



# Drivers of carbonate chemistry variability in an inland sea at Friday Harbor Laboratories



Aaron Ninokawa\* & Emily Carrington\*\*

\*State University of New York, Environmental Science and Forestry, Department of Chemistry

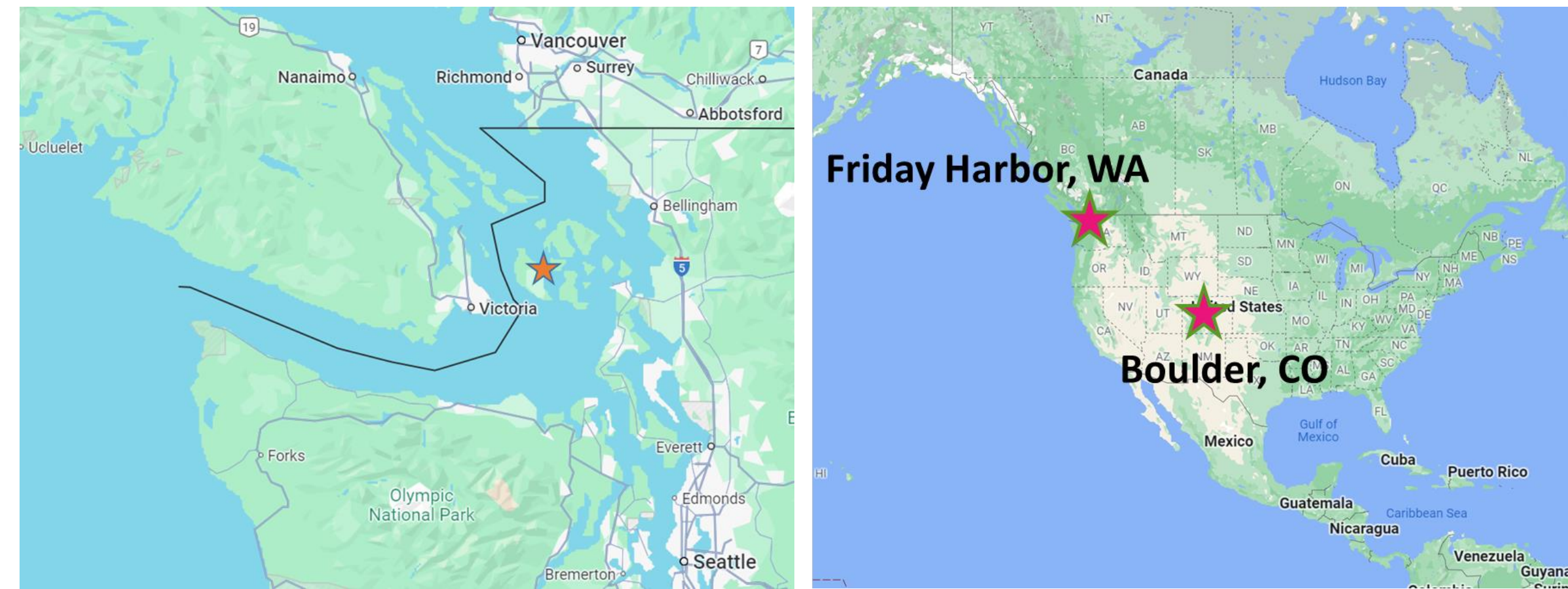
\*\*University of Washington, Biology & Friday Harbor Laboratories

## Abstract

Ocean acidification, the lowered pH resulting from increased anthropogenic carbon dioxide, is a threat to marine ecosystems globally. However, detecting acidification and predicting its impacts is difficult in coastal environments due to high natural variability driven by the mixing of marine and terrestrial inputs coupled with further modification by local organisms. Here, we present sensor data from the Friday Harbor Laboratories Ocean Observatory (FHLOO), a fixed sensor array located in the surface waters of the central Salish Sea in Washington state, combined with bottle samples collected between 2021 and 2023. The empirical relationship between salinity and alkalinity remained stable throughout the summer when salinity variability depended on discharge from the Fraser River. Because of the robustness of this relationship, we also examine how aerial heat waves impact carbonate chemistry variability by affecting the timing and intensity of freshwater input to the site. Although extreme heat events were observed in multiple years of the dataset, there were variable consequences for local alkalinity (salinity) depending on tides and snowpack. These findings highlight the complex connections between warming and chemistry that can challenge modeling and predictions in the coastal zone.

