JOURNAL OF GEOPHYSICAL RESEARCH

Supporting Information for "Underway pCO$_2$ surveys unravel CO$_2$ invasion of Lake Superior from seasonal variability"

D. E. Sandborn[1,2], E. C. Minor[1,3]

[1]Large Lakes Observatory, University of Minnesota Duluth, Duluth MN 55812 USA

[2]Water Resources Science Program, University of Minnesota, St. Paul, MN 55108 USA

[3]Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, MN 55812 USA

Contents of this file

Introduction

This Supporting Information document includes data and graphics supplementing those presented in our study. Text S1 describes statistical analysis of our dataset for diel variability. Equations S1-S3 present seventh-order regressions of time series, illustrated

---

Corresponding author: D. E. Sandborn, Large Lakes Observatory, University of Minnesota Duluth, Duluth, MN 55812 (sandb425@umn.edu)

to aid replication of our work. Figures S1-S4 provide extra context for statements given in our publication.

Text S1: Diel variability

To test the potential effect of diel variability on observed surface water $p\mathrm{CO_2}$, observations were separated into "light" and "dark" categories determined by sunrise and sunset times on the 15th day of each month at the approximate center of Lake Superior. 41 of 69 cruises included only daylight observations. For 28 cruises with both light and dark observations compared with a t-test, 26 (93%) had significantly ($p<0.01$) different distributions of $p\mathrm{CO_2}$ under dark and light conditions, with 18 of those 26 cruises (69%) indicating increased $p\mathrm{CO_2}$ associated with dark conditions. No apparent seasonal or spatial pattern was observed in the differences between light and dark $p\mathrm{CO_2}$. These equivocal results point to no significant diel differences in sea surface $p\mathrm{CO_2}$, which is supported by a repeated measures ANOVA (Python package Statsmodels) performed on $p\mathrm{CO_2}$ values separated by cruise and light and dark conditions, which indicated no significant difference between the $p\mathrm{CO_2}$ values observed during light and dark conditions for the whole dataset ($F = 1.1$, $p = 0.3$); similar results were obtained for the pelagic ($F = 0.55$, $p = 0.5$) and riverine ($F = 0.62$, $p = 0.4$) subsets. These results are insufficient in temporal coverage to pick out drivers such as diurnal heating, primary production, and respiration at the diel scale. The majority (65%) of observations in the underway dataset are in daytime, but there is no basis for suggesting that the $p\mathrm{CO_2}$ values reported in this study are biased by time of measurement.

Equations S1-S3: Regression of pCO_2 driver deconvolutions

Power regressions (seventh order) of measured pCO_2 and its thermal and biophysical drivers were produced as visual aids and rough approximations of relative driver dominance. They are reproduced below.

$$
\begin{aligned}
p\mathrm{CO}_2 \;=\; & -1.45x10^{-12}x\mathrm{DOY}^7 + 1.89x10^{-9}x\mathrm{DOY}^6 - 1.01x10^{-6}x\mathrm{DOY}^5 + 2.91x10^{-4}\mathrm{DOY}^4 \\
& -4.82x10^{-2}x\mathrm{DOY}^3 + 4.63x\mathrm{DOY}^2 - 2.37x10^2x\mathrm{DOY} + 5.42x10^3 \qquad (1)
\end{aligned}
$$

$$
\begin{aligned}
p\mathrm{CO}_{2\,\mathrm{T}} \;=\; & 1.57x10^{-13}x\mathrm{DOY}^7 - 2.59x10^{-10}x\mathrm{DOY}^6 + 1.90x10^{-7}x\mathrm{DOY}^5 - 7.85x10^{-5}\mathrm{DOY}^4 \\
& +1.90x10^{-2}x\mathrm{DOY}^3 - 2.64x\mathrm{DOY}^2 + 1.92x10^2x\mathrm{DOY} - 5.24x10^3 \qquad (2)
\end{aligned}
$$

$$
\begin{aligned}
p\mathrm{CO}_{2\,\mathrm{BP}} \;=\; & -1.05x10^{-12}x\mathrm{DOY}^7 + 1.45x10^{-9}x\mathrm{DOY}^6 - 8.37x10^{-7}x\mathrm{DOY}^5 + 2.64x10^{-4}\mathrm{DOY}^4 \\
& -4.93x10^{-2}x\mathrm{DOY}^3 + 5.42x\mathrm{DOY}^2 - 3.24x10^2x\mathrm{DOY} + 8.51x10^3 \qquad (3)
\end{aligned}
$$

