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Multi-century record of anthropogenic impacts on an urbanized mesotidal estuary: Salem Sound, MA

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Abstract

Salem, MA, located north of Boston, has a rich, well-documented history dating back to settlement in 1626 CE, but the associated anthropogenic impacts on Salem Sound are poorly constrained. This project utilized dated sediment cores from the sound to assess the proxy record of anthropogenic alterations to the system and compared the proxy records to the known history. Proxies included bulk stable isotopes of organic matter, magnetic susceptibility, and trace metal concentrations. Our data reveal clear changes in organic matter composition and concentration associated with land use changes and twentieth century sewage disposal practices. Further, metals data correspond with local industrial activity, particularly the historic tanning industry in Peabody, MA. Although conservation practices of past decades have improved the state of Salem Sound, the stratigraphic record demonstrates that the environment is still affected by anthropogenic influences, and has not attained conditions consistent with pre-anthropogenic baseline. The approach and results of this study are applicable to coastal embayments that are being assessed for remediation, especially those with scant historic or monitoring data.

Keywords

Sewage effluent; legacy contaminant; stable isotopes; sediment core; Anthropocene

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Conflict of Interest

The authors declare that they have no conflict of interest.

Introduction

Industrialized coastal embayments have been affected by anthropogenic activities, including both detrimental (contaminant inputs, land use changes, habitat destruction) and beneficial (contaminant mitigation, changes in harmful practices) effects on the environments (e.g. Kennish 2002). Most of these industrialized coastal systems have not had the benefit of long-term monitoring programs, however, and knowledge gaps remain in our understanding of systems' responses to anthropogenic forcings. As a result, it is difficult to quantify the magnitude of anthropogenic effects on these coastal systems. This challenge is especially evident with regard to understanding baseline (*i.e.* pre-anthropogenic alteration) conditions, thus inhibiting remediation and restoration efforts and environmental protections.

One method that has been used to reconstruct past environmental conditions and investigate responses to known forcings is the utilization of dated sediment cores to establish a time series of environmental conditions within a coastal system (Cantwell et al. 2015; Hubeny et al. 2009; King et al. 2008; Sowers and Brush 2014; Valette-Silver 1993; Willard et al. 2003). Such proxy records can help to constrain past productivity, sedimentation rates, organic matter source material, and input of allochthonous material, including contaminants. Further, if the sediment records represent enough time, the pre-anthropogenic baseline conditions can be interpreted and understood (Bindler et al. 2011; Birch and Olmos 2008).

The purpose of this study is to reconstruct environmental conditions within Salem Sound, Massachusetts, USA, and to compare these conditions to the well-documented history of the region. Our research questions are: 1) Does the stratigraphic record preserve historic anthropogenic changes in the watershed, and 2) Have mitigation strategies employed over past decades returned the system to baseline conditions? A better comprehension of the fundamental issues these questions represent is important in any effort to understand both the natural state of and the human influences on the system. Specific to Salem Sound, our efforts may assist in future remediation work in the region. More broadly, we aim to provide a framework in which other similar water bodies can be assessed and quantifiable remediation strategies can be developed, if appropriate.

We hypothesize that multiple proxies in dated sediment cores will be sensitive to anthropogenic changes that have occurred since colonial times. Specifically, we expect that Salem Sound has experienced quantifiable detrimental effects from land use changes, the historic tanning industry, the construction of a sewage outfall pipe to the central portion of the sound, and the construction of a power plant in the mid-20th century. We also expect to observe positive effects in the record associated with the demise of the tanning industry in the mid-20th century, and enhanced sewage treatment procedures over the past four decades.

Our experimental approach is focused on measuring multiple proxies from a transect of dated sediment cores in Salem Sound (Fig. 1). Physical proxies, including basic sediment lithology (Schnurrenberger et al. 2003), density, and magnetic susceptibility (Evans and Heller 2003; Nowaczyk 2001) provide basic constraints on the bulk sediment inputs to the embayment, and are expected to be sensitive to changing sediment sources and fluxes. Preserved organic matter is expected to be sensitive to both land use changes (by

examination of source provenance) and to estuarine productivity, interpreted through the quantification of bulk organic matter (Dean 1974; Heiri et al. 2001) as well as isotopic and elemental interparametric ratios of carbon, nitrogen, and sulfur (Bates et al. 1995; Meyers 1994). Finally, since specific heavy metal concentrations in sediment are indicative of past industrial activities and input of these contaminants to the water body, metals will be used to assess the industrial influences on the system (e.g. Deely and Fergusson 1994).

Salem Sound is not atypical for industrialized coastal embayments, and is well suited for this study due to well-constrained histories of land use practices, sewage treatment, and industrial activity. The scientific approach and results of this study will be applicable to the interpretation and prediction of anthropogenic activity to other embayments.

Site Description

Salem Sound, located 24km north of Boston, is a vertically-mixed, tide-dominated, mesotidal coastal embayment within Massachusetts Bay (Fig. 1). The area is 36.6 km², average depth is 9.15 m MHW (Jerome et al. 1967), the mean semi-diurnal tide range is 2.75 m, and the flushing time is on the order of 2 days. Salinity within Salem Harbor averages *ca.* 29-30 psu, chlorophyll *a* averages *ca.* 6.6 µg/l, and suspended particulate matter is *ca.* 12.7 mg/l (Hubeny et al. 2017). Salem Sound is underlain primarily by Ordovician-Silurian-aged Salem Gabbro-Diorite, with Silurian-Devonian-aged Cape Ann Granite and Beverly Syenite in the northeastern watershed (Toulmin 1964; Zen et al. 1983). The region has been glaciated multiple times during the Quaternary Period, and ice most recently retreated by *ca.* 16,500 ± 700 cal BP (Ridge 2003; Ridge 2004; Stone et al. 2004). Sub-bottom geophysical surveys of Salem Sound reveal glaciomarine sediments overlying bedrock (Boglione and Hubeny 2014), consistent with a regional relative sea level highstand immediately following ice retreat (Hein et al. 2012; Oldale et al. 1993). Salem Sound was subaerially exposed due to isostatic rebound, likely within a millennium of ice retreat, and then inundated again during the mid-Holocene transgression, *ca.* 6800 cal BP for sill height of -12m (Annadale et al. 2017; Hein et al. 2012; Oldale et al. 1993).

The Salem Sound region was inhabited by Native Americans prior to initial European settlement in 1626, and it is well established that European settlement had large effects on the land use and ecosystems of New England (Cronon 1983). In colonial time (1626 - 1776), agriculture and fishing were the primary industries, and lumber mills were in use as early as the 1630s. The agriculture of Essex County was mixed, with corn as the staple grain, meadowlands for hay, a diversity of livestock including cattle, pigs, and sheep, and oxen were the principle draft animals (Vickers 1994). Over the first few generations forest was converted to settled farmland at a steady pace, and by 1700 all land in Salem was parsed, with residences primarily at the town center and agricultural fields along the outer portions of town (Perley 1933). Over the course of the 18th century, the poor local soils became progressively more stressed, and a general shift in agricultural strategy from tillage to pasturage occurred. Although quantitative data are lacking from the Salem Sound watershed, between 1680 and 1771 nearby Salisbury (Essex County, MA) saw increases in total farmland acreage (740% increase) as well as sheep (340% increase), cattle, and pig populations (both 120% increase) (Vickers 1994). During the early colonial period coastal

fisheries were also strong, and the salt processing of cod was done on shore. By 1725 larger schooners took over as the dominant fishing vessels, which largely moved the fishery off-shore, with longer voyages and processing at sea (Vickers 1994).

