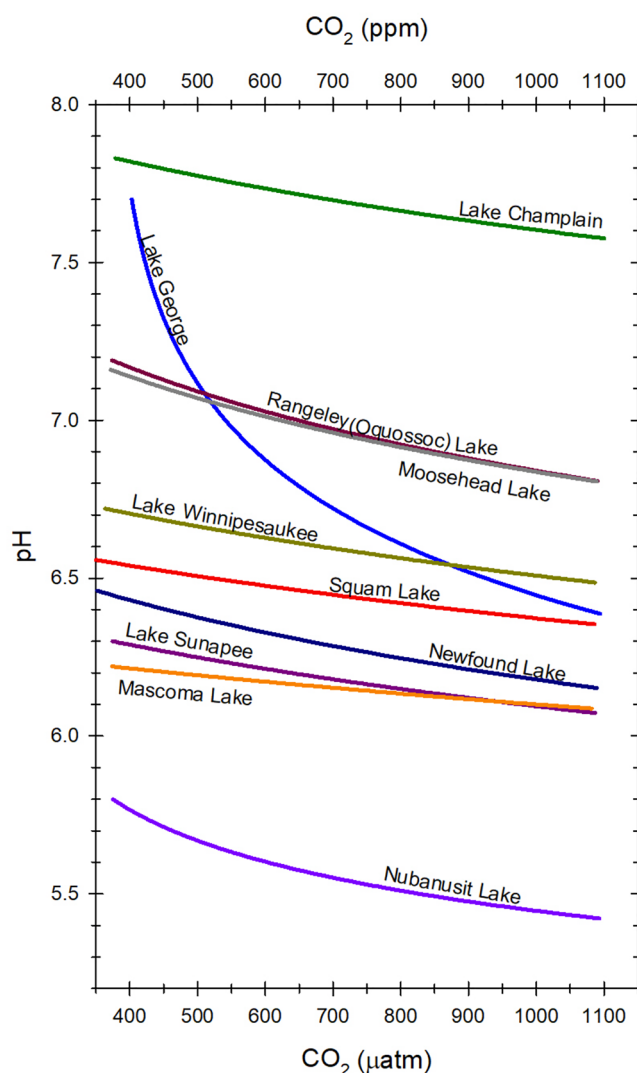


Figure 1. Predicted changes in pH owing to rising $p\text{CO}_2^{\text{atm}}$ for 10 lakes from northeastern USA. Additional results for eight other lakes are presented in Figure S3 in Supporting Information S1.

Pond. Nevertheless, all the studied lakes are expected to become more acidic as $p\text{CO}_2^{\text{atm}}$ increases, because $p\text{CO}_2^{\text{water}}$ will also increase (e.g., McKinley et al., 2020; Phillips et al., 2015). Predicted pH changes in the studied lakes are shown in Figure 1 and Figure S3 in Supporting Information S1. Modeled changes in pH, the activity of carbonate species (i.e., $a_{\text{H}_2\text{CO}_3^*}$, $a_{\text{HCO}_3^-}$, and $a_{\text{CO}_3^{2-}}$), and the saturation state of aragonite and calcite as a function of increasing $p\text{CO}_2^{\text{atm}}$ for three lakes that span the range of pH buffering capacity of the studied lakes are presented in Figure 2. All results for the other 15 lakes investigated are shown in Figures S5–S10 in Supporting Information S1.

