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A Centennial Record of Paleosalinity Change in the Tidal Reaches of the Potomac and Rappahannock Rivers, Tributaries to Chesapeake Bay

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ABSTRACT

Gravity and push cores from the Potomac and Rappahannock Rivers (Virginia Tidewater) were collected from central and proximal estuarine zones with known seasonal salinity stratification. The lowermost microfossil associations in the cores comprise alternating ostracode populations of *Cyprideis salebrosa* and *Cytheromorpha*. This microfossil association gives way to an oligohaline association dominated by the freshwater ostracode *Darwinula stevensoni*. Stable oxygen isotope values ($\delta^{18}O$) of Rapphannock *Cyprideis salebrosa* are highly variable ranging between -6.6 to -3.2‰ VPDB. $\delta^{18}O$ values for Potomac *Cytheromorpha fuscata* range from -8.2 to -3.2‰ VPDB. Positive excursions in $\delta^{18}O$ values are synchronous with population peaks for both *Cyprideis* and *Cytheromorpha* indicative of increased marine influence and/or higher salinities. Microfossil paleoecology coupled with oxygen isotope values record a marked shift towards gradual freshening and deterioration of the salinity structure in the tidal tributaries during the mid-to late 19th century. We attribute these trends to both decadal climate trends and aggressive land use practices in the Chesapeake Bay watershed during the late 19th to middle 20th centuries.

INTRODUCTION

Estuaries are physically, chemically, and biologically complex environments at the convergence of continental and marine processes. In the Chesapeake Bay, the recent combination of anthropogenic watershed modification and sea-level rise are forcing mechanisms that have potentially influenced mixing of fresh and marine waters in the tidal reaches of the major tributaries (Colman and Bratton 2003; Boon 2012). To test this hypothesis, sediment cores were collected from the proximal and central reaches

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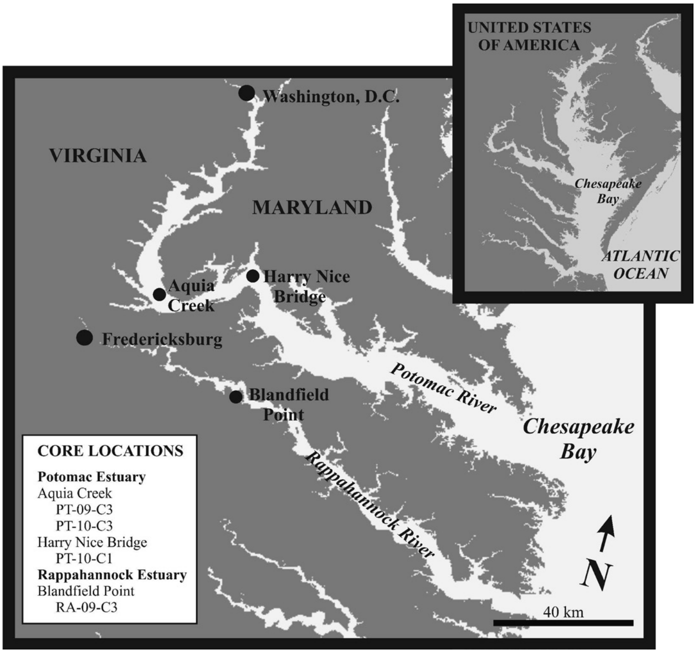

FIGURE 1. Sediment cores were collected from the Potomac and Rappahannock estuaries, both of which are tributaries to Chesapeake Bay, the largest estuary in the eastern United States (Colman and Mixon, 1988).

of the Potomac and Rappahannock estuaries for microfossil and stable isotopic analyses. Paleosalinity indicators were established on the basis of ostracode paleoecology (population abundances and pore morphometrics) and oxygen isotope values ($\delta^{18}O$). The paleosalinity trends were considered in the context of sedimentation history based on ^{137}Cs dating, organic matter concentrations, and magnetic susceptibility of collected cores. Cumulative results of these analyses indicate that salinity gradients in both estuaries have changed markedly since the beginning of the 19th century which is suggestive of anthropogenic influence on estuarine processes in the Chesapeake Bay.