After independence in 1776, international maritime trade expanded and Salem became a world-leading seaport until the middle of the 19th century. During this time the agricultural industry expanded to larger farms and operations and continued the 18th century trend toward less tillage and expansion of grass fields for hay (Vickers 1994). Comparison of maps from 1700 (Perley 1933), 1804 (Bowditch 1834), and 1851 (McIntyre and Taylor 1851) reveals that development along the shoreline was substantial, including the construction of wharves and land expansion through filling. By mid-19th century, much of the local maritime trade had moved to Boston and New York, and Salem's economy shifted to manufacturing. This shift was led by a world-leading tanning industry (Cultrera et al. 1991) along the banks of Salem Sound's major inflows, primarily the North River (Fig. 1). Population grew rapidly during the late 18th and 19th centuries due to the international shipping trade, subsequent manufacturing, and the construction of the Eastern Railroad Company rail line from East Boston to Salem in 1838 (Felt 1845). The tanneries fell into decline in the mid-20th century, after World War II.

In the 20th century population steadied, and the region expanded its municipal services. In 1905 a sewage outfall pipe was put into operation to transport raw sewage from Peabody and Salem to the central portion of the sound, near Haste Rock (Wright 1935) (Fig. 1). The South Essex Sewerage District (SESD) was established in 1925, and an updated sewage outfall was put into operation in 1928. Primary treatment of the effluent, however, did not commence until 1977 (Chase et al. 2002). In 1998 SESD upgraded to secondary sewage treatment, and a diffuser was added to the Haste Outfall pipe. A coal- and oil-burning power plant was constructed at Salem Harbor in 1952, and phased out operations in 2014.

Methods

Sample Collection

Sediment cores were collected in May 2010 using a modified Kullenberg-type gravity piston corer deployed from a 24' pontoon research vessel. Three coring locations were selected to represent a transect from the inner Salem Harbor (SH10), to outer Salem Harbor (SHM10), to the central portion of Salem Sound adjacent to the modern location of the SESD outfall pipe near Haste Rock (HO10) (Fig. 1). At each location two adjacent cores were taken (Table 1). The first was split horizontally, logged, and subsampled for all proxy analyses. The second core was subsampled vertically for ⁷Be, ¹³⁷Cs, and ²¹⁰Pb analyses.

All cores had quality sediment/water interfaces, as indicated by clear water in the core tube immediately above the sediment. The tops of the cores were stabilized with Zorbitrol (Tomkins et al. 2008) before transport and storage at 4°C at the Salem State University Environmental Sedimentology Lab.

In addition to the core samples, particulate organic matter (POM) was sampled from the surface water in order to: 1) assess the homogeneity of POM among our sampling locations,

and 2) assess the ability of sedimentary isotopic and interparametric ratios to record the POM characteristics of the source material. Surface water was sampled at each coring location on seven separate days from May 2010 until April 2011. Each sample was filtered through a pre-combusted glass fiber filter (VWR type 696). All sampling equipment was rinsed three times with sample water prior to sample collection, and the volume of water filtered was recorded. Filters were folded in half, wrapped in aluminum foil, and stored frozen until analysis.

Age Models

Age models have been calculated for each sediment core location using the Bayesian age-depth modeling software Bacon 2.2 (Blaauw and Christen 2011). Chronostratigraphic inputs for the models include ^7Be , ^{137}Cs , ^{210}Pb , ^{14}C , benzotriazole (BZT) concentrations, and *Ambrosia* pollen data. Sediment cores HO10KC2, SHM10KC2, and SH10KC2 were extruded vertically in 1.5cm increments for radionuclide analyses within 24 hours of collection. Each subsample was oven-dried at 50°C, homogenized, sealed in a plastic-lined aluminum can and analyzed by gamma spectrometry using an ultralow-background, high-resolution Canberra Broad Energy Germanium planar detector equipped with Canberra Genie 2000 MCA microprocessor. All counts were normalized by sediment dry mass, yielding values of mBq/g, and ^{210}Pb data were calculated as excess ^{210}Pb . An age model was calculated for each core with the ^{210}Pb data assuming a constant initial concentration (CIC) model (Appleby 2001). Cesium-137 was used to confirm the ^{210}Pb age models, and its agreement to the CIC model validated the CIC model as opposed to the alternative Constant Rate of Supply (CRS) model (Appleby 2001; Lima et al. 2005). Beryllium-7 was analyzed in the upper sediment samples to assess the depositional nature of each site (Zhu and Olsen 2009). An additional chronostratigraphic constraint was afforded in the HO10 core by the identification of the BZT horizon associated with this chemical's patent date of 1961 (Cantwell et al. 2015).

One accelerator mass spectrometry (AMS) radiocarbon date was analyzed from each core location (Table 2). Organic samples from the outer and inner harbor cores were treated with an acid-base-acid (ABA) procedure (Olsson 1986) prior to analysis. In the Haste core, bivalve shell fragments were the only datable macrofossils available, and fragments sampled from a core depth of 72.5 cm were dried and analyzed. Samples were dated at the National Science Foundation-Arizona AMS Laboratory and calibrated using the Bacon 2.2 program. The Intcal3 calibration data set was used to calibrate the terrestrial macrofossils, and the Marine 13 calibration data set was used for the bivalve shell material (Reimer et al. 2013). A local marine reservoir correction ($R = 60 \pm 15$) was used based on the only local bivalve (*Mya arenaria*) listed in the CALIB marine reservoir correction database (Beverly, MA; distance 4km) (McNeely et al. 2006; Reimer et al. 2013). Note that the next closest *Mya arenaria* was from Plymouth, MA (75km south of study site), and its local reservoir correction ($R = 100 \pm 60$) did not change the calibration appreciably.

Sediment samples were processed for pollen analysis using standard techniques (Faegri and Iversen 1989) that were modified to preserve more susceptible palynomorphs (McCarthy et al. 2011). A tablet containing $10,850 \pm 200$ *Lycopodium clavatum* spores was added during

HC1 treatment to allow palynomorph density to be estimated (Stockmarr 1971). Palynomorphs were identified (McAndrews et al. 1973) at 400X magnification, and a minimum pollen sum of 100 arboreal grains was used to establish the horizon of increased *Ambrosia* and non-arboreal pollen associated with European contact (1629 CE) and concomitant land use changes.

Sediment Core Logging

Split sediment cores were described visually, identifying color, bedding, macrofossils, and qualitative grain size (Schnurrenberger et al. 2003). Ten subsamples were taken from core HO10 for quantitative grain size analysis. All samples were prepared and analyzed via laser diffraction at the U.S. Environmental Protection Agency's Narragansett, RI laboratory.

Magnetic Susceptibility

Volume magnetic susceptibility (κ) was measured with a Bartington MS2E high-resolution sensor. Measurements were taken at 1 cm intervals down the split face of each core, zeroing the sensor between each measurement.

Frequency dependence of magnetic susceptibility (X_{FD}) was measured on 8 cm³ cube samples from the Haste core. Samples were measured three times each at low frequency (0.46 kHz, X_{lf}) and high frequency (4.6 kHz, X_{hf}) on a Bartington MS2B sensor. Mean values of X_{lf} and X_{hf} were used to compute X_{FD} as: $(X_{lf} - X_{hf}) / X_{lf} * 100\%$.

