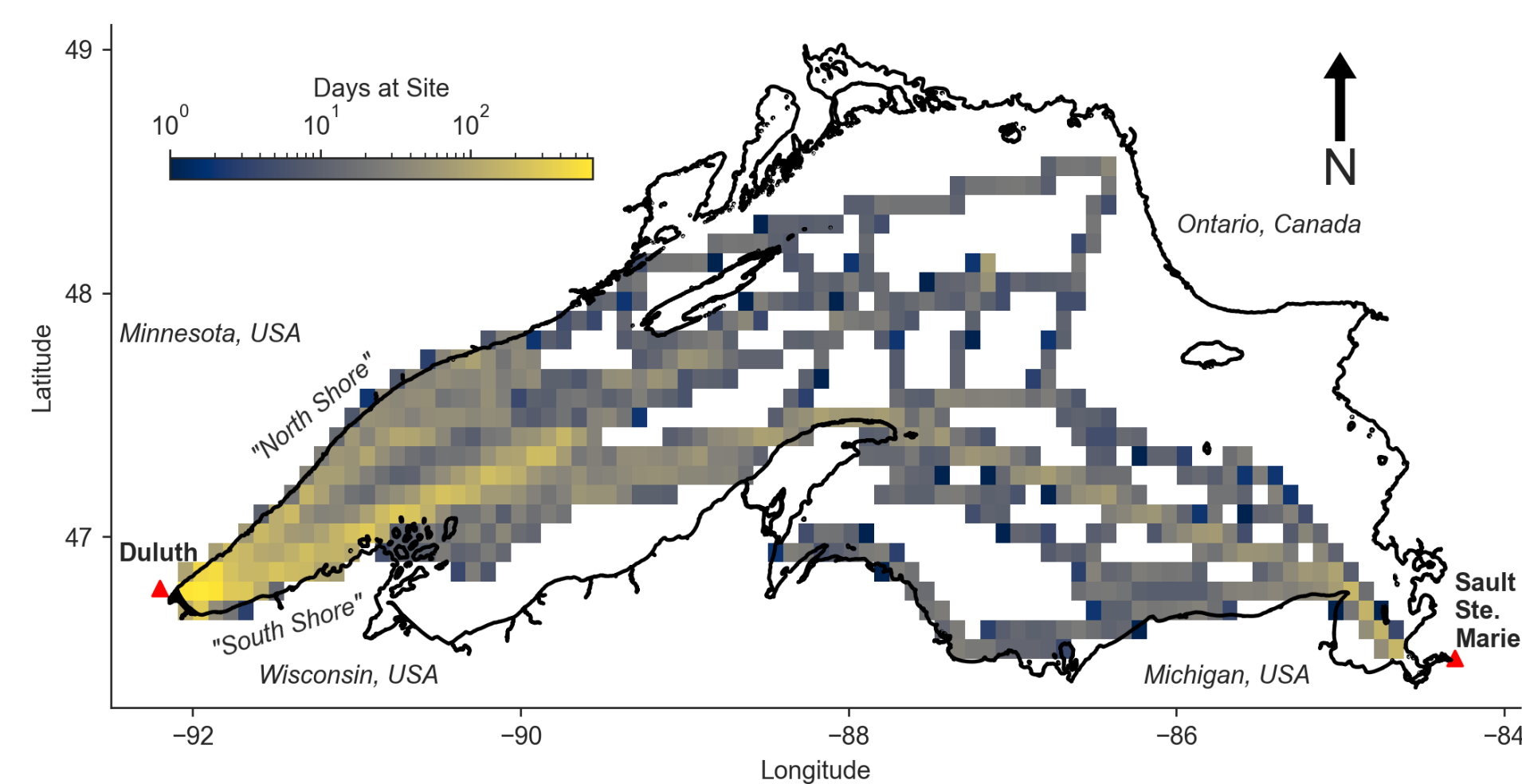


## Introduction

Lake Superior is Earth's largest freshwater body by area. Its great societal importance, immense size, ultraoligotrophic state, low buffering capacity, and rapid mixing period (compared to deep ocean water) highlight its suitability for study in the context of the ongoing perturbation to Earth's C cycle. Acidification of freshwater by CO<sub>2</sub> parallel to ocean acidification has been hypothesized (Phillips et al. 2015) but confounding drivers and few, short, and/or high-uncertainty timeseries of inorganic C parameters have inhibited study of the effects of CO<sub>2</sub> infiltration. **This study presents the first multiannual time series of high-accuracy surface water pCO<sub>2</sub> measurements of Lake Superior.**