Text S2: pCO_2 thermal sensitivity calculation

```
import PyCO2SYS as pyco2

import numpy as np

from scipy import stats

from sklearn.linear_model import LinearRegression


PAR1 = 840 #Assume average total alkalinity of 840 micromol/kg

PAR2 = 400 #Assume pCO2 near atmospheric equilibrium

PAR1TYPE = 1  # 1=TA microM, 2=DIC microM, 3=pH, 4=pCO2 microatm, 5=fCO2 microatm, 6=CO32-

PAR2TYPE = 4

kwargs = {

'salinity': 0.05,  # practical

'temperature': 10,  # degC

'pressure': 0,  # dbar

'pressure_out': 0,  # dbar

'total_silicate': 10,  # silicate microM

'total_phosphate': 0,  # microM

'total_calcium': 13.62/40.078/1000*1000000,

'total_sulfate': 3.85/1000/96.06*1000000,

'opt_pH_scale': 3,  # 1=Total, 2=Seawater, 3=Free, 4=NBS

'opt_k_carbonic': 15,  # WMW14

'opt_k_bisulfate': 3

}
```

```
results = pyco2.sys(par1=PAR1, par2=PAR2, par1_type=PAR1TYPE,
par2_type=PAR2TYPE, temperature_out=10, **kwargs)
print("pH at 10 °C: " + str(round(results["pH_out"], 3)))

# %%
TEMP = np.linspace(0, 20)
pCO2array = np.zeros(len(TEMP))
lnpCO2 = np.zeros(len(TEMP))

for i in range(len(TEMP)):
results = pyco2.sys(par1=PAR1, par2=PAR2, par1_type=PAR1TYPE,
par2_type=PAR2TYPE, temperature_out=TEMP[i], **kwargs)
new = results["pCO2_out"]
pCO2array[i] = new
lnpCO2[i] = np.log(new)

Y = lnpCO2.reshape(-1, 1)
X = TEMP.reshape(-1, 1)
linear_regressor = LinearRegression()  # create object for the class
regression = linear_regressor.fit(X, Y)
dlnpCO2dT = regression.coef_
print("dlnpCO2dT = " + str(round(dlnpCO2dT[0][0], 8)) + "/°C")
```

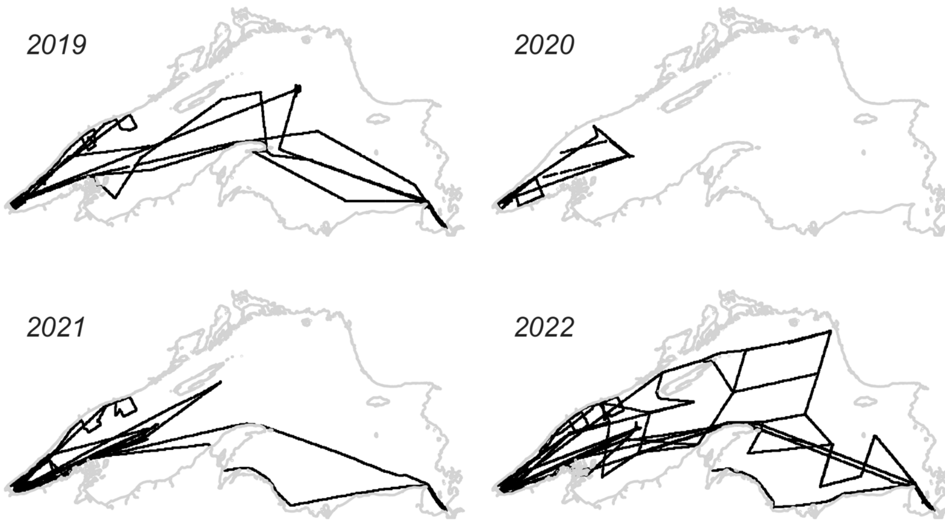

Figure S1. Transects across Lake Superior during 2019-2022.

