Chesapeake Community Research Symposium 2024
Session 19: Carbon cycling in Chesapeake Bay

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The Chesapeake Carbon and Alkalinity Study (CHALK)

A key feature of the global carbon cycle is the transport of carbon and alkalinity (acid-neutralizing capacity) from land to the open ocean. Before reaching the open ocean, the carbon and alkalinity carried by rivers must past through estuaries, where significant transformations take place. While many such transformations are mediated by microbiota (phytoplankton and bacteria), these transformations are also influenced by macrobiota, such as oysters, clams, salt marshes, mangroves, and seagrasses. However, macrobiota are generally ignored in conceptual and computational models of carbon transformations in estuaries. In this presentation, we provide an overview of a new three-year project funded by the National Science Foundation, the Chesapeake Carbon and Alkalinity Study (CHALK), whose objective is to improve understanding of the role that macrobiota play in estuarine carbon and alkalinity dynamics. CHALK is a coordinated program of field measurements, laboratory experiments, historical data analysis, and numerical modeling. Research is focused on two contrasting tidal tributaries of the Chesapeake Bay, the Potomac River Estuary and the York River Estuary. Our interdisciplinary research team is evaluating hypotheses about the role of tidal wetlands, benthic fauna, and submerged vegetation in estuarine carbon and alkalinity dynamics. The research plan includes seven main elements: (1) carbonate system measurements, (2) benthic fauna distribution measurements, (3) measurements of macrobiota carbon and alkalinity fluxes, (4) extrapolation of those fluxes across space and time, (5) historical analysis of carbonate system measurements, (6) 3-D numerical modeling, and (7) a meta-analysis that extends findings to other systems. Mentoring and inclusion occur through the development of a research affinity group connecting existing regional undergraduate research programs. This research will advance the understanding of how macrobiota influence estuarine carbon and alkalinity dynamics and, ultimately, the large-scale marine cycles of carbon and alkalinity.

Riley Westman, Raymond Najjar, Edward Stets, Bryn Stewart, Devon Kerins, Li Li

Geology and Hydrology Drive Substantial Variations in the Carbonate Chemistry of Rivers Feeding the Chesapeake Bay

Carbonate chemistry of rivers is important because it buffers against rapid pH changes and can prevent acidification of receiving water bodies like the coastal ocean. Dissolved inorganic

carbon (DIC) and the relative abundance of its components (CO_3^{2-}, HCO_3^-, and CO_2) directly impact carbon dioxide emissions from rivers and aragonite (calcium carbonate) saturation (ΩA), which is critical to the growth and survival of shell-constructing organisms. We investigated spatial and temporal variability of the carbonate chemistry of seven large rivers draining into the Chesapeake Bay, focusing on the time period 1980–1995, where data availability was highest. Calcium, alkalinity, pH, water temperature, and discharge data originated from the United States Geological Survey National Water Information System. ΩA and components of DIC were calculated using the PHREEQC and Seacarb packages in R. Values of each parameter vary spatially between the rivers, with alkalinity, calcium, DIC, and ΩA being highest in the Potomac River, with ΩA sometimes >1, indicating the oversaturation of aragonite, and lowest in the Mattaponi River, with ΩA always <<1, from 1980–1995. These findings match pH differences between the rivers in this period (Potomac = 8.01, Mattaponi = 6.58). Mean calcium, alkalinity, and DIC are highly correlated with the fraction of surficial carbonate in the watersheds. Monthly average ΩA peaks in late summer and reaches a minimum in late winter/early spring, representing a potentially major control on bivalve growth. This pattern is inversely related to discharge and directly related to water temperature. pCO_2 is well above saturation, with mean values for some rivers approaching an order of magnitude greater than atmospheric pCO_2. These findings can be used to better understand dominant drivers of carbon cycling and ecology of rivers in the Chesapeake Bay watershed.

Novia Mann, Hunter Walker, Quinn Roberts, Emily Rivest, Raymond Najjar, Zhaohui Aleck Wang, Amber Hardison

Seasonal and Spatial Variability of Dissolved Inorganic Carbon in the York and Potomac River Estuaries

