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Jennifer C. Phillips
University of Wisconsin-Madison

Galen A. McKinley
University of Wisconsin-Madison

Val Bennington
University of Wisconsin-Madison

Harvey A. Bootsma
University of Wisconsin-Milwaukee

Darren J. Pilcher
University of Wisconsin-Madison

See next page for additional authors

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Authors

Jennifer C. Phillips, Galen A. McKinley, Val Bennington, Harvey A. Bootsma, Darren J. Pilcher, Robert W. Sterner, and Noel Urban

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The Potential for CO₂-Induced Acidification in Freshwater

A Great Lakes Case Study

By Jennifer C. Phillips, Galen A. McKinley,
Val Bennington, Harvey A. Bootsma, Darren J. Pilcher,
Robert W. Sterner, and Noel R. Urban

ABSTRACT. Ocean acidification will likely result in a drop of 0.3–0.4 pH units in the surface ocean by 2100, assuming anthropogenic CO₂ emissions continue at the current rate. Impacts of increasing atmospheric $p\text{CO}_2$ on pH in freshwater systems have scarcely been addressed. In this study, the Laurentian Great Lakes are used as a case study for the potential for CO₂-induced acidification in freshwater systems as well as for assessment of the ability of current water quality monitoring to detect pH trends. If increasing atmospheric $p\text{CO}_2$ is the only forcing, pH will decline in the Laurentian Great Lakes at the same rate and magnitude as the surface ocean through 2100. High-resolution numerical models and one high-resolution time series of data illustrate that the pH of the Great Lakes has significant spatio-temporal variability. Because of this variability, data from existing monitoring systems are insufficient to accurately resolve annual mean trends. Significant measurement uncertainty also impedes the ability to assess trends. To elucidate the effects of increasing atmospheric CO₂ in the Great Lakes requires pH monitoring by collecting more accurate measurements with greater spatial and temporal coverage.

INTRODUCTION

Ocean pH is predicted to drop by 0.3–0.4 units by 2100 if humans continue to consume fossil fuels under “business as usual” scenarios. This projected change will result in an increase of hydrogen ion concentrations $[H^+]$ of up to 150% and a 50% decrease in carbonate ion (CO_3^{2-}) concentrations in seawater (Orr et al., 2005). Though our understanding of ocean acidification has advanced in the last decade, the question of how increasing atmospheric CO_2 concentrations may affect freshwater systems has been left largely unanswered.

The Laurentian Great Lakes constitute the largest freshwater system on Earth, containing roughly 18% of global liquid surficial freshwater and 84% of North America’s surface freshwater. In addition to sustaining the region’s 34 million people (US EPA, 1988), the lakes support a strong tourism and fishing industry, generating US\$62 billion annually (Vaccaro and Read, 2011). Myriad anthropogenic stressors such as climate change, pollution, habitat alteration, and coastal development impact the lakes (Allan et al., 2013), and the potential additional stressor of CO_2 -induced acidification needs to be considered. Here, we summarize the evidence that the Laurentian Great Lakes, and by extension other freshwater systems, may become acidified due to increases in the partial pressure of CO_2 in the atmosphere ($pCO_2^{atmosphere}$).

Many small lakes are net CO_2 emitters because they are loci for the accumulation and processing of carbon from their associated watersheds (Hanson et al., 2004; Alin and Johnson, 2007; Cole et al., 2007). However, even if a lake is a CO_2 source, it will not necessarily be protected from the influence of acidification induced by increasing atmospheric CO_2 concentrations. Instead, this increase will reduce the efflux from the lake because of a reduced water-to-air pCO_2 gradient. Lakes with large positive water-to-air pCO_2 gradients (Sobek et al., 2005) will experience smaller reductions in efflux than those with small water-to-air

gradients because of the smaller proportional change in the gradient. But, all else being equal, they will still acidify. Assuming no other changes, lakes with a present-day pCO_2 of 1,000 and 2,500 μatm that experience a $pCO_2^{atmosphere}$ increase of 550 μatm will show a pH decline of -0.19 and -0.09 units, respectively (Figure 1). The conclusion that acidification should not be prevented by a positive water-to-air pCO_2 gradient is consistent with findings from the equatorial Pacific, where the surface ocean pCO_2 is above $pCO_2^{atmosphere}$ (Takahashi et al., 2009). Here, acidification is proceeding at rates comparable to the rest of the ocean (Orr et al., 2005; Feely et al., 2006).

The degree to which inorganic carbon dynamics affects $pCO_2^{atmosphere}$ in the Great Lakes is difficult to assess because the carbon cycles of these lakes are poorly constrained by existing data (Eadie and Robertson, 1976; Urban et al., 2005; Atilla et al., 2011; McKinley et al., 2011; Bennington et al., 2012). However, if the pCO_2 of these lakes is responsive to $pCO_2^{atmosphere}$, acidification should occur throughout the water column because the lakes are dimictic (mix from the surface to the bottom twice a year), and thus the entire water column should equilibrate with the atmosphere each year.

