Investigating Trends of Organic Alkalinity in Estuaries of the Gulf of Maine

Jessica Hinckley, Dr. Joseph Salisbury | jah1108@wildcats.unh.edu | University of New Hampshire

Summary

Estuaries exhibit a noticeably high organic alkalinity signature that diminishes towards the ocean where inorganic species dominate alkalinity.[1,6,7] This shift in alkalinity from a low salinity to high salinity environment has not been sufficiently studied. The goal of this investigation is to better understand the role organic alkalinity plays in the buffering of coastal ecosystems. Ten estuaries that feed into the Gulf of Maine were selected for sampling ranging from Maine, U.S.A to New Brunswick, Canada. River endmember samples were collected and will be serially diluted with seawater to simulate river water mixing with the ocean. For each series of dilutions, total alkalinity, organic alkalinity and dissociation constants (pK_as) will be determined through titration analysis. Understanding the contribution of organic alkalinity to the buffering ability of estuaries is essential to predict the future resilience of these ecosystems. Acidification in estuaries threatens the habitat of many shellfish and fish species.[8] This investigation will not only further develop the ability to estimate the total alkalinity of a coastal ecosystem, but can aid in analysis of estuary health and fisheries management.

Introduction

- Increased concentrations of atmospheric Carbon dioxide (CO_2) are driving the acidification of coastal ecosystems through the dissolution of CO_2 in marine waters.[2,5]
- Alkalinity is the aquatic systems ability to buffer changes in acidity. Total alkalinity is comprised of both inorganic and organic species that neutralize a change in pH through chemical bonding (Figure 1).[3]
- Inorganic alkalinity is relatively well studied, but much is unknown about organic alkalinity and its potential importance to the buffering of coastal ecosystems.
- Estuaries are key coastal ecosystems under the threat of acidification. With unique acid-base properties, studies have shown that estuaries display signs of high organic buffering.[1,6,]
- Organic alkalinity diminishes towards the ocean where inorganic alkalinity dominates. Salinity has been hypothesized to cause this decrease in organic alkalinity through impacting the acid-base properties of organic alkalinity (Obj. 2) and enhancing flocculation (Obj. 3).[7,9]

OBJECTIVES:

1. ***Quantify the impact of river and ocean water mixing on the organic alkalinity of an estuary.***
2. ***Determine the effect of salinity on the dissociation constants (pK_as) of organic alkalinity. Compare pKa values throughout and of different estuaries in the Gulf of Maine.***
3. ***Identify the influence of increasing salinity on the coagulation and settling of organic particles out of solution.***

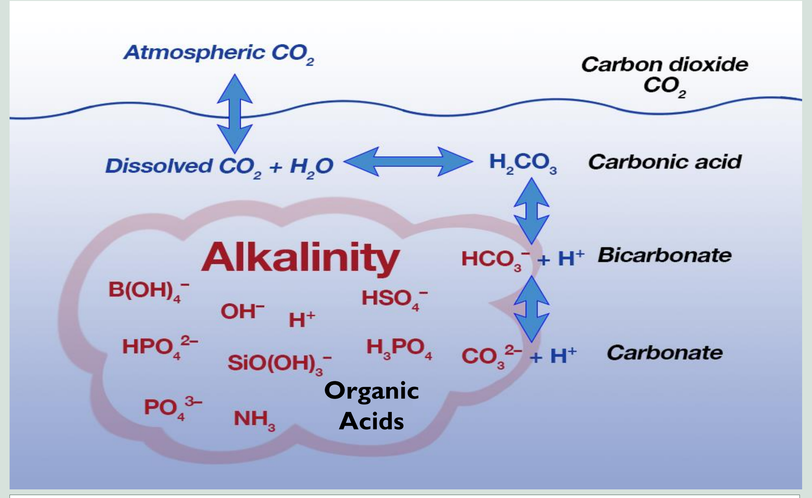

Figure 1: Interaction of Carbonate System and Total Alkalinity in marine waters (adapted from NASA).