## Methods

Surface water pCO<sub>2</sub> was measured during *RV Blue Heron* transects of Lake Superior 2019-2022 using a SuperCO<sub>2</sub> instrument. Instantaneous flux was parameterized by measurements of wind velocity (Ho et al. 2006). Four years' underway data were combined into a single year to generate a synthetic April-May time series of pCO<sub>2</sub> and CO<sub>2</sub> flux, from which drivers and interannual trends were inferred. A pathway towards a data-based pCO<sub>2</sub> product spanning Lake Superior using non-linear ML regression is presented along with the first wintertime under-ice pCO<sub>2</sub> time series of Lake Superior.

## Laurentian Great Lakes in a High-CO<sub>2</sub> World: What's Next?

The outcomes of pCO<sub>2</sub> infiltration alone include acidification, decreasing Ω, changes to trace metal speciation, metabolic effects on plankton, and other phenomena paralleling ocean acidification.

- however -

Poorly-understood drivers modify acidification outcomes:

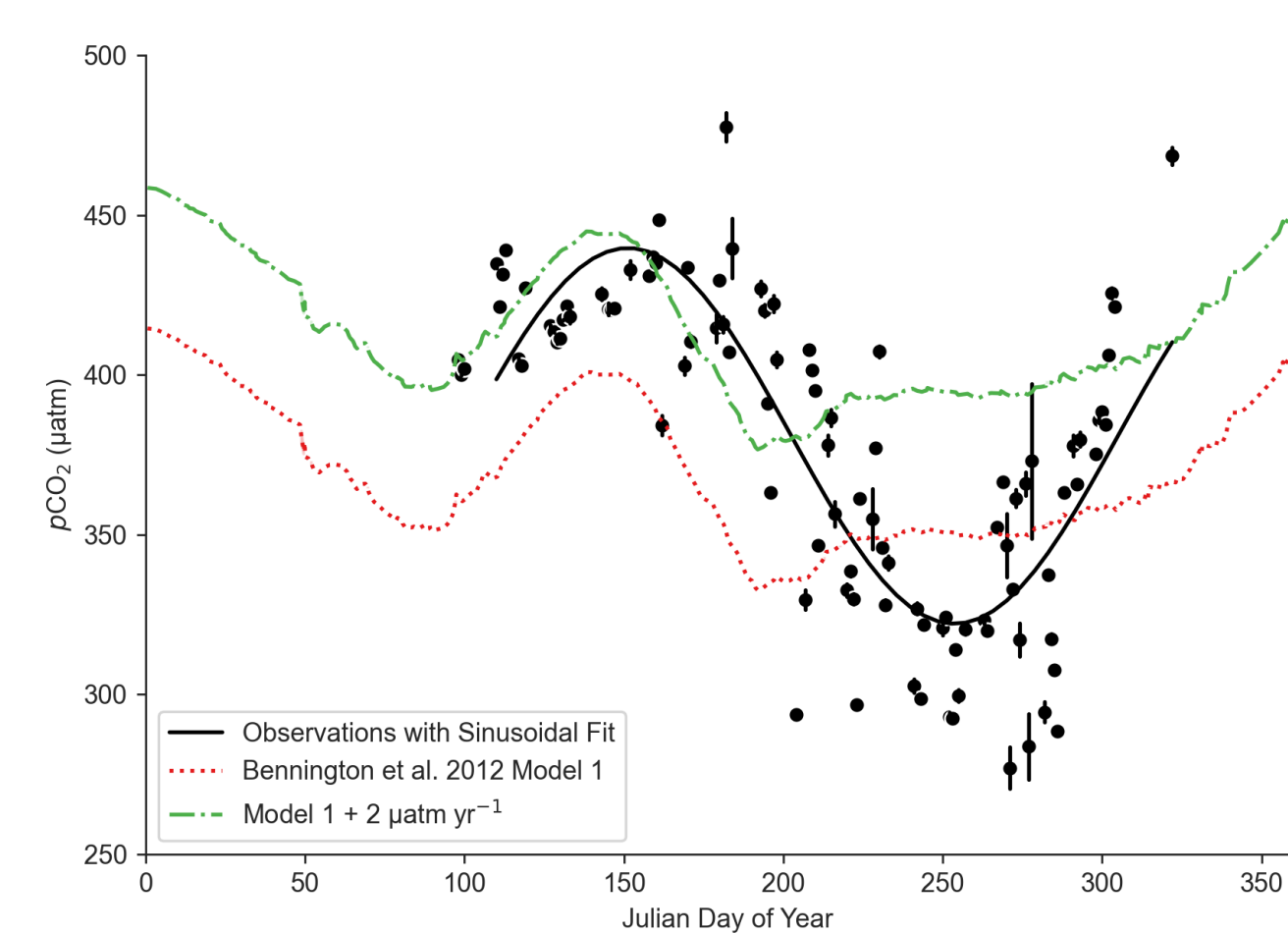
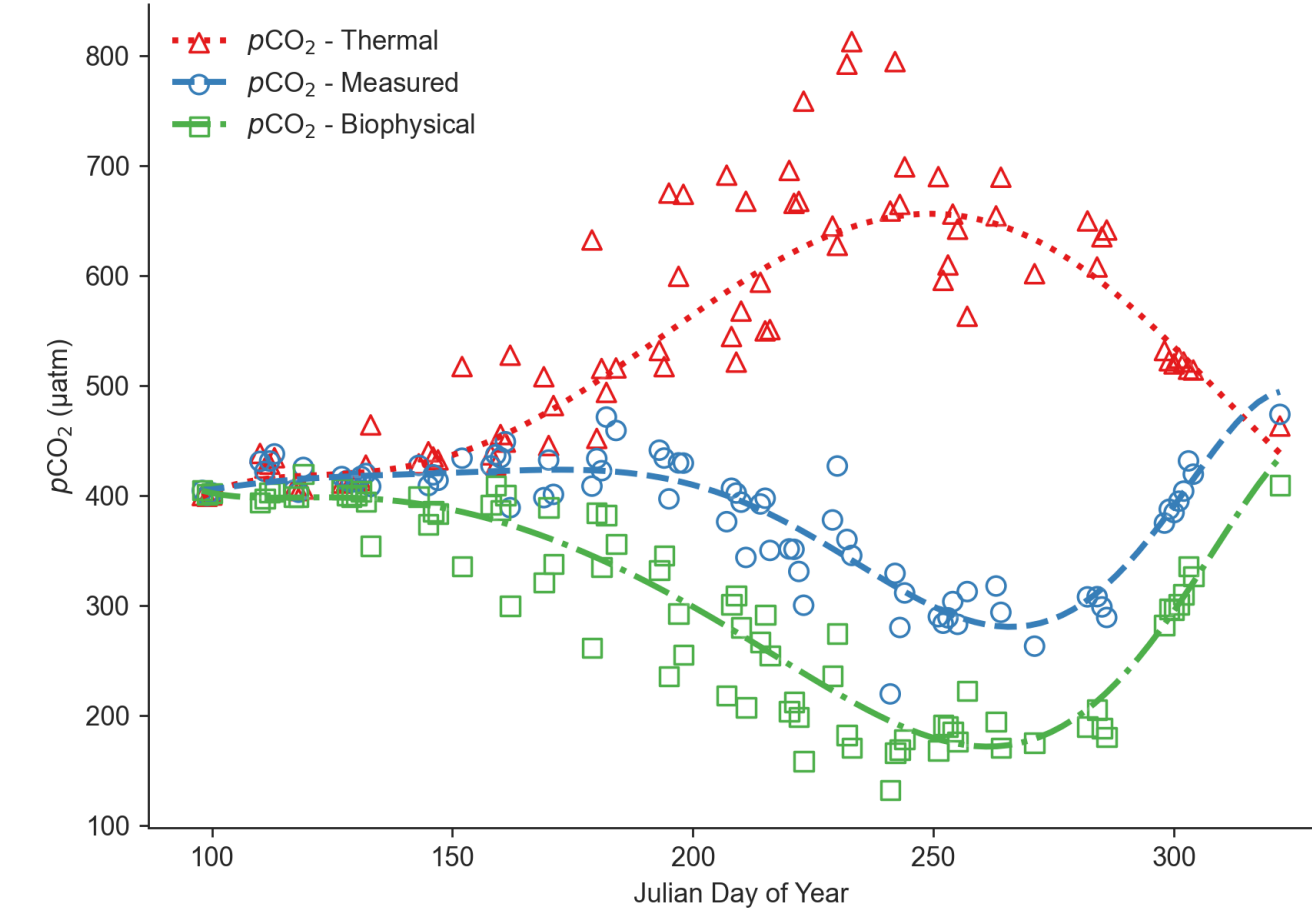
- Alkalinization/sediment buffering
- Increasing water temperature
- Strengthening lake stratification
- Shifting ice phenology