The degree to which the Laurentian Great Lakes are comparable to the ocean in terms of their biogeochemistry and carbon cycling is one way to initially consider the likely influence of $pCO_2^{atmosphere}$ on the pCO_2 of large lakes. Primary production (PP) in the Great Lakes and in the

“ Like the coastal ocean, freshwater systems such as the Laurentian Great Lakes have the potential to be natural laboratories for monitoring change in carbonate chemistry and for better understanding of the complex interactions of numerous stressors. ”

ocean strongly impacts pCO_2 seasonality (Bennington et al., 2012), and the magnitude of Great Lakes PP is comparable to the ocean. Karl et al. (1998) report annual average PP at Station ALOHA in the subtropical North Pacific of $172 \text{ gCm}^{-2} \text{ yr}^{-1}$. Cotner et al. (2004) report annual PP of $119\text{--}128 \text{ gCm}^{-2} \text{ yr}^{-1}$ for Lake Michigan, and $73\text{--}110 \text{ gCm}^{-2} \text{ yr}^{-1}$ for Lake Superior. Sterner (2010) reports $94 \text{ gCm}^{-2} \text{ yr}^{-1}$ for Superior. In the most productive part of the Laurentian Great Lakes, western Lake Erie, $320\text{--}370 \text{ gCm}^{-2} \text{ yr}^{-1}$ was recently reported (Fitzpatrick et al., 2007), similar to coastal upwelling regions of the global ocean (Sarmiento and Gruber, 2006).

Another factor that makes the Laurentian Great Lakes similar to the ocean is the relatively small biogeochemical effects from their watersheds. Small temperate lakes tend to respire allochthonous organic carbon and emit CO_2 to the atmosphere (Cole et al., 1994; Hanson et al., 2004). The delivery of alkalinity and dissolved inorganic carbon (DIC) and dissolved organic carbon from catchments to lakes have been shown to be major factors in alkalinity and carbon budgets for small lakes (McConnaughey et al., 1994; Einsele et al., 2001; Alin and Johnson, 2007; Stets et al., 2009). The input of allochthonous organic carbon to the Laurentian Great Lakes, in contrast, is believed to be small because of the relatively small watershed-to-lake surface area ratios (ranging from 1.6:1 in Lake Superior to 3.4:1 for Lake Ontario; <http://www.worldlakes.org>). In a study of Finnish boreal lakes, areal C evasion

diminished strongly with lake area, also indicating that larger lakes are typically closer to equilibrium with $p\text{CO}_2^{\text{atmosphere}}$ than small lakes (Kortelainen et al., 2006).

Of the five Laurentian Great Lakes, Lake Superior's inorganic carbon dynamics are the best understood and thus can be assessed in more detail (Atilla et al., 2011; Bennington et al., 2012). Available data suggest that summer lake-average $p\text{CO}_2$ in Lake Superior nearly equals $p\text{CO}_2^{\text{atmosphere}}$ while the spring lake-average $p\text{CO}_2$ is slightly elevated above $p\text{CO}_2^{\text{atmosphere}}$ (Atilla et al., 2011). An eddy-resolving coupled hydrodynamic-biogeochemical model, the Massachusetts Institute of Technology General Circulation Model for Superior (MITgcm.Superior), captures these observations, and offers an estimate of the full annual cycle of $p\text{CO}_2$ in which summertime CO_2 uptake due to biological drawdown is largely balanced by efflux of respired CO_2 during the other seasons (Bennington et al., 2012). Stable

isotope analyses indicate that the $\delta^{14}\text{C}$ of DIC in Lake Superior is close to atmospheric values and suggests that DIC cycles across the air-lake interface on a time scale of three years (Zigah et al., 2011). These studies support the conclusion that air-water equilibration strongly influences the $p\text{CO}_2$ in Lake Superior on multiyear time scales. If this is the case, the lake's $p\text{CO}_2$ should rise with $p\text{CO}_2$ in the atmosphere, and CO_2 -induced acidification should occur.

Another approach to determining the relative importance of air-water flux to lake-wide carbon budgets is to summarize published estimates of autochthonous and allochthonous carbon fluxes. Despite large uncertainties, this method suggests that Lakes Superior, Michigan, and Huron are slight CO_2 sources and Lakes Erie and Ontario are slight CO_2 sinks (McKinley et al., 2011). Lakes Erie and Ontario are sinks because they have higher productivity and shallower depths, leading to burial

of a larger fraction of primary production (Eadie and Robertson, 1976).

It is important to distinguish acidification caused by increased atmospheric CO_2 from that caused by acidic precipitation. The reaction of sulfur and nitrogen oxides from fossil fuel combustion with atmospheric water vapor produces strong acids (HNO_3 and H_2SO_4) that can be deposited to water bodies. For the coastal and open ocean, these effects are only a few percent of the pH change expected from acidification due to atmospheric CO_2 (Doney et al., 2007). The literature does not suggest strong acid rain impacts on the Great Lakes due to their large volumes and positions largely upwind of industrial sources (Environment Canada & US EPA, 2009). Thus, similar to the ocean, it can be expected that pH impacts from the steady and persistent source of CO_2 from the atmosphere will have a greater impact on Great Lakes pH.

Here, we present projections for future pH of the Laurentian Great Lakes. We use high-resolution numerical models to assess whether or not the available data have sufficient temporal and spatial coverage to be able to assess annual mean pH trends. While this assessment is regionally focused, it has direct implications for the potential for acidification from increasing atmospheric $p\text{CO}_2$ across freshwater systems.

