Final Report

Karin A. Block-Cora, Ph.D. The City College of New York and CUNY Graduate Center

Project Title: Sclerochronology of bivalves in the Hudson River estuary

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Abstract

Over the last three decades the frequency of sudden rainstorms that produce flash flooding and combined sewer overflows into the Hudson River estuary has increased as a result of climate change. These events affect the estuary by increasing turbidity, introducing contaminants, and potentially affecting water conditions such as temperature, salinity, and dissolved oxygen. Oysters build their shells during the growing season, with years represented as bands of calcium carbonate that grow outward from bivalve hinge to shell edge and containing trace amounts of metals that reflect the immediate environment. They therefore serve as high resolution record-keepers of the estuarine environment. Oysters filter vast amounts of water and provide habitat for other species in the estuarine ecosystem and are important indicators of the general health of the estuary. We collected live oysters at three locations in Hudson River Park, the Pier 26 Tide Deck, Gansevoort Peninsula beach, and at the Pile Fields near Pier 40 in early and late summer of 2025 with the intent to hone protocols to assess how variations in environmental conditions during the growing season are captured in the hard tissue major, trace, and isotope chemistry, mineralogy, and morphology. Our initial results show measurable variations in element ratios indicative of changes in salinity and water chemistry across the different collection sites. We also observed differences in calcite structure that show a larger volume and preferential elongation of the crystal lattice along the c-axis of the unit cell in samples from shallower collection locations, suggesting an effect of location and greater salinity gradients on the Gansevoort Peninsula and Pier 26 Tide Deck oysters.

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1. Introduction

Acute rainfall events (> 44.5 mm/hr) have increased in frequency in the New York City metropolitan region over the last three decades (Mossel et al., 2024). These events produce large influxes of fresh water from excessive runoff and combined sewer overflows that cause sudden change in water conditions in the Hudson River, potentially disrupting the habitat of estuarine species. Marine bivalves such as oysters grow in seasonal cycles, thus capturing environmental changes in their carbonate exoskeletons (Mouchi et al., 2025; Vereycken and Aldridge, 2023). These organisms can adapt to a variety of temperature, salinity, and pH conditions as evident from their > 260 Ma evolutionary history. Oysters can live > 20 years, and therefore, they keep a continuous record of acute estuary stressors in their shell composition, structure, and morphology.

Mg/Ca, Mn/Ca, and Ba/Ca measurements of bivalve shell growth bands, combined with oxygen isotope ratios, provide seasonal scale reconstructions (Mouchi et al., 2025). These proxies potentially can be combined to assess resiliency of bivalves in the face of increasingly frequent acute rainfall events. Other proxies such as those obtained from bivalve shell microstructure analysis, have successfully correlated measurements to hypoxia events and temperature variations (Höche et al., 2023; Milano et al., 2017). This study seeks to establish field and laboratory protocols to monitor the impact of environmental and climate change on the Hudson River estuary through sclerochronological studies of oysters. These invertebrates are important to estuarine ecology and readily capture changes in water chemistry through rapid seasonal growth of their hard tissues. We conducted field and laboratory experiments to determine the feasibility of these methods in tracking flash flooding and pollution events using X-ray fluorescence, X-ray diffraction, electron microscopy and isotopic analysis. Our goal is to establish workflows and procedures to develop a sample library at the City College of New York that establishes a record of the effects of climate-induced changes in weather patterns on the estuary and provides students and collaborators with research opportunities that meet the Park's science goals.

The ultimate goal of this work is to answer the following overarching **research questions**:

1. How are oyster shell structure and composition affected by extreme precipitation/flash flooding events?
2. How do the growth habits of oysters vary across location and physiographic features?
3. How does the record environmental (pollution) and hyposalinity events compare across specific species and their habitats in the estuary (e.g., Pier 26 Tide Deck vs. Pier 54 pile fields)?

This work complements ESMP Research and Habitat Enhancement Action 1.4 to characterize the physical environment, including sediment types and seasonal variations; and Action 1.6, which reviews data on indicators associated with CSO and storm water discharge. Additionally, this work connects to Action 1.8, which seeks to study common climate change indicators such as frequency of flooding events.