For scenario SSP5-8.5 of the IPCC's Sixth Assessment Report in which $p\text{CO}_2^{\text{atm}}$ attains 1,100 ppm by 2100, the modeling indicates that pH would decrease between a low of 0.13 pH units in Mascoma Lake (New Hampshire) to as much as 1.31 pH units in Lake George (New York), with an average decrease across the 18 lakes of 0.32 pH units (Johannesson, 2023a). These pH decreases translate to increases in the activity of the hydrogen ion (i.e., a_{H^+}) of between 30% and 180%, with an average increase of 65% across all 18 lakes. If instead atmospheric CO_2 only attains a concentration of 600 ppm by 2100 (scenario SSP2-4.5), then the pH of surface waters of the studied lakes would decrease by between 0.05 and 0.83 pH units, with an average decrease of 0.15 pH units (Johannesson, 2023a). Hence, for scenario SSP2-4.2, the models indicate that, on average, a_{H^+} would increase by ca. 30% in the studied lakes. These changes are similar, albeit, slightly lower than predicted pH decreases for the ocean of 0.3–0.4 pH units and up to a 150% increase in a_{H^+} (Orr et al., 2005; Phillips et al., 2015).

There is a weak to moderate inverse correlation (i.e., $R^2 = 0.39$) between the buffering capacity of the 18 studied lakes and the model predicted changes in pH, which is statistically significant at the 95% confidence level (Figure S4 in Supporting Information S1). Hence, lower buffering capacity indicates a greater likelihood that rising atmospheric CO_2 will lead to a larger decrease in surface water pH. Nonetheless, testing this relationship requires careful monitoring of how $p\text{CO}_2^{\text{water}}$, pH, and alkalinity of lakes respond to changing $p\text{CO}_2^{\text{atm}}$.

The modeling demonstrates that carbonate anion activities, $a_{\text{CO}_3^{2-}}$, would decrease by between 23.4% and 180%, and exhibit an average decrease of 49%, if $p\text{CO}_2^{\text{atm}}$ rises according to scenario SSP5-8.5, whereas $a_{\text{CO}_3^{2-}}$ would decrease between 8% and 146%, with an average decrease of 24%, assuming

that increases in $p\text{CO}_2^{\text{atm}}$ more closely follow scenario SSP2-4.5. The average predicted decrease in $a_{\text{CO}_3^{2-}}$ for all 18 lakes is thus of the same magnitude as the expected 50% decrease in CO_3^{2-} concentrations in ocean surface waters (Orr et al., 2005; Phillips et al., 2015). If Nubanusit Lake and Mendums Pond (both in New Hampshire) are excluded, the average decrease in $a_{\text{CO}_3^{2-}}$ rises to 59% and 29% for scenarios SSP5-8.5 and SSP2-4.5, respectively. Decreases in the saturation state of the studied lakes with respect to aragonite and calcite are predicted to be nearly identical (Figure 2 and Figures S5–S10 in Supporting Information S1). Specifically, aragonite and calcite saturation states (i.e., $\log Q/K = \log \Omega$) would decrease between approximately 20% to 179% for scenario SSP5-8.5 (average decrease $\sim 45\%$), and 7%–145% for scenario SSP2-4.5 (average decrease $\sim 21\%$).

Although the effect of rising atmospheric CO_2 on ocean acidification and hence marine calcifying organisms has elicited substantial concern (Andersson et al., 2008; Kawahata et al., 2019; Kleypas et al., 1999), the potential impact to freshwater calcifiers from increasing $p\text{CO}_2^{\text{atm}}$ has only recently been addressed (Ninokawa & Ries, 2022). Rising atmospheric CO_2 increases the carbonic acid concentrations (H_2CO_3^*) of surface waters according to Henry's Law (i.e., $a_{\text{H}_2\text{CO}_3^*} = K_{\text{CO}_2} p\text{CO}_2^{\text{atm}}$), which subsequently dissociates to HCO_3^- and H^+ , shifting the carbonate buffer system toward HCO_3^- as CO_3^{2-} reacts with H^+ (Orr, 2011; Orr et al., 2005).