Organic Matter

The loss-on-ignition method (Dean 1974) was used to calculate dry bulk density (DBD) and percent organic matter (OM). One cubic centimeter of sediment was subsampled from the split core at each location at 1 cm intervals. Each sample was dried at 100°C overnight, and the dry mass was used to calculate DBD (g/cm³). The dry sample was ignited at 550°C for 1 hour, and the mass lost was used to compute the percentage of organic (ignitable) matter in each sample.

Isotopic and Light Elemental Analysis

A continuous flow elemental analyzer/stable isotope ratio mass spectrometer (EA/IRMS) was used to quantify stable carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), and sulfur ($\delta^{34}S$) isotope ratios and elemental concentrations for 68 samples from core HO10KC1. In addition, 21 samples of POM from glass fiber filters were dried and analyzed. Mass of particulate matter was determined as the difference in mass between the pre-combusted filter and the dry filter with sample on it.

Two rounds of analyses were conducted in order to avoid complications of N analysis associated with acidification techniques to remove inorganic carbon necessary for $\delta^{13}C$ analyses (Brodie et al. 2011). For $\delta^{15}N$ and $\delta^{34}S$ analyses dry homogenized sediment, or one quarter of a glass fiber filter, was weighed into tin capsules. The $\delta^{13}C$ samples (dry homogenized sediment or a hole punch of glass fiber filter) were acidified through fumigation for six hours in silver capsules (Harris et al. 2001). After drying, samples and silver capsules were wrapped in tin capsules, and 3 times the sample weight of tungsten

trioxide was added to assist in sample combustion. Standard reference samples (USGS-40, USGS-41, IAEA S-2, and IAEA S-3) were measured for calibration, and isotopic composition of all samples were expressed in standard format relative to VPDB, AIR, and VCDT, respectively. Reference gas stability on the EA/IRMS was quantified as 0.01‰, 0.02‰, and 0.02‰ for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$, respectively. Ratios of OC/N and OC/S were calculated from element concentration data.

Metal Analysis

Concentrations of Cr, Pb, Zn, Cu, and Ni were quantified using an Innov-X X-50 X-ray Fluorescence (XRF) Spectrometer. One-centimeter wide subsamples were taken from core HO10KC1 to a depth of 42cm. Each sample was dried at low temperature and any large particles were removed. Samples were ground, homogenized, and placed in clean plastic bags in preparation for analysis. Samples were analyzed three times on the XRF and the average value is reported. The metal concentrations are reported in parts per million (ppm), and quality control was ensured with the analysis of standard reference materials, National Research Council Canada's MESS-3 and PACS-2 marine sediments.

Statistics

Basic statistical computations were performed using StatPlus® and Excel® software and the PAST statistical package (Hammer et al. 2001). Hypothetical changes in proxy data associated with the timing of known anthropogenic forcings or spatial distribution in the field area were tested for significance through classic two-sample or several-sample tests. Prior to selection of test, a Shapiro-Wilk test was performed to confirm a normal distribution of data, which dictated if a parametric or non-parametric test should be used. If a normal distribution of data was confirmed, then samples were compared using two-sample t-tests assuming equal variances. In cases of non-normality, the non-parametric two-tailed Mann-Whitney test was performed to check for equal medians. In the case of more than two samples, the one-way ANOVA test was used for normally distributed data and the non-parametric Kruskal-Wallis test was used for non-normal data. Significant differences were interpreted when the distribution returned a p value ≤ 0.05 .

Multivariate ordination was performed using principal components analysis (PCA) on the correlation matrix of data in the PAST statistical package (Hammer et al. 2001). The analysis results in calculated principal components (PCs) that account for common variance in the multivariate data, and it is useful in the reduction of data into primary variables. The correlation of the original data variables (proxies) to the calculated PCs allows for an evaluation of the association of proxies to each other and their association with interpreted common forcings or variables (*i.e.* productivity, sediment provenance, etc). Further, the PCA approach can assist in testing hypotheses associated with responses to changing environmental conditions by grouping samples by known conditions and testing for separation of these groups within a PCA biplot.

Results

Sediment Core Stratigraphy

All three stratigraphic sequences consist of estuarine sandy muds and muddy sands. The two Salem Harbor cores are massive, with no visible stratigraphic variability. The Haste core contained five distinct color zones with minimal grain size variability (Fig. 2), however there was no visible bedding within the core. The lower portion of the core was light – medium gray silty sand that transitioned to light grey – medium brown silty sand at 56cm. At 42cm, the color darkened to a medium – dark grey, and from 24 – 8cm the sediment was dark gray to black and fined to sandy silt in the upper portion of this zone. The upper 8cm of the core was medium brown – medium gray sandy silt. Clay percentage was minimal throughout the core, with values ranging between 0.6% and 1.6%.

Figure 2 also shows changes in OM, DBD, and κ with depth in the Haste core. The lower portions of the cores likely represent background conditions before major anthropogenic influences, and certain patterns emerge. OM exhibits a trend of decreasing values moving away from the inner harbor out to the central Sound (Haste). In the same intervals, a similar trend of increasing DBD with distance out of the inner harbor is apparent. Magnetic susceptibility is similar between sites.

In the upper portion of the cores, the OM and DBD records of the Haste and outer harbor cores shift toward values more similar to those observed in the inner harbor. Further, all three locations exhibit elevated κ values, with the outer harbor having the clearest signature.

Sediment Chronologies

The Bayesian age-depth models for all three cores provide chronological constraints on the stratigraphic records (Fig. 3). For the Haste core, the ^{210}Pb age model agrees well with the ^{137}Cs peak known to occur in 1963 associated with atmospheric bomb testing (Appleby 2001) and with the BZT peak known to occur with the 1961 patent date of this chemical marker (Cantwell et al. 2015). Further, the presence of ^7Be ($t_{1/2} = 53$ days) in the uppermost sample provides evidence of continued active sedimentation and a high-quality sediment water interface (Zhu and Olsen 2009). The *Ambrosia* pollen horizon agrees well with the calibrated ^{14}C age from the core (Table 2). Since all age indicators of the Haste core correspond with each other, we interpret the chronology from the Haste core to be robust, with relatively tight chronological control since the late 19th century, modest chronologic control in the middle part of the record, and increased chronologic uncertainty below the ^{14}C control point. A modest increase in sedimentation rate from 0.12 to 0.14 cm/yr is observed after European contact (as interpreted from *Ambrosia* horizon). A second increase in sedimentation rate to 0.22 cm/yr is observed above 36cm (*ca.* 1835), roughly in line with the timing of increased population, international maritime trading, and early industrialization in the watershed.

The inner harbor and outer harbor cores' age models rely upon the ^{210}Pb age model, *Ambrosia* horizon, and calibrated ^{14}C age. Neither core had measurable ^7Be in the surface sample, suggesting that local scouring, erosion, or non-deposition has occurred. Further, the ^{137}Cs profiles lack a clear peak to correspond with the ^{210}Pb age model, suggesting that

bioturbation may be more of a factor in these cores as compared to the Haste core. Although ^7Be and ^{137}Cs results suggest a non-continuous archive of sedimentation and increased error in the models, the age models for these cores provide chronologic control of the records that can be used with noted caution (Fig. 3).

Based on the stratigraphy and superior chronologic control of the Haste core, we decided to proceed with our multi-proxy analysis with this core. In our interpretations, we will utilize the inner and outer harbor cores where appropriate, acknowledging the chronological uncertainties associated with the two age models.

