Tidal Influence on Alkalinity-Salinity Relationships in the Murderkill River

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Abstract

A reliable total alkalinity (TA) and salinity relationship will allow users to convert high frequency and easy to acquire salinity data to TA and other key carbonate system parameters such total dissolved inorganic carbon (DIC) and carbonate mineral saturation state, which are needed for understanding carbon cycle and assessing conditions for aquaculture industrial. The purpose of this study was to understand how flood and ebb tides affect the total TA and salinity relationship in the Murderkill River watershed in Delaware (DE), U.S.A., which is characterized by nutrient-rich water, surrounding salt marshes, and a wide salinity range . Alkalinity and salinity relationships are controlled tidally via two main endmembers, the Delaware Bay and estuarine outflow. These parameters were measured through discrete samples, USGS sensors, as well as SeapHOx sensors. Tidal fluctuations were measured via water gauge data. We found that TA and salinity increased during the flood tide and decreased during the ebb tide. However, DE bay water rapidly increased the salinity on the flood tide. To further distinguish the flood and ebb tides, pH and DIC data were incorporated as part of the analysis. The accuracy of each daily tidal TA-S relationship was determined by calculating RMSE and R^2 values. This study demonstrated a unique understanding of tidal influences on TA-S in an estuary (Murderkill). However, if sampling were less sporadic during the Sept 2015- Aug 2016 period, more concluding observations could be made.

Introduction

- Alkalinity is one of the four measurable carbon parameters used to measure and characterize the marine inorganic carbon cycle.
- Total Alkalinity (TA) is defined as the number of moles of the hydrogen ion equivalent to the excess proton acceptors over proton donors found in 1kg of water (Dickson 1981).
- Alkalinity can be thought of as a charge balance or buffering effect. If we have a larger alkalinity, there is a higher resistance to change in pH.
- Tidal periods analyzed in this work are flood and ebb tides, which correspond to the incoming and outgoing tides, respectively.
- There were two main endmembers to consider when studying the Murderkill Estuary-Delaware Bay System (Bowers, DE, USA): (1) the more saline Delaware Bay water with higher TA that dominated on the flood tide and during high tide periods and (2) the fresher Murderkill Estuarine outflow with lower TA that dominated on the ebb tide and during low tide periods.
- Since total alkalinity and salinity mix conservatively in most two-endmember river-dominated estuarine systems, mixing relationships between TA and salinity (hereafter referred to as TA-S relationships) are an important tool in the toolbox of resolving marine inorganic carbon cycling in nearshore systems.

Objective

The purpose of this study was to understand differences between TA-S relationships on the ebb and flood tides, in the Murderkill Estuary-Delaware Bay System by using gauge height (or water level), TA, and salinity data for three sampling days in the summer of 2016.

Methods

- Discrete water samples for TA were collected on June 1st, June 29th, and August 2nd in summer 2016 over full tidal cycles.
- An automated Gran titration (TA Titrator from Apollo SciTech) was used to measure discrete alkalinity samples.
- Salinity was measured using a Sea-Bird Electronics Conductivity-Temperature Sensor (SBE37) integrated into the SeapHOx sensor.
- Discharge and water gauge height data were taken from the United States Geological Survey (USGS) database from station 01484085 (Murderkill River at Bowers Beach, DE) that was co-located with the SeapHOx sensor.
- Discharge and water gauge were measured every 6 minutes, which were then separated out into 30-minute intervals to match the discrete water sample and SeapHOx timestamps.
- Tides were determined by increasing (denoting flood tide periods) or decreasing (denoting ebb tide periods) water gauge heights, whereas Delaware Bay data was found by plotting salinity and water gauge height together.
- Linear regression was created in Microsoft Excel.