4. Methods

a. Field sampling

Live *C. virginica* specimens were collected in July and September of 2025 with the assistance of the Trust science team. Five specimens were collected in July in the piling fields by the diving team and another five collected at the Pier 26 Tide Deck. The September collection comprised of six specimens from the Pier 26 Tide Deck and twelve from the beach at the Gansevoort Peninsula. A complete list of specimens, their collection date, and relevant metadata is included in Table A1 of the Appendix.

b. Sample preparation

After field sampling, oysters were submerged in 200 proof ethanol and transported to the City College of New York. Soft tissue was discarded in the lab, and the top valve of the oyster shell was selected for processing. Each top valve was cut in half using a Buehler Isomet saw for further processing. All samples were placed in labeled bags and photographed prior to analysis. One half of each top valve was powdered by hand in an agate mortar samples for bulk XRD and XRF analysis. A subset of half valve was shipped for thin section preparation and another subset set aside for micromilling in preparation for isotope analysis.

c. X-ray diffraction

XRD patterns were acquired with a Malvern PANalytical X'Pert Pro equipped with a chromium cathode tube producing Cu Kα radiation at 1.5418 Å; a Ni foil filter to attenuate Cu Kβ emission; and a PixCel 1-D detector array. A divergence slit of 1° and an anti-scatter slit of 5.7 mm were used to minimize background scatter. Scans were run in the range of 20° to 70° 2θ at a step size of 0.02°. Patterns were then processed with GSAS-II open source software from the U.S. Department of Energy Argonne National Laboratory (Toby and Von Dreele, 2013) for Rietveld refinement to obtain lattice parameters (calcite unit cell measurements).

d. X-ray fluorescence

X-ray fluorescence (XRF) analysis was conducted to determine bulk elemental composition of shell samples using a Bruker Tracer V pXRF equipped with a rhodium X-ray tube at a 50 kV potential and 20 µA current integrated over 10 s. Spectra were collected in Artax software and processed for element identification and deconvolution. A suite of USGS certified reference powdered rock standards was analyzed using the same instrument parameters to calibrate detector counts and obtain element concentrations. Precision of concentrations is estimated at > 90%.

e. Kiel Carbonate analysis

Two specimens from each of the sampling locations were sectioned hinge to edge with a Buehler Isomet saw in preparation for cross-lamellar thermometry and salinity microanalysis seasonal growth bands representing the last five years of each oyster's life. Oyster sections were mounted on epoxy molds to stabilize each shell half. Each band was drilled with a micromill at the CUNY Advanced Science Research Center. ^{13}C and ^{18}O will be collected by Kiel carbonate analysis normalized to the Pee Dee Belemnite standard.

f. Imaging (electron microscopy)

The remaining shell sections were sent to Spectrum Petrographics in Vancouver, WA for preparation of polished thin sections mounts for electron microscopy and future X-ray fluorescence and X-ray diffraction microanalysis. Sections were cut to 70 µm thickness and mounted on oriented quartz slides to produce detailed imaging at a resolution of up to 5µm.

5. Results

a. *Mineral structure*

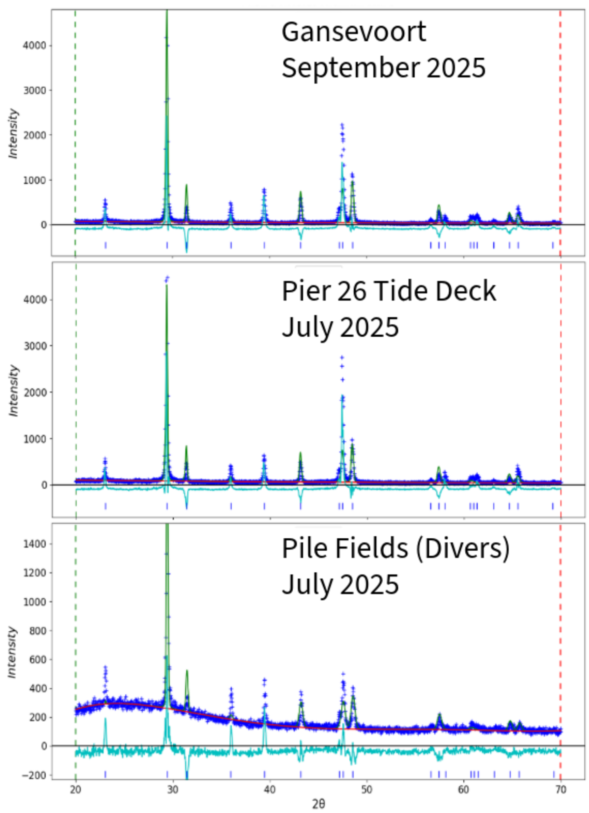

Figure 1 Representative X-ray diffraction patterns of samples from the three sites with idealized calcite peaks. Peaks represent Miller Indices for calcite structure. Differences in peak intensity and position are indicative of overall differences in the growing conditions at the three locations.