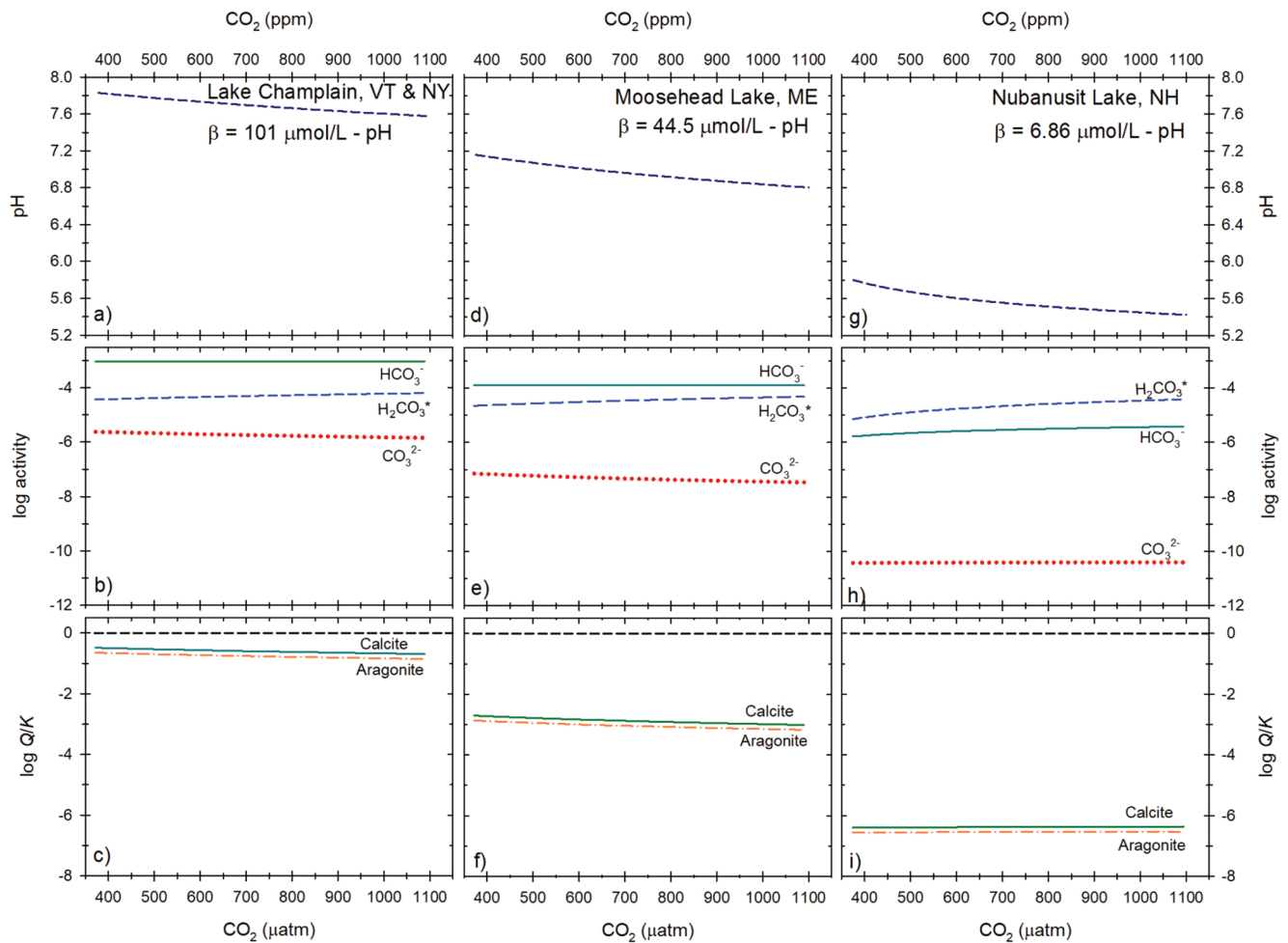


Figure 2. Model results for three lakes that span the pH buffering capacity (i.e., β) of the 18 lakes studied (Table S1 in Supporting Information S1) that could result if $p\text{CO}_2^{\text{atm}}$ increases to 1,100 ppm by 2100. Panels (a), (d), and (g) show the predicted changes in pH for Lake Champlain (Vermont—New York border), Moosehead Lake (central Maine), and Nubanusit Lake (southwestern New Hampshire). Panels (b), (e), and (h) present the log activity of H_2CO_3^* , HCO_3^- , and CO_3^{2-} that would accompany the decreasing pH, and panels (c), (f), and (i) demonstrate how carbonate mineral saturation states (i.e., $\log Q/K = \log \Omega$) of each lake would change. The horizontal dashed lines in panels (c), (f), and (i) represent saturation for each mineral.