BACKGROUND

Geographic Location

The Chesapeake Bay is the largest estuarine system in the United States that is located between Virginia and Maryland on the Atlantic Coastal Plain (Colman and Mixon 1988). This study focuses on the upper tidal reaches of the Potomac and Rappahannock Rivers where they transition from estuarine-to fluvial conditions (Fig. 1). Sediment cores were collected near the boundary between proximal (oligohaline) and central estuary (mesohaline) near Aquia Creek in the Potomac estuary and Blandfield Point in the Rappahannock estuary (Ellison and Nichols 1970, 1976; Ellison 1972; USEPA 1998). Since the 1980s, these estuaries have produced the highest annual

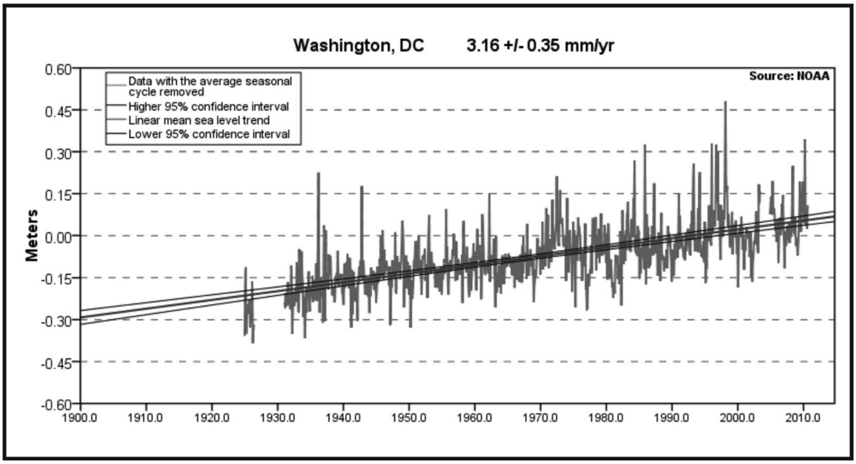

FIGURE 2. Historic sea level data for Washington, D.C. illustrates a constant rise in sea level over the last century for the Potomac estuary (NOAA 2008).

sediment yields for all major Chesapeake Bay tributaries (Langland and Cronin 2003). In general, the relatively high sedimentation rates in Chesapeake Bay are related to ongoing sea-level rise and anthropogenic watershed modification (Fig. 2) (Colman and Mixon 1988; Brush 1989; Colman and Bratton 2003; Boon and others 2010; Boon 2012).

Estuarine Circulation

The convergence of fluvial and marine waters creates a dynamic circulation pattern that impacts sedimentary processes in estuarine environments. Where freshwater outflow meets incoming saltwater in a partially mixed estuary like the Chesapeake Bay, the seasonal halocline (salinity gradient) forms a relatively impermeable surface to sediment transport that frequently coincides with the estuarine turbidity maximum (ETM)(Langland and Cronin 2003). In the Potomac estuary, the maximum extent of saltwater intrusion occurs near Aquia Creek (Elliott 1976). In the Rappahannock estuary, the maximum extent of saltwater intrusion occurs near Blandfield Point (Ellison and Nichols 1970). Our preliminary assessment of modern salinity structure revealed oligohaline conditions and/or weak haloclines near Aquia Creek and Blandfield Point during June 2009 (Fig. 3).

Microfossils

Ostracodes are aquatic crustaceans that are sensitive to changes in salinity and temperature (Frenzel and Boomer 2005) and their ecological associations have been used to make inferences about past environmental conditions in the Chesapeake Bay (Elliott and others 1966; Cronin and Grinbaum 1999; Cronin and others 2005, 2010). When used in conjunction with $\delta^{18}O$ values of their calcite carapaces, ostracodes can be used to develop paleosalinity proxies in the context of both climate induced evaporation and mixing of marine and freshwaters (Anderson and Arthur 1983; Anadón