## Water chemistry of an inland sea

- San Juan Island in Central Salish Sea along west coast of North America
- Region has unique carbonate chemistry
  - Naturally high CO<sub>2</sub> and nutrient-rich<sup>1</sup>
  - Influenced by biological activity<sup>2</sup>
- Alkalinity an important parameter
- River input from different sources can have different effects on alkalinity<sup>3</sup>



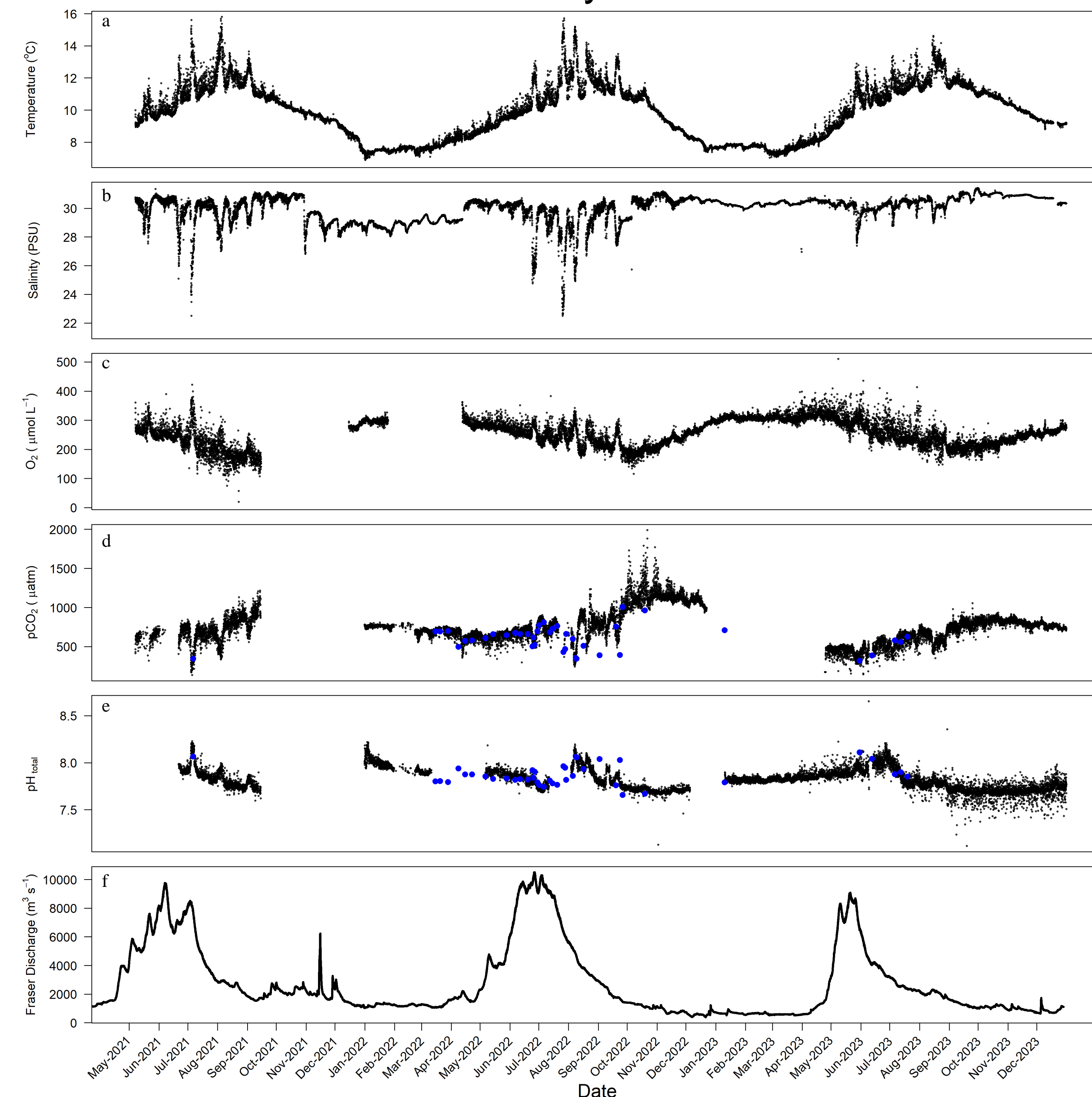
## Friday Harbor Laboratories Ocean Observatory (FHLOO)