Magnetic Stratigraphy

The magnetic record of the Haste core (Fig. 4) contains a typical κ profile in which low values dominate the lower portion of the core ($5.4 \times 10^{-5} \pm 0.7 \times 10^{-5}$ SI below 30cm), and a general increasing trend is observed from the start of the Industrial Revolution to present. The clearest and most defined increasing trend is from 12cm to the top of the core, representing from *ca.* 1950 to present, and the maximum value (19.9×10^{-5} SI) is observed at the top of the core.

The X_{FD} record is also reported, and the 3% line is represented in the figure, since values above 3% represent samples with a significant fraction of superparamagnetic grains relative to single- and multi-domain magnetic grains (Oldfield et al. 1985). In the lower half of the core, the X_{FD} signal is dominated by values below 3%. From *ca.* 40-15cm (*ca.* 1806 – 1950), the X_{FD} signal is variable, with periods of significant superparamagnetic grains within the core. Above 14cm (*ca.* 1950), the record is dominated by low X_{FD} values, suggesting a period of reduced superparamagnetic grains in the most recent 6 decades.

Organic and Stable Isotope Stratigraphy

Organic matter and DBD show an inverse relationship to each other, in which background values are low for OM and higher for DBD (Fig. 4). Starting at *ca.* 44cm (late 18th century), OM begins to increase and DBD begins to decrease. At this same interval, $\delta^{13}\text{C}$ experiences a step shift to more depleted values and OC/N has a similar step increase to higher values. Such shifts are consistent with increased terrigenous organic matter reaching the estuary (Meyers 1994). Both $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ become more enriched during this interval. $\delta^{13}\text{C}$ and OC/N remain relatively consistent until *ca.* 23-24cm, when organic matter abruptly increases. At this point of the core (*ca.* 1905), $\delta^{13}\text{C}$ becomes enriched by *ca.* 2‰ and OC/N decreases by almost 2, indicating a shift from significant terrigenous organic matter input to organic matter dominated by marine phytoplankton. Organic matter stays high until *ca.* 6-7cm (*ca.* 1977) when it decreases to the top of the core. During the 20th century, $\delta^{13}\text{C}$ and OC/N trend erratically to more depleted and higher values, respectively. $\delta^{34}\text{S}$ reaches its most enriched value at *ca.* 15cm, approximately mid-century.

In addition to the sediment core analysis, we analyzed particulate organic matter (POM) filtered from the surface waters of the three coring locations to assess the modern homogeneity of POM between the sites. In addition, we test the hypothesis that sedimentary isotopes and interparametric ratios are statistically representative of the POM at the time of deposition, and therefore represent past conditions (Fig. 5). The isotopic signature of POM

was not significantly different between field sites for $\delta^{13}\text{C}$ (ANOVA: $F = 0.655$, $p = 0.531$), $\delta^{15}\text{N}$ (ANOVA: $F = 1.341$, $p = 0.287$), or $\delta^{34}\text{S}$ (ANOVA: $F = 0.576$, $p = 0.573$). Further, POM OC/N (Kruskal-Wallis: $H = 0.423$, $p = 0.809$) and OC/S (Kruskal-Wallis: $H = 0.733$, $p = 0.693$) values from the three field locations are not significantly different from each other. The POM results demonstrate that Salem Sound surface waters are well mixed and that POM characteristics in one location are representative of the rest of the embayment.

No significant difference was found with OC/N between Haste POM and sediment core samples (t-test: $t = -1.027$, $p = 0.308$). $\delta^{13}\text{C}$ (t-test: $t = -4.723$, $p < 0.001$), $\delta^{15}\text{N}$ (Mann-Whitney: $z = -2.246$, $p = 0.025$), and OC/S (Mann-Whitney: $z = -2.138$, $p = 0.033$) were significantly higher in the sediment core samples as compared to POM. Since sewage treatment can affect isotopic fractionation, we reran the analyses with only the core samples deposited since 1998 (post-secondary treatment) and found no significant difference in $\delta^{13}\text{C}$ (Mann-Whitney: $z = -1.257$, $p = 0.209$), $\delta^{15}\text{N}$ (Mann-Whitney: $z = -1.029$, $p = 0.304$), or OC/S (Mann-Whitney: $z = -1.823$, $p = 0.068$) between the sediment and POM samples. $\delta^{34}\text{S}$ values from the sediment core are significantly depleted as compared to POM samples for the whole core record (Mann-Whitney: $z = -4.033$, $p < 0.001$) and for the post-secondary treatment period (Mann-Whitney: $z = -2.195$, $p = 0.028$). The POM/sediment core results (Fig. 5) demonstrate that sedimentary $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, OC/N, and OC/S reliably record the POM signature of Salem Sound, and that the sedimentary $\delta^{34}\text{S}$ values are significantly depleted with respect to POM.

A principal components analysis (PCA) of the sediment core organic matter proxies was calculated to reduce the proxy time series to common variability (Fig. 6A). The PCA was successful in representing most of the variance with two principal components (PCs), with PC1 explaining 53.8% of the variance and PC2 explaining 25.0% of the variance. PC1 is driven primarily by variability in DBD, $\delta^{34}\text{S}$, OM, and OC/S (correlations to PC1: -0.945 , 0.929 , 0.925 , 0.821 , respectively). PC1 is interpreted as representing productivity/OM preservation. PC2 is driven primarily OC/N, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ (correlations to PC2: 0.840 , -0.679 , 0.649 , respectively). PC2 is interpreted as representing OM provenance, with larger values indicative of terrigenous source and smaller values indicative of planktonic source. The PCA biplot shows clear separation of chronologic samples from the Haste stratigraphic record that are associated with distinct historic periods.

Trace Metal Stratigraphy

Fig. 7 plots the concentrations of Pb, Cr, Zn, Cu, and Ni for the top 42cm of the Haste core. Pb, Cr, and Zn display nearly identical profiles, which start with relatively low values, gradually increase to 24 cm (*ca.* 1902), abruptly increase at 21 cm (*ca.* 1915), then decrease steadily from 11 cm (*ca.* 1960) to the top of the core. The background value for each metal is defined here as the minimum value in the bottom portion of the core, with values of 26 ppm, 43 ppm, and 36 ppm for Pb, Cr, and Zn, respectively. Peak values for the metals are 416 ppm, 4534 ppm, and 511 ppm, respectively. At the top of the core (modern surface), values are 62 ppm, 486 ppm, and 97 ppm, respectively.

Copper follows a similar trend to the first three metals below 14 cm (*ca.* 1947). Above this point, Cu increases to 120 ppm, and does not start a large decline until 8 cm (*ca.* 1974).

These observations suggest that Cu had a common source to Cr, Pb, and Zn up until the mid-20th century, and then a likely additional source of Cu occurred. Alternatively, it is possible that preservation potential may be slightly different between metals due to changing redox conditions in the sediment. Nickel has relatively low concentrations at the base of the core (background: 24 ppm), has a one-point peak at 21 cm with the large increase in other metals, and then is variable for the rest of the record. Such behavior suggests that Ni has a separate source from the other metals.

A PCA of metals data was calculated to reduce the proxy data to common variability (Fig. 6B). The PCA was successful in representing most of the variance with two principal components (PCs), with PC1 explaining 81.3% of the variance and PC2 explaining 16.2% of the variance. PC1 is driven primarily by variability in Pb, Cr, Zn, and Cu concentrations (correlations to PC1: 0.991, 0.985, 0.9980, 0.956, respectively). PC2 is driven primarily by Ni concentrations (correlations to PC2: 0.871).