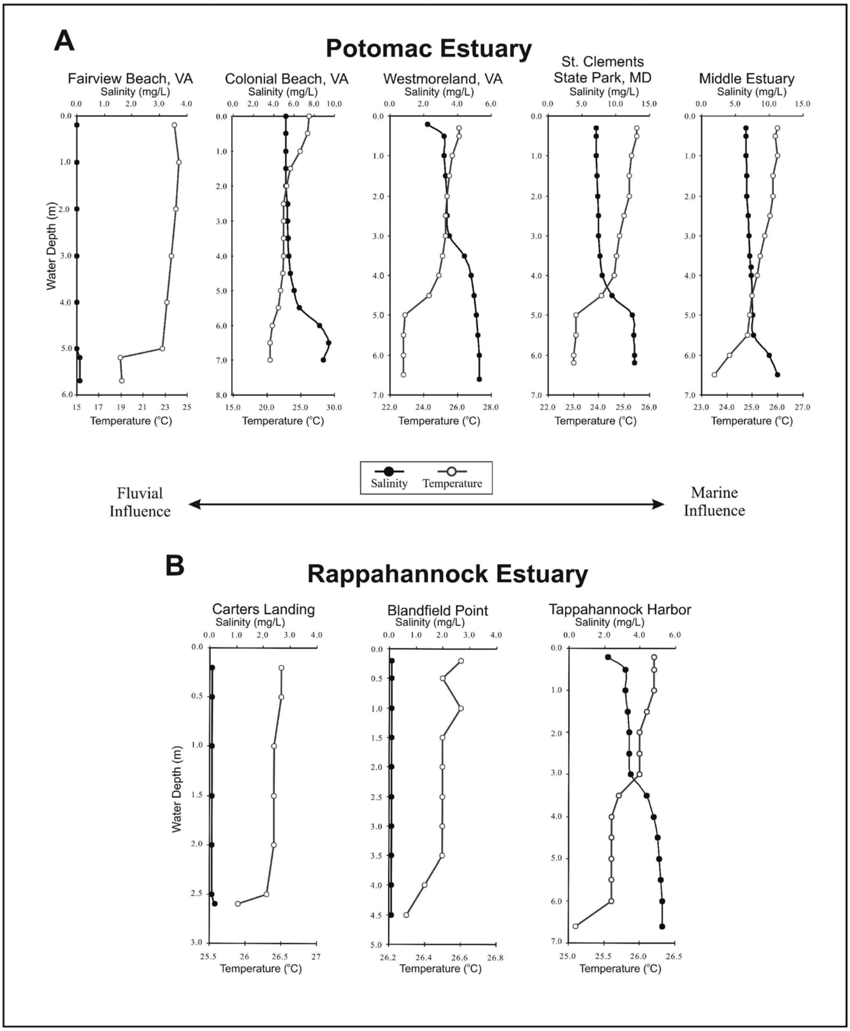

FIGURE 3. Late spring salinity (mg/L) and temperature (°C) profiles measured from the (A) Potomac and (B) Rappahannock estuaries. This analysis was part of an unpublished assessment of water quality during June 2009.

and others 2002; Holmes and Chivas 2002; Ito and others 2003). Studies by Medley and others (2008) demonstrated that the shape of the sieve pores on the external surface of the carapace (Type C of Puri 1974) varies significantly with salinity which further improves the potential for past salinity determinations using ostracoda.

METHODS

Sediment cores were collected from the Rappahannock and Potomac estuaries with Ogeechee and Gravity (Wildco Inc.) corers (Fig. 1). The longer Ogeechee cores (>100 cm) were analyzed with a Bartington MS2C Core Logging Sensor, and subsequently partitioned into 1 cm segments for loss on ignition and microfossil processing. The shorter gravity cores (40 cm) were divided into 2 cm segments and samples sent to Core Scientific International (Winnipeg, MB, Canada) for ^{137}Cs analysis *via* gamma spectrometry.

Microfossil census counts were completed at 2 cm intervals using the methods outlined in Medley and others (2008). Sediment samples were rinsed on a 125 μm mesh sieve and wet samples were examined with a stereoscopic zoom microscope (Nikon SMZ1500). Select ostracodes were photographed using a variable pressure scanning electron microscope (Hitachi S-3400N). Morphometric shape analysis was completed according to the methods described by Medley and others (2008). Sieve pores on external valves of *Cyprideis* were traced to determine the areas and shapes using *ImageJ 1.3.1v* (*National Institutes of Health by Wayne Rasband*). Values for circularity were calculated using the following formula: Circularity = 4π (area/perimeter^2). The best-fit trendline of circularity versus area crossplots was used to determine the pore slope values.

Ostracode carapaces were bathed in deionized water and sent to the Saskatchewan Isotope Laboratory (Saskatoon, SK, Canada) for oxygen and carbon isotope analysis *via* stable isotope ratio mass spectrometry (SIRMS). SIRMS preparation entails the heating of samples *in vacuo* to dissipate contaminants (e.g. organic matter and water that may influence isotope values) prior to analysis with a Finnigan Kiel-IV carbonate preparation device directly coupled to a Finnigan MAT 253 isotope ratio mass spectrometer. Data is expressed relative to the VPDB scale and calibrated to the NBS-19 standard (δ^{13}C=1.95‰ VPDB; δ^{18}O=-2.2‰ VPDB).

Sediment accumulation rates were determined following the ^{137}Cs analysis method of Robbins and Edgington (1975). Cesium-137 is a radioactive isotope (half life=~30 years) that was released into the atmosphere during nuclear testing and simple gamma spectrometry can measure its concentration in sediment (USEPA 2010). Given that atmospheric levels of ^{137}Cs peaked in 1963, a sampling site's average sedimentation rate can be calculated using the simple stratigraphic thickness above the peak divided by the time in years since 1963. To ensure accurate gamma spectroscopy results, at least 2 g of sediment were removed from the center of each core segment. Forty samples from two Potomac estuary cores were analyzed by Core Scientific International (Winnipeg, Manitoba). Select samples were pretreated for radiocarbon dating at the University of Pittsburgh following the methods outlined by Abbott and Stafford (1996). AMS ^{14}C analyses were performed at the University of Arizona's Accelerator Mass Spectrometry Laboratory.