Estuaries are among the most productive ecosystems and are critical zones for carbon cycling. However, the fate of carbon in these systems is complex and typically system-specific. Estuaries often receive large allochthonous organic matter loads, supporting strong rates of remineralization, driving the system to net heterotrophy, or net dissolved inorganic carbon (DIC) production. Estuaries can also have high nutrient concentrations, supporting primary production, driving the system to net autotrophy (i.e., net DIC uptake). This study aims to (1) identify the seasonal and spatial patterns of DIC concentrations in two tidal tributaries of the Chesapeake Bay (the Potomac River Estuary and the York River Estuary), and (2) determine potential drivers of these patterns. We sampled 12 stations in the York River and 12 stations in the Potomac River seasonally for one year (spring 2023 to winter 2024). The stations spanned the salinity gradient from the river mouths to the tidal fresh zones. Surface water was collected at each station, and bottom water was collected if the water column was stratified. Additional CO_2 system parameters such as total alkalinity, pH, and pCO_2 were measured at each station. Profiles of temperature, salinity, dissolved oxygen, chlorophyll-a, and turbidity were also measured to contextualize the CO_2 system data. Preliminary analysis suggests that DIC concentrations differ greatly between the two estuaries, with the Potomac generally having higher DIC concentrations than the York. Further analysis will examine spatial and seasonal patterns, and potential environmental controls. Information garnered in this study could provide

insight into how the carbonate chemistry of these tidal tributaries changes with space and time. Additionally, as the York and Potomac are two tidal tributaries of the Chesapeake Bay, these results could be useful in helping to characterize the impact of riverine DIC on the carbonate system in the Chesapeake Bay.

Zhaohui Aleck Wang, Sophie Kuhl, Kate Morkeski, Emily Rivest, Amber Hardison, and Raymond Najjar

Impacts of organic alkalinity on carbonate chemistry and carbon fluxes in the two tidal tributaries of the Chesapeake Bay

The linkage between dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) stocks in natural waters exerts a significant control on carbon cycling. As part of this linkage, organic acid species within the DOC pool that contribute to total alkalinity (TA), known as organic alkalinity (OrgAlk) can significantly influence the carbonate system and CO2 fluxes in organic-rich aquatic environments. As such, biogeochemical processes that influence organic acid species may also impact the carbonate system via this linkage. Where present, OrgAlk can influence pH, carbonate speciation, buffering capacity, and air-water CO2 fluxes of natural waters. Previous studies have found that OrgAlk can exist as a significant proportion of TA in riverine, estuarine, and coastal waters, which contradicts the traditional assumption that OrgAlk is insignificant when studying the carbonate system. Here we investigate the connections between carbonate chemistry and the distribution and composition of OrgAlk throughout two tidal tributaries of the Chesapeake Bay—the York River Estuary (YRE) and Potomac River Estuary (PRE)—which differ in their carbonate system characteristics as low alkalinity and high alkalinity environments, respectively. Water samples were collected throughout the YRE and PRE ranging from polyhaline to tidal and non-tidal fresh conditions and analyzed for pH, TA, DIC, and OrgAlk. From these data, we demonstrate the behavior of OrgAlk within these differing environments and its effects on the carbonate system through changes to pH, carbonate speciation, buffering capacity, and CO2 fluxes. We will also examine the internal consistency of carbonate system calculations in the presence of OrgAlk, and the viability of predicting OrgAlk using DOC and commonly measured carbonate system variables.

Alexa K Labossiere, Marjorie A.M. Friedrichs, Pierre St-Laurent, Raymond Najjar

Impact of Tropical Storms on the Carbonate Chemistry of Two Contrasting Tidal Tributaries in the Chesapeake Bay

Carbon cycling in coastal environments is strongly influenced by short-term variability from extreme events like tropical storms. These storms bring high winds and heavy rainfall, which can lead to enhanced mixing, storm surge, and increased river discharge, but little is known about their impact on estuarine carbon cycling, and specifically on total alkalinity (TA), the acid-neutralizing capacity of a water body. We address this knowledge gap by focusing on two tributaries of the Chesapeake Bay with different background carbonate chemistry conditions. The Potomac River Estuary is characterized by high-TA river inputs (~2000

micromol/kg), contrasting with the York River Estuary, a tributary draining a much smaller watershed with low-TA river inputs (~400 micromol/kg). A coupled 3-D hydrodynamic–biogeochemical model was run from 1985 to 2020 and captured the impact of 37 hurricanes and tropical storms. Typically, in the initial stage of a storm, storm surge and mixing dominate and cause increases in TA, whereas in the second stage, river discharge increases, decreasing TA. Although storms cause both tributaries to exhibit lower TA upstream due to high freshwater discharge, the tributaries differ in their downstream response. Throughout the York, TA generally decreases after a storm, but the gradient of TA, increasing downstream, is maintained. In contrast, throughout the Potomac, the patterns become more spatially complex with areas of higher and lower TA. During high-discharge events, the high TA at the head of the Potomac can decrease by more than 50% and the high-TA waters are moved further downstream. The resulting dramatic shifts in TA over just a few days can detrimentally impact the local ecosystem, specifically in naturally highly alkaline rivers. Improving knowledge of how estuarine carbonate chemistry responds to extreme events is critical for local stakeholders, including shellfish aquaculturists, restoration managers, and those interested in pursuing marine carbon dioxide removal techniques.