Discussion

In the following subsections, we analyze the sedimentary proxy records of three chronologic zones associated with distinct anthropogenic forcings: 1) Land use changes associated with agriculture, and watershed development, 2) Sewage treatment practices during the 20th and 21st centuries, and 3) Industrialization in the 19th and 20th centuries. Our goal is to clearly discuss the known forcings and the proxy recordings of each event. Table 3 presents a summary of anthropogenic events and their historic timings, proxy recordings of these events, and a summary of the specific mechanisms that the proxies record. We find clear evidence of anthropogenic influences in Salem Sound, and our findings will guide future research aimed at interpreting similar water bodies for anthropogenic influences.

History of pre-20th Century Land Use Change

As outlined in the introduction, Salem Sound's watershed experienced large land use changes from the early 17th century through modern time, associated with clear cutting, changing agricultural practices, and coastal development. Such modifications to the watershed likely made soils more susceptible to erosion, suggesting that sedimentary proxies should show indicators of increased flux of sediment and organic matter from the watershed as compared to values before 1626. Natural baseline conditions prior to significant human disturbance to Salem Sound can be interpreted from data below 67 cm in the Haste core (Fig. 4), and therefore we can quantitatively compare proxy data to data below this horizon. PCA demonstrates that productivity was relatively consistent (PC1) and that although the primary source of organic matter was algae, the source (PC2) was variable representing episodic inputs of allochthonous organic material (Fig. 6).

Based on age constraints, we note a modest increase in sedimentation rates, from 0.12 to 0.14 cm/yr (Fig. 3), after European contact, which is consistent with the known history. Magnetic properties of sediments can provide additional constraints on erosion since superparamagnetic magnetite is produced during pedogenesis in watershed soils (Oldfield et al. 1985). As a result, pedogenic ferromagnetic minerals have been shown to be a mixture of superparamagnetic and single-domain grains with elevated X_{FD} values, perhaps as high as

10% (Mullins 1977). Reworked glacial sediments and anthropogenically-produced magnetic particles (combustion of coal and other fossil fuels, etc) contain mostly single and multi-domain grains, with low X_{FD} . Therefore, soil-derived magnetic particles will contain larger frequency dependence than magnetic particles from other sources.

Utilizing this simple magnetic model, we identified zones in the stratigraphic record that are above and below a 3% criterion, representing a lower analytical threshold for detection of superparamagnetic grains. In the early part of the record (pre-contact), most of the samples do not display significant frequency dependence, suggesting that soil erosion was reduced during this interval in time. Soil fluxes increased after settlement (evidenced by more frequently elevated X_{FD} values) and became much more frequent at the beginning of the 19th century (Fig. 4).

With increased erosion on the land, we expected an increase of organic matter with characteristics of terrigenous vegetation to be evident. OM does not increase from pre-contact through the 18th century and is a minor component of the sedimentary record, with mean values of $1.33 \pm 0.36\%$. The organic matter was composed primarily of marine algae, as interpreted from $\delta^{13}C$ and OC/N values, and not of terrigenous origin. These results suggest that the organic proxies are insensitive to the early changes known to have occurred on land, and that magnetic and sedimentation data are moderately sensitive to the changes. There are a number of possibilities for these discrepancies. First, it is possible that erosion associated with early farming practices was smaller than expected and that the impacts were minimal. Second, much of the material eroded from the watershed may not be transported to the depositional site that we sampled. This possibility could be explained by a combination of two phenomena. First, it is possible that the early dams associated with lumber mills may have sequestered much of the sediment within their impoundments, thus prohibiting its transport and deposition in the central portion of the sound. There is also a possibility that sedimentation occurred further up-estuary. Salem Sound is well mixed, with coring site salinities of 29-30 psu. The estuarine turbidity maximum (ETM) zone, associated with the front between fresh and salt water, is further upstream on the small tributaries of the system. Clays and OM are known to flocculate and become deposited in the ETM zone, it is possible the early sedimentary signal simply did not reach our coring site.

A step shift was crossed in a number of organic proxies at the end of the 18th century, concomitant with an inflection in the OM record (Fig. 4 and 6). During the 19th century the population of the region experienced a large increase. During this century, OM increased in the core record to 5.71%, and an average value of $3.61 \pm 1.09\%$. Since the clay content is low throughout the core, this increase in OM is interpreted as a productivity signal, and not a grain-size artifact. PC1 shows a clear increase in productivity over the century. A decrease in $\delta^{13}C$ and increase in OC/N early in the century (increased PC2) provide constraints to the origin of this OM. These shifts are indicative of mixing of additional C3 terrestrial vegetation with marine phytoplankton. Such an influx of allochthonous material is likely due to increased erosion of land associated with human development in the watershed. The abrupt shifts in these proxies suggest that the allochthonous OM was rather non-bioavailable. Otherwise, such an influx of OM might be expected to fertilize phytoplankton in the system, which might mask the terrigenous signal recorded here.

In addition to the increased OM and changing provenance, we observe an increase in sedimentation rates to 0.22 cm/yr at the beginning of the 19th century. The increased sedimentation, coupled with the abrupt shift to a more terrigenous signature of the organic matter, suggests new influx of sediment from the watershed. Development along the shoreline increased markedly starting at the end of the 18th century as wharves were constructed and tidal land was filled (Bowditch 1834; Perley 1933). These activities would have remobilized sediments and soils on the shoreline, seaward of the dams and ETM zone that may have restricted sediments from earlier agriculture from reaching the central sound. This sediment reworking occurred due to shoreline development associated with the international maritime trade industry, and the subsequent industrialization of the region.

An additional component of the agricultural activity is livestock. The numbers of these animals increased through the colonial and pre-industrial time as population increased and soil resources became stressed. Data from nearby Salisbury, MA show that from 1680 to 1771 the number of cattle and pigs increased by 120% and the number of sheep increased by 340% (Vickers 1994). Mammals tend to enrich nitrogen through trophic fractionation, with diet to fecal matter $\delta^{15}\text{N}$ values of +3.0‰ to +3.1‰ for sheep (Sutoh et al. 1993; Wittmer et al. 2011), +0.4‰ to +2.0‰ for cattle (Steele and Daniel 1978; Sutoh et al. 1987), and +1.2‰ for pigs (Sutoh et al. 1987). There may have been an additional source of enriched nitrogen from the cod waste associated with the salting process (heads, guts), since the higher trophic status of this fish likely produced more enriched organic matter. Salem Sound $\delta^{15}\text{N}$ data appear sensitive to the enriched nitrogen source from the watershed, and a trend is observed from European contact until industrial times (Fig. 4).

The $\delta^{34}\text{S}$ record largely mimics the OM record from European contact until the mid-20th century (Fig. 4), which is supported by the tight correlation between OM, $\delta^{34}\text{S}$, and PC1 (Fig. 6A). All $\delta^{34}\text{S}$ values are very depleted as compared to marine sulfate values of +21.24‰ (Tostevin et al. 2014). Further, they are much more depleted than expected terrestrial source matter, as estimated by mean values of +1.00‰ to +9.20‰ in a comprehensive study of the Susquehanna River watershed (Cravotta 1997). These observations suggest that sulfate is being reduced by sulfate reducing bacteria in the sediments of Salem Sound. Such reduction has been shown to fractionate sulfur, with sulfide values typically ~40‰ more depleted than the parent sulfate, consistent with the significant depletion in $\delta^{34}\text{S}$ of sediment core samples as compared to POM samples (Fig. 5C). In cases of abundant sulfate availability (*i.e.* marine/estuarine environments) fractionation is more pronounced (*i.e.* up to 60‰) when reaction rates are slow, as would be expected in environments with limited organic matter and/or available Fe, and less pronounced when reaction rates are accelerated. The beginning of the Salem Sound record, when $\delta^{34}\text{S}$ is ~ -30‰, organic matter concentrations were small and likely limited sulfate reduction rates. As organic matter increased, $\delta^{34}\text{S}$ became less depleted, likely a result of more efficient sulfate reduction rates.

