Multi-faceted monitoring of estuarine turbidity and particulate matter provenance: Case study from Salem Harbor, USA

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Abstract

Turbidity is a water quality parameter that is known to adversely affect aquatic systems, however the causes of turbid water are often elusive. We present results of a study designed to constrain the source of particulate matter in a coastal embayment that has suffered from increased turbidity over past decades. Our approach utilized monitoring buoys to quantify turbidity at high temporal resolution complemented by geochemical isotope analysis of suspended sediment samples and meteorological data. Results reveal a complex system in which multiple sources are associated with particulate matter. Weight of evidence demonstrates that phytoplankton productivity in the water column, however, is the dominant source of particulate matter associated with elevated turbidity in Salem Harbor, Massachusetts. Allochthonous matter from the watershed was observed to mix into the pool of suspended particulate matter near river mouths, especially in spring and summer. Resuspension of harbor surface sediments likely provides additional particulates in the regions of boat moorings, especially during summer when recreational boats are attached to moorings. Our approach allows us to constrain the causes of turbidity events in this embayment, is helping with conservation efforts of environmental quality in the region, and can be used as a template for other locations.

Key words: (up to 6) stable isotopes, phytoplankton, water quality, monitoring buoy, time series analysis, Salem Sound

1. INTRODUCTION

Turbidity, which is an optical property that quantifies light transmission through the water column, is a key water quality parameter due to its direct influence on the photosynthetic compensation depth. Specific ecologic effects of high turbidity, and associated suspended particulate matter, include light limitation of submerged aquatic vegetation such as eelgrass (Dennison et al., 1993; Moore et al., 1997; Nielsen et al., 2002; Olesen, 1996) and the associated reduced dissolved oxygen; increases in water temperature as particles suspended absorb and scatter sunlight (Paaijmans et al., 2008); various effects on

pelagic and benthic invertebrates associated with clogging of filtration systems, burial, and substrate alteration (Wilber and Clarke, 2001; Zweig and Rabeni, 2001); and effects on fish through gill clogging and associated reduced resistance to disease, and stress to migrating, spawning, and developing fish eggs and larvae (Newcombe, 2003; Newcombe and Jensen, 1996; Wilber and Clarke, 2001).

A number of studies have identified major causal factors that may contribute to elevated turbidities in coastal waters. Elevated turbidities are frequently attributable to resuspension of bottom sediments (Koch, 2001; Newell and Koch, 2004). Resuspension may occur by a number of mechanisms such as heavy wind, tidal currents, precipitation, and storm events over the water surface (Davis et al., 2004; Mitchell et al., 2003; Ogston et al., 2000; Uncles and Stephens, 1993), and the persistent shift of boat moorings (Hastings et al., 1995; Walker et al., 1989). Moreover, turbidity may also result from the suspension of allochthonous material flushed in from the watershed via storm water runoff and elevated stream discharges (Berto et al., 2013; Dalzell et al., 2005). Finally, numerous studies have found that elevated turbidities in coastal waters indirectly result from chronic nitrogen eutrophication, which leads to phytoplankton blooms that block light transmission through the water column (e.g. Cederwall and Elmgren, 1990; Kemp et al., 1983; Lapointe and Clark, 1992; Nixon, 1995). In order to address elevated turbidities in coastal systems, it is important to tease out the balance of different mechanisms that are forcing turbidity dynamics in a given system (Chen et al., 2005; Mitchell et al., 2003; Uncles and Stephens, 1993).

Turbidity has become a water quality parameter of concern in Salem Sound, Massachusetts (USA) over recent decades. This concern has led to funding from Massachusetts state agencies with the applied goal of constraining the dominant source of particulate matter in the coastal embayment so that a remediation strategy can be developed. Of note, *Zostera marina*, a species of submerged aquatic vegetation known for its importance in ecosystem services (Kemp et al. 2004, Heck et al. 1995), has experienced the largest decline in Salem Sound of any coastal region in Massachusetts since 1995 (Costello and Kenworthy, 2011). Over this time turbidity at the harbor mouth has increased, with Secchi depth measurements declining from 3.5 meters in 1997 (Chase et al., 2002) to 3.2 meters in 2010 - 2011

(unpublished data). Further, a station within inner Salem Harbor had an average Secchi depth value of 2.5 meters in 2010 – 2011, demonstrating comparatively high turbidity within the inner harbor. Although not definitive, the connection in timing between turbidity increases and eelgrass declines warrant the further study of turbidity in Salem Harbor.