- Sensors below FHL dock
  - 2 m depth
- Hourly observations:
  - Temperature
  - Salinity
  - Dissolved Oxygen
  - pH
  - pCO<sub>2</sub>
- Bottle samples collected and analyzed for pH and total alkalinity
  - Weekly during summer 2022 and 2023, one sample 2021
  - Daily during some low salinity events

## Motivating Question: How does freshwater discharge affect carbonate chemistry dynamics at the FHLOO?

### Seasonal variability at the FHLOO



### Consistent alkalinity-salinity relationship for FHLOO

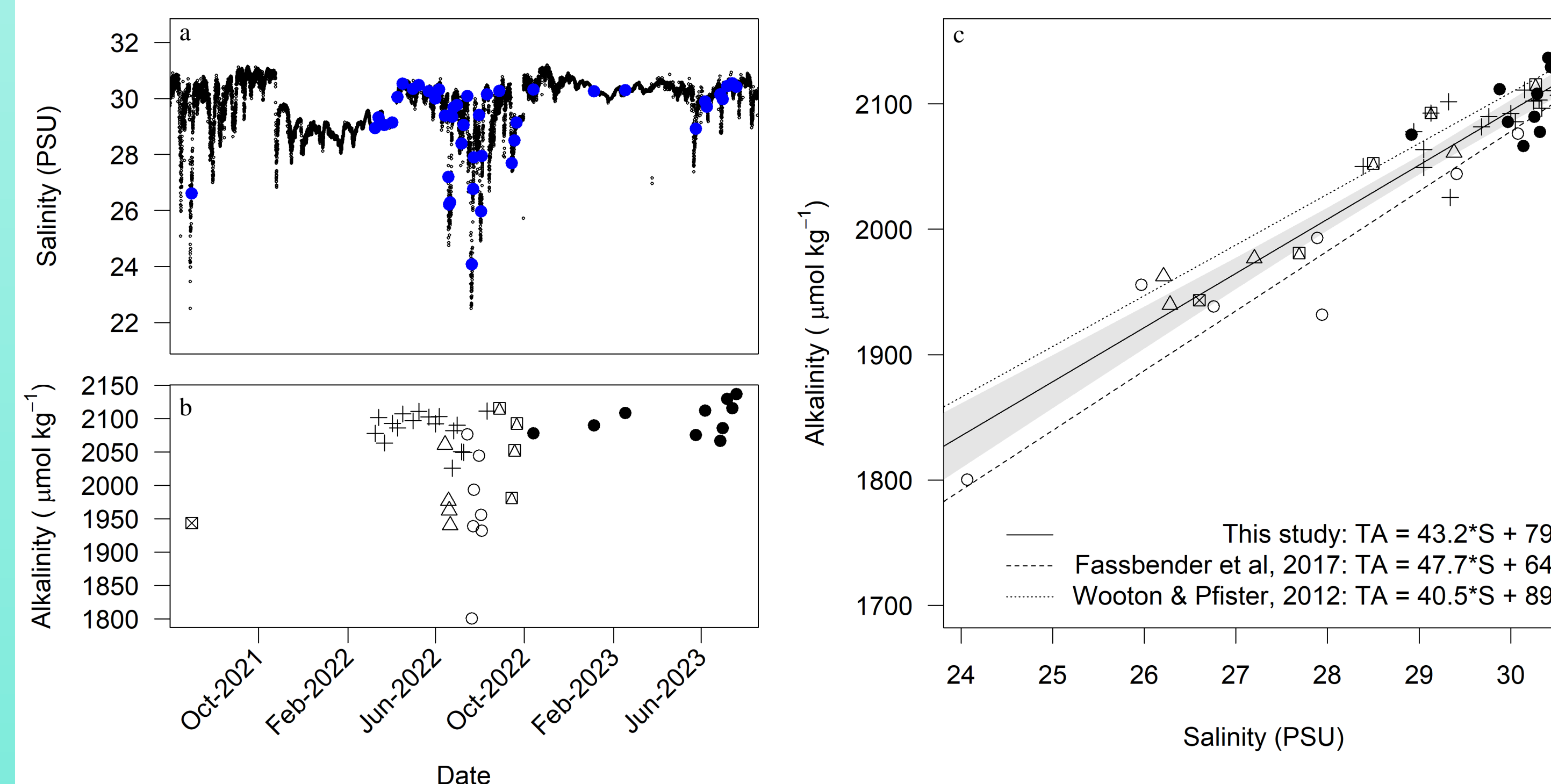


Figure 2. Relationship between salinity and alkalinity at the FHLOO. a) Salinity time series collected by the sensors. Blue dots indicate when we collected bottle samples. b) Alkalinity time series determined from bottle samples indicated in Fig 2a. Symbols indicate either the background alkalinity (pluses and closed circles) or a respective low salinity events (other symbols). c) Plot of alkalinity versus salinity for the time period. Symbols match those in Fig 2b to demonstrate that the alkalinity-salinity relationship did not differ through the season. Solid line indicates the best fit line from a linear model and gray region shows the 95% confidence interval. Slope estimate was  $43.2 \pm 2.4$  and intercept estimate was  $799 \pm 70.4$  (estimate  $\pm$  standard error).

**Alkalinity-salinity relationship stable and consistent with Fraser River origin for freshwater source ( $851 \mu\text{mol L}^{-1}$ )<sup>4</sup>**