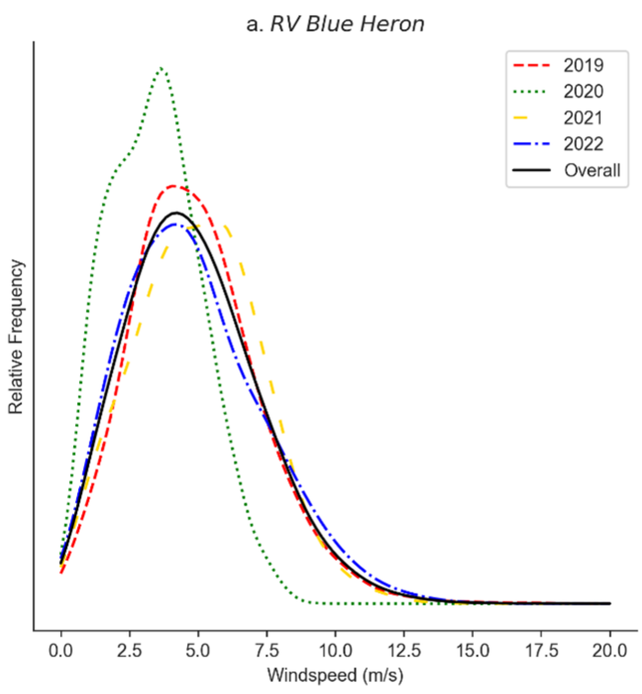

Figure S2. Wind speed distributions observed during transects of *RV Blue Heron* on Lake Superior, 2019-2022

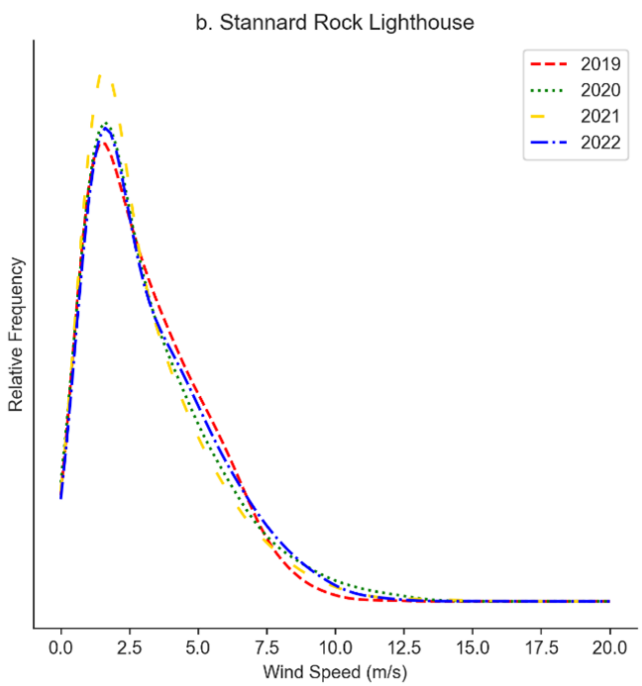

Figure S3. Wind speed distributions observed April-November (inclusive) at Stannard Rock Lighthouse via NOAA-NDBC instrumentation.

