

The Effect of Salinity on Lithium Isotope and Element Ratios in the Eastern Oyster, *Crassostrea virginica*

Alexandra Schaffer¹, Michael Kipp¹, Gordon Williams¹, Gary Dwyer¹, Rosa Grigoryan¹
¹Division of Earth & Climate Sciences, Nicholas School of the Environment, Duke University

Abstract



GAIA Lab

Geoscience Applications of Isotopic Analysis

Duke

NICHOLAS SCHOOL of the ENVIRONMENT

References & Acknowledgements:

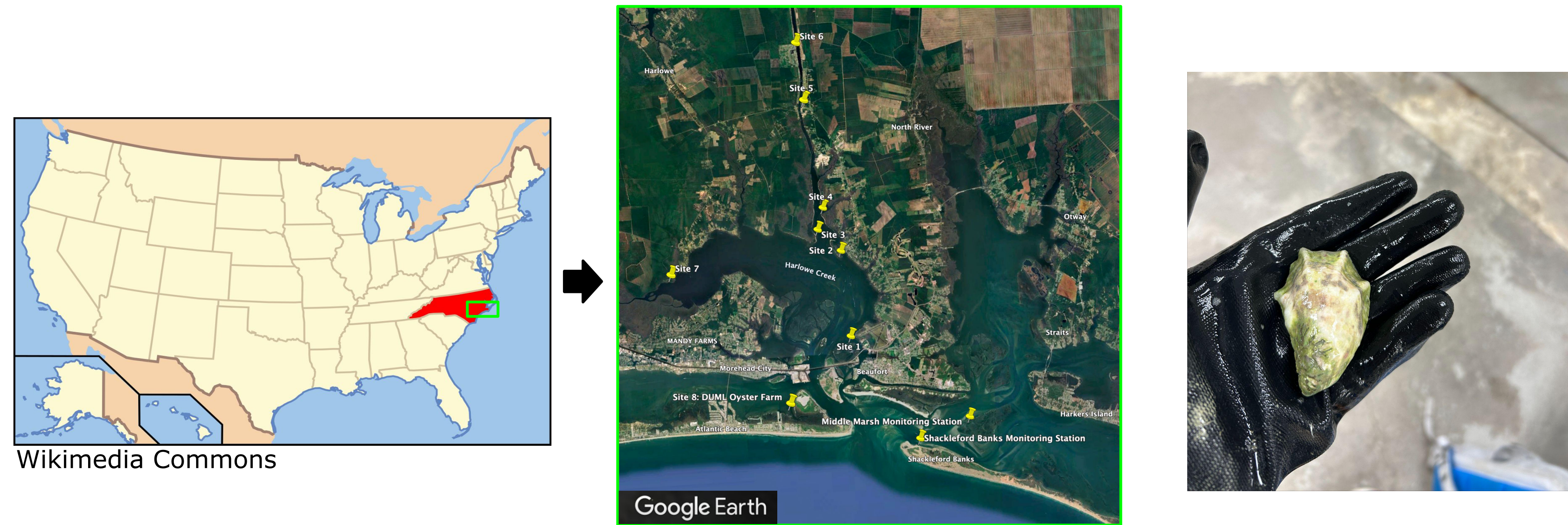


Background

- Oyster shells are abundant in the fossil record and can be used to estimate paleo- $\delta^7\text{Li}$.
- $\delta^7\text{Li}$ values and Li concentration ratios serve as proxies for silicate weathering congruency^{3, 9}, temperature^{3, 7}, and cycling between rivers, which have relatively low Li concentrations ($0.0015 \mu\text{g/g}$)², and the ocean, which has higher Li concentrations ($0.18 \mu\text{g/g}$)⁸.
- Ancient $\delta^7\text{Li}$ and element ratio values in water can be estimated by measuring fossil shells.
- However, Li isotope fractionation or preferential element uptake due to factors such as salinity could reduce the shell's ability to serve as a faithful paleo-archive.¹ This effect has yet to be studied in many paleo-proxies.
- Marriott et al. 2004⁶ found no relationship with salinity for both $\delta^7\text{Li}$ and Li/Ca in inorganically grown carbonates and benthic foraminifera.
- We analyzed $\delta^7\text{Li}$, Li/Mg, Mg/Ca, Sr/Ca, and more as they relate to salinity in low-Mg calcite oyster shells and water samples in the Newport River Estuary in coastal North Carolina.