Because calcifying organisms like mollusks require the CO_3^{2-} anion to precipitate their shells, this decrease in the carbonate ion concentration forces these organisms to consume more energy to regulate their internal shell forming metabolic processes. The impact of CO_2 -induced acidification on carbonate mineral saturation states is particularly problematic for larval stages of calcifying organisms (Gledhill et al., 2015; Waldbusser et al., 2015). Unlike the ocean, freshwater systems are commonly undersaturated with respect to aragonite and calcite. Hence, freshwater calcifying organisms can tolerate substantially lower carbonate mineral saturation states than marine calcifiers (Ninokawa & Ries, 2022). Nevertheless, the much lower alkalinity and pH buffering capacity of freshwater systems compared to the ocean can still negatively impact freshwater calcifiers (Ninokawa & Ries, 2022), especially as rising atmospheric CO_2 drives these systems to progressively lower saturation states with respect to carbonate minerals (Beaune et al., 2018). Our modeling demonstrates that $a_{\text{CO}_3^{2-}}$ will decrease in the studied lakes as $p\text{CO}_2^{\text{atm}}$ increases during the 21st century, pushing carbonate mineral saturation states to even more undersaturated conditions (Figure 2). The impact of these changes on indigenous calcifying organisms is currently unknown.

In addition to calcifiers, other freshwater organisms can also be adversely impacted by CO_2 -induced acidification and rising temperatures. For example, acidification can negatively impact freshwater crustaceans by lowering the activity of calcium ions in solution (Beaune et al., 2018; Tagliarolo, 2018). Moreover, increasing $p\text{CO}_2^{\text{water}}$ has been shown to hamper growth rates and embryonic development of pink salmon (*Oncorhynchus gorbuscha*)