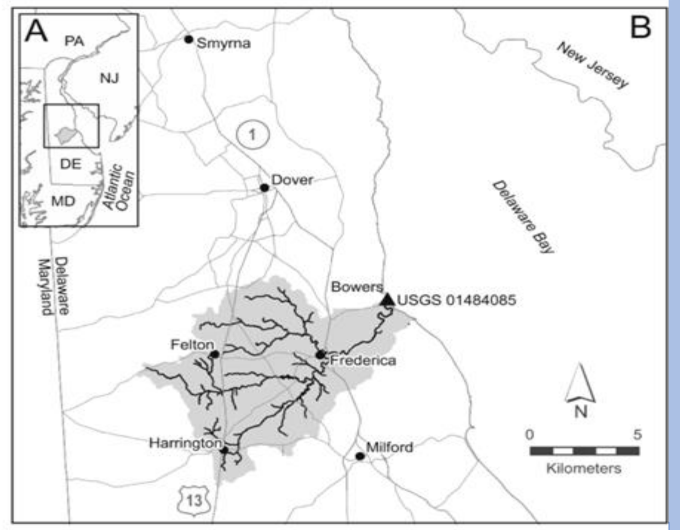

Fig 1 Map of the Murderkill Watershed and sensor location. Location of the Murderkill Watershed in the Mid-Atlantic and State of Delaware (A, inset). The Murderkill Watershed (grey) and the USGS gauging station (DE01484085) in Bowers, DE (triangle) at the confluence of the Murderkill Estuary and Delaware Bay (B). An autonomous SeapHOx sensor was co-located at the USGS gauging station during Summer of 2016.

(a)

(b)

(c)

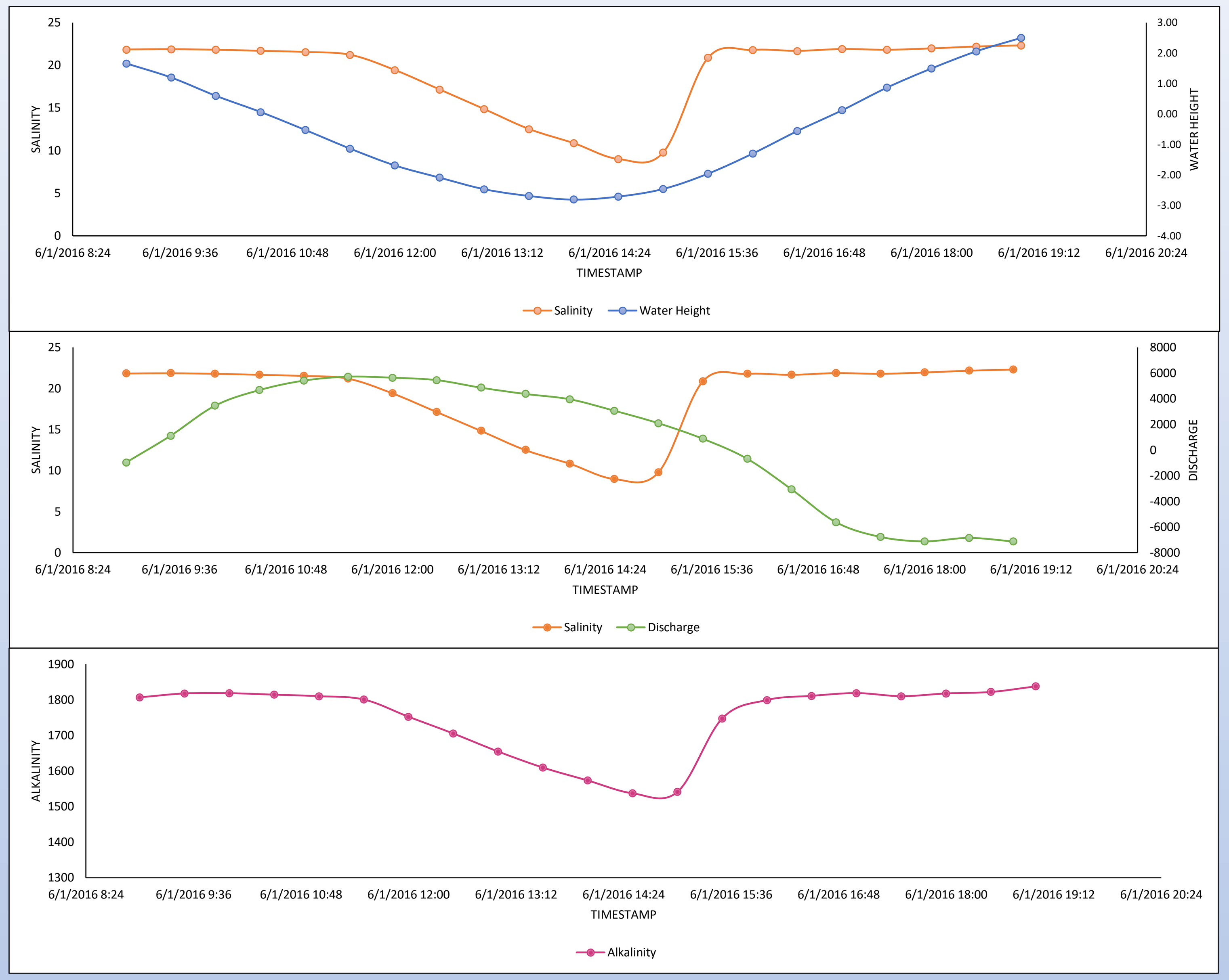

Fig 2 June 1st, 2016, sampling day composite timer-series of **(a)** water gauge height and salinity, **(b)** discharge (ft^3/sec) and salinity and **(c)** alkalinity between times 0900-1900.