• Lake Superior lacks sediment carbonate, but other lakes (e.g. Michigan) may benefit from solid-phase buffering.

• No long-term chemistry timeseries exists with sufficient accuracy to detect acidification in Lake Superior.

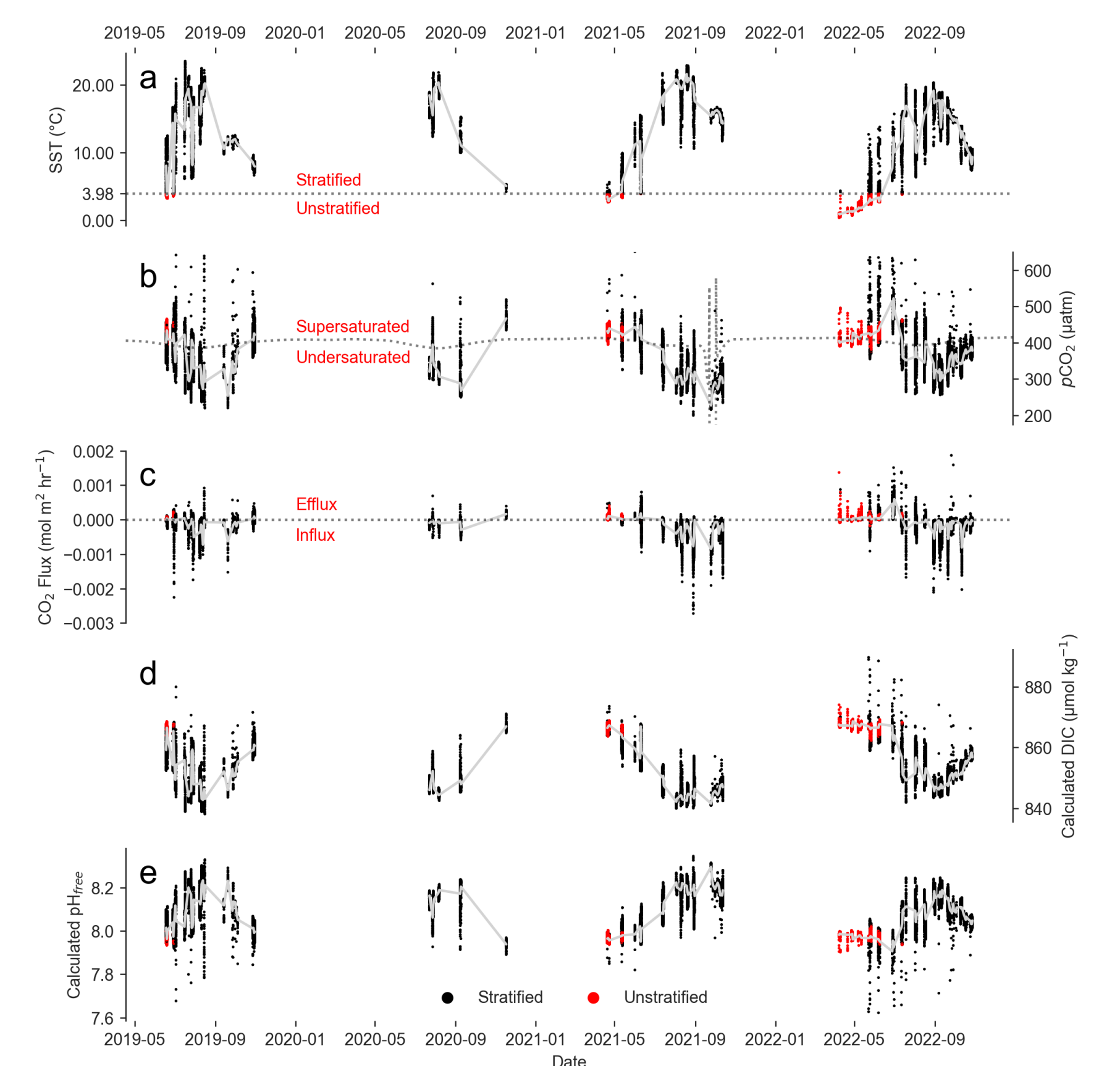
• The C budget of Lake Superior is as-yet unconstrained, highlighting the need for a spatially- and temporally-comprehensive understanding of CO<sub>2</sub> cycling and flux.