METHODS

Data

High-Resolution Time Series

In western Lake Superior, high-frequency measurements were taken 7.5 km offshore of Split Rock Lighthouse (47.19°N, 91.34°W) at 12 m depth using a subsurface mooring equipped with a Submersible Autonomous Moored Instrument for $p\text{CO}_2$ (SAMI- CO_2 ; Baehr and DeGrandpre, 2004; Atilla et al., 2011) and a temperature sensor. Data were collected every half hour from June 6, 2001, through September 11, 2001. Calculation of pH assumed a constant alkalinity of 838 meq m^{-3} (Table 1) and freshwater dissociation constants using the National

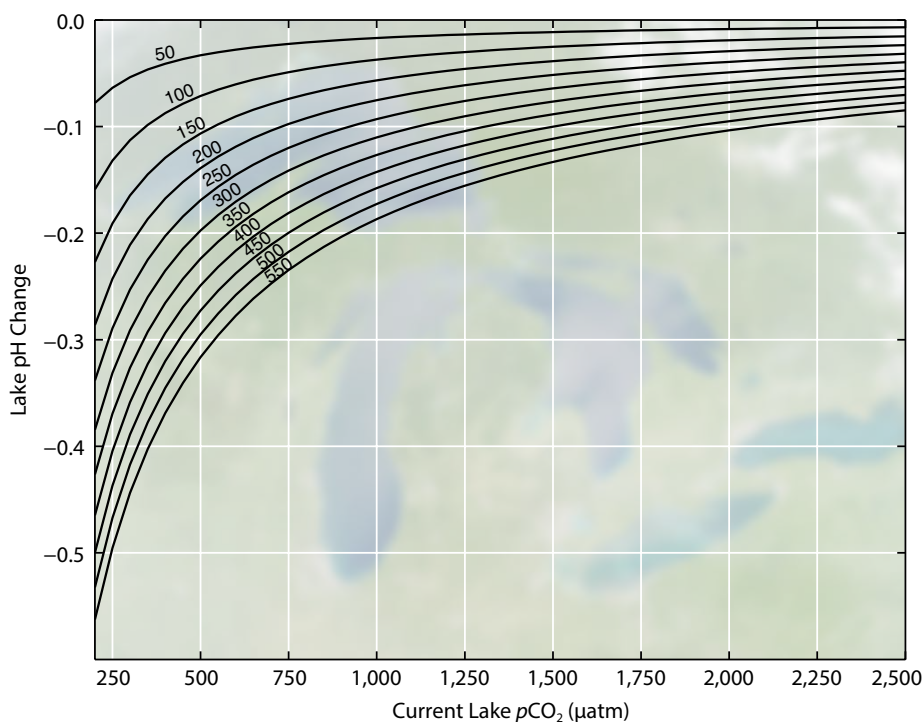


FIGURE 1. Demonstration of the effect of increased $p\text{CO}_2$ on freshwater pH across a range of current lake surface $p\text{CO}_2$ (250–2,500 μatm , consistent with observed values across global freshwater lakes; Sobek et al., 2005). Contours indicate a positive change in $p\text{CO}_2$, or $\Delta p\text{CO}_2$, from 50 to 550 μatm . These increases are consistent with current IPCC projections for the growth in atmospheric $p\text{CO}_2$ from the present to 2100. These results are independent of alkalinity, which is held constant (i.e., for mean alkalinity ranging from 800–2,500 meq m^{-3} , contours of change are indistinguishable from one another).

Bureau of Standards (NBS) scale (Millero et al., 1979; Dickson, 1990; Wanninkhof, 1992; Atilla et al., 2011).

US EPA Biannual Survey

The US Environmental Protection Agency (US EPA) surveys all the Great Lakes biannually in the spring and summer (typically April and August) at 8–20 sites per lake. For example, in Lake Superior, pH, alkalinity, and temperature measurements are recorded at 19 sites, with four depths per site in April and six depths per site in August. Data are available since 1986, except in Lake Superior since 1996 (http://www.epa.gov/greatlakes/monitoring/data_proj/glenda). This monitoring supports the US commitment to the US/Canada Great Lakes Water Quality Agreement. Data through 2011 are analyzed.

US EPA measures pH with potentiometric electrodes after the samples have been warmed to 25°C (Atilla et al., 2011). The potentiometric approach is less accurate than measuring pH with a spectrophotometer and indicator dye (Dickson et al., 1993; French et al., 2002; Dickson et al., 2007); calculating pH from a combination of $p\text{CO}_2$, DIC, and alkalinity (Dickson et al., 2007); or using automated pH sensors that are increasingly employed in marine environments (Martz et al., 2010). French et al. (2002) found a negative bias of 0.137 pH units using electrodes in comparison to the spectrophotometric approach. Additionally, measurements by the US EPA are made at any time of day, which may alias diurnal variability (5–190 μatm ; Atilla et al., 2011). Measurement uncertainty (0.17 pH units) is estimated from the standard deviation across 672 pairs of replicate pH observations by US EPA. Despite these significant uncertainties, the US EPA data are the only long-term pH record available across the Great Lakes and thus must be considered in this assessment.

For the months of April and August, all pH data above 3 m water depth are averaged to determine lake-mean mean surface pH. Uncertainty due to spatial

sampling is estimated from the standard deviation across observations within each lake. This estimate is combined with the measurement uncertainty (by square root of the sum of squares) to arrive at the total monthly uncertainty. April and August mean pH is the mean of April and August data in each year, with uncertainty combined using the square root of the sum of squares.

Projections and Models

Carbon Chemistry Projection

For 1970 to 2100, we assume IPCC IS92a (the business as usual scenario) and A1FI (the fossil fuel intensive scenario) $p\text{CO}_2^{\text{atmosphere}}$ projections. Each lake is assumed to equilibrate with this $p\text{CO}_2$ at a constant alkalinity for each lake (Table 1), and pH is calculated (Millero, 1979; Dickson, 1990; Atilla et al., 2011). For sensitivity tests with warming, we include a linear trend leading to an upper-bound 8°C warming of lake surface temperatures by 2100 (Wisconsin Initiative on Climate Change Impacts, 2011).