RESULTS

Physical Stratigraphy

Core PT-09-C3 from Aquia Creek (Potomac River) comprises 134 cm of dark grey clay with a layer of fine sand in the basal 10 cm (Figs. 1, 4). Magnetic susceptibility values average 38.7 SI Units with a minimum value of 18.7 (124 cm) and a maximum value of 166.7 (134 cm). Total organic matter (TOM) averages 6.59 % with a minimum value of 1.42% (132 cm) and a maximum value of 9.68% (11 cm). The maximum concentration of ^{137}Cs occurs between the 20-22 cm cored interval (Fig. 5).

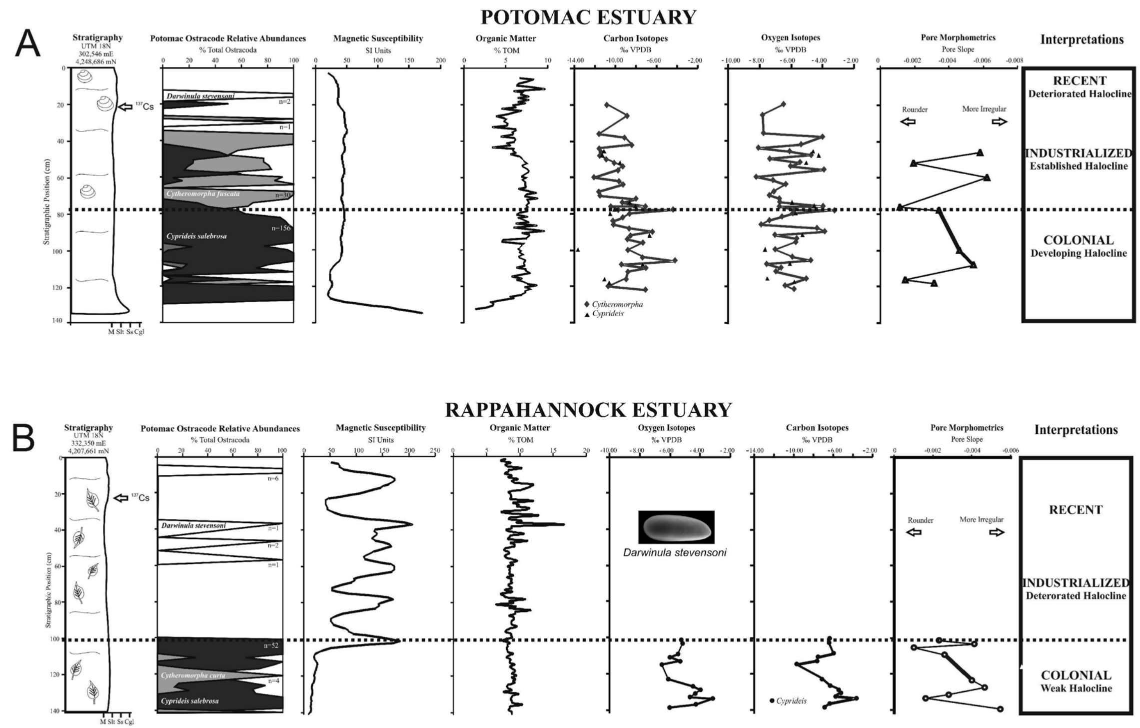

FIGURE 4. (A)Potomac Estuary and (B) Rappahannock Estuary: physical stratigraphy, ostracode populations, magnetic susceptibility, total organic matter, ostracode oxygen isotope values, ostracode carbon isotope values, and *Cyprideis* pore morphometric data. These results are interpreted in the context of three distinct paleosalinity intervals (see Figure 7).