Methods

Sample collection: Collected **50 oysters** from a total of **eight** sites around the Newport River Estuary on the coast of North Carolina



Adopted digestion and Lithium purification methods from Dellinger et al. 2018¹:
Digestion: Ground ~ 100 mg pieces from each shell into a fine powder, subjected to an ammonium acetate leach, and dissolved in 0.05 M HCl ($\sim 90\%$ dissolution).
Lithium purification: Used columns containing 4 mL Biorad AG50W X-12 resin to isolate Li in the samples (~ 1 -10 ng for shells, ~ 100 ng for water).
MC-ICP-MS Analysis: Li was measured at 2.5-10 ppb on Nu Sapphire (HE mode) in the low-resolution mode. microFAST Isotope2 (ESI) was connected to an Apex Ω HF desolvation nebulizer system⁴.
ICP-MS Analysis: Element ratios were measured on a Thermo X-series ICP-MS in 2% HNO₃ at a uniform Ca concentration of 40 ppm⁵.

Results

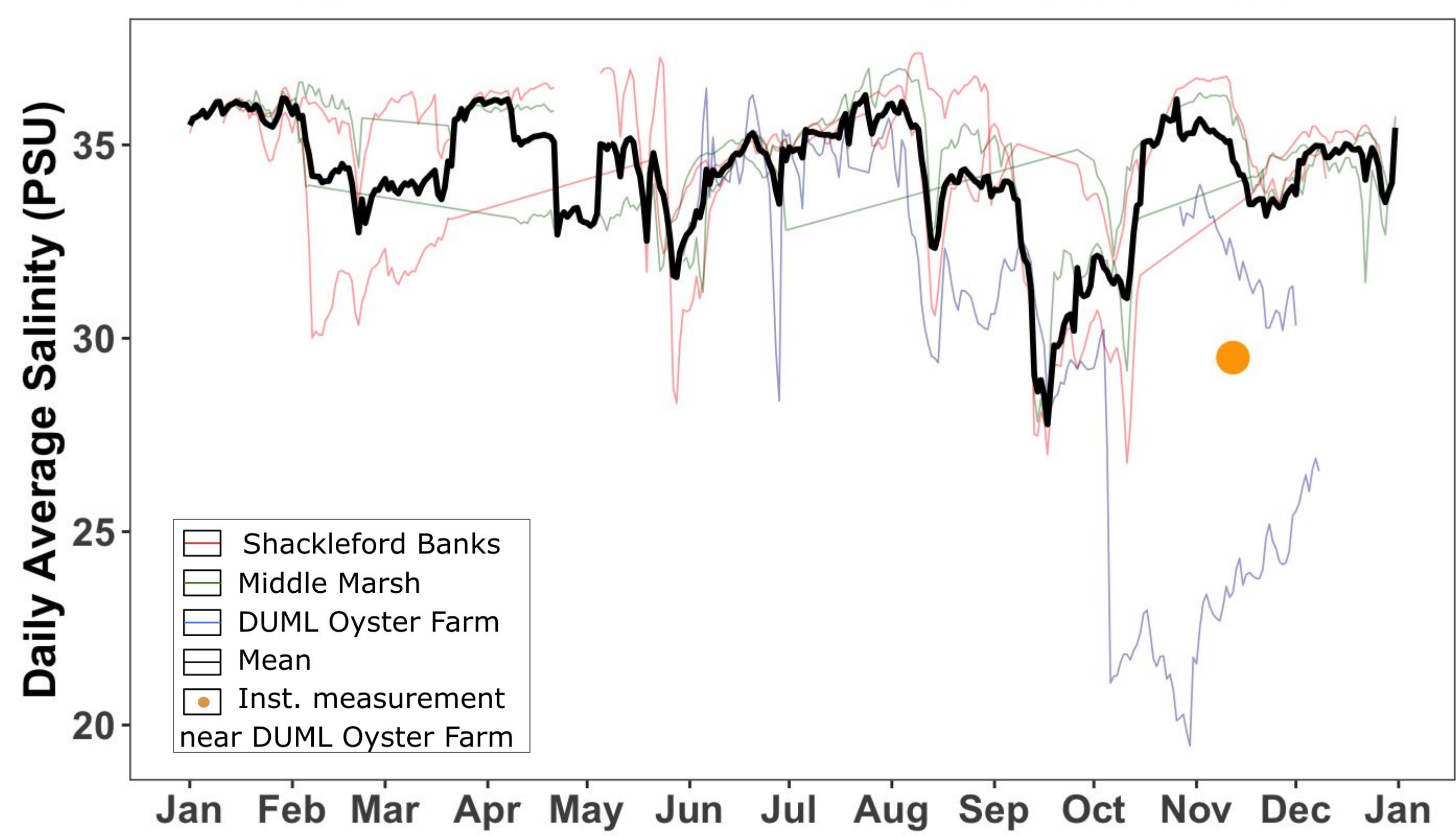


Figure 1. Average daily salinity over the last three years at one sampling site (DUML oyster farm) and two National Parks Service monitoring stations close to the sampling sites (Shackleford Banks and Middle Marsh). National Parks Service data acquired from NPS Aquarius web portal¹⁰. Oyster farm data acquired from Duke Marine Lab.