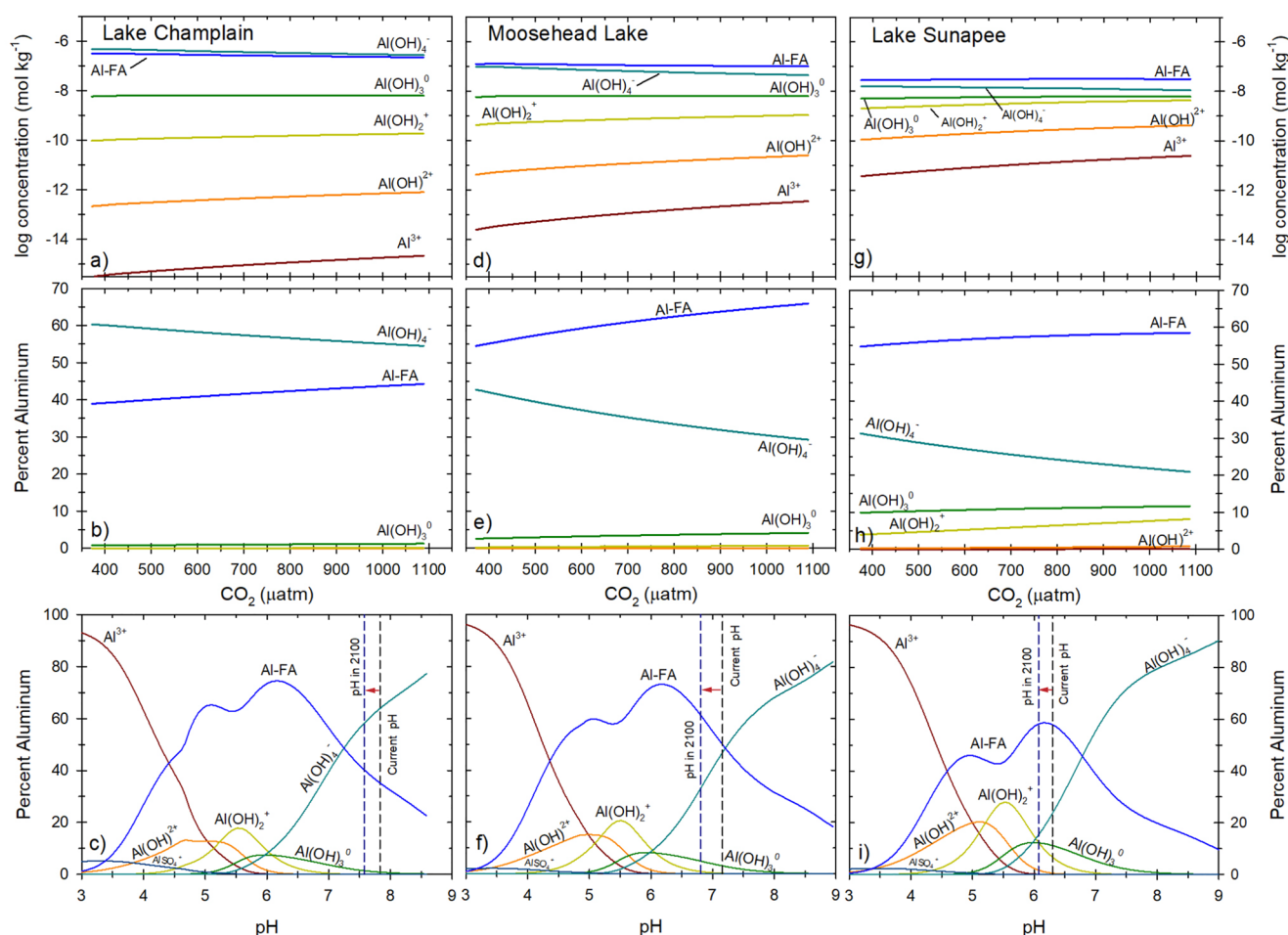


Figure 3. Aluminum speciation for three lakes from northeastern USA as a function of rising atmospheric CO_2 concentrations. In each panel Al-FA (bright blue curves) represents Al complexed with fulvic acid. Results for Lake Champlain are shown in panels (a), (b), and (c), Moosehead Lake in panels (d), (e) and (f), and Lake Sunapee (central New Hampshire) in panels (g), (h), and (i). Panels (a), (d), and (g) show predicted changes in Al species concentrations (as log [mol kg⁻¹]). Panels (b), (e), and (h) show the same results as percent total aluminum. Panels (c), (f), and (i) show percent Al versus pH for each lake. Dashed vertical black line in panels (c), (f), and (i) represents the current mean pH of surface waters in each lake, whereas the dashed blue vertical line to the left indicates pH in 2100 assuming scenario SSP5-8.5 of the IPCC's Sixth Assessment Report (Arias et al., 2021). Small red arrow shows the modeled acidification of these lakes.

during their freshwater development as well as egg hatchability, growth, and survival in brook trout, arctic char (*Salvelinus alpinus*), and Atlantic salmon (*Salmo salar*) among other economically important sport fish (Jagoe & Haines, 1983; Lacroix, 1985; Ou et al., 2015; Peterson et al., 1980).

Decreasing pH also commonly enhances concentrations of potentially toxic metals such as lead (Pb), mercury (Hg), and aluminum (Al), which together with pH stress, can have particularly negative impacts on freshwater biota (Cleveland et al., 1986; Parkhurst et al., 1990; Wang et al., 2016). Although amelioration of Al toxicity has been reported for lakes and streams in New York's Adirondack Mountains owing to substantial decreases in strong acid deposition (Baldigo et al., 2020; Michelena et al., 2016), future acidification of these freshwater environments by rising anthropogenic-sourced CO_2 could potentially reverse gains in these lakes and streams, as well as those of northern New England.