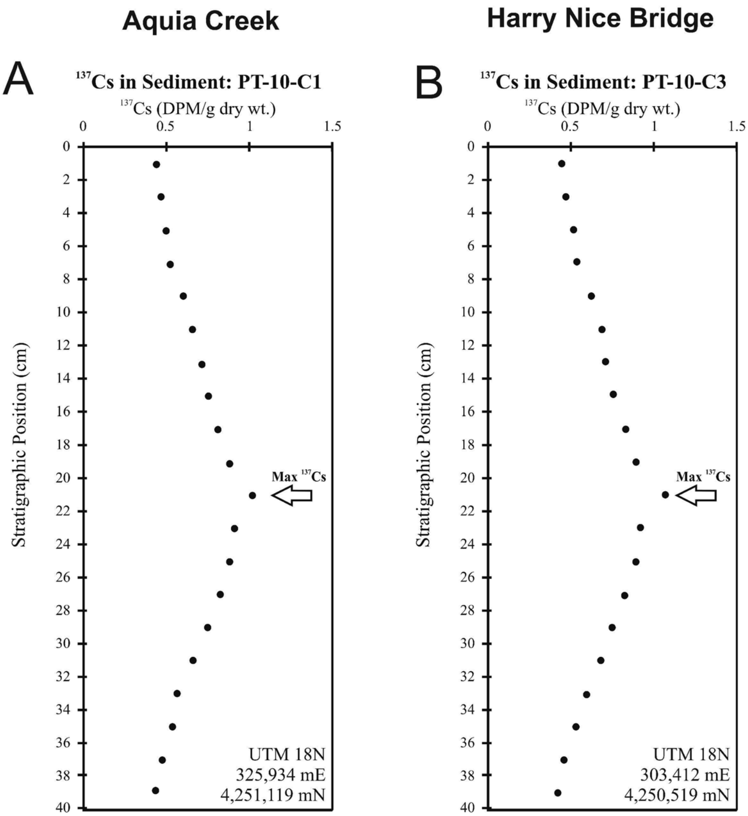

FIGURE 5. Results of ^{137}Cesium analysis of sediment collected near (A) the Harry Nice Bridge and (B) Aquia Creek. ^{137}Cs disintegrations per minute (DPM) were greatest between 20 and 22 cm in both cores.

Core RA-09-C3 at Blandfield Point (Rappahannock River) comprises 141 cm of brown-to-grey clay (Figs. 1, 4). Magnetic susceptibility in this core averages 86.3 SI Units with a minimum value of 8.9 (141 cm) and a maximum value of 206.3 (37 cm). Total organic matter averages 8.47% with a minimum value of 6.02% (81 cm) and a maximum value of 16.2% (37 cm). The maximum concentration of ^{137}Cs occurs between the 20-22 cm cored interval (Fig. 5).

Ostracode Paleoecology (Census and Pore Morphometrics

Ostracodes observed at Aquia Creek include *Cyprideis salebrosa*, *Cytheromorpha fuscata*, and *Darwinula stevensoni* (Figs. 4A, 6). *Cyprideis salebrosa* dominates the 128-20 cm interval with a relative abundance maximum at 84 cm (n=146).

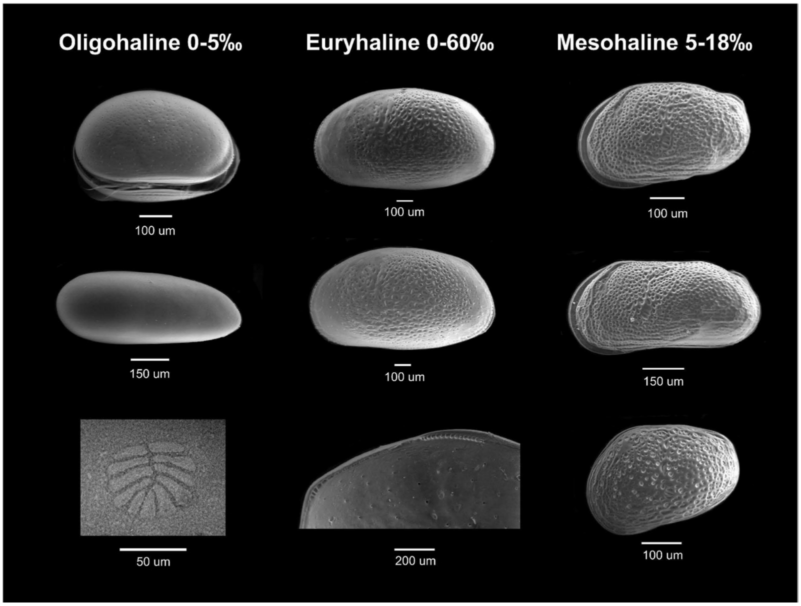

FIGURE 6. Oligohaline (*Darwinula stevensoni*), euryhaline (*Cyprideis salebrosa*), and mesohaline (*Cytheromorpha fuscata* and *Cytheromorpha curta*) ostracodes observed in sediment cores from the Rappahannock and Potomac Rivers. Salinity classification adopted from Belt and others (2005).

Cytheromorpha fuscata is relatively common within the 118-20 cm interval with a relative abundance maximum at 70 cm (n=30). *Darwinula stevensoni* is sparsely distributed with single valves observed above the 116 cm position (Fig. 4A).

Ostracodes at Blandfield Point include *Cyprideis salebrosa*, *Cytheromorpha curta* and *Darwinula stevensoni*. *Cyprideis salebrosa* is relatively common within the 139-101 cm interval with a relative abundance maximum at 107 cm (n=52) (Fig. 4B). *Cytheromorpha curta* is sparsely distributed with relative abundance peaks at 123 cm and 121 cm. *Darwinula stevensoni* is sparsely distributed with occurrences above the 57 cm position (Fig. 4B).