Various tools have been used by coastal oceanographers to determine the origin of particles that lead to turbid conditions in coastal embayments. Continuous turbidity sensors, automated sensors, and remotely sensed data have had success in generating time series of turbid conditions in various systems (Glasgow et al., 2004; Mitchell et al., 2003), however information on suspended particulate matter (SPM) provenance is often desired. Numerous studies have studied the role of nutrients and phytoplankton in coastal turbidity zones to better understand spatio-temporal dynamics of this potential driver for turbid conditions (Bužancic et al., 2016; Carstensen et al., 2015; Llebot et al., 2011; Lugoli et al., 2012; Meler et al., 2016; Reed et al., 2016). In addition, modeling efforts have been used to better constrain forcings on phytoplankton for a particular system (Artigas et al., 2014). Although SPM consists of a mixture of organic and mineral particles, quantifiable proxies of the particulate organic matter (POM) fraction of the SPM has yielded robust constraints on the provenance of the particulates. Successful approaches have included the study of particulate organic carbon (POC) and nitrogen from elemental (Etcheber et al., 2007; Veyssy et al., 1999) and isotopic (Berto et al., 2013; Savoye et al., 2003) perspectives.

The objective of this study is to utilize a multi-faceted approach to constrain the causes of turbid estuarine conditions using monitoring buoys, stable isotopic analyses of SPM, and meteorological data. Specifically we addressed the causes of increased turbidity in Salem Harbor, an urban mesotidal coastal embayment north of Boston, Massachusetts, USA. As compared to more sophisticated automated sensors and remotely sensed data (e.g. Glasgow et al., 2004), this approach did not have large start up and maintenance costs, and it directly addressed the provenance of particulate matter in the water column. The four hypotheses examined in this study are:

1. Elevated turbidities are associated with resuspension of seafloor surface sediments, caused by either a) shift in mooring chain position on the seafloor as wind events consisting of high velocities and shifts of prevailing direction occur, or b) tidal currents.
2. Elevated turbidities are caused by precipitation events and associated increases in storm water runoff and stream discharge, both of which transport allochthonous matter to the water body..
3. Elevated turbidities are caused by phytoplankton blooms.
4. Elevated turbidities are caused directly by turbid sewage effluent from a local wastewater treatment facility's (WWTF) discharge pipe.

2. METHODS

2.1 Project Location

Salem Sound (Fig. 1) is a vertically mixed drowned river estuary with semi-diurnal tides (2.75 meter range). It is approximately 24 km northeast of Boston, MA, is relatively large (35.6 km²) and shallow (mean depth 9.15 m). Average surface salinity from eight discrete sampling days in 2010-2011 was 30.2 ± 0.3 psu (unpublished data). Freshwater inflow was reported in 1997 to average 1.10 m³/s from the local WWTF and 0.99 m³/s from rivers (Chase et al., 2002). Salem Harbor, the focus of this study, constitutes the lower portion of the Sound between Marblehead and Salem, draining the Forest and South River watersheds with 1997 average discharges of 0.044 m³/s and 0.051 m³/s, respectively (Chase et al., 2002). As a result of the large tidal range and small fluvial input, approximately 70% of water in Salem Sound is exchanged over the course a tidal cycle (Jerome et al., 1967), implying a relatively rapid flushing rate (on the order of approximately two days) in Salem Harbor (Chase et al., 2002). Mean dissolved oxygen in surface waters was found to be >100% throughout the year in 1997, and bottom water dissolved oxygen never dropped below 75.3% (Chase et al., 2002). Annual 1997 chlorophyll *a* concentrations averaged 1.24 ± 0.29 µg/l (n=15), and had a greater than four fold increase in concentration in July – September as compared to the rest of the year (Chase et al., 2002) Data collection

occurred at five buoys in the harbor, and nine additional sites from inland waters and shore side storm water outfalls (Fig. 1, Table 1).

The Salem region has been glaciated multiple times during the Quaternary Period, and ice most recently retreated by *ca.* 16,500 $\pm$ 700 cal BP (Ridge, 2003; Ridge, 2004; Stone et al., 2004), resulting in a thin veneer of glacial drift throughout the watershed (Kaye, 1978). From the mid-18th to mid-19th century, Salem was a major international maritime port, and by the end of the 19th century the region had shifted toward an industrial base. In 1905 a sewage outfall pipe was constructed to transport raw sewage to the central portion of Salem Sound (Wright, 1935). 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 started in 1977 (Chase et al., 2002), and in 1998 SESD upgraded to a secondary treatment WWTF and added a diffuser to the outfall pipe. Currently the watershed is urban, with residential, commercial, industrial, and urban land use accounting for nearly 60% of land area (Chase et al., 2002). The population of the watershed has remained stable at ~170,000 since the mid-1960s (Chase et al., 2002).