Aluminum speciation as a function of rising $\text{pCO}_2^{\text{atm}}$, and hence decreasing pH is shown in Figure 3 for Lake Champlain, Moosehead Lake, and Lake Sunapee, 3 of the 6 (out of 18) lakes we examined for which Al concentration data are available. The models indicate that in Moosehead Lake and Lake Sunapee Al chiefly occurs as complexes with naturally occurring dissolved organic matter (i.e., fulvic acid complexes), whereas the $\text{Al}(\text{OH})_4^-$ species predominates in Lake Champlain, followed closely by organic complexes (Figure 3). As $\text{pCO}_2^{\text{atm}}$ rises, the fraction of Al complexed with fulvic acid should increase in all three lakes, although the

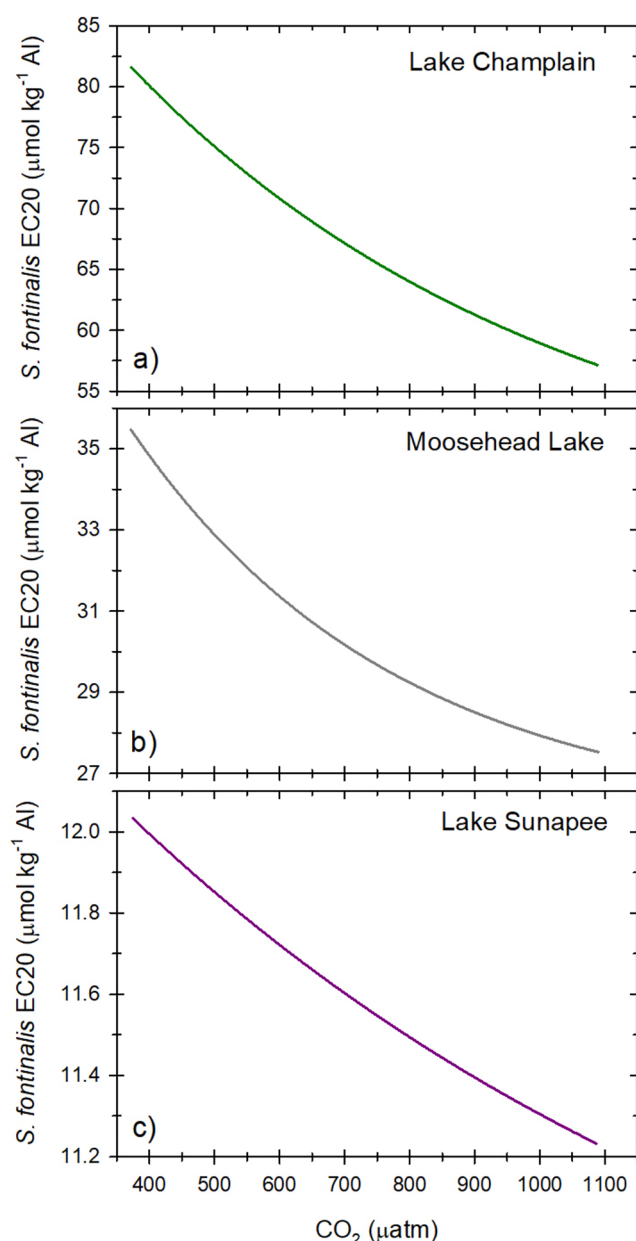


Figure 4. Predicted 20% effect concentrations (EC20) values of Al as a function of increasing $p\text{CO}_2^{\text{atm}}$, and thus decreasing surface water pH in panel (a) Lake Champlain, panel (b) Moosehead Lake, and panel (c) Lake Sunapee for brook trout (*Salvelinus fontinalis*) computed using the biotic ligand model (Santore et al., 2018). The predicted changes in pH in each lake are shown in Figure 1 as a function of rising $p\text{CO}_2^{\text{atm}}$.