Coupled Hydrodynamic-Biogeochemical Models of Lakes Superior and Michigan

Coupled hydrodynamic-biogeochemical models are used to estimate spatio-temporal variability and to assess the ability of the US EPA monitoring program to capture lake-wide, annual-average pH. The MITgcm (Marshall et al., 1997) was configured for Lake Superior (Bennington et al., 2010). Within this eddy-resolving physical model (MITgcm.Superior), a

biogeochemical-carbon module including complete carbon chemistry, air-water CO_2 fluxes, a lower food web module, and biogeochemical inputs from rivers (Bennington et al., 2012) was integrated for 1997–2001. Model pH is calculated from local concentrations of DIC, alkalinity, and temperature. MITgcm.Superior was modified to simulate the physics and biogeochemistry of Lake Michigan (MITgcm.Michigan) for 2007–2010 (Pilcher et al., 2015).

RESULTS

Projected Great Lakes pH Trends

Future rates and effects of CO_2 -induced acidification in the Great Lakes are projected using only carbon chemistry and the assumption that lake $p\text{CO}_2$ follows $p\text{CO}_2^{\text{atmosphere}}$ until 2100. Though other changes should factor into the carbon balance of these ecosystems over the coming century, including changing nutrient loading, internal alkalinity loss or generation, food web shifts or watershed carbon inputs, we focus here on elucidating the impacts on pH of only air-lake CO_2 equilibration. This approach is consistent with early ocean acidification studies (Orr et al., 2005).

Across the Great Lakes, mean alkalinity and associated carbonate parameters vary greatly due to the geographic and geologic setting of each lake and its position along the flow path through the series of lakes (Table 1). Lake Superior has low alkalinity because it sits upon the granitic Canadian Shield where slow weathering and shallow soils result in low carbonate inputs.

TABLE 1. Physical and biogeochemical characteristics of the Laurentian Great Lakes.¹

| Lake | Surface Area ($\text{m}^2 \times 10^{10}$) | Water Residence Time (yr) | Mean (Max) Depth (m) | Mean Alkalinity (meq m^{-3}) |
|----------|--|---------------------------|----------------------|---|
| Superior | 8.21 | 174 | 149 (406) | 838 |
| Michigan | 5.78 | 104 | 85 (282) | 2,181 |
| Huron | 5.96 | 21 | 59 (229) | 1,561 |
| Erie | 2.57 | 2.6 | 19 (64) | 1,817 |
| Ontario | 1.90 | 7.3 | 86 (244) | 1,836 |

¹Surface area, residence time, and mean and max depth values are from *The Great Lakes: An Environmental Atlas and Resource Book* (US Environmental Protection Agency, 1988) and mean alkalinity from the Great Lakes Environmental Database (http://www.epa.gov/greatlakes/monitoring/data_proj/glenda/#query).

The other lakes reside in carbonate basins and are more alkaline. These differences largely explain the pH offset from lake to lake (Figure 2a). Despite these differences in initial pH, the magnitude of change in pH across all of the lakes is the same from these water-chemistry-only based projections: a 0.33 unit decline by 2100 under the IS92a scenario. Under A1FI, the projected decline is 0.46 units by 2100. Surface water warming of 8°C by 2100 reduces CO₂ solubility in the lakes, modulating the pH decline to -0.29 units by 2100 for the IS92a scenario (Figure 2a). Across the lakes, there is variation in the trajectories for carbonate ion concentration, with the greatest change in Lake Michigan and the least change in Lake Superior (Figure 2b). Lake Michigan has a higher initial carbonate ion concentration and is not flushed with low-alkalinity water from Superior, as is Lake Huron.

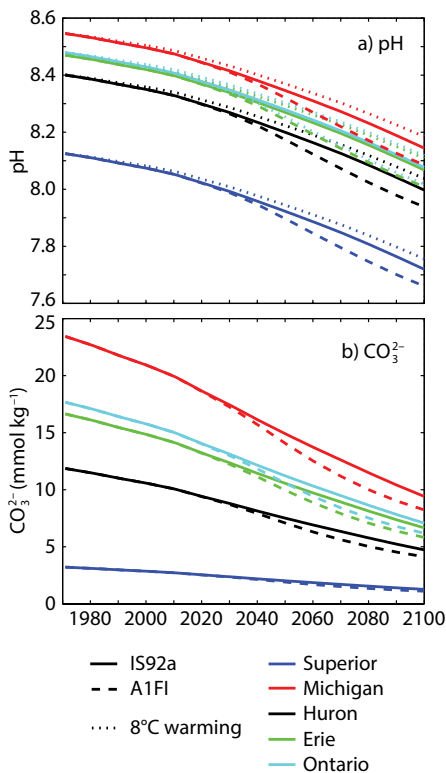


FIGURE 2. Projected mean annual (a) pH and (b) carbonate ion concentration for the five Laurentian Great Lakes under IPCC atmospheric CO₂ forcing: IPCC IS92a (the business as usual scenario) or A1FI (the fossil fuel intensive scenario). Also shown on (a) is an 8°C warming by 2100 scenario. Details are provided in the text.

Observed Great Lakes pH

Is the observed record of sufficient resolution in space and time to corroborate or to invalidate these pH trend estimates?