## Observation



← Daily mean sea surface pCO<sub>2</sub> observed 2019-2022, with power series regression as a visual aid. Decomposition into **thermal** and **biophysical** drivers indicates **equal dominance of the two drivers on annual scales**. **Thermal** drivers dominate early-season pCO<sub>2</sub>, while late-season **biophysical** drivers force a local minimum mid-September.

← Daily mean sea surface pCO<sub>2</sub> (±se) observed 2019-2022 exhibited a sinusoidal seasonal cycle. **Decadal-scale pCO<sub>2</sub> increase is indicated by agreement of early-season predictions from process modeling (Bennington et al. 2012) after adjustment for atmospheric CO<sub>2</sub> increase.** Observations displayed greater seasonal variability (>50 µatm) than previous observations or models.



↑ Complete 4-year time series of underway observations. CO<sub>2</sub> flux parameterized from wind speed (Ho et al. 2006); pH and DIC are calculated using assumed A<sub>T</sub> = 850 µmol kg<sup>-1</sup>.

## Questions

- How do pCO<sub>2</sub> and CO<sub>2</sub> flux vary seasonally? Spatially?
- What drives seasonal pCO<sub>2</sub> variability?
- What is the ice-free-season net CO<sub>2</sub> flux?
- Is L. Superior pCO<sub>2</sub> keeping pace with the atmosphere?

Lake Superior's seasonal pCO<sub>2</sub> variability is larger than the equatorial North Atlantic. Riverine influence induces both high- and low-pCO<sub>2</sub> deviations from the cycle.

Thermal and biophysical drivers are evenly-balanced on an annual scale. SST dominates variability in spring; biophysical drivers effect a summertime drawdown.

A net influx on the order of 20 Gmol C was observed April-November, exceeding process model estimates.

**Yes.** A rapid CO<sub>2</sub> equilibrium timescale (τ<sub>eq,CO2</sub>) on the order of 100 d. combined with decadal-scale surface pCO<sub>2</sub> increase indicate **Lake Superior is undergoing CO<sub>2</sub> infiltration.**