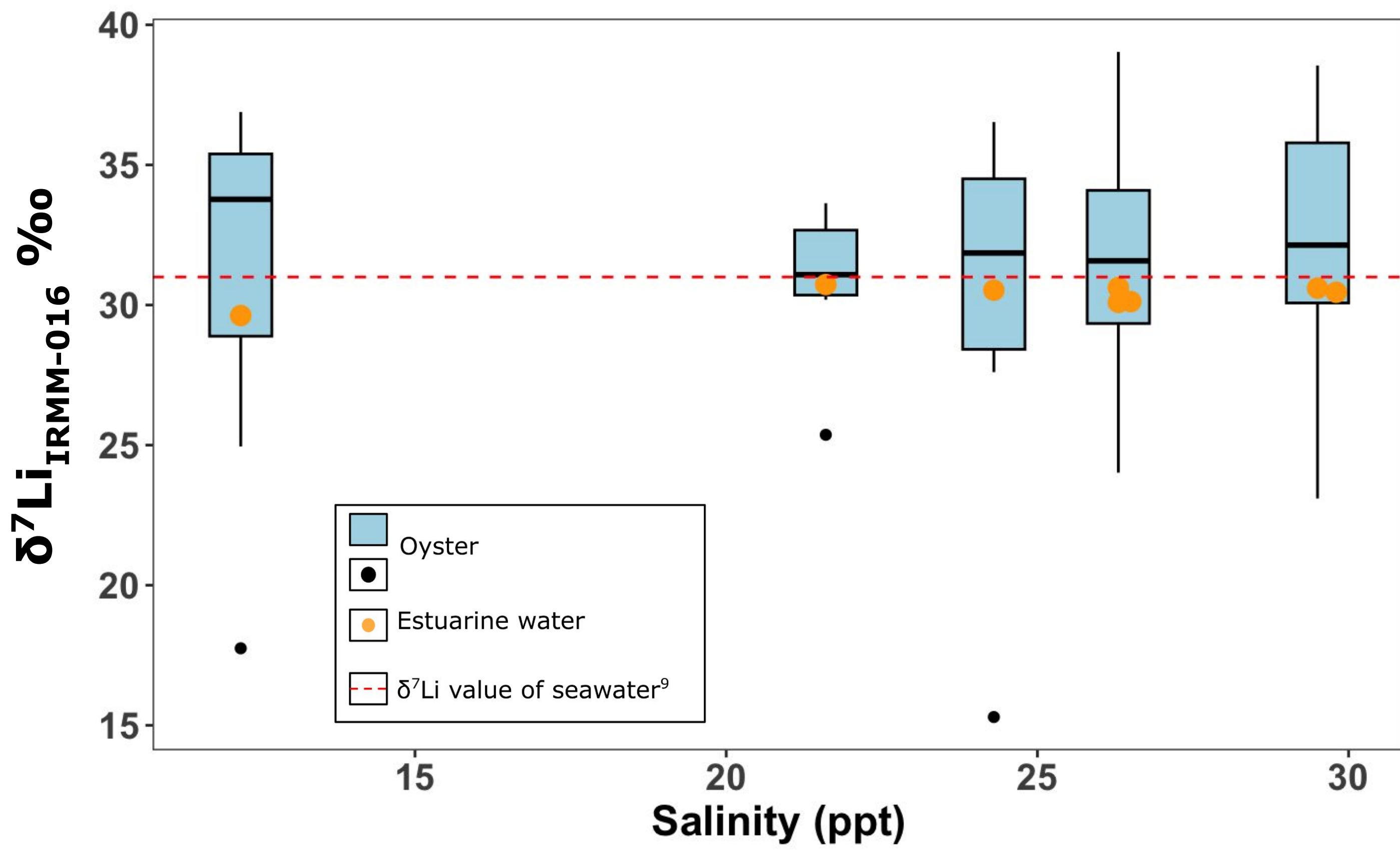


Figure 2. Relationship between salinity and $\delta^7\text{Li}_{\text{IRMM-016}}$ ‰ in oyster and estuarine water samples, grouped by sampling site. Sites with a <2 ppt salinity difference are grouped together as one.

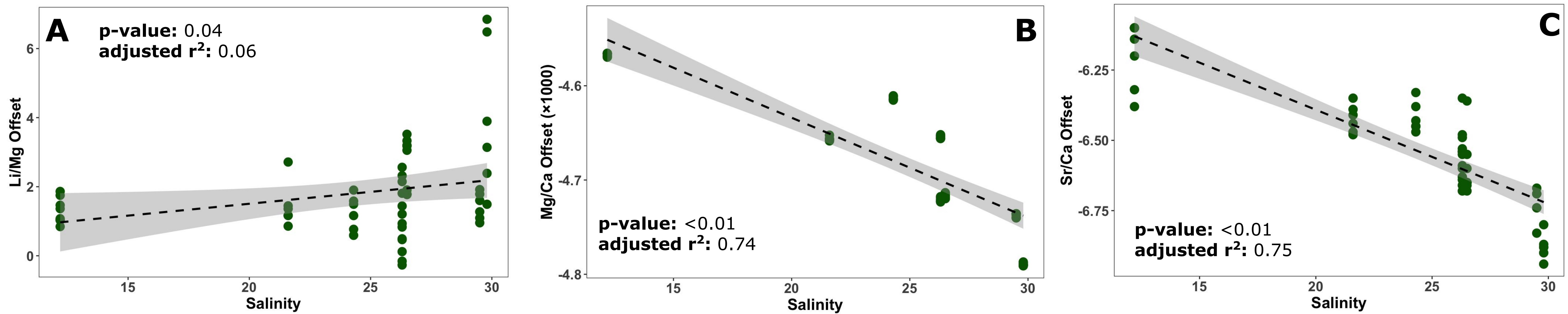


Figure 3. Relationship between salinity and offset of oyster and estuarine water values (oyster value - estuarine water value) for (A) Li/Mg, (B) Mg/Ca, and (C) Sr/Ca.

Discussion

- We found no relationship between $\delta^7\text{Li}$ and salinity in oyster shell samples and estuarine water samples**
 - Since $\delta^7\text{Li}$ values are not confounded by salinity, fossil oysters that once lived in estuarine environments with highly variable salinity might still serve as faithful archives of silicate weathering congruency, temperature, water cycling patterns, and other environmental conditions.
- Salinity in the Newport River Estuary is highly variable throughout the year**
 - We aim to resample salinity from all sites in late August to obtain maximum values before hurricane season, which likely caused the annual drop in salinity observed during the fall months. This will increase the preciseness of our salinity measurements.
- The offsets between oyster and water values for Li/Mg, Mg/Ca, and Sr/Ca increase in magnitude with increasing salinity**
 - As we move closer to the ocean, the shells are less representative of the elemental composition of the water. The offsets can be influenced by changing oyster values while water values are kept constant, which we observed in Sr/Ca, or by changing of both oyster and water values.