High-Resolution Time Series

In the western arm of Lake Superior, pH varies from 7.95 to 8.73, a range of 0.78 pH units from June to September 2001, with a temporal standard deviation of 0.13 pH units (Figure 3). MITgcm.Superior indicates similar variability at this location (Bennington et al., 2012), and suggests that within the months of April and August 2000, daily pH at any one location can vary by more than 0.1 units (see online Supplemental Figure S1).

MITgcm.Michigan also illustrates large pH variability (Figure 4). For April and August of 2008, the pH range at any location is 0.35 and 0.25 units, respectively (Figure 4a,b). On a single day in either month, the maximum range is 0.35 units in April and 0.10 in August for the open lake outside of Green Bay (Figure 4c,d). Model results are consistent with pH estimated from in situ pCO₂ observations and assumed constant alkalinity on the Lake Express ferry from Milwaukee, Wisconsin, to Muskegon, Michigan; away from direct coastal influences, pH can span up to 0.05 units in a single day (author Bootsma, unpublished data).

These models and data from

Lakes Superior and Michigan are consistent with observations in the coastal ocean, where there can be a large seasonal variability in pH due to the interplay of physical and biogeochemical processes (Hauri et al., 2013). As a whole, these findings support the conclusion that substantial high-frequency pH variability occurs in Lakes Michigan and Superior, and presumably also in the other Laurentian Great Lakes.

US EPA Biannual Survey

Data from the US EPA are sparse in time across the annual cycle, but do have reasonable spatial coverage for April and August. In each Great Lake, these data indicate pH spans several tenths of a pH unit between stations, and the difference between April and August can be up to 0.5 pH units (not shown). Across the decades, there is substantial interannual variability in the mean of April and August data (April–August mean, Figure 5). Though the mean estimates do suggest a positive trend in all lakes except Michigan, when the large uncertainty is considered, only a few points can actually be distinguished from any other in its time series.

In Figure 5, pH trends from the IS92a carbon chemistry projections (Figure 2) are superimposed on the observed estimates (solid line). Estimated trends from CO₂-induced acidification are very

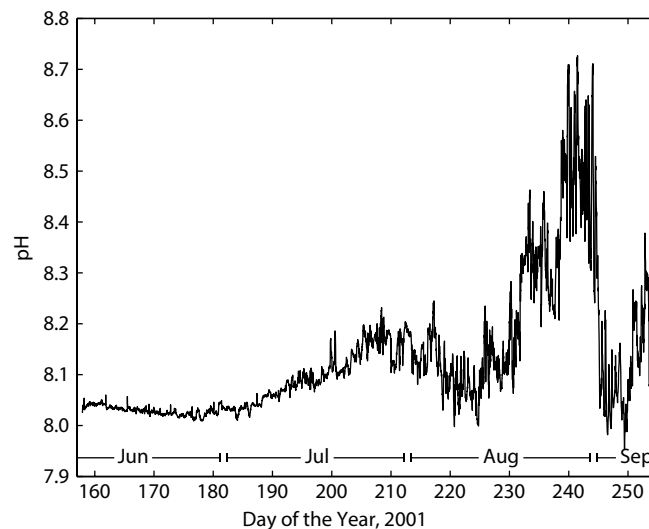


FIGURE 3. pH estimated from observed pCO₂ and constant alkalinity in the western arm of Lake Superior near Split Rock Lighthouse (47.19°N, 91.34°W) from June 6, 2001, through September 11, 2001. See text for details.

slight compared to the uncertainty in the observed record. If we ignore the large uncertainties and focus only on the mean estimates, the observed April–August mean pH appears to have a positive trend over time that contrasts to the projections that suggest a negative trend for annual average pH in all lakes. If these April–August mean data give a robust estimate of the annual mean surface pH, then we must conclude that air–water equilibration is not the dominant process controlling the long-term trend in annual mean pH, and that the effects of CO₂-induced acidification are not yet noticeable, given these other controls. This conclusion, however, hinges on the assumption that the April–August mean accurately represents annual mean pH.

We can use MITgcm.Superior and MITgcm.Michigan to assess

the relationship between the April–August mean pH from US EPA biannual observations and annual mean pH. In this Observing System Simulation Experiment (OSSE), the models are sampled in time and space at the corresponding model grid cell of sites where data were collected. This “sampled” result is compared to the true annual average using all points in space across the full annual cycle (Figure 6). Uncertainty on the sampled model is only the spatial standard deviation (i.e., we ignore measurement uncertainty here).

In Lake Superior for 1997–2001, the OSSE indicates that the spatial and temporal distribution of the biannual observations leads to a positive bias of the April–August mean with respect to the annual average of up to 0.05 units, as well as substantially exaggerated interannual

variability (Figure 6a). In Lake Michigan for 2007–2010, the April–August mean can have either negative or positive bias with respect to the annual average, consistent with its exaggerated interannual variability. In both lakes, the uncertainty from the sampled estimates is large enough to obscure the interannual variability that actually occurred. These OSSEs indicate that the current monitoring of Great Lakes pH cannot resolve temporal trends at resolution sufficient to resolve acidification due to increasing $p\text{CO}_2^{\text{atmosphere}}$.