2.2 Analytic approach

We investigated the major contributions to elevated turbidities using two methods: 1) characterization of turbidity trends using multiprobe sensors housed in buoys (readings every 15 minutes), and 2) characterizing the provenance of suspended particulate matter by stable isotope analysis of particulates from the harbor and from adjoining freshwater inputs. The first approach permits the characterization of elevated turbidity in terms of event frequencies and magnitudes, with events defined as turbidity readings or sequences of readings above a critical threshold of 15 nephelometric turbidity units (NTU). This paradigm will enable analysis of the frequency and magnitude of events throughout the year, yielding a more nuanced understanding of seasonal turbidity conditions in Salem Harbor.

The second approach, geochemical analysis of stable isotope signatures, will enable the validation of findings yielded by the event analysis and will independently enable an assessment of the origins of the particulates causing elevated turbidities. In coastal environments, organic matter is a significant

component of total suspended particulate matter. Due to trophic and biogeochemical factors, particulate organic matter can be identified to a geographic or taxonomic source by use of geochemical proxies. These proxies include the elemental concentrations and ratios of carbon, nitrogen, and sulfur (CNS) as well as the relative concentrations of heavy and light stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$) (Bates et al., 1995; Chambers and Trudinger, 1979; Cline and Kaplan, 1975; Meyers, 1994; Schlesinger and Bernhardt, 2003).

2.3 Sampling protocols

2.3.1 Monitoring buoys

Continuous water quality monitoring was conducted at five moored stations in Salem Harbor from 2012-2014. Two stations were located within mooring fields (B and C), two at the mouths of the South and Forest Rivers inputs to the harbor (D and E, respectively) and the fifth was a site located just inside the mouth of the Harbor (A) (Fig. 1). Each monitoring buoy housed a Eureka Manta2 multiprobe with sensors to measure temperature, turbidity and conductivity (which was used to calculate salinity) in surface waters (0.2 meters). The temperature probe was factory calibrated. The turbidity probes were optical sensors of the type ISO 7027 with integrated wiper. They were calibrated in the field using a two-point calibration with 0 and 100 NTU calibration solutions. The conductivity probes were four-electrode sensors with graphite electrode. They were calibrated in the field using a two-point calibration with 0 and 58,670 $\mu\text{S}/\text{cm}$ calibration solutions. The Manta2 is designed for long-term deployment in marine waters and has antifouling components, such as a wiper for the turbidity sensor, though these components proved inadequate without regular maintenance. Multiprobes were configured to analyze and record each parameter at a 15-minute sampling interval. In addition to the multiprobes, one station (B) was equipped with a HOBO U20 water level sensor mounted to the buoy anchor that was corrected to atmospheric pressure to yield water level in the harbor.

2.3.2 Water sampling

Salem Harbor water samples were collected in 1-liter bottles from a boat at 0.1 to 0.2 meter depth. River water samples were collected directly into a bottle. All samples were collected during discreet field sampling dates from 2010 – 2014, and represent all seasons, although summer was the most frequently sampled season due to field access. Effluent from the SESD WWTF was sampled directly from the facility in March 2015 using the same procedures as above. Wide mouth, dark brown, 1-liter plastic bottles were used to collect the water to be tested for chlorophyll *a* (only taken during summer 2014), while opaque white 1 liter bottles were used for isotope analysis. Each of the plastic containers was field-rinsed three times with site water before samples were collected and samples were stored on ice in the field until transferred to a refrigerator at the end of the field day.

2.3.3 Bottom sediment sampling

Surface sediments were collected from 53 equally spaced sites within Salem Harbor in September and October 2013. Even spacing was ensured using a hexagonal grid overlay of the harbor (Supplemental Material). Sediment samples (upper 1cm) were collected using a Van Veen-style bottom grab sampler, stored in Whirl-Pak bags, and stored on ice in the field until transferred to a refrigerator at the end of the field day.