(a)

(b)

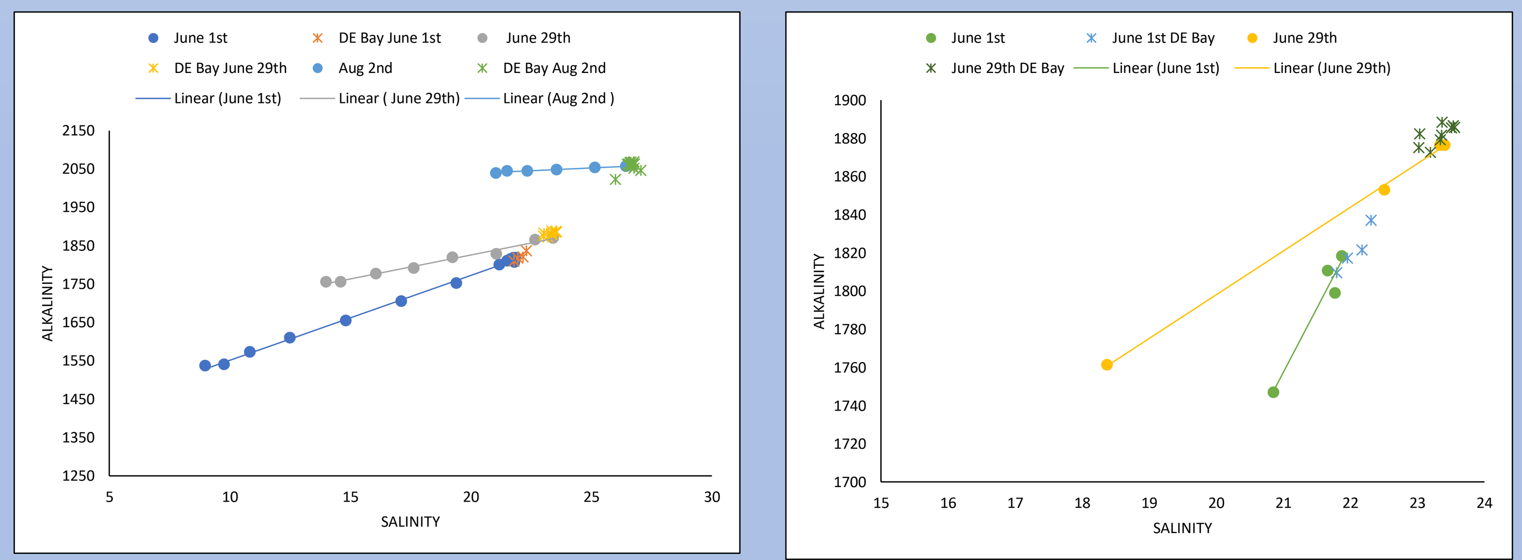

Fig 3 **(a)** Ebb tide and **(b)** Flood tide TA-S relationship for June 1st, June 29th, and Aug 2nd, 2016 (ebb tide only), along with DE Bay water from each sampling day plotted

Table 1 Regression relationships from Fig 2. S being salinity, N being the number of observations, and RMSE being the root mean squared error.

Date	Tide	Regression Relationship	R^2	N	Salinity Range	TA Range	RMSE
June 1st	Ebb	TA=22.122*S+1330.3	0.999	15	8.99-21.86	1536.69-1818.10	5.09
June 1st	Flood	TA=67.166*S+346.67	0.940	4	20.86-21.88	1746.99-1818.38	6.83
June 29th	Ebb	TA=12.498*S+1575	0.985	10	14.01-23.43	1755.27-1869.56	5.16
June 29th	Flood	TA=22.883*S+1340.4	0.998	4	18.38-23.41	1761.30-1876.43	1.56
Aug 2nd	Ebb	TA=3.01*S+1977	0.952	6	21.06-26.45	2038.50-2056.23	1.31