Taken as a whole, these data and models support the conclusion that spatio-temporal variability in the Great Lakes is large enough that the long-term record from the US EPA April and August sampling at 8–20 stations per lake does not accurately represent long-term annual average change in Great Lakes pH. This

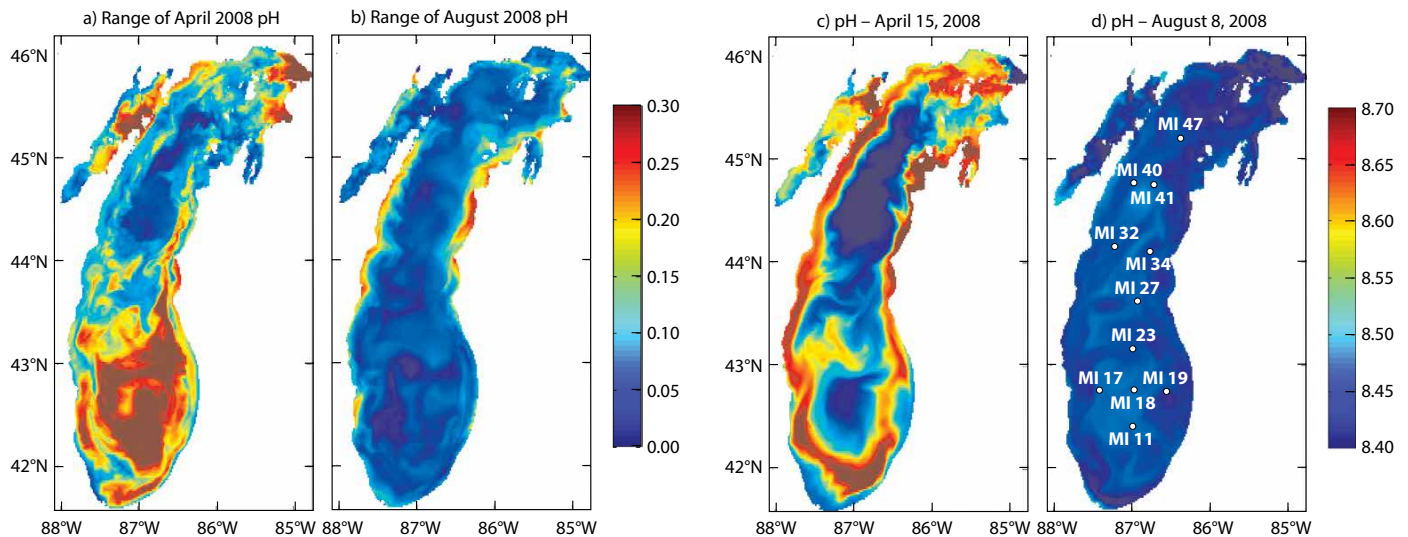


FIGURE 4. MITgcm.Michigan modeled pH. Monthly range of daily average pH (a) in April 2008 and (b) in August 2008; and daily average pH on the days (c) April 15, 2008, and (d) August 8, 2008. Lake-wide monthly mean in pH is 8.56 in April 2008 to 8.46 in August 2008. In (d), the US EPA biannual monitoring sites are indicated.

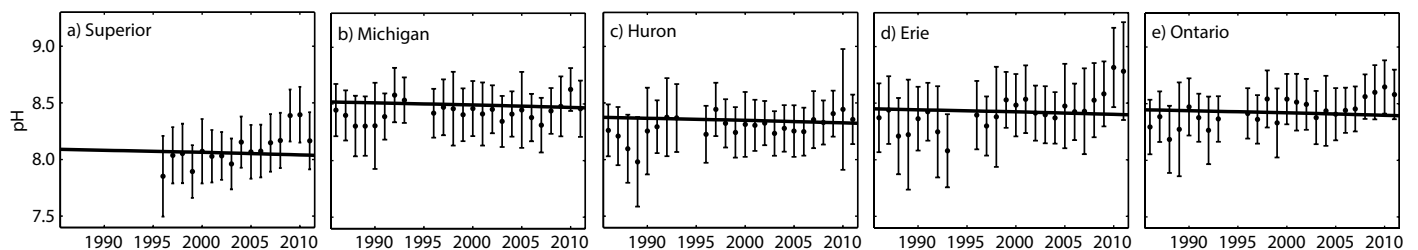


FIGURE 5. Mean of April and August pH observations from US EPA biannual survey. Solid lines are the pH estimates for annual pH based on the IS92a emissions scenario of the carbon chemistry projection (Figure 2).

result is compounded by the fact that the methodology used for the US EPA pH measurements has low precision (Dickson et al., 2007). Nonetheless, the observed changes in April–August mean pH, despite their large uncertainty, are worthy of further investigation to determine whether they are due to methodological changes or to real phenomena such as secular trends in spring bloom timing. To reduce the large uncertainty in both monthly and annual mean pH, spatial variability must be better characterized and its driving mechanisms understood.

Ecosystem Impacts

Impacts of CO₂ acidification on the Great Lakes have not yet been studied, but the ocean acidification literature may provide insight into potential effects. Studies in coastal and estuarine environments likely have particular relevance

to the Great Lakes as they are similarly affected by a suite of anthropogenic stressors; their carbonate chemistry is influenced by biological responses to nutrient delivery by rivers, groundwater, and the atmosphere (Borges and Gypens, 2010); and spatiotemporal variability is large (Hauri et al., 2013). Coastal ocean acidification can also be significantly modified by interactions with other natural and anthropogenic forcings (Feely et al., 2008; Cai et al., 2011) to accelerate local declines in pH and saturation states.