Record of Sewage Treatment Practices

The 20th and early 21st centuries are highlighted by a stabilization of population in the region, and the onset of sewage management in the watershed. In this section we will assess

the proxy record of OM and how it corresponds to the known changes in sewage treatment practices. Proxy data during this period include much higher and more variable OM concentrations ($9.46 \pm 2.13\%$ for the period; Fig. 4). Further, $\delta^{13}\text{C}$ and OC/N values approach pre-anthropogenic baseline values, suggesting a return to phytoplankton dominance of the OM preserved. PCA analysis suggests an increase in productivity (PC1) along with a return to a phytoplankton-dominated source of the organic matter (PC2) (Fig. 6).

An outfall pipe was constructed in 1905 to deliver raw sewage to the region of Haste Rock, just west of the Haste core location (Fig. 1). In the proxy data, an abrupt increase in OM occurs at the beginning of the 20th century and is likely associated with this outfall pipe. We interpret that this direct transport of sewage to the core location increased available nutrients, and fertilized previously nutrient-limited phytoplankton in the sound. In 1925 the pipe was extended as SESD was established. At this time in the core record, our proxies appear to reach a new status with higher OM preserved. The likely reason for the contemporary nature of this shift is two fold: first, the outfall became more proximal to the core location, and second, the establishment of SESD likely encouraged more people to hook into the sewer system.

In 1977 SESD began primary sewage treatment prior to discharging effluent at the Haste Outfall. Through this process, sludge (which would previously help fertilize the waters of Salem Sound) was removed, limiting the nutrient input to the system. A significant decrease in OM after 1977 from $10.61 \pm 2.53\%$ during the time of raw sewage input to $8.06 \pm 1.63\%$ (Mann-Whitney: $z = -2.221$; $p = 0.026$), demonstrates that OM is sensitive to this change and clearly illustrates the role that sewage has in primary productivity during the 20th century. The composition of the OM ($\delta^{13}\text{C}$ and OC/N) after the shift to primary treatment suggests a shift to organic input similar to that of the 19th century, in which allochthonous material was more significant than prior to European settlement. SESD upgraded to secondary treatment in 1998, and this change is represented by the three uppermost samples of the core record. Organic matter decreases to $7.72 \pm 0.84\%$ in these three samples, and $\delta^{13}\text{C}$ and OC/N data suggest a further shift toward 19th century-like organic matter. Organic matter in these three samples is not statistically different from that during the time of primary treatment (6.72 ± 0.84 vs. $8.06 \pm 1.62\%$; Mann-Whitney: $z = -1.237$; $p = 0.216$). Organic matter since secondary treatment is statistically reduced as compared to the period of raw sewage input (6.72 ± 0.84 vs. $10.61 \pm 2.53\%$; Mann-Whitney: $z = -2.516$; $p = 0.012$), but is still significantly higher than the period prior to construction of the effluent pipe (6.72 ± 0.84 vs. $2.61 \pm 1.33\%$; Mann-Whitney: $z = -2.834$; $p = 0.005$).

Further information on the spatial effects of the effluent pipe is afforded by examining all three sediment cores from Salem Sound (Fig. 8). Before the sewage discharge pipe was constructed, Salem Sound displayed a sedimentation pattern in which low DBD values and higher OM were deposited in the inner harbor, while further from shore DBD increased as OM contribution decreased (Fig. 8). Since the sewage pipe installation in 1905, a pattern of increased effects is observed as one moves closer to the point source (Fig. 8). Only the Haste and outer harbor cores display significant increases in OM since the construction of the pipe, with the Haste core showing the more dramatic increase in OM. In fact, since the

construction of the pipe, the Haste OM ($9.66 \pm 4.32\%$) is not significantly different from that of the inner harbor ($8.87 \pm 1.58\%$) (Fig. 8; Mann-Whitney: $z = -1.809$; $p = 0.071$).

All three core locations display significant decreases in DBD since the construction of the sewage pipe, although Haste has the most dramatic decrease (Fig. 8). Dry bulk density variability is influenced by both the relative contribution of sedimentary components, *i.e.* organic vs. siliciclastic matter, and by the degree of post depositional compaction. Due to the compaction influence, it is not surprising that all three locations display a significant decrease in DBD at the top of the core. The magnitude of the Haste step-shift decrease, however, is unusual and further supports the conclusion that the nature of sedimentation in this region of Salem Sound has fundamentally been altered by the construction of the Haste sewage outfall pipe.

These observations demonstrate that the effects of sewage discharge to Salem Sound are relatively local to the point source. The reason for the localized signal is likely due to the high flushing rate of the sound that has the effect of purging the estuarine system rather quickly of excess nutrients, thereby limiting the signal primarily to the region of the effluent pipe. Primary and secondary treatment of the waste has significantly reduced the OM at the Haste site, however OM is still significantly elevated from baseline, or even 19th century conditions.

Record of Industry

Much of the industrial history of the Salem Sound region is tied to the leather tanning industry. Peabody, MA, within the Salem Sound watershed, was the world's major supplier of leather products for close to 5 decades, peaking from 1900-1930 CE, and declining after World War II (Cultrera et al. 1991). In 1972, the Environmental Protection Agency passed the Clean Water Act, which had large effects on the industry.

The down-core metals data (Fig. 7) and the summarized PCA results of the metals time series (Fig. 6B) clearly record the industrial history of the region. PC1, which describes 81.3% of the variability in the metals series, is driven by the concentrations of Cr, Pb, Zn, and Cu, all known to be utilized in the tanning process (Mwinyihija 2010). Although there are likely other anthropogenic sources of these metals, the tight coupling suggests that these metals have a common source, most likely the local tanneries. Further, there is clear separation on the PCA biplot between samples representing the early part of the record, those deposited during the major tannery operations, and those deposited after the Clean Water Act of 1972. By 1855, there were 51 leather tanning facilities in the region (Fig. 7), and PC1 started to increase from background levels (Fig. 6C). PC1 climbs exponentially until a peak value in 1918, in line with the 1919 designation of Peabody as the largest leather producer in the world. PC1 is relatively steady through World War II, and then decreased relatively steadily from the late 1950s to present. Although clay content can affect metal concentrations in sediment due to affinity of some metals to clay particles, the low clay content in the core (Fig. 2) suggests that the metals curves represent changes in metal input, not a grain-size artifact. The maximum subsurface enrichment factors from baseline at the Haste site are: Cr: 105; Pb: 10; Zn: 12; Cu: 12, and Ni: 2.4.

The extent of contamination in this system is afforded by placing the individual metal concentration in context with sediment quality guidelines (SQGs). In marine and estuarine sediments, SQGs have been established to define concentrations of a given contaminant that have a biological effects range-low (ERL) and those that have a biological effects range-median (ERM) (Long et al. 1995). Although SQGs for metals have been established using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses, we interpret that for non-regulatory purposes our XRF concentrations compare adequately. Utilizing these SQGs, it is evident that the level of historic and legacy pollution is large (Fig. 7). All metals analyzed have exceeded the ERL value in the record. Cr and Pb have both exceeded the ERM value as well, with Cr peak values of 4534 ppm in the early 1930s more than 12 times the ERM value (Long et al. 1995). Such a high concentration of Cr is remarkable: for comparison, it is an order of magnitude higher than the highest Cr concentration (666 ppm) reported from Boston Harbor (MacDonald 1991).