Acknowledgements and References

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1. *Hunt, C. et al. (2021). Variability of USA East Coast surface total alkalinity distributions revealed by automated instrument measurements. Marine Chemistry, 232, 1-17*
2. *Millero, F. J. (2007). The marine inorganic carbon cycle. Chemical reviews, 107(2), 308-341.*
3. *Joesoef, A. et al. (2017). Seasonal variability of the inorganic carbon system in a large coastal plain estuary. Biogeosciences, 14, 4949-4963.*
4. *Gonski, S. et al. (2017). Assessment of the Durafet based sensors for pH measurement in dynamic estuarine environments. Estuarine Coastal and Shelf Science, 200, 152-168.*
5. *Gonski, S. F., Cai, W. J., Ullman, W. J., Joesoef, A., Main, C. R., Pettay, D. T., & Martz, T. R. (2018). Assessment of the suitability of Durafet-based sensors for pH measurement in dynamic estuarine environments. Estuarine, Coastal and Shelf Science, 200, 152-168.*
6. *Voynova, Y. G., Lebaron, K. C., Barnes, R. T., & Ullman, W. J. (2015). In situ response of bay productivity to nutrient loading from a small tributary: The Delaware Bay-Murderkill Estuary tidally-coupled biogeochemical reactor. Estuarine, Coastal and Shelf Science, 160, 33-48.*
7. *Pettay, D. T. et al. (2020). The ebb and flow of protons: A novel approach for the assessment of estuarine and coastal acidification. Estuarine, Coastal and Shelf Science, 160, 1-11.*

Results

- Alkalinity and salinity were in a positive, linear relationship during both flood and ebb tides.
- Generally, when the tide is flooding, alkalinity and salinity increased, and conversely when ebbing, alkalinity and salinity decreased with time.
- Once salinity began to stabilize a couple hours into high tide, that is when the Delaware Bay water predominated.
- The Delaware Bay water recharged rapidly upstream into the estuary at 15:30 on June 1st, 2016, in Fig 2, therefore changing the salinity quite abruptly.
- A tidal node in the Murderkill River resulted in a weaker flow of water toward the bay coming out, and a much stronger flow from the Bay into the river as expected of a flood-dominant system.
- Two data points previously determined to be on the flood tide were then moved to the ebb tide because of extremely low salinities.
- The flood tide data from August 2nd was not sufficient to create a meaningful relationship, therefore only the August 2nd ebb tide data is charted.
- Discharge was inversely related to salinity with respect to water gauge height.

Discussion

- All relationships were strongly correlated, with $R^2 \geq 0.94$.
- June 1st had the lowest salinity and alkalinity on the ebb tide, likely because of larger freshwater flows and greater river influences at the sensor site, or another physical anomaly. DIC and pH (data not shown) agreed with this conclusion.
- Discharge was not an accurate determinant of differentiating between ebb and flood tides, however the strength of the tides at a certain time of day were analyzed, which was useful in visualizing and determining when the Delaware Bay water recharged upstream.
- In Fig 2. (b), in the middle of the 30-minute period of rapid salinity increase, discharge was 0 and continued to decrease as salinity stabilized around slack ebb tide.
- The bay water was coming in as discharge kept decreasing on the flood tide.
- The tide was ebbing more rapidly than it was flooding, with most of each sampling day having a large influx of Delaware Bay water.
- August 2nd had the least amount of TA-S data out of the three sampling days, with a large majority of tidal influence coming from bay water, which is most likely why there was such a small slope and range of salinity.
- In Fig 3 (b), the slope of the relationships were steeper than the ebb tide relationships in (a) because of high salinity bay water abruptly rapidly recharging upstream.

Conclusion

- There is a strong relationship between tidal variations and TA-S in the Murderkill River.
- When the tide and bay water was coming in, salinity was generally higher and vice versa.
- Each sampling day had its own precise, unique relationship.
- This study allowed a baseline understanding of what creates variations in TA-S in the Murderkill Estuary-Delaware Bay System.
- As single parameter studies of marine inorganic carbon cycling dynamics in estuarine and coastal ocean systems become more common, the development of TA-S relationships in these systems will allow for scientists and environmental managers to use salinity (a commonly measured water quality parameter) to calculate high-frequency TA. With two parameters, the remainder of the marine inorganic carbon system can then be calculated.

Future Outlook

Light and time were limitations when sampling in the colder months for this study, which limited analysis to simply summer data. In the future for a continuation of this study, sampling more frequently would be recommended. Every 15 minutes instead of 30 minutes would give a more accurate tidal differentiation (especially on flood tide periods).