2.3.4 Meteorological data

A meteorological station was in operation on the roof of Meier Hall, Salem State University (Fig. 1), for the first year of this project (2012). The station provided precipitation, average wind speed, and average wind direction at 1-hour temporal resolution for this period.

2.4 Sample Analyses

2.4.1 Chlorophyll *a*

Seawater designated for analysis of chlorophyll *a* was stored on ice in the dark until filtration. All samples were filtered through a pre-combusted 47 mm 1.2 micron glass fiber filter the evening of collection. Samples were filtered until the sample was exhausted or the filter reached refusal, and the filtered volume was noted. Filters were folded in half and stored in aluminum foil packets frozen at -10°C immediately after filtration. All equipment was rinsed with deionized water between samples. Frozen samples were stored for up to eight months in the dark before being analyzed for chlorophyll *a* and phaeophytin at the Center for Coastal Studies in Provincetown, MA according to EPA method 445.0. Briefly, chlorophyll *a*/phaeophytin was extracted from the cells retained on the filter by a 16-24 hour steep in 90% acetone at 4°C. The extract was analyzed using a fluorometer. 150 µL of 0.1 N HCl was added to the extract and the extract was remeasured after 90 seconds to determine phaeophytin concentrations.

Due to extended storage time before analyses, samples may have undergone some chlorophyll degradation. In order to assess this we analyzed the ratio of phaeophytin: chlorophyll (Reuss et al., 2005). Samples with a ratio larger than 0.75 (Reuss et al., 2005) were interpreted as having large degradation affects and were not used in the analysis. Further, it is possible that the chlorophyll data presented are underestimates of true field conditions.

2.4.2 Isotope analyses

Water collected for isotope analysis was filtered as above. Stable isotope analyses were conducted at SSU's Viking Environmental Stable Isotope Lab (VESIL).

$\delta^{13}\text{C}$ samples: Filtered water samples were dried and massed, and uniformly sized sub-samples were separated from each filter using a hole punch. The sub-samples were then placed in open silver capsules and fumigated with 12M HCl in a desiccator for six hours to remove inorganic carbon components (Harris et al., 2001). The samples were then dried at 60°C and placed in tin capsules with 6mg of tungsten trioxide, crimped shut, pressed, and placed in assay trays. Sediment samples were dried,

ground, and placed into open silver capsules for fumigation with 12M HCl and subsequently treated as above.

$\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ samples: Filtered water samples were dried, massed, and filters were cut into quarters. One quarter from each sample was placed in a tin capsule, crimped, pressed, and placed on assay trays. Sediment samples were dried, ground, placed into tin capsules, massed, pressed, and placed on assay trays.

All prepared samples were analyzed using a continuous flow Elementar micro cube elemental analyzer/ Isoprime 100 isotope ratio mass spectrometer (EA/IRMS), producing data that were calibrated using USGS 40 and USGS 41 standards for $\delta^{13}\text{C}$ (VPDB) and $\delta^{15}\text{N}$ (AIR), and IAEA S2 and S3 standards for $\delta^{34}\text{S}$ (VCDT). Reference gas stability on the EA/IRMS system 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.

The isotopic composition of carbon is denoted by $\delta^{13}\text{C}_{\text{VPDB}}$, defined as:

$$\delta^{13}\text{C}_{\text{VPDB}} = \frac{R(^{13}\text{C}/^{12}\text{C})_P - R(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}}{R(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}}$$

where $R(^{13}\text{C}/^{12}\text{C})_P$ is the ratio $N(^{13}\text{C})_P/N(^{12}\text{C})_P$, and $N(^{13}\text{C})_P$ and $N(^{12}\text{C})_P$ are the numbers of the two isotopes of carbon, ^{13}C and ^{12}C , respectively, in a sample P (Coplen, 2011). In a similar manner, $R(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}$ is the equivalent carbon isotope ratio of the international isotopic measurement standard VPDB.

The isotopic composition of nitrogen is denoted by $\delta^{15}\text{N}_{\text{AIR}}$, defined as:

$$\delta^{15}\text{N}_{\text{AIR}} = \frac{R(^{15}\text{N}/^{14}\text{N})_P - R(^{15}\text{N}/^{14}\text{N})_{\text{AIR}}}{R(^{15}\text{N}/^{14}\text{N})_{\text{AIR}}}$$

where $R(^{15}\text{N}/^{14}\text{N})_P$ is the ratio $N(^{15}\text{N})_P/N(^{14}\text{N})_P$, and $N(^{15}\text{N})_P$ and $N(^{14}\text{N})_P$ are the numbers of the two isotopes of nitrogen, ^{15}N and ^{14}N , respectively, in a sample P (Coplen, 2011). In a similar manner, $R(^{15}\text{N}/^{14}\text{N})_{\text{AIR}}$ is the equivalent carbon isotope ratio of the international isotopic measurement standard AIR.