Valves of *Cyprideis salebrosa* from the Potomac River were analyzed for pore morphometric shape at nine stratigraphic positions within the 118-46 cm interval (Fig. 4A). An average of 39 pores were measured per ostracode valve whereas the calculated pore slope values that range from -0.0062 at 60 cm to -0.0011 at 76 cm. Valves of *C. salebrosa* from Blandfield Point (RA-09-C3) were selected for pore analyses at nine stratigraphic positions between 139-101 cm (Fig. 4A). An average of 43 pores were measured per ostracode whereas pore slope values range from -0.0054 at 139 cm to -0.0009 at 105 cm and exhibit a trend toward more positive slope values in the uppermost core.

Oxygen and Carbon Stable Isotope Values

Cytheromorpha fuscata

Oxygen isotope values measured in valves of *Cytheromorpha fuscata* at Aquia Creek average -6.1‰ VPDB . The minimum $\delta^{18}O$ value is -8.2‰ VPDB (60 cm) and the maximum value is -3.2‰ VPDB (78 cm) (Table 1)(Fig. 4A). $\delta^{18}O$ values are variable with the highest values recorded within the 122-78 cm and 57-38 cm intervals. Values decrease significantly above the 36 cm position.

Carbon isotope values for *C. fuscata* average -9.1‰ VPDB . The minimum $\delta^{13}C$ value is -12.0‰ VPDB (60 cm) and the maximum value is -4.2‰ VPDB (106 cm)(Table 1)(Fig. 4A). $\delta^{13}C$ values are most positive at the core's base, and gradually decreasing from -7.0 to -12.0‰ VPDB above the 78 cm position. Prominent positive excursion peaks mark the 78 and 106 cm positions (Fig. 4A).

Cyprideis salebrosa

Oxygen isotope values of *Cyprideis salebrosa* at Aquia creek average -5.6‰ VPDB. The minimum $\delta^{18}O$ value is -7.6‰ VPDB (100 cm) and the maximum value is -4.2‰ VPDB (48 cm) (Table 2)(Fig. 4A). $\delta^{18}O$ values of *Cyprideis salebrosa* gradually become higher in the top of the core. $\delta^{18}O$ values of *Cyprideis salebrosa* valves from Blandfield Point average -5.1‰ VPDB. The minimum value is -6.6‰ VPDB (115 cm) and the maximum value is -3.2‰ VPDB (134 cm) (Table 3)(Fig. 4B).

Carbon isotope values of *Cyprideis salebrosa* at Aquia Creek are more positive at the base of the core and shift to more negative values above the 78 cm position (Fig. 4A). $\delta^{13}C$ values average -9.8‰ VPDB. The minimum value is -13.6‰ VPDB (100 cm) and the maximum value is -6.6‰ VPDB (92 cm) (Table 2) (Fig. 4A). $\delta^{13}C$ values at Blandfield Point average -6.4‰ VPDB . The minimum value is -9.7‰ VPDB (115 cm) and the maximum value is -3.6‰ VPDB (134 cm) (Figure 4B). The maxima of both $\delta^{18}O$ and $\delta^{13}C$ are synchronous with both trending to lower values within the 134-115 cm interval (Table 3) (Fig. 4B).

Core Geochronology and Sedimentation Rates

Gravity cores (PT-10-C1 and PT-10-C3) collected from the Potomac estuary yield maximum ^{137}Cs decay rates between 20 and 22 cm that indicates an average sedimentation rate of 0.45 cm/yr since 1963 (Fig. 5). An earlier ^{137}Cs study at Blandfield Point (Rappahannock River) (Baliwag and others 2010) yielded an average sedimentation rate of the 0.54 cm/yr (see Tibert and others 2013). A single AMS ^{14}C radiometric date from a core in the Rappahannock River (upstream of Blandfield Point) yielded an uncorrected date of 245±15 that suggests a longer term sedimentation rate of 0.36 cm/yr. The collective summary of the sedimentation rates and the AMS ^{14}C in the Rappahannock and Potomac Rivers indicates basal core ages that approximate middle-to late 18th century colonial times (1767±15).

DISCUSSION/INTERPRETATIONS

Paleosalinity Indicators

Ostracodes reported from the tidal reaches of the Potomac and Rappahannock Rivers have well known ecological tolerances in estuarine environments (Frenzel and Boomer 2005). Species of *Cytheromorpha*, including *C. fuscata* and *C. curta*, are often

TABLE 1. Stable isotope values of *Cytheromorpha* spp. from the Potomac River.