Maria Herrmann, Raymond Najjar, Caroline Spengler, Jacqueline Kiszka

Upper Potomac River Estuary contributes disproportionately to the carbon dioxide outgassing of Chesapeake Bay

The role of estuaries in global and regional carbon cycling is made uncertain by the inherently large spatial and temporal variability of estuarine biogeochemical processes. The uncertainty in estuarine outgassing of carbon dioxide can be reduced by exploiting the large number of historical measurements of pH and alkalinity, which can be used to compute the surface partial pressure of carbon dioxide and the air–water carbon dioxide flux. Here we focus on the upper portion of the Potomac River Estuary (PRE), which is a tidal tributary of the Chesapeake Bay, a large, coastal-plain estuary in the eastern United States. pH, alkalinity, and numerous other water quality parameters have been measured approximately monthly for more than three decades at 14 monitoring stations along the main axis of the upper PRE. The computed pCO2 is very high, with long-term means at all stations exceeding 1000 atm and at three tidal fresh stations exceeding 2000 atm. pCO2 is also highly seasonal, typically peaking in the summer, and exhibits long-term decreasing trends of varying magnitude at all stations. The annual cycles and long-term trends are anti-correlated with the departure of oxygen from saturation, suggesting a biological driver for both temporal patterns. CO2 outgassing follows the same spatial and temporal patterns as pCO2. The long-term mean net integrated outgassing of the upper PRE is 75 Gg yr–1, only slightly less than the mainstem of the Chesapeake Bay, which has an area 15 times that of the upper PRE. This work supports the utility of pH and alkalinity measurements for improving estimates of estuarine CO2 outgassing and emphasizes the importance of tidal tributaries as contributors to this outgassing.

A. Whitman Miller

High frequency, continuous measurements reveal strong diel and seasonal cycling of pCO2 and CO2 flux in a mesohaline reach of the Chesapeake Bay

We estimated hourly air-water gas transfer velocities (k600) for carbon dioxide in the Rhode River, a mesohaline subestuary of the Chesapeake Bay. Gas transfer velocities were calculated from estuary-specific parameterizations developed explicitly for shallow, microtidal estuaries in the Mid-Atlantic region of the United States, using standardized wind speed measurements. Combining the gas transfer velocity with continuous measurements of pCO2 in the water and in the overlying atmosphere, we determined the direction and magnitude of CO2 flux at hourly intervals across a 3-year record (01 July 2018 to 01 July 2021). Continuous year-round measurements enabled us to document strong seasonal cycling whereby the Rhode River is net autotrophic during cold-water months (Dec–May), and largely net heterotrophic in warm-water months (Jun–Nov). Although there is inter-annual variability in CO2 flux in the Rhode River, the annual mean condition is near carbon neutral. Measurement at high temporal resolution across multiple years revealed that CO2 flux can reverse during a single 24-hour period. pCO2 and CO2 flux are mediated by temperature effects on biological activity and are inverse to temperature-dependent physical solubility of CO2 in water. Biological/biogeochemical carbon fixation and mineralization are rapid and extensive, so sufficient sampling frequency is crucial to capture unbiased extremes and central tendencies of these estuarine ecosystems.

Anna Hildebrand, John Pohlman, Lee-Gray Boze, Michael Casso, Josh Dean, Laura Lapham

Quantifying dissolved methane concentrations in surficial sediments and water column of the Chesapeake Bay

Estuaries are highly dynamic systems that are typically net heterotrophic emitters of carbon dioxide (CO2) and methane, both powerful greenhouse gases. Estimates of fluxes of both of these gases from estuaries remain poorly constrained due to high spatial and temporal variability. Some variability in emissions is inherent (for example- a salinity gradient), while other factors that control variability have the potential to worsen with climate change (such as hypoxic events and seasonal storms). As one of the largest estuaries in the world, Chesapeake Bay can be used to better constrain these estuarine estimates, especially given that it is underlain with at least 30% methane gas as bubbles. From a July 2022 cruise spanning the salinity gradient of Chesapeake Bay, we demonstrate here a characterization of methane concentrations from the sediments to the air. We utilized “discrete” measurements from 12 stations (gravity cores, CTD rosette) as well as “continuous” survey methods (chirp sonar, CO2/methane surface mapping) in order to develop a “bottom-up” approach from the sediments, to the water column, and ultimately to the atmosphere. In this talk, we will (1) characterize distributions of methane and CO2 within Chesapeake Bay, (2) estimate methane and CO2 flux to the atmosphere using a continuous underway system, and (3) hypothesize which processes are responsible for these distributions, including estimates of methane oxidation that limit atmospheric release. Stable

isotopes for carbon will also be discussed that were used to characterize sources. Results from this project can be used as a building block to develop a greenhouse budget and inform targeted greenhouse gas reductions in estuaries.