The isotopic composition of sulfur is denoted by $\delta^{34}\text{S}_{\text{VCDT}}$, defined as:

$$\delta^{34}S_{VCDT} = \frac{R(^{34}S/^{32}S)_P - R(^{34}S/^{32}S)_{VCDT}}{R(^{34}S/^{32}S)_{VCDT}}$$

where $R(^{34}S/^{32}S)_P$ is the ratio $N(^{34}S)_P/N(^{32}S)_P$, and $N(^{34}S)_P$ and $N(^{32}S)_P$ are the numbers of the two isotopes of sulfur, ^{34}S and ^{32}S , respectively, in a sample P (Coplen, 2011). In a similar manner, $R(^{34}S/^{32}S)_{VCDT}$ is the equivalent carbon isotope ratio of the international isotopic measurement standard VCDT.

2.4.3 Turbidity time-series data treatment and processing

Turbidity time-series exhibited several characteristics that justified the designation of individual turbidity readings as “events” or “non-events.” A turbidity reading was classified as an “event” when an individual reading was equal to or greater than 15 NTU, a threshold used by the Chesapeake Bay Interpretative Buoy System (<http://buoybay.noaa.gov/observations/parameters-measured>; accessed 22 June 2016) for sea grass health. The first concerning characteristic was autocorrelation between consecutive turbidity readings. Because the duration of autocorrelation was precisely known, turbidity readings could not be corrected for autocorrelation, which establishes observations as a function of a time lag between them. Therefore, consecutive 15-minute turbidity readings from the same buoy could not be treated as independent or randomly sampled. Moreover, turbidity readings taken in aggregate did not display a normal distribution, further precluding the use of individual readings in parametric statistical tests. Turbidity showed continuous stochasticity, fluctuating through time as a function of the physical conditions of the water column.

For each set of buoy-collected time-series turbidity data, the proportion of daily readings greater than or equal to 15 NTU was calculated. Additionally, an event magnitude was determined by finding the average NTU by which event-classified readings exceeded the threshold value. This enabled the calculation of turbidity event summary statistics for each range of sampling dates at each buoy (SI Table 2). These summary statistics were pooled seasonally across years and across buoys to assess general trends regarding the magnitude and duration of turbidity events in Salem Harbor.

The decision to pool turbidity datasets seasonally was based on the observation that calculated daily mean turbidities tended to reach radically larger maxima in the summer than in the winter, and that during the winter, turbidity tended to be higher during months associated with greater daily light integrals (DLI), measures of the total amount of photosynthetically active radiation (PAR) delivered per day, which was not measured locally but which can be generalized by latitude and month (Korczynski et al., 2002). Though no linear correlations could be established between turbidity and temperature during any month or season, it was nevertheless considered worthwhile to examine turbidity event duration and magnitudes by season to gain a clearer understanding of event patterns throughout the year.

Especially in spring, summer and fall datasets, there was a tendency for turbidity readings to be heavily inflated by biofouling after sensors had spent a certain period of time in the water. Although the sensors contain wiper blades designed to prevent biofouling by wiping the sensor lens, field observations revealed that marine growth on the outer sensor guard eventually grew large enough to violate the space of the sensor. At this threshold point of marine growth, the wiper blade motor was no longer strong enough to clear the growth in the zone of measurement. Plotting turbidity against the number of days the sensor had been submerged identified the threshold of biofouling. Data collected on days after which daily mean turbidities began an exponential increase and subsequently failed to fall back below a plausible maximum of 100 NTU were simply excluded from the analysis; the period before which exclusion occurred varied by dataset, ranging from 8 to 40 days depending upon the site and growing conditions.

Salinity data were processed by removing anomalous points outside the reasonable range of salinities for the harbor. Most of these points were either associated with a poor field calibration (resulting in a step function of data at the time of recalibration) or with timing of biofouling that was identified via turbidity data as described above. In the second case, biofouling that exceeded the threshold of the sensor guard would grow between the electrodes of the conductivity sensor and reduce conductivity. Once processes daily arithmetic means were calculated for analyses.