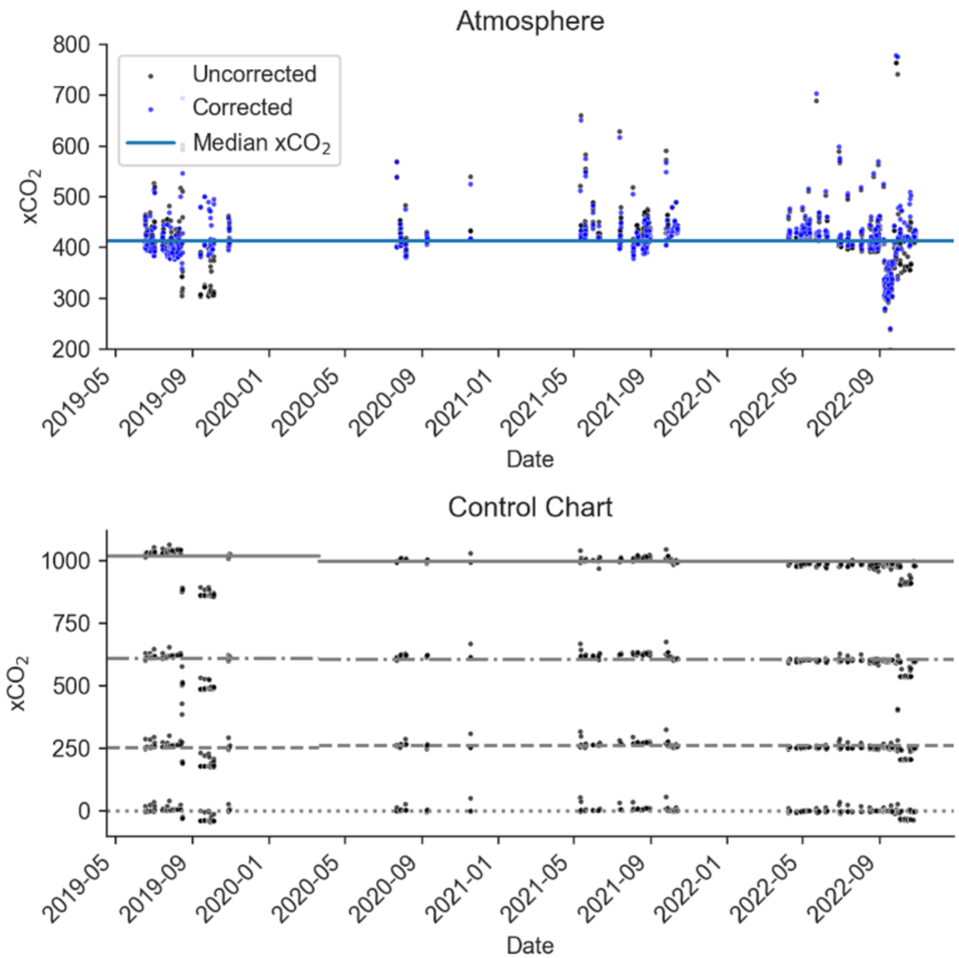

Figure S4. xCO_2 measurements of atmosphere and standard gases performed by SuperCO2 instrumentation during 69 transects of Lake Superior, 2019-2022. **a.** Pre- and post- standard correction atmospheric xCO_2 measurements demonstrate large biases from reliable atmospheric time series. **b.** Standard gas xCO_2 indicated by horizontal lines, measured concentrations by points. Several periods of bias from known standard gas xCO_2 are visible, demonstrating the need for cruise-level standard curve correction of surface water xCO_2 measurements. Standard gases were changed between the 2019 and 2020 field seasons, as indicated by breaks in the known standard concentrations.

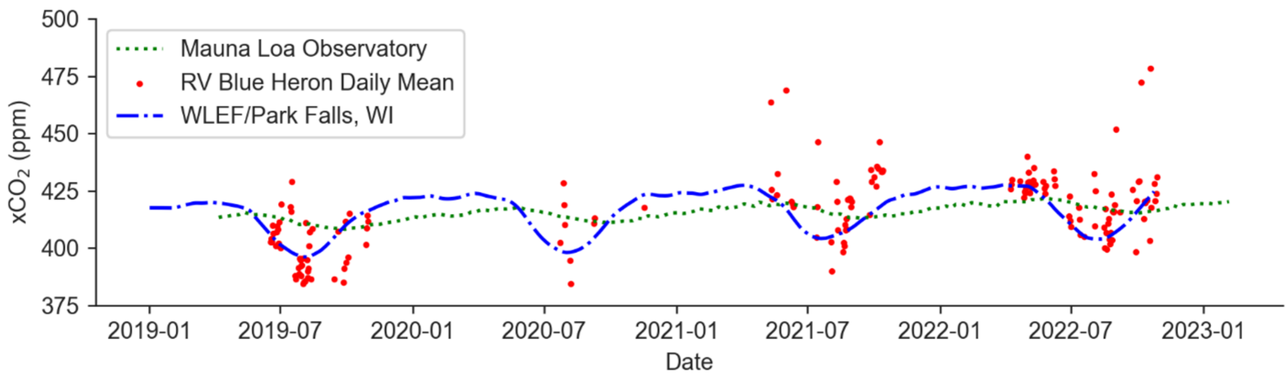

Figure S5. Daily mean atmospheric xCO_2 from the underway system (red dots), the Mauna Loa time series (green dotted line) and the Park Falls/WLEF tower (blue dash-dotted line). Anomalously depressed atmospheric xCO_2 values in September 2022 not shown.