The metals are a legacy contaminant despite the reduction in concentrations in sediments deposited since the height of the tanning industry. Modern surface enrichment factors are: Cr: 11.3, Pb: 2.4; Zn: 2.7; Cu: 2.6, and Ni: 1.3. Surface enrichment factors demonstrate that the modern bottom of the region of Salem Sound has elevated metals concentrations as compared to the baseline conditions one might expect in Salem Sound based on our sediment core analyses. Further, surface sediment values of Cr exceed ERM values, and Pb and Ni both exceed ERL values. Such legacy contamination is relevant in Salem Sound due to a shellfish harvesting ban for human consumption, with no clear mechanism for ending such a ban.

As the tanning industry was in decline, a coal-burning power plant was constructed in Salem in 1952. The activity of coal combustion has been recorded in the sedimentary record, primarily in κ , X_{FD} and $\delta^{34}S$. Samples deposited prior to the 1952 construction of the Salem Power plant are characterized by κ values of $5.7 \pm 1.0 \times 10^{-5}$ SI units, and X_{FD} values of $2.1 \pm 1.5\%$. Samples deposited after 1952 are characterized by κ values of $11.6 \pm 3.7 \times 10^{-5}$ SI units, and X_{FD} values of $1.1 \pm 1.0\%$. Mann-Whitney tests reveal that the differences pre- and post- power plant construction are significant for both κ and X_{FD} ($z = -4.989$; $p < 0.001$, and $z = -2.350$; $p = 0.019$, respectively). These results are consistent with increased fluxes of fly ash from coal combustion at the plant, as fly ash is characterized by increased κ , and negligible X_{FD} due to the oxidation of Fe resulting in the production of multi-domain magnetite particles (Evans and Heller 2003; Heller et al. 1998).

Further, $\delta^{34}S$ has an inflection point in the record in the mid-twentieth century that cannot be explained by the covariance of organic matter and $\delta^{34}S$ in the earlier record (*i.e.* PC1, Fig. 6A). From this inflection point to almost the top of the core, $\delta^{34}S$ become more depleted to a low of *ca.* -25% . Coal $\delta^{34}S$ normally average between -26% and -23% (Sharp 2006). Significant input of such depleted $\delta^{34}S$ values appear to have influenced the sedimentary $\delta^{34}S$ since the construction of the power plant. The uppermost relatively enriched $\delta^{34}S$ value may be a result of this sample being above the redox boundary of the sedimentary column and not fully reduced.

Perspective on Current State of Salem Sound

It is clear from the historic and stratigraphic records that humans have had impacts on Salem Sound through land use changes, sewage disposal practices, and industry, and that the sedimentary proxy record has preserved evidence of this history. Over the past decades, steps have been made to improve the quality of this coastal system, in large part associated with the Clean Water Act of 1972. In 1998 SESD upgraded to secondary sewage treatment. This step, in combination with primary treatment started in 1977, has reduced the amount of OM in Salem Sound. However, the stratigraphic record demonstrates that this reduction is not sufficient to bring the system to baseline, or even pre-industrial conditions. Salem Sound currently experiences reduced water quality associated with turbid conditions and phytoplankton blooms (Hubeny et al. 2017), and nutrients from the SESD outfall pipe likely contribute to the productivity. Based on our core results, the response time of estuarine productivity to upgrades in sewage treatment practices is short, however the introduction of effluent still provides nutrients to the system. A true recovery to baseline conditions of organic input is unlikely in Salem Sound due to the population and associated organic waste. Our results suggest that a readjustment period is short and that further mitigation efforts will result in decreased organic matter quickly.

The legacy contamination of Salem Sound, as investigated through metals concentrations, is also a note of concern. The demise of the tanning industry has resulted in a decrease in metals concentrations in the upper portion of the sediment column. The combined effects of a slow sedimentation rate (0.22 cm/yr) and likely remobilization of contaminants from elsewhere in the watershed/embayment have kept the concentrations relatively high, particularly for Cr. These results demonstrate that Salem Sound is still within the recovery period of the historic contamination almost forty years after regulation terminated the direct input of metals into Salem Sound. One of the regions economically valuable infauna, *Mya anenaria*, is known to burrow up to 25 cm into intertidal sediments (Blundon and Kennedy 1982), which would expose such organisms to the maximum concentration depth zone (~10-25 cm) observed in Salem Sound. If we assume a lack of bioturbation or remobilization of the legacy metals, we can project the recovery period forward using sedimentation rates and depth zones of infauna. We calculate that it would take close to 115 years to accumulate 25cm of sediment. This is a minimum estimate of recovery time, however, since remobilization of legacy contaminants is apparent from the elevated concentrations noted at the top of the core.

Conclusions

The goal of this study was to ascertain the extent to which the stratigraphic record of a mesotidal urban estuary preserves a record of anthropogenic alterations to the coastal system. We were able to demonstrate that a multi-proxy approach using dated sediment cores yielded a record of human activity since European contact that is consistent with the historic record due to the sensitivity of specific proxies to anthropogenic forcings. Further, we were able to quantify the effects of the forcings on the system and to document the recovery of the system associated with conservation practices. We conclude that modern conditions in Salem Sound are improved over those experienced during previous centuries,

however proxy data reveal significant differences between the modern conditions and those of pre-anthropogenic baseline conditions reconstructed from the older portion of the sediment record. This study can serve as a model for the investigation of anthropogenic impacts on other such coastal embayments, including ones with a less robust historic record.

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Fig. 1. Locus map and bathymetric chart of Salem Sound, MA. Inner harbor (SH10), outer harbor (SHM10), and Haste (HO10) core locations shown with black dots. Modern SESD sewage outfall (hollow square), Salem power plant (hollow hexagon), and North River are also noted

Fig. 2. Stratigraphic plots of organic matter (OM), dry bulk density (DBD) and volume magnetic susceptibility (κ) for the three Salem Sound sediment cores. Grain size plot shows cumulative percent clay, silt, and sand from ten samples in the Haste core (note that clay percentage is too small to note variability at this scale). Haste stratigraphy defines distinct color zones in the Haste core (see text)

Fig. 3.

Age vs. depth models for Haste Outfall core (HOIO), Outer harbor core (SHM10), and inner harbor core (SH10). Age constraints from ^{210}Pb CIC age model, AMS ^{14}C dates, ^{137}Cs , ^7Be , Ambrosia pollen, and Haste core benzotriazoles (Cantwell et al. 2015) chronostratigraphic horizons. Darker gray shading represents more likely calendar ages, and outer dashed lines represent 95% confidence intervals

Fig. 4.

Physical and organic sediment proxy data from Salem Sound Haste core. From left to right: volume magnetic susceptibility (κ), frequency dependence of magnetic susceptibility (X_{FD}), dry bulk density (DBD), organic matter (OM%), Salem population *1000 (US Census data), stable carbon isotopic composition ($\delta^{13}C$), organic carbon: nitrogen ratio (OC/N), stable nitrogen isotopic composition ($\delta^{15}N$), stable sulfur isotopic composition ($\delta^{34}S$), and organic carbon: sulfur ratio (OC/S). Age model from Fig. 3. Horizontal Events include time periods (vertical boxes): pre-European contact (Pre-contact), Agricultural and fishing industry (Agriculture), International Maritime Trade (Maritime), Industrial period (Industrial), and post-Clean Water Act (CWA); and specific events (horizontal lines): European contact (EC), construction of Haste sewage pipe (SP), construction of Salem power plant (PP), Start of primary sewage treatment (PT), and start of secondary sewage treatment (ST)

Fig. 5. Box and whisker plots of isotopic (A) $\delta^{13}\text{C}$, (B) $\delta^{15}\text{N}$, (C) $\delta^{34}\text{S}$, and elemental ratios (D) OC/N, and (E) OC/S data from Salem Sound. Inner Harbor, Outer Harbor, and Haste refer to POM samples filtered from surface waters on 7 sampling days (May 2010 – April 2011), while Haste Core refers to data from the Haste sediment core (Fig. 4)

Fig. 6.