Once clipped, continuous datasets were classified by season based on the months during which the most readings were taken, although some series overlapped slightly with a different season. Winter series had majorities of data points from December, January and February; spring series corresponded to March, April, and May; summer series to June, July and August; and fall series to September, October and November.

2.4.4. Data analysis

All data were initially pooled, curated and organized in Excel.

Sample groups were established that represented marine water locations within Salem Harbor and hypothesized SPM source areas (Fig. 1; Table 1). Marine samples were divided into locations representing control, mooring field, river mouth, and shoreline samples. Source areas were divided into samples from rivers, storm water outfall, and the SESD WWTF effluent (Table 4).

Subsequently, all data analysis, statistical tests and graphs were run in R version 3.2.1 and PAST version 3.12 (Hammer et al., 2001). Selection of appropriate parametric or non-parametric hypothesis tests was made based on evaluation of dataset adherence to each tests' respective assumptions, following the statistical principles outlined in Sokal and Rohlf (2011). Statistical tests employed include two-sample Welch's T-test, linear regression, χ^2 test of independence, one-way ANOVA, and Tukey's Honest Significance Test. Spectral analyses of turbidity and tide time series were calculated in kSpectra version 3.4 using the multi-taper method, with AR(1) red noise significance testing (Mann and Lees, 1996).

3. Theory: Hypothesis Examination and Predictions

3.1 Sediment Resuspension

The likelihood of resuspension of bottom sediments by wind events via mooring shifts or tidal currents will be established by comparing the $\delta^{34}\text{S}_{\text{VCDT}}$ of suspended particulates at buoys in mooring fields to those of particulates collected from buoys outside of mooring fields as well as to sediments.

Further, time series analysis of the turbidity series as compared to tidal currents will constrain the roles of such currents on these processes. If resuspension of bottom sediments were the forcing mechanism for turbidity events, we would expect the following:

1) suspended particulates collected from the water column have similar geochemical profiles as samples collected from the surface sediments;

2) if driven by shifting boat moorings, particulate isotope profiles from the mooring fields have significantly different from samples taken outside the mooring fields.

3) if driven by tidal currents, a spectral analysis of the turbidity time series will show significant periods of variability consistent with tidal periods.

3.2 Runoff and Stream Discharge

Precipitation or storm events could initiate turbidity events by increasing the amount of storm water runoff and stream discharge into the harbor, thereby flushing the harbor with riverine sediments increasing the quantity of suspended particulate matter. This hypothesis can be tested by three methods: first, by comparing the geochemical composition of suspended particulates gathered in the harbor to particulates sampled from freshwater tributaries to the harbor. It would also be possible to establish the presence or absence of a link between precipitation and turbidity by regressing daily mean turbidity against daily precipitation data, and finally, by evaluating the possibility of an association between decreases in salinity (high-resolution proxy for precipitation events) and increases in turbidity. If this hypothesis is supported, it is expected that:

1) turbidity events are statistically correlated with precipitation events;

2) turbidity events are statistically correlated with decreases in salinity recorded by the monitoring buoys;

3) geochemical characteristics of particulate matter collected from the water column are similar to those of particulate matter collected from major inflows to the harbor.

3.3 Phytoplankton Blooms

Nutrient fluxes and seasonal light cycles may increase phytoplankton biomass and particulate matter in the water column, elevating turbidity and attenuating light through the water column. To infer whether phytoplankton blooms account for high turbidities, the geochemical signature of the organic particulate matter in the harbor will be compared to published values for coastal phytoplankton (Meyers, 1994). Moreover, seasonal turbidity trends will be evaluated to determine whether turbidity event duration and magnitudes occur during periods of peak light availability. If this hypothesis is supported, it is expected that:

- 1) Chlorophyll *a* concentrations correlate positively and significantly with turbidity;
- 2) Turbidities are most elevated during peak phytoplankton growing season (late spring through early fall, with low turbidities in winter overall).
- 3) Geochemical profiles of suspended particulate matter from the harbor match the known geochemical profiles of marine phytoplankton.

3.4 Sewage Effluent

Sewage effluent can introduce particulate matter to a system directly, or can fertilize the system by the addition of excess nutrients, and lead to phytoplankton blooms. Sewage effluent produced by WWTFs using secondary treatment have been shown to have distinct nitrogen isotopic signatures (King et al., 2008). If this hypothesis is supported, it is expected that geochemical characteristics of harbor particulate matter will closely match those of effluent from the local WWTF.