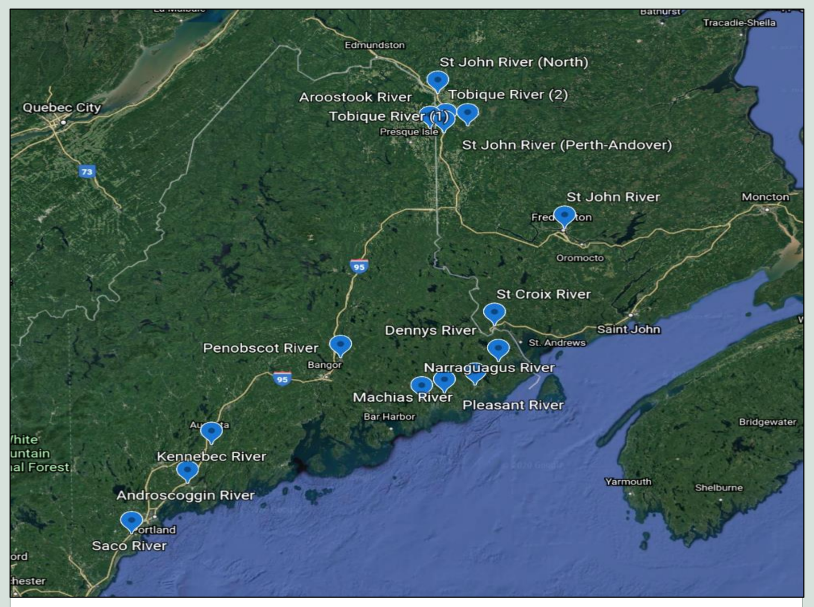

Figure 2: Map of sampling locations.

Methodology

Freshwater samples were collected at 15 sites, to represent the river endmembers of the ten estuaries selected for sampling (Figure 2). The samples will be serially diluted with a saltwater standard to target salinities. Before and after each dilution, a portion of sample will be looked at under a microscope for evidence of flocculation. The total alkalinity, organic alkalinity and pKa's for the series of dilutions will be determined through a Gran + Whole titration (Figure 3).[1]

Figure 3: Procedure of Gran + Whole Titration Analysis

Gran
- Hydrochloric Acid (HCl) slowly added until the sample reaches a pH of 3
- Total Alkalinity calculated from amount HCl used

Back-Titration
- Sample stoppered and Nitrogen gas bubbler inserted to prevent re-dissolution of CO_2
- CO_2 free Sodium Hydroxide (NaOH) added to sample until a pH of 10 is achieved

Whole
- HCl is slowly added to the sample until a pH of 3 is reached
- A titration curve is produced, and transferred into MATLAB
  - Organic Alkalinity calculated twice
  - pKa's calculated from equivalence points

Expected Results

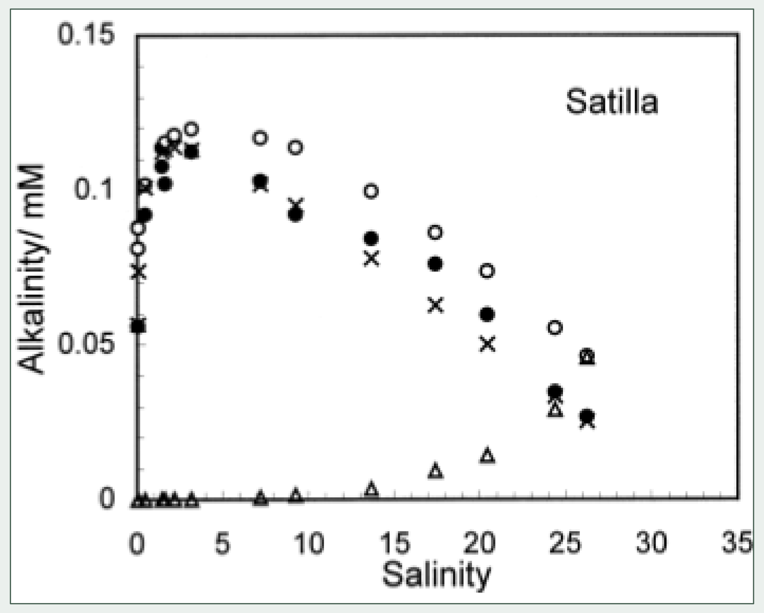

Figure 4: Data from the Satilla River in Georgia pulled from Cai et al. 1998. Overall, organic alkalinity (black dots) decreases with increasing salinity. Prior to the decrease, there is an increase of organic alkalinity within the initial few ppt increase of salinity.