(A) Principal Components Analysis (PCA) of organic proxy data from Haste sediment core. Labeled vectors project the original variables in PCA space, and data symbols represent individual samples. Four chronologic zones (pre-contact, Colonial, Watershed Development, and post Haste outfall) are highlighted with 95% confidence ellipses, (B) PCA of metal concentration data from Haste sediment core. Labeled vectors project the original variables in PCA space, and data symbols represent individual samples. Three chronologic zones (Early, Tanneries, and post Clean Water Act) are highlighted with 95% confidence ellipses,

(C) Time series of Salem population (US Census data), Organic Principal Component 1 (PC1) (representing productivity, see text), Organic PC2 (representing organic matter source, see text), and Metals PC1 (representing industrial activity, see text). Vertical gray lines highlight the time of European Contact (settlement), construction of Haste sewage discharge pipe (pipe), and the Clean Water Act (CWA)

Fig. 7.

Metals concentration data from Salem Sound Haste core. From left to right: volume magnetic susceptibility (κ), dry bulk density (DBD), organic matter (OM%), lead concentration (Pb), chromium concentration (Cr), Zinc concentration (Zn), copper concentration (Cu), nickel concentration (Ni), Principal Component 1 of metals PCA analysis (PC1, Figure 6), Salem population *1000 (US Census data), number of Peabody leather workers (triangles), and Peabody leather factories (squares). All metals concentrations reported in parts per million (ppm) normalized to dry mass sediment, and error bar show standard deviation of three replicate analyses. Age model from Fig. 3. Vertical gray boxes highlight the historic times of International Maritime Trade (Maritime), Tannery Industry (Tanneries), and the Clean Water Act (CWA). Metal concentrations exceeding effects range-low (ERL) shaded light gray and those exceeding effects range-median (ERM) shaded dark gray (Long et al. 1995)

Fig. 8.

(A) Organic matter and (B) dry bulk density data (mean with standard deviation error bars) from three core locations in Salem Sound, separated into samples deposited before (gray square) and after (black circle) construction of Haste sewer outfall pipe in 1905.

Significance (p values) of Mann-Whitney between before and after data are shown for each proxy at each core location (see text)

Table 1

Sediment core metadata from Salem Sound, including location, geographic coordinates, core length, and analyses performed on each core

Core	Location	Latitude	Longitude	Core Length (m)	Analyses
HO10KC1	Central Sound	42°32.11'N	070°49.81'W	1.00	Multi-proxy, ¹⁴ C
HO10KC2	Central Sound	42°32.11'N	070°49.81'W	0.51	²¹⁰ Pb, ¹³⁷ Cs, ⁷ Be
SHM10KC1	Harbor Mouth	42°31.31'N	070°51.95'W	0.87	Multi-proxy, ¹⁴ C
SHM10KC2	Harbor Mouth	42°31.31'N	070°51.95'W	0.76	²¹⁰ Pb, ¹³⁷ Cs, ⁷ Be
SH10KC1	Inner Harbor	42°30.75'N	070°52.48'W	1.24	Multi-proxy, ¹⁴ C
SH10KC2	Inner Harbor	42°30.74'N	070°52.46'W	0.60	²¹⁰ Pb, ¹³⁷ Cs, ⁷ Be

Table 2

Radiocarbon chronostratigraphic data from Salem Sound. All analyses were conducted at the University of Arizona AMS Facility. Calibrations were calculated using the CALIB 7.1 program using Marine13 and IntCal13 calibration datasets (Reimer et al. 2013)

Core	Depth (cm)	Lab ID	Material	$\delta^{13}\text{C}$	^{14}C age (yr BP)	Delta R	2 σ calibrated age (yr A.D.)	Relative area under distribution	Calibration Dataset
HO10 KC1	72.5	AA93757	Bivalve shell fragments	1.0	746 $\pm$ 35	60 $\pm$ 15	1525-1687	1.000	Marine13
SHM10 KC1	79	AA92034	Wood	-26.3	1,553 $\pm$ 39	N/A	417-590	1.000	IntCal13
SH10 KC1	110	AA92033	Vascular organic matter	-9.9	793 $\pm$ 98	N/A	1027-1318 1352-1390	0.943 0.057	IntCal13

Table 3

Summarized table of known historic events and timing in Salem Sound region, the proxy signature preserved, and the forcing agent responsible for the proxy record. See text for detailed discussion of events and proxy record

Historic Event	Timing in Salem Sound	Proxy Signature	Forcing Agent
Coal-burning power plant	1952 - 2014	<ul style="list-style-type: none"> • Increased κ • Reduced X_{FD} • Reduced $\delta^{34}S$ signal 	Flux of fly ash with specific magnetic properties
Secondary sewage treatment	1998	<ul style="list-style-type: none"> • Decrease in organic matter • $\delta^{13}C$ decrease and OC/N increase 	Secondary treatment further reduces nutrient fluxes to Salem Sound
Primary sewage treatment	1977	<ul style="list-style-type: none"> • Decrease in organic matter • $\delta^{13}C$ decrease and OC/N increase 	Primary treatment decreases nutrient fluxes to Salem Sound allowing relative allochthonous component of OM to increase
Input of raw sewage	1905	<ul style="list-style-type: none"> • Increased organic matter deposition • $\delta^{13}C$ increase and OC/N decrease • Separation in PC space from previous conditions • $\delta^{34}S$ continues to become less depleted and parallels OM 	Release of raw effluent to Haste Outfall fertilizes marine algae
Tanning industry, manufacturing population growth	1850-1970s	<ul style="list-style-type: none"> • Increased trace metal concentrations, particularly Cr, Pb, Zn, Cu • Separation in PC space once tanneries start operations and a second PC shift closer to background after CWA regulations 	Release of metal salt waste from tanning process into tributary rivers with slow reduced inputs of metals after CWA and reduction of tanneries
Maritime trading industry, continued agriculture, population growth	1780-1850	<ul style="list-style-type: none"> • Increased organic matter • Step-wise $\delta^{13}C$ decrease and OC/N increase • $\delta^{15}N$ becomes more enriched • $\delta^{34}S$ becomes less depleted and parallels OM • Increased number of elevated X_{FD} events • Separation in PC space from previous conditions 	Erosional input of allochthonous organic matter and sediment due to land development, especially associated with shoreline development
European contact: Initial agriculture and fishing industry in watershed	1626-1780	<ul style="list-style-type: none"> • <i>Ambrosia</i> horizon at contact • OM fairly steady • Slight increase in $\delta^{15}N$ and OC/N and decrease in $\delta^{13}C$ • Single event of increased X_{FD} • Lack of separation in PCA analysis from pre-contact 	Agriculture and land use change in watershed as agriculture is established; Livestock became more important during 18 th century
Pre-European contact	Pre-1626	<ul style="list-style-type: none"> • "background" or baseline conditions are established in this portion of the record 	Natural variability with minor influence by Native Americans