X-ray diffraction results are consistent across all samples with low-Mg calcite, a hexagonal mineral in the R32c space group. The results of XRD unit cell refinements are shown in Table A1 in the Appendix.

Some of the diffraction peaks show a marked change in intensity without a change in position. For example, at 2θ = 47.58°, which corresponds to the 018 family of planes, and 2θ = 48.58° , which corresponds to to the 116 are indicative of preferential growth direction in the crystal for each sample.

b. *Bulk shell composition*

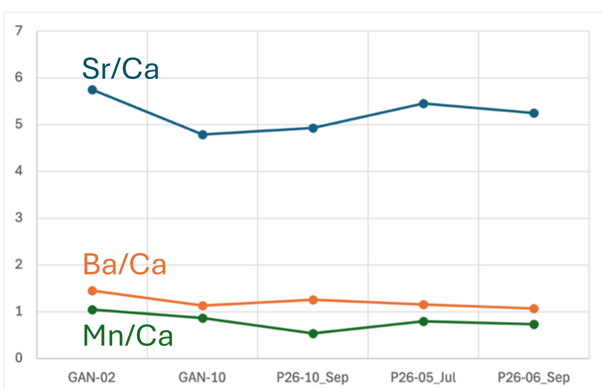

Figure 2 Sr/Ca, Ba/Ca, Mn/Ca ratios (mmol/mol) in Gansevoort (GAN) and Tide Deck (P26) samples

Elemental ratios (Sr/Ca, Ba/Ca, Mg/Ca, and Mn/Ca) were calculated using the calibrated concentration values (Table A3 in the Appendix) to assess spatial and temporal variability in shell geochemistry and are shown in Figure 2. Sr/Ca ratios (mmol/mol) show some variability across all samples, with values ranging from 4.78 to 5.75. Samples from both Gansevoort and Pier 26 display similar Sr/Ca values, suggesting broadly comparable conditions during shell growth across sites. Ba/Ca ratios range from 1.06 to 1.44 (mmol/mol) and exhibit similar pattern variability to Sr/Ca except for the Pier 26 July sample. Mn/Ca ratios range from 0.53 to 1.05 (mmol/mol) and follow a pattern opposite to Ba/Ca and Sr/Ca ratios, suggesting an inverse relationship.

Mg/Ca ratios are generally low and highly variable among samples, including very low values in some Pier 26 samples. Mn/Ca ratios display moderate variability across all samples, with values ranging from 1.1 to 1.6. Overall, samples from Pier 26 exhibit a wider range of Ba/Ca, Mg/Ca, and Mn/Ca ratios compared to samples from Gansevoort.

6. Discussion

The goal of this study was to develop protocols and determine the viability of oyster shells as recorders of environmental change as captured in the variation in chemical composition and mineral structure. Since oysters are sensitive to water conditions, the impact of flash flooding events is presumably recorded in the hard tissues as they develop during the growing season. The three oyster collection sites are characterized by distinctly different growing conditions which manifest as differences in bulk structure and chemistry.

The DC (July), GAN (September) and P26 (July and September) samples exhibited a well-defined calcite structure. However, the XRD patterns reveal that the oysters collected by the divers possess a structure nearly identical to an idealized calcite, whereas the oysters from Gansevoort Peninsula and the Pier 26 Tide Deck exhibit an elongation along the c-axis of the unit cell, and resulting in a larger cell volume. This variation was consistent in both bulk and individual growth band measurements, indicating a c-axis sensitivity in these samples and perhaps increased heterogeneity as a result of exposure to greater salinity gradients and environmental stress. Differences in preferred crystal growth direction among Pier 26 Tide Deck and Gansevoort Peninsula samples supports greater intra-shell heterogeneity associated with the specific habitat of each oyster within the Park.

Differences in Ba, Mg, Ca, and Mn in Pier 26 and Gansevoort samples suggest that samples at each location might experience different temperature and salinity conditions despite the relatively small distance between locations. Mg/Ca and Mn/Ca are often used as proxies for temperature in oysters (Mouchi et al., 2025). While Ba/Ca has not been applied to oysters as a salinity proxy, *M. edulis* shells have shown an inverse correlation between Ba/Ca and salinity (Gillikin et al., 2006; Marali et al., 2017; Steinhardt et al., 2016). We posit that the Ba/Ca variations we expect to see in *C. virginica* samples from the Park are related to salinity stress.

Oxygen-18 isotope analysis has been shown to provide accurate counts of growth bands of *C. virginica* (Zimmt et al., 2019) as well as paleotemperature (Milano et al., 2017). We hypothesize that when combined with Mg/Ca and Mn/Ca measurements (Mouchi et al., 2025) our measurements will elucidate whether these variations are related to salinity disturbances associated with flash flood impacts at the two locations.