Stratigraphic Position (cm)	$\delta^{18}O$ (‰ V-PDB)	$\delta^{13}C$ (‰ V-PDB)
20	-6.46	-10.75
26	-7.80	-8.78
36	-7.75	-11.51
38	-3.98	-9.06
42	-5.34	-8.36
44	-8.05	-11.50
46	-6.08	-11.35
48	-4.70	-11.41
50	-7.35	-10.80
52	-5.42	-10.06
54	-6.02	-9.30
56	-3.90	-9.68
60	-8.19	-12.00
62	-7.16	-9.59
68	-7.09	-11.55
74	-6.69	-9.25
76	-3.94	-7.03
76	-6.73	-10.40
78	-5.74	-9.68
78	-3.22	-4.37
80	-5.86	-8.52
64	-6.32	-9.17
70	-7.38	-11.42
72	-6.74	-7.96
82	-6.57	-9.24

TABLE 1. Continued

Stratigraphic Position (cm)	$\delta^{18}O$ (‰ V-PDB)	$\delta^{13}C$ (‰ V-PDB)
84	-7.38	-10.14
86	-7.86	-10.12
88	-4.32	-8.63
90	-3.83	-6.40
92	-6.97	-8.49
94	-5.61	-8.75
96	-5.69	-7.28
100	-6.99	-8.71
104	-5.90	-7.31
106	-4.47	-4.21
108	-7.53	-9.34
110	-6.62	-6.97
112	-6.93	-8.74
116	-5.04	-8.92
120	-6.35	-10.61
122	-5.79	-7.05

associated with mesohaline conditions (mesohaline = ~7-15 ‰), while *Darwinula stevensoni* is restricted to oligohaline waters (oligohaline = 0-5 ‰)(Elliot and others 1966; Cronin and Vann 2003). *Cyprideis salebrosa*, on the other hand, is common in both hyposaline and hypersaline environments, and can therefore has a wide salinity tolerance (euryhaline = 0-60‰)(Sandberg and Plusquellec 1974; Carbonnel 1983).

Cyprideis salebrosa has been used to reconstruct Holocene paleosalinity histories in lagoonal and lacustrine deposits in the Dominican Republic (Medley and others 2008). This studies show that synchronous positive excursions of the $\delta^{18}O$ values coupled with increased sieve pore irregularity are viable indicators for times of increased aridity and salinity. Although the $\delta^{18}O$ values of Potomac River water are more lower than those reported from Lago Enriquillo (a hydrologically closed lake), they do closely match $\delta^{18}O$ values of foraminiferal calcite reported in the Chesapeake Bay (Cronin and others 2005). The isotope values considered in the context of sieve shape variability serve as confirmation for significant changes in salinity spanning the past several centuries.

TABLE 2.Stable isotope values of *Cyprideis salebrosa* from the Potomac River.

Stratigraphic Position (cm)	$\delta^{18}O$ (‰ V-PDB)	$\delta^{13}C$ (‰ V-PDB)
46	-4.58	-11.05
48	-4.22	-11.21
52	-5.02	-9.49
74	-5.91	-8.56
76	-4.51	-7.99
78	-4.83	-10.01
80	-5.68	-10.43
92	-5.25	-6.60
100	-7.61	-13.57
108	-6.04	-7.26
116	-7.47	-10.99
118	-5.77	-10.51

A Centennial Record of Paleosalinity for the Virginia Tidewater

Basal core intervals in the Potomac River are characterized by euryhaline ostracodes with inconsistent oxygen isotope values that support our interpretation of a highly variable annual salinity range during late colonial times (Fig. 7). Trends in $\delta^{18}O$ values reflect the ostracodes' preference to live close to the landward extent of the marine salt wedge in the partial mixed estuary. Given that this interval pre-dates the industrial period, the seasonal stratification in this partially mixed Chesapeake Bay estuary maintained a salinity gradient that was not significantly impacted by natural storm events.

The middle intervals in the cores exhibit $\delta^{18}O$ values that trend toward their maximum values. This pronounced variability in the isotopic variability is coincident with a paleoecological shift to a *Cytheromorpha fuscata*-dominated ostracode association, thus recording the transition from near-oligohaline (~5-10 ‰) to increased mesohaline (~7-15 ‰) salinities. Within this interval, $\delta^{18}O$ values vary over 5‰ highlighting the magnitude of the salinity gradient at this time (Fig. 7). The relative abundance of *Cyprideis salebrosa* with irregular pore shapes supports our interpretation for elevated salinities likely due to increasing marine influence due to sea-level rise during the early-late 19th century.

The uppermost core intervals show a sharp decline in *Cytheromorpha fuscata* and a marked decrease in $\delta^{18}O$ values. Because fresh water has lower $\delta^{13}C$ and $\delta^{18}O$ values than marine water (Patterson and Walter 1994, Patterson 1998), the lower $\delta^{13}C$ and $\delta^{18}O$ values of ostracode carapaces were likely forced by a transition to less saline water.