Cassie Gurbisz, Theresa Murphy, Meghan Stevens, Lilianna Bowman, Matthew S. Fantle, Amber Hardison, Maria Herrmann, Lora Harris, Alexis Putney, Emily Rivest, Quinn Roberts, Hunter Walker, Zhaohui Aleck Wang, Ryan Woodland, Raymond Najjar

Submersed aquatic vegetation modifies estuarine inorganic carbon and alkalinity dynamics

Submersed Aquatic Vegetation (SAV) beds are often thought of as carbon sinks because they convert CO2 to organic carbon, which is then, in part, buried in the underlying sediments. SAV can also modify the inorganic carbon system in ways that may affect air-sea CO2 flux but are not typically included in carbon models or sequestration estimates. For instance, SAV beds have high metabolic rates, and they can alter sediment redox chemistry and calcium carbonate saturation states. These processes, in turn, can affect dissolved inorganic carbon (DIC) and total alkalinity (TA) such that CO2 is either increasingly absorbed from or released to the atmosphere, potentially increasing or offsetting carbon sequestration rates derived from organic carbon fixation. The overarching goal of this study is to clarify the role of SAV in estuarine inorganic carbon cycling. We used benthic chambers to measure in-situ DIC and TA fluxes in SAV beds in the York and Potomac estuaries, which encompass the range of alkalinities and salinities typically found in temperate estuaries. Preliminary results suggest that SAV beds, indeed, affect water column DIC and TA, but the magnitude and direction of these effects vary across sites and seasons. We plan to continue seasonal sampling through 2024 to further quantify these processes and assess their underlying mechanisms. This work is part of the Chesapeake Carbon and Alkalinity Study (CHALK), a coordinated multi-institution research program assessing the role that macrobiota play in estuarine carbon and alkalinity dynamics.

Victoria J. Hill, Richard C. Zimmerman

Assessing submerged aquatic vegetation blue carbon in The Chesapeake Bay from high resolution satellite imagery

Blue Carbon emphasizes the role of aquatic plants in the carbon cycle. However, the global importance of submerged aquatic vegetation (SAV) is highly uncertain, as <10% of this resource has been mapped. Satellite technology now provides daily coverage of the global coastal environment at 3 m resolution, enabling the mapping of Blue Carbon system dynamics at spatial and temporal scales not previously attainable. We employed satellite imagery from the Planet/Dove constellation to quantify the monthly dynamics of SAV Blue Carbon potential at five locations in the Chesapeake Bay ranging from the upper Bay dominated by freshwater SAV to the oceanic coastal lagoons exclusively vegetated by eelgrass (Zostera marina L.). Weemployed machine learning to classify the images and a physics-based model of reflectance to quantify Blue Carbon abundance. Since 2018, the SAV meadows occupying the oceanic coastal lagoons were temporally stable, supporting a mean above-ground biomass of 40 g C

m-2.Meadows in the polyhaline lower Bay supported less biomass (~34 g C m-2) with a seasonal amplitude characterized by winter declines and summer re-growth. SAV meadows coveredextensive mudflats in the freshwater uppermost portion of the Bay at extremely high density (>40 g C m-2) in summer but disappear almost completely during winter. Our efforts to quantify the seasonal dynamics of SAV from satellite imagery will improve the assessment of Blue Carbon in the Chesapeake Bay and provide an automated workflow environment that can be scaled to routine assessment of SAV dynamics across the globe.

Jill M. Arriola, Raymond G. Najjar, Maria Herrmann, Seyi Ajayi, Amber Hardison, Quinn Roberts, Hunter Walker, Emily Rivest, Alexis Putney, Zhaohui Aleck Wang

Seasonality of carbon and alkalinity export from a well-constrained brackish tidal marsh along the York River, Virginia