Our future work seeks to examine shell microstructure through µXRF and µXRD imaging of oyster cross-lamellar thin sections to reveal ultra-high-resolution changes possibly related small growth increments. Additionally, Höche et al.(2023) have found that imaging analysis of disturbance lines may serve as an indicator of hypoxic events, such as those caused by excessive nutrients in the estuary after a storm.

7. Acknowledgments

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Appendix

Table A1. List of specimens and collection date. The table also notes analytical data collected or in progress with an "x". Number of subsamples from yearly growth bands are noted in parentheses for carbon-13 and oxygen-18 analyses.

Sample #	Collection date	XRF	XRD	Thin Section	13C; 18O
Diver Collected Samples					
DCo71625-01	7/16/25				
DCo71625-02	7/16/25				
DCo71625-03	7/16/25		x		x (5)
DCo71625-04	7/16/25				
DCo71625-05	7/16/25				
Pier 26 Tide Deck					
P2671725-01	7/17/25	x		x	
P2671725-02	7/17/25				
P2671725-03	7/17/25				
P2571725-04	7/17/25				
P2671725-05	7/17/25	x	x	x	
P2691625-06	9/16/25	x	x		
P26091625-01	9/16/25				x (2)
P26091625-04	9/16/25				x (3)
P26091625-02	9/16/25				x (2)
P26091625-03	9/16/25				x (3)
Gansevoort Peninsula Beach					
GAN91625-01	9/16/25				x (3)
GAN91625-02R	9/16/25	x	x		
GAN91625-03	9/16/25		x		
GAN91625-04	9/16/25				x
GAN91625-05	9/16/25				x
GAN91625-06R	9/16/25				
GAN91625-07	9/16/25				x (4)
GAN91625-08	9/16/25				x (2)
GAN91625-09R	9/16/25	x	x		
GAN91625-10	9/16/25	x			
GAN91625-11	9/16/25	x			
GAN91625-12	9/16/25				x

Table A2. Lattice parameters and unit cell volume derived from XRD pattern Rietveld refinement.

Index	Sample ID	Collection Date	Length_a (A)	d of _a(A)	*Length_b(A	Length_c (A)	d_c (A)	VOL (A^3)	d_VOL (A^3)
1	DC071625-03_Hinge	7/16/2025	4.981	3.10E-05	4.981	17.030	5.00E-05	365.929	2.40E-03
2	DC071625-03_3.Band	7/16/2025	4.981	3.10E-05	4.981	17.030	5.00E-05	365.929	2.40E-03
3	DC071625-03_5.Band	7/16/2025	4.981	3.10E-05	4.981	17.030	5.00E-05	365.929	2.40E-03
4	DC071625-03_Outer	7/16/2025	4.981	3.10E-05	4.981	17.030	5.00E-05	365.929	2.40E-03
5	HRP-05 (Pier 26)	9/16/2025	4.991	2.00E-04	4.991	17.080	5.00E-04	368.457	1.90E-02
6	HRP-06b (Pier 26)	9/16/2025	4.991	2.00E-04	4.991	17.080	5.00E-04	368.457	1.90E-02
7	Gan091625-02	9/16/2025	4.991	2.00E-04	4.991	17.080	5.00E-04	368.457	1.90E-02
8	Gan091625-03	9/16/2025	4.991	2.00E-04	4.991	17.080	5.00E-04	368.457	1.90E-02
9	Gan091625-09rB	9/16/2025	4.991	2.00E-04	4.991	17.080	5.00E-04	368.457	1.90E-02

Table A3. Select metal analyses of samples from the Gansevoort Peninsula beach (GAN) and the Pier 26 Tide Deck (P26).

Sample	Ca (wt%)	Sr (ppm)	Ba (ppm)	Fe (wt%)	Mn (ppm)	Sr/Ca	Ba/Ca	Mn/Ca
GAN-02	43.15	542.28	214.22	0.06	61.89	5.75	1.45	1.05
GAN-10	44.23	462.76	171.51	0.09	52.23	4.78	1.13	0.865
P26-10_Sep	44.88	483.39	192.70	0.07	33.09	4.93	1.25	0.54
P26-05_Jul	43.06	513.34	170.15	0.07	46.77	5.45	1.15	0.79
P26-06_Sep	43.48	498.98	159.21	0.07	43.73	5.25	1.07	0.73

Table A4. Updated schedule of analyses