TABLE 3. Stable isotope values of *Cyprideis salebrosa* from the Rappahannock River.

Stratigraphic Position (cm)	$\delta^{18}O$ (‰ V-PDB)	$\delta^{13}C$ (‰ V-PDB)
101	-5.25	-6.33
103	-5.17	-6.39
109	-5.48	-5.93
111	-5.98	-7.51
113	-5.34	-7.60
115	-6.55	-9.67
123	-6.12	-7.13
127	-4.47	-6.28
129	-3.98	-5.44
131	-4.32	-5.20
133	-4.66	-5.73
134	-3.18	-3.62
137	-4.30	-6.31
139	-6.02	-6.84

Sedimentation rates during this interval indicate an average rate of 0.45 cm/yr that also corresponds to a paleoecological shift to the freshwater ostracode *Darwinula stevensoni* . Population shifts, pore shape analyses, and isotope trends indicate decreased salinity and weakening salinity gradient near Aquia Creek during the early 20th century (Figs. 4, 7).

Climate Forcing and Sediment Loading

Cronin and others (2005) evaluated oxygen and carbon isotopes from calcareous foraminifera, and magnesium-calcium ratios from ostracode carapaces that generally oscillate in-phase for the last ~150 years in the Chesapeake Bay. Similar in-phase variations characterize the isotope record from Rappahannock and Potomac ostracodes (e.g., $\delta^{18}O$ and $\delta^{13}C$ maxima at 78 cm) (Fig. 4). The variability in our paleosalinity proxy indicators suggests that global climatic events, including the last vestiges of the Little Ice Age (Cronin and others 2003), may have influenced late 18th and early 19th century salinity variability in both the Rapphannock and Potomac estuaries. Cronin and Vann (2003) and Cronin and others (2005, 2010) analyzed ostracode and foraminifera populations collected from the mouth of the Patuxtent estuary. Their results indicate that decadal climate variability in the Chesapeake Bay is potentially influenced by the

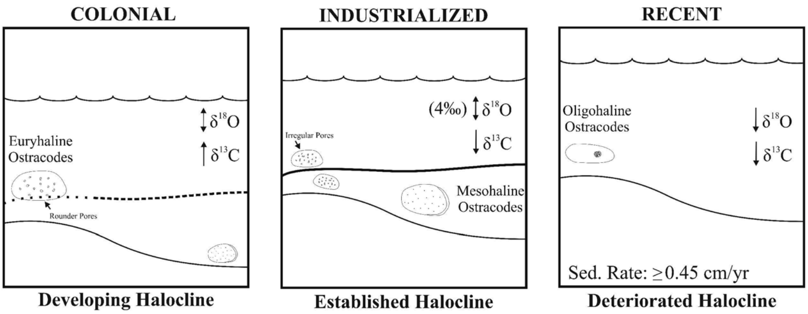

FIGURE 7. Model of paleosalinity change in based on microfossil populations, geochemistry, and stratigraphy of the Potomac estuary, and supported by supplementary results from the Rappahannock estuary. Three stages of halocline (A) development/strengthening, (B) establishment, and (C) deterioration were reconstructed for the last two centuries in the tidal reaches of these estuaries.

North Atlantic Oscillation and possibly El Niño Southern Oscillation (ENSO). The apparent decadal variability in our paleosalinty data substantiates their hypothesis.

Between 1983 and 2000, the Rappahannock and Potomac Rivers produced the greatest average annual sediment yields for all major Chesapeake Bay tributaries (Langland and Cronin 2003). Sedimentation rates and patterns are variable across the bay due to its tributaries' variable physiographic identities and land use histories (Brush 1989; Langland and Cronin 2003). Brush (1989) linked recently altered sedimentation rates and patterns in Chesapeake Bay tributaries to aggressive post-colonial land development. However, the amount of this "legacy sediment" stored in Chesapeake Bay watersheds, as well as time required for it to reach the bay, currently remains unquantified (Langland and Cronin 2003).

CONCLUSIONS

The paleosalinity history for the Potomac and Rappahannock Rivers is likely related to both natural climate change and anthropogenic forcing mechanisms. The initial shift from euryhaline-to mesohaline dominated ostracode associations was attributed to increasing salinity associated with ongoing Holocene sea-level rise. Despite the increasing marine influence due sea-level rise, sediment deposited in the tidal reaches during the 20th century was characterized by increased abundances of oligohaline ostracodes with decreasing $\delta^{18}O$ and $\delta^{13}C$ values. While the exact cause of decreasing salinity during a period of 20th century is unknown, our results corroborates the hypothesis that anthropogenically-induced salinity change, post-Industrial times, has had a significant impact on seasonal salinity gradient development in the tidal reaches of the Potomac and Rappahannock Rivers.

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