**Between relationships for Puget Sound and WA outer coast<sup>5</sup> and coastal northwest WA<sup>6</sup>**

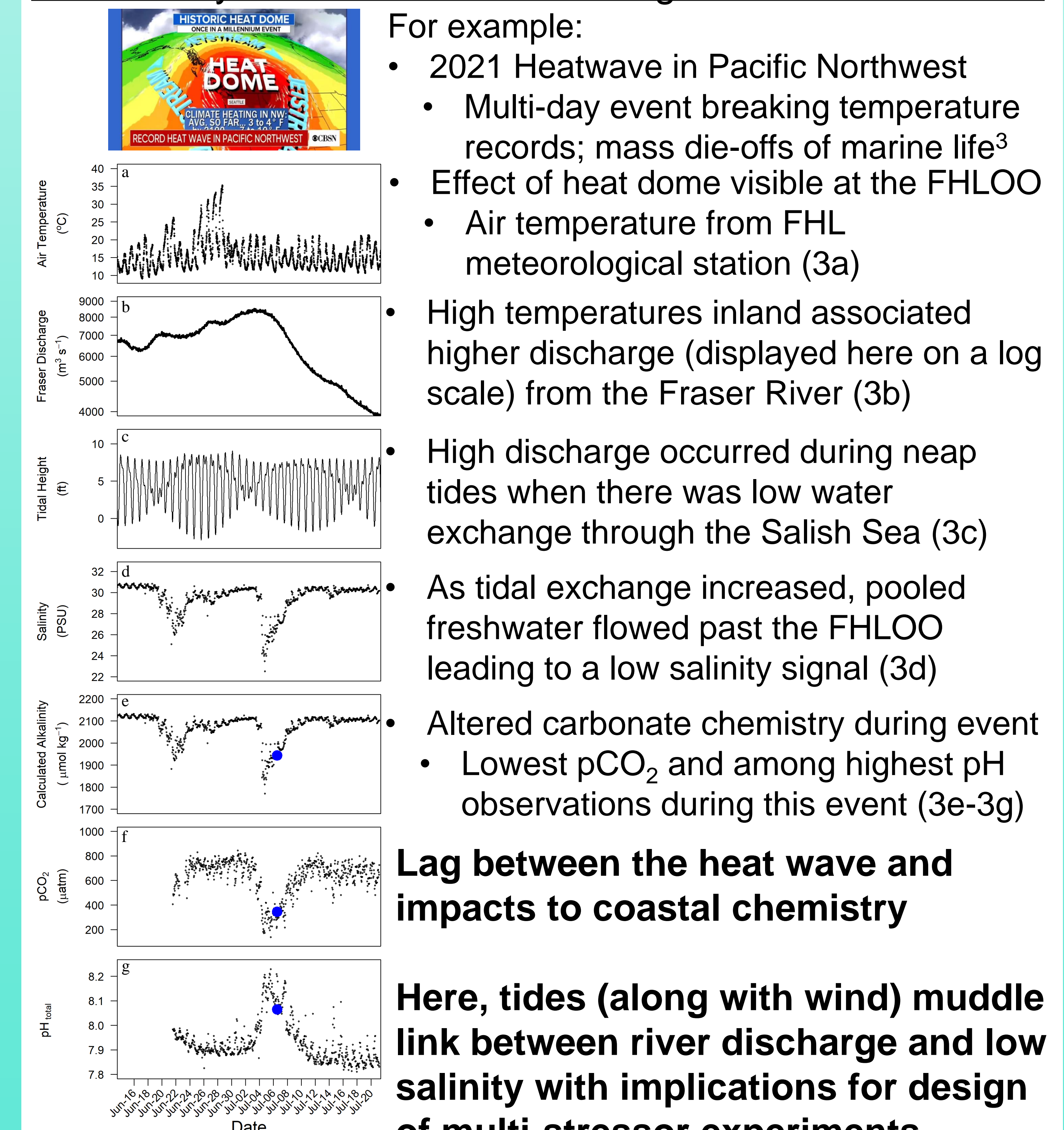
### Acknowledgements

Thank you to those that have helped establish and maintain the FHLOO including K. Sato, A. Gagnon, E. Lessard, J. Newton, B. Swalla, K. Sebens, K. Kull, E. Finn, K. Murie, J. Little, Y. Li, J. Pineda, and K. Davis. This project was supported by NSF FSNL-1418875 and NSF OCE-2126719

### References

<sup>1</sup>Murray et al, 2015; <sup>2</sup>Lowe et al, 2015; <sup>3</sup>Aufdenkampe et al, 2011; <sup>4</sup>Voss et al, 2014; <sup>5</sup>Fassbender et al, 2017; <sup>6</sup>Wootton & Pfister, 2012

### Low salinity events linked to discharge/snowmelt and tides



For example:

- 2021 Heatwave in Pacific Northwest
  - Multi-day event breaking temperature records; mass die-offs of marine life<sup>3</sup>
- Effect of heat dome visible at the FHLOO
  - Air temperature from FHL meteorological station (3a)
- High temperatures inland associated higher discharge (displayed here on a log scale) from the Fraser River (3b)
- High discharge occurred during neap tides when there was low water exchange through the Salish Sea (3c)
- As tidal exchange increased, pooled freshwater flowed past the FHLOO leading to a low salinity signal (3d)
- Altered carbonate chemistry during event
  - Lowest pCO<sub>2</sub> and among highest pH observations during this event (3e-3g)

**Lag between the heat wave and impacts to coastal chemistry**

**Here, tides (along with wind) muddle link between river discharge and low salinity with implications for design of multi-stressor experiments**

Figure 3. FHLOO data for the period between June 15, 2021 and July 21, 2021. Each panel described above. Blue points indicate bottle data and Fraser River discharge accessed as in Fig 1. Tidal height data accessed from tidesandcurrent.noaa.gov for Friday Harbor (9449880).

## Apparent seasonality in seawater conditions

## Variability in summer due to influence of Fraser River