4. Results and Discussion

4.1 Salem Harbor Physical and Chemical Parameters

Average surface water values for measured physical and chemical parameters of Salem Harbor in 2012-2014 are presented in Table 3. Temperatures represent the seasonal variability in this mid-latitude

coastal system. Salinity values center at ~ 30 psu, similar to results from 2010-2011 (30.2 ± 0.3 psu). The largest standard deviation for salinity was observed at Station E, which is located at the mouth of the Forest River (Fig. 1). Turbidity values average as low as 11.0 NTU at Station C and as high as 297 NTU at Station D, and all stations have high standard deviations indicative of the dynamic nature of turbidity in Salem Harbor. The spectral analysis results of the turbidity time series and tidal variability are plotted in Fig. 2. Spectral analysis of the tidal data collected in Salem Harbor returned expected lunar periodic components 12.4 hours (M_2), and 23.9 hours (K_1), as well as the half tide peak (6.1 hours) and a higher frequency peak at 4.1 hours (Fig. 2). Spectral analyses of the turbidity time series do not show clear and significant peaks at the tidal periods (highlighted with gray in Fig. 2), however Station C had significant indistinct spectral peaks in the lower frequency portion of the broad tidal region.

Chlorophyll *a* values range from 2.8 ± 0.5 to 4.4 ± 1.1 $\mu\text{g/l}$, which are the same and higher than the highest samples recorded in 1997 (Chase et al., 2002). These values suggest that the concern of underestimation of the chlorophyll *a* data in this study due to longer than recommended holding times (Section 2.4.1) may not be large. SPM values range from 11.4 ± 4.5 to 13.9 ± 12.6 mg/l, with the highest standard deviation at Station C, within a mooring field. The percentage of POC varies from 2.7 ± 1.8 to 5.0 ± 3.5 %, within the range expected from a phytoplankton source (Veyssy et al., 1999).

POC:Chlorophyll *a* ratios center just under the 200 threshold below which phytoplankton source matter is likely (Savoye et al., 2003), however the large values and high standard deviations suggest that there are likely additional less dominant sources of organic matter in addition to phytoplankton (Fig. 3). Station E, located at the mouth of the Forest River, has a mean value of 256.2 ± 155.8 , suggesting increased influence from a terrigenous source.

Carbon biomass from water samples was calculated for Salem Harbor samples and plotted against sample month (Fig. 4). Although there is abundant variability, higher C biomass is clearly observed during the summer and fall months as compared to the winter and spring, consistent with 1997 monthly chlorophyll *a* data (Chase et al., 2002). Further, summer and fall are the seasons with the highest mean turbidity excesses over 15 NTU, and summer has the highest proportion of a given day in which turbidity

exceeds 15 NTU. Using constraining data from eight coastal system in the northern hemisphere (Carstensen et al., 2015), it is possible to constrain the C biomass for coastal phytoplankton blooms to between 30 and 600 mg C/m³. These values can be refined to a threshold of ~500 mg C/m³ by focusing on systems at approximately the same latitude as Salem Harbor, and such a constraint demonstrates that a large proportion of the C biomass values from Salem Harbor exceed this value, especially in the summer and fall.

4.2 Particulate Matter Source Proxy Data

Potential particulate matter sources include surface sediments, river inflow, storm water inflows, SESD WWTF effluent, and phytoplankton. Samples for each of the sources, with the exception of phytoplankton, are presented in Table 4 and used as constraints on biplots presented in Figs. 5-7. Results show clear differences between specific proxy data from different sources. For instance, surface sediments are the only source with negative $\delta^{34}\text{S}_{\text{VCDT}}$ values, and $\delta^{15}\text{N}_{\text{AIR}}$ values for SESD effluent and storm water samples are more depleted than the other sources (Table 4). Phytoplankton were not sampled directly in this study, and we used well-established elemental and isotopic values for this source as found in the literature for POC (Veyssy et al., 1999), $\text{C}_{\text{org}}/\text{S}$ (Berner and Raiswell, 1984), $\delta^{13}\text{C}_{\text{VPDB}}$ and $\text{C}_{\text{org}}/\text{N}$ (Meyers, 1994), and $\delta^{15}\text{N}_{\text{AIR}}$ and $\delta^{34}\text{S}_{\text{VCDT}}$ (Sharp, 2006) in Figs. 5-7. These results again show clear separation in proxy data for different sources of SPM, for instance the relative enrichment in $\delta^{13}\text{C}_{\text{VPDB}}$ for phytoplankton and surface sediments as compared to terrigenous sources (Fig. 6).