Studies of the impacts of ocean acidification on calcification have particular significance for Great Lakes bivalves, including native unionids and the invasive dreissenids, zebra (*Dreissena polymorpha*) and quagga (*D. rostriformis bugensis*) mussels whose shells are made up primarily of aragonite, which is more soluble than the predominantly calcite shells of marine bivalves (Mucci, 1983). The metabolism of sodium and calcium in dreissenids may be particularly sensitive to acidification because dreissenids are recent immigrants from the sea (Vinogradov et al., 1987). Juvenile zebra mussels only grow when the water's pH is greater than 8.3 (Hincks and Mackie, 1997), and a pH near 7.4 is lethal for the veliger stage (Mackie and Kilgour, 1994). Our projection for Great Lakes mean pH under the IS92a and A1FI scenarios ranges from 7.65 to 8.20 by 2100 (Figure 2a), and the spatial heterogeneity is large enough that these lower thresholds will likely be achieved, at least in some locations.

While our understanding of the role of dreissenids within Great Lakes biogeochemical cycles and trophic ecology is incomplete, they appear to be key players within these systems. In the pelagic zone, they have altered trophic dynamics by removing a significant fraction of phytoplankton from the water column (Fahnenstiel et al., 2010), which in turn has impacted energy flow to higher trophic levels (Nalepa et al., 2009). Reductions in phytoplankton abundance have resulted in improved water clarity, which has led to a resurgence of nuisance

algae such as *Cladophora* spp. (Auer et al., 2010). Any changes in the population dynamics, health, and calcification of dreissenids will likely have cascading impacts on noncalcifying species.

DISCUSSION AND CONCLUSIONS

Under the assumption of lake $p\text{CO}_2$ equilibration with $p\text{CO}_2^{\text{atmosphere}}$ through 2100 and a business as usual emission scenario, pH in the Laurentian Great Lakes is projected to decline by 0.29–0.49 units by 2100 (Figure 2a), similar to predictions for the surface ocean (Orr et al., 2005). A survey of the scientific community also illustrates broad concurrence that acidification is likely (Box 1). Yet, the evidence from observations and models that we present here indicates that current monitoring is insufficient to determine whether long-term changes in pH are actually occurring. There is a need to establish a pH monitoring program in the Laurentian Great Lakes designed to determine if long-term, but relatively gradual, pH trends driven by increasing $p\text{CO}_2^{\text{atmosphere}}$ are occurring. The NOAA Ocean and Great Lakes Acidification Research Plan (NOAA Ocean Acidification Steering Committee, 2010) laid out a plan for this type of monitoring, but implementation has not yet begun.

In the Laurentian Great Lakes, pH data can be obtained from both autonomous sensors on moorings and volunteer observing ships, and such data should be combined with calibration surveys (Fabry et al., 2008; Read et al., 2010). Autonomous pH sensors with accuracy of ± 0.002 pH units (Dickson et al., 2007) are needed. Complementary $p\text{CO}_2$ observations would be of great use to characterize the CO₂ system more fully spatially and temporally. Better quantification of whole-lake carbon and alkalinity budgets is also needed in order to provide the mechanistic basis with which observed pH variability and trends can be understood. Following protocols established for marine research (Dickson et al., 2007; Riebesell et al.,

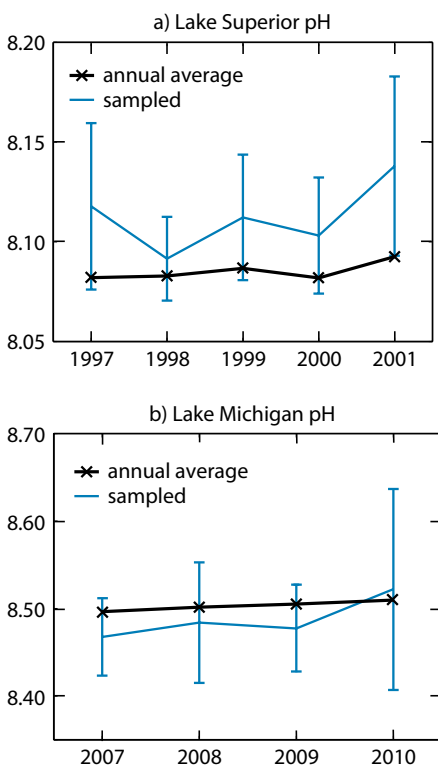


FIGURE 6. Observing System Simulation Experiment for (a) Lake Superior and (b) Lake Michigan. Surface pH from stations as sampled by US EPA and annual average from MITgcm.Superior and MITgcm.Michigan. Uncertainty on the sampled estimate is only from the spatial standard deviation across the sampled points in each month.

Box 1. Survey of Great Lakes Scientists

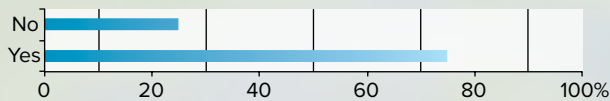
Given the unknowns about impacts of acidification on lakes, we conducted a survey of Great Lakes scientists. Similar approaches have been employed to discuss uncertainties in the global climate system (Zickfeld et al., 2010) and to assess ecosystem vulnerability to ocean acidification in the California Current (Teck et al., 2010). We developed a three-question survey and addressed it to active Great Lakes scientists. The pool of potential respondents consisted of 371 research scientists from government

agencies, universities, consulting firms, and nonprofit organizations. Experts were identified using Web of Science to search the phrase “Great Lakes” and key words associated with potential stressors. Individual scientists contacted collectively possessed a wide breadth of knowledge and experience with technical Great Lakes issues (Sigrid Smith, University of Michigan, *pers. comm.*, November 30, 2011). Eighty-nine (89) scientists responded to the survey, with most answering all questions.