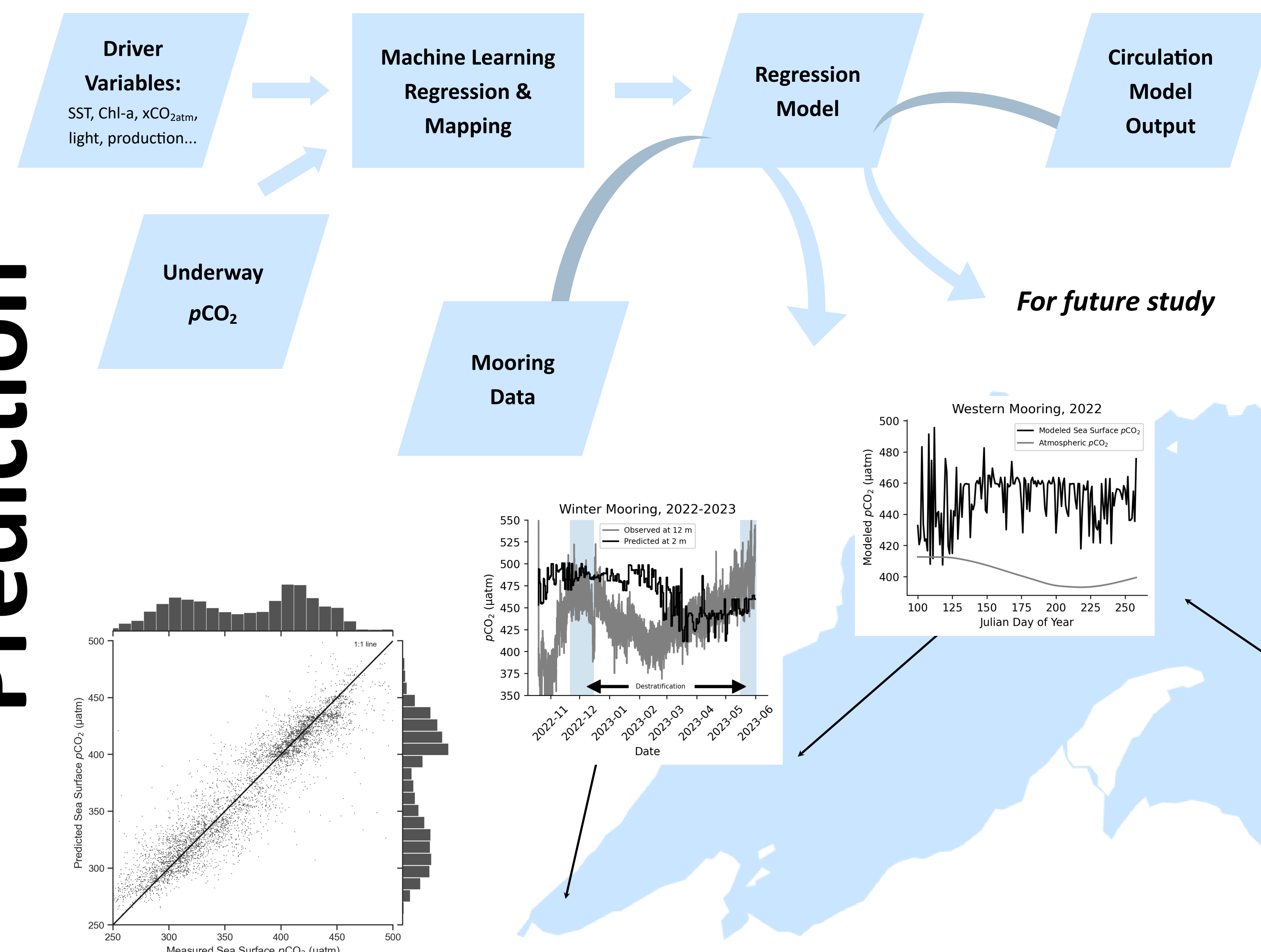
## Results

FFNN regression yields very good (R<sup>2</sup>>0.9) agreement between modeled and underway-measured pCO<sub>2</sub>.

Application to mooring data demonstrates scalability as well as challenges to signal reproduction at the limit of training conditions.

A lake-spanning model driven by circulation models (e.g. GLOFS) and remotely-sensed parameters (e.g. VIIRS/MODIS) may provide an unprecedented window into CO<sub>2</sub> dynamics and flux.

## Prediction

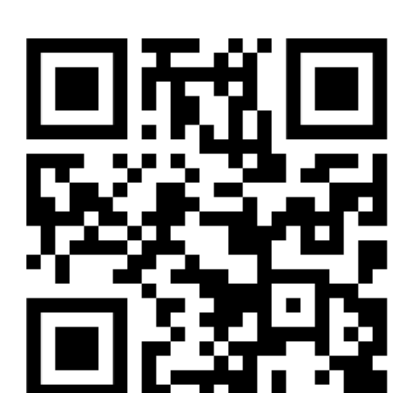


## Conclusions

Surface water inorganic C complex measurements of unprecedented accuracy and spatiotemporal breadth have allowed inference of CO<sub>2</sub> cycling drivers and flux in Lake Superior. This research described the relative dominance of competing thermal and biophysical drivers, confirmed decadal increase in sea surface pCO<sub>2</sub>, and lays the foundation for development of a data-based CO<sub>2</sub> flux product with the potential to reshape the understanding of large lakes as significant players in regional and global C cycles.

## Acknowledgements

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