Surface sediments were characterized by 53 surface grab samples evenly sampled using a hexagonal grid pattern. The majority of sampling locations (49 out of 53) yielded muddy sediments, which characterizes the harbor bottom as fine-grained as opposed to a coarser-grained fluvial-dominated system. This observation is relevant since the fine-grained sediments sampled to characterize this source of SPM are the same as the sediments that might be resuspended via physical disturbance. This is different from coarser-grained fluvial-dominated systems in which there can be a separation of fine- and

coarse-grained sediments due to threshold energy requirement for different grain sizes to be eroded from the substrate.

4.3 Harbor Particulate Matter

Geochemical data from Salem Harbor SPM are presented in Figs. 5-7 as biplots with source proxy data included to constrain the SPM provenance. The biplot of POC vs. $C_{org}:S$ shows clustering of samples with low values of each proxy (Fig. 5). The majority samples plot in an overlapping region of phytoplankton, surface sediment, and low POC storm water sources. Samples with higher values than this region appear to represent a partial mixing line to include river and/or SESD influence. Many of these samples were taken from near the mouths of the two river inflows to the harbor, but samples from other locations in the harbor are identified as well. The majority of these anomalous samples were taken in the spring and summer months.

$\delta^{13}C_{VPDB}$ and $C_{org}:N$ data illustrate a clustering of data in the phytoplankton and/or SESD region, although the spread of data are not consistent with the tight spread of SESD data (Fig. 6). A number of samples, primarily from the mooring field locations (Stations B and C) have elevated $C_{org}:N$ values, suggesting that surface sediments may at times have an influence on the SPM presumably through resuspension of surface sediments in the harbor. Many of these high $C_{org}:N$ samples represent summer months in which most moorings are occupied with a boat, as opposed to winter months when either buoys or winter sticks are the only surface expression of the mooring. A relatively even distribution of samples representing the control, mooring, and river mouth locations had depleted $\delta^{13}C_{VPDB}$ data consistent with mixing of storm water and/or river water. Most of these low $\delta^{13}C_{VPDB}$ samples represent summer sampling.

$\delta^{15}N_{AIR}$ and $\delta^{34}S_{VCDT}$ data are not as tightly clustered as the above proxies, however patterns emerge (Fig. 7). The majority of $\delta^{15}N_{AIR}$ data are within the 3-18‰ range for phytoplankton (Sharp, 2006), however their range is also consistent with river water and surface sediment samples, complicating the interpretation. $\delta^{34}S_{VCDT}$ of surface sediments are very depleted as compared to other sources,

presumably due to sulfate reduction in the surface sediments driving isotopic fractionation. The majority of $\delta^{34}\text{S}_{\text{VCDT}}$ data fall around the river region of the plot, however this range could also be interpreted as a mixing zone between phytoplankton and resuspended surface sediments. A relatively small percentage of extremely $\delta^{34}\text{S}_{\text{VCDT}}$ depleted surface sediment SPM mixed with the narrow range of phytoplankton $\delta^{34}\text{S}_{\text{VCDT}}$ values could reasonably explain the grouping. In fact the majority of depleted SPM samples are from the mooring field locations where the potential of mooring chain physical disturbance may play a role in resuspension.

4.4 SPM provenance hypothesis evaluation

4.4.1 Hypothesis 1: Resuspension

The most clearly separated surface sediment proxy data are $\delta^{34}\text{S}_{\text{VCDT}}$, as illustrated in Fig. 7. A two-sample T-test comparing means of harbor bottom sediments from the 53 seafloor sites to suspended sediments taken from the water column at the five harbor buoys indicated that the two groups had significantly different mean $\delta^{34}\text{S}_{\text{VCDT}}$ values ($p < 2.2e^{-16}$), with $\delta^{34}\text{S}_{\text{VCDT}}$ means of 12.49‰ for suspended sediment samples and -17.39‰ for harbor bottom samples (Fig. 7). These results demonstrate that sediments in Salem Harbor are more depleted than particulate matter on average by almost 30‰, presumably due to sulfate reduction in anoxic sediments, leading to depleted sulfide. Further, since oxidation of sulfide does not involve a significant fractionation of sulfur isotopes, if resuspension was the dominant forcer of SPM, then we would expect greater similarities