to decrease from 85.3%–81.9% of the total Al in Lake Champlain, 81.2%–76.8% of the total Al in Moosehead Lake, and 63.9%–56.3% of the total Al in Lake Sunapee as $p\text{CO}_2^{\text{atm}}$ increases and these lakes acidify over the 21st century. Aluminum oxyhydroxides may form by direct precipitation from the saturated to nearly saturated lake waters, or within fish gills when acidic to circumneutral pH lake waters with relatively high Al concentrations encounter the more alkaline environment characteristic of fish gills (e.g., Gensemer & Playle, 1999; Gensemer et al., 2018; Playle & Wood, 1990). Indeed, the positive surface charge of Al oxyhydroxides (i.e., isoelectric point for gibbsite is ~9; Drever, 1988) will facilitate their adsorption onto the negatively charged gill sites, leading to toxic respiratory effects (Gensemer & Playle, 1999; Teien et al., 2006; Wilkinson et al., 1993).

relative increase is lowest in Lake Sunapee (Figure 3). Complexation of Al with dissolved organic ligands is thought to decrease the metal's toxicity (e.g., Driscoll et al., 1980; Fakhraei & Driscoll, 2015; Gensemer & Playle, 1999).

Nevertheless, the protective effect of organic complexation is compromised at circumneutral pH owing to the precipitation of amorphous to poorly crystalline, colloidal Al oxyhydroxides like amorphous gibbsite [i.e., $\text{Al}(\text{OH})_{3(s)}$], which contributes to Al toxicity by binding to the surfaces of fish gills (Gensemer & Playle, 1999; Gensemer et al., 2018; Poléo et al., 1997). Lake Champlain and Moosehead Lake are saturated with respect to gibbsite and will remain so as $p\text{CO}_2^{\text{atm}}$ increases during the 21st century, whereas Lake Sunapee is slightly undersaturated with respect to gibbsite (Figure S11 in Supporting Information S1).

Speciation modeling further demonstrates that even though Lake Sunapee has the lowest reported Al concentrations of the studied lakes, the concentration of positively charged inorganic Al species [i.e., Al^{3+} , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_2^+$] occur at substantially higher concentrations than in either Lake Champlain or Moosehead Lake (Figure 3 and Figure S12 in Supporting Information S1). Specifically, the sum of the concentrations of these species is 36-fold higher in Lake Sunapee compared to Lake Champlain, and 8 times higher in Lake Sunapee than in Moosehead Lake. These positively charged ionic species can adsorb onto negatively charged brachial surfaces within fish gills leading to toxic osmoregulatory effects (e.g., Gensemer & Playle, 1999; Teien et al., 2006).

The biotic ligand model (BLM; Santore et al., 2018) predicts that the amount of Al complexed to the biotic ligand associated with brook trout in Lake Sunapee ($15.8 \text{ nmol gw}^{-1}$) is 3-fold higher than in Lake Champlain (5.2 nmol gw^{-1}) and 3.5 times greater than in Moosehead Lake (4.4 nmol gw^{-1}), indicating a greater threat from Al in Lake Sunapee. Moreover, the BLM reveals that the 20% effect concentrations (EC20) for brook trout will decrease dramatically in these lakes as $p\text{CO}_2^{\text{atm}}$ increases and the lakes acidify (Figure 4). EC20 values reflect the total Al concentration in each lake that will cause a sub-lethal response in 20% of the resident brook trout population (Wright & Welbourn, 2002). Hence, the Al concentration required to cause sub-lethal effects in 20% of the resident brook trout population will decrease in each lake as $p\text{CO}_2^{\text{atm}}$ increases and pH decreases. Consequently, if total Al concentrations remain approximately constant in each lake, greater percentages of the resident brook trout populations would experience the effects of Al toxicity as the lakes acidify. The effects of Al toxicity to brook trout are currently greatest in Lake Sunapee and will remain so as $p\text{CO}_2^{\text{atm}}$ increases and the lake acidifies during the 21st century.