Question 1

Survey participants were first asked **Question 1: In your opinion, are the Laurentian Great Lakes likely to experience a drop in pH as atmospheric CO₂ rises (i.e., analogous to ocean acidification)?** Responses from 89 scientists, shown below, indicate that most scientists agree that acidification should occur.

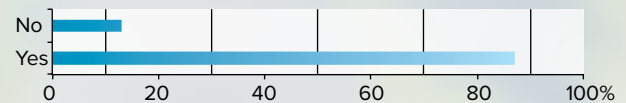
Responses to Question 1



Question 2

Next, respondents were shown projections for Lake Superior and global ocean declines in pH under IPCC emission scenarios (Meehl et al., 2007), both of which were similar to Figure 2a, and asked **Question 2: Please examine the following projections from a simple model for Lake Superior under six IPCC Special Report on Emission Scenarios (SRES) and the IS92a emission scenario, and compare them to published projections for the surface ocean. Based on these figures, do you think the Laurentian Great Lakes are likely to experience a drop in pH as atmospheric CO₂ rises (i.e., analogous to ocean acidification)?** Responses from 85 scientists, shown below, indicate a slight increase in the confidence that acidification should occur.

Responses to Question 2



Question 3


Finally, survey participants were asked **Question 3: If the Great Lakes are acidified by increasing atmospheric CO₂, how might some organisms or ecological conditions be affected? Please rank the options on the given negative to positive scale.** Responses from at least 79 scientists, shown on the right, indicate most confidence with respect to negative impacts on water quality, biodiversity, and both early and adult life stages of calcifying organisms.

Responses to Question 3

| | | Strong negative impact | Weak negative impact | Neutral or no impact | Weak positive impact | Strong positive impact | Unsure |
|----------------------|--|------------------------|----------------------|----------------------|----------------------|------------------------|--------|
| Water quality | | 5% | 52% | 25% | 0% | 1% | 16% |
| Water clarity | | 0% | 14% | 32% | 28% | 3% | 24% |
| Primary productivity | | 5% | 35% | 16% | 20% | 3% | 20% |
| Biodiversity | | 8% | 46% | 23% | 4% | 0% | 20% |
| Early Life Stages | Native amphipods | 13% | 34% | 25% | 0% | 0% | 29% |
| | Calcifying organisms (including mussels) | 33% | 47% | 8% | 4% | 0% | 9% |
| | Macroalgae | 6% | 25% | 22% | 23% | 1% | 23% |
| | Fish | 8% | 29% | 34% | 4% | 0% | 25% |
| Adult Stages | Native amphipods | 6% | 37% | 28% | 3% | 0% | 27% |
| | Calcifying organisms (including mussels) | 29% | 46% | 11% | 4% | 0% | 10% |
| | Macroalgae | 3% | 30% | 24% | 20% | 1% | 22% |
| | Fish | 4% | 30% | 37% | 3% | 0% | 27% |

2010), but modified for freshwater, will help to align the Great Lakes research community with the ocean acidification research community.

Impact assessments will also be needed for freshwater systems. They can be performed using laboratory manipulations, mesocosms, and in situ CO₂ perturbation experiments (Fabry et al., 2008). For the Laurentian Great Lakes, one particular genus that should be studied across its life stages is the dreissenid mussel, as these mollusks have significantly shaped the ecosystem since their invasion (Fahnenstiel et al., 2010; Nalepa et al., 2010; Chapra et al., 2012), greatly stress the already-declining native mussels, and make their shells out of aragonite.

In this assessment, the multiple stressors that are known to affect Laurentian Great Lakes and other large freshwater system biogeochemistry, such as invasive species and eutrophication, have not been directly considered. The ocean acidification literature and our recent survey of the Great Lakes scientific community (Box 1) suggest where research on organismal and ecological impact studies are most needed, keeping in mind that it will be the combined effects of CO₂-induced acidification and other drivers of change to which all freshwater ecosystems, large and small, will have to adjust (Breitburg et al., 2015, in this issue). Like the coastal ocean, freshwater systems such as the Laurentian Great Lakes have the potential to be natural laboratories for monitoring change in carbonate chemistry and for better understanding of the complex interactions of numerous stressors (Feely et al., 2010). 

SUPPLEMENTARY MATERIALS. Supplemental Figure S1 is available online at http://www.tos.org/oceanography/archive/28-2_phillips.html.

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AUTHORS. Jennifer C. Phillips (jennifer.phillips@resources.ca.gov) was a graduate student in the Nelson Institute for Environmental Studies, University of Wisconsin-Madison, Madison, WI, USA, and is currently Program Manager, California Ocean Protection Council, Sacramento, CA, USA. Galen A. McKinley is Associate Professor, Department of Atmospheric and Oceanic Sciences, University of Wisconsin-Madison, Madison, WI, USA. Val Bennington is Research Scientist, Center for Climatic Research, University of Wisconsin-Madison, Madison, WI, USA. Harvey A. Bootsma is Associate Professor, School of Freshwater Sciences, University of Wisconsin-Milwaukee, Milwaukee, WI, USA. Darren J. Pilcher was a graduate student in the Department of Atmospheric and Oceanic Sciences at University of Wisconsin-Madison, Madison, WI, USA, and is now a National Research Council postdoctoral fellow at the National Oceanic and Atmospheric Administration Pacific Marine Environmental Laboratory, Seattle, WA, USA. Robert W. Stern is Director, Large Lakes Observatory and Professor, Department of Biology University of Minnesota Duluth, Duluth, MN, USA. Noel R. Urban is Professor, Civil & Environmental Engineering, Michigan Technological University, Houghton, MI, USA.

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