Alkalinity influences key estuarine carbon cycle processes, such as calcium carbonate precipitation and dissolution. Although it is known that alkalinity is generated in tidal wetland soils via sulfate reduction, measurements of alkalinity export to neighboring rivers and estuaries are rare. The goal of this research is to quantify lateral fluxes of carbon and alkalinity from a well-constrained brackish marsh system on the York River, Virginia, over a two-year period in order to improve the representation of tidal wetlands in estuarine biogeochemical models. Seasonal water samples were collected in Taskinas Creek, which drains the marsh, hourly over a 24-hour period and analyzed for dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC), total alkalinity (TA), and calcium ion concentrations [Ca2+]. To extrapolate these measurements to non-sampling periods, we will develop a statistical model relating them to continuous measurements of temperature, salinity, dissolved oxygen, pH, and dissolved organic matter fluorescence (fDOM). Lateral fluxes will be computed by combining the modeled analyte concentrations with flow directly measured in the creek via an ADCP, as well as a hydrodynamic model that accounts for flow over the marsh platform. Preliminary results show that during summer 2023 DIC and TA concentrations peaked at low tide, whereas fDOM peaked at high tide. Concentrations of DIC, TA, and fDOM ranged between 1650–2100 µmol/kg, 1500–2200 µmol/kg, and 25–125 QSU, respectively. Future directions of this research are to estimate the fluxes of carbon and alkalinity per marsh unit area along Taskinas Creek using SCHISM, a tidal marsh model, and then scale up these fluxes to wetlands along the tidal tributaries of Chesapeake Bay.

Fei Da, Marjorie A.M. Friedrichs, Pierre St-Laurent, Raymond G. Najjar, and Elizabeth H. Shadwick

Controls on the carbonate system of a coastal plain estuary: rivers, tidal wetlands, and tidal cycles

Estuarine dissolved inorganic carbon (DIC) and total alkalinity (TA) dynamics are sensitive to multiple ocean and watershed drivers, including tidal cycles and inputs from wetlands and rivers. However, development and application of numerical models that simultaneously address

these drivers are limited. In this study, controls on the carbonate system of a coastal plain estuary are investigated using a 3-D coupled hydrodynamic-biogeochemical model forced with empirical inputs from tidal wetlands. The model was applied to the York River estuary, a small tributary of the Chesapeake Bay, and experiments were conducted both with and without tidal wetlands to explore their impacts. Results show that on average, wetlands account for 20-30 % of TA and DIC inputs to the estuary, and double estuarine CO2 outgassing. Strong quasi-monthly variability in estuarine DIC and TA is driven by the tides, which cause fluctuations between net heterotrophy and net autotrophy. Model results also show that in wetter years, decreased primary production relative to biological respiration (i.e., greater net heterotrophy) is largely responsible for substantial increases in net DIC production and CO2 outgassing. Additionally, in wetter years advective exports of DIC and TA to the Chesapeake Bay increase by a factor of three to four, pushing spatial maxima of biological sources and sinks downstream by ~20 km, and resulting in lower concentrations of DIC and TA. Quantifying the impacts of these complex drivers is not only essential for better understanding coastal carbon and alkalinity cycling, but also helps assess the health and functioning of coastal ecosystems and provide insights into ecosystem responses to climate change.

Seyi Ajayi, Raymond Najjar, Emily Rivest, Ryan Woodland

Relationship between benthic biomass and environmental conditions in Chesapeake Bay

The Chesapeake Bay is vital in transforming carbon and alkalinity transferred between land and ocean. Estuarine numerical models have tended to include microbiota but not macrobiota to understand biogeochemical transformations. However, macrobiota, such as benthic fauna, could also significantly affect carbon and alkalinity transformation within estuaries. For example, it was recently posited that the bivalve Corbicula fluminea contributes to a large alkalinity sink within the Potomac River Estuary. Our study examines historic benthic fauna data collected each summer from 1995 to 2022 by the Chesapeake Bay Program's long-term Benthic Monitoring Program. Data include ash-free dry weights of different benthic species, species abundances, and various water property measurements (such as dissolved oxygen, water temperature, and salinity). We spatially interpolated data from the Chesapeake Bay Water Quality Monitoring Program to add additional water property measurements (such as chlorophyll-a, total nitrogen, total phosphorous, and pH) to each benthic monitoring location. We used climate-associated and water chemistry variables and sediment characteristics as predictors of benthic biomass data using generalized additive models. Preliminary results show important relationships between salinity and biomass, with biomass highest at the lowest salinities. Bivalves dominate the biomass of benthic organisms overall and, of the most abundant bivalve species, C. fluminea strongly prefer the tidal fresh zone, whereas the bivalve Rangia cuneata dominate the oligohaline. Dissolved oxygen is also positively correlated with biomass; benthic biomass disappears in hypoxic zones. Overall, a suite of water property measurements explains over 30% of the variance in biomass. Our findings highlight the different environmental factors that influence the abundance of estuarine benthic fauna, knowledge that can be leveraged to understand the impact of benthic fauna on estuarine carbon and alkalinity transformations in future work.