Most of the toxic effects from Al on brook trout in these lakes will be from precipitated Al oxyhydroxides like amorphous gibbsite (Figure S13 in Supporting Information S1). The relative percent of precipitated Al oxyhydroxides contributing to toxic effects (i.e., EC20) in brook trout is predicted

Therefore, Al oxyhydroxide precipitates represent the greatest Al toxicity threat to brook trout in these lakes (Santore et al., 2018). Aluminum stress on brook trout may also be exacerbated as rising lake water temperatures decrease the solubility of dissolved oxygen, which is necessary for aerobic respiration (e.g., Jane et al., 2021).

Brook trout spawn in the autumn and require well aerated sandy and gravel-rich substrates to build their spawning beds. As such, they commonly migrate up streams from lakes to spawn. During the spring runoff, stream pH can attain values as low as 4 (Burns et al., 2019; Fakhraei & Driscoll, 2015). Many of the streams used by brook trout for spawning in northern New England and New York are also poorly buffered and can exhibit negative acid neutralizing capacities (e.g., Fuss et al., 2015; Gbondo-Tugbawa & Driscoll, 2003; Hall et al., 1985). Consequently, Al toxicity will be most dire for brook trout fry shortly after hatching in the spring when they are most vulnerable to the combined harmful effects of acidity and dissolved and precipitated Al species (e.g., Cleveland et al., 1986, 1989, 1991; Ingersoll et al., 1990; Mount et al., 1990; Wood et al., 1990). Additional research should thus focus on $p\text{CO}_2^{\text{atm}}$ driven acidification of lakes and streams in the northeastern USA in combination with study of changing Al speciation and that of other metals/metalloid and their toxic effect on indigenous biota.

4. Conclusions

Rising $p\text{CO}_2^{\text{atm}}$ resulting from anthropogenic activities will lead to acidification of the oceans and freshwater lakes during the 21st century. Reaction path models for lakes from the northeastern USA in which $p\text{CO}_2^{\text{atm}}$ is forced using scenarios from the IPCC Sixth Assessment Report suggest that lake pH could decrease between 0.08 and 0.84 pH units and 0.13–1.31 pH units in the studied lakes depending on whether $p\text{CO}_2^{\text{atm}}$ attains a level of 600 ppm or 1,100 ppm, respectively, in 2100. These changes translate to mean increases of 31%–65% for the hydrogen ion activity (i.e., a_{H^+}), which compares well with predictions for the oceans. The impact of acidification on indigenous calcifying organism is not currently known but is likely to be detrimental. The acidification of the lakes is also expected to increase the amount of Al complexed with natural dissolved organic ligands (i.e., fulvic acid), but because these lakes are saturated, or nearly so, with respect to gibbsite, Al oxyhydroxide precipitates represent the greatest Al toxicity threat to brook trout (*Salvelinus fontinalis*). As the lakes acidify over the course of the 21st century, the effects of Al toxicity to brook trout will increase. Consequently, lake acidification by rising anthropogenic $p\text{CO}_2^{\text{atm}}$ could potentially reverse important gains in water quality that have resulted since implementation of environmental legislation like the Clean Air Act helped to alleviate strong acid deposition and the acidification of freshwater ecosystems from acid rain.

Data Availability Statement

Data employed in this study were compiled from published papers, reports, and on-line sources maintained by several northeastern states. Specifically, the data are available through Boylen et al. (2014), Hintz et al. (2020), Hollocher and Yuskaitis (1993), Solomon et al. (2013), Weiler (1978), the Maine Department of Environmental Protection (2023), the New Hampshire Department of Environmental Services (2022), the Vermont Department of Environmental Conservation, and the New York Department of Environmental Conservation (2019). A summary of the model results is available via Zenodo (Johannesson, 2023a). Example scripts for simulating acidification of Lake Champlain and Lake Superior with version 14.0.01 and higher of the Geochemist's Workbench® software package are also available at Zenodo (Johannesson, 2023b).

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