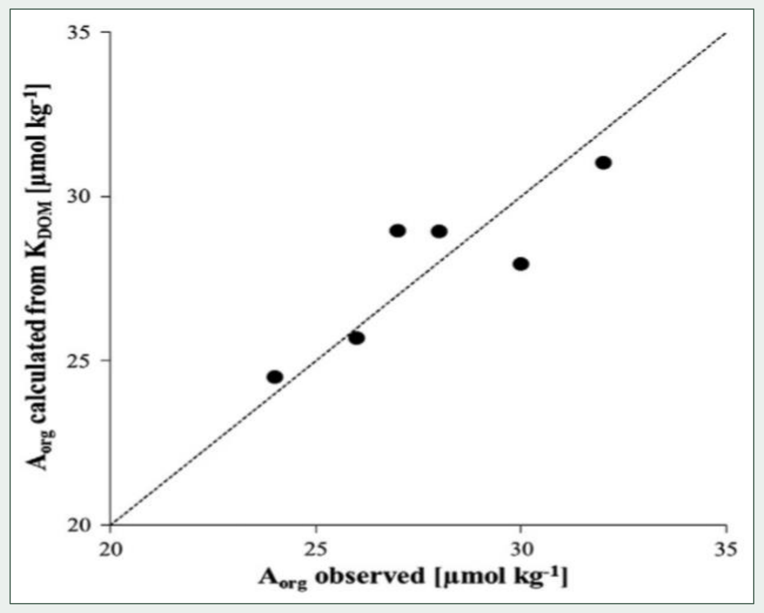

Figure 5: Data from the Baltic Sea pulled from Kulinski et al. 2014. Observed organic alkalinity values closely matched that of organic alkalinity values calculated using pK_as. With increasing salinity, changes in pK_as could be reflected in organic alkalinity values.

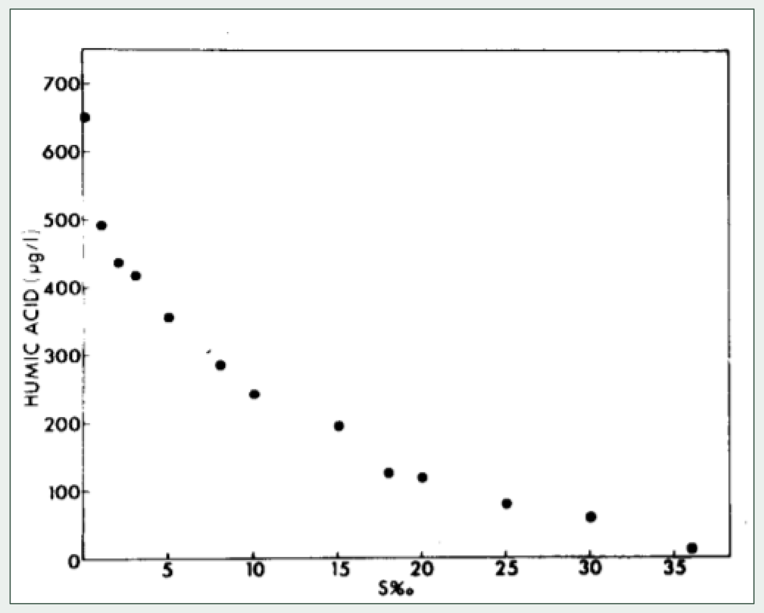

Figure 6: Data from the Amazon estuary pulled from Sholkovitz et al. 1978. When water from the Amazon River was mixed with Atlantic seawater, the flocculation of humic acids greatly increased with increasing salinity. Removing species of organic alkalinity available to the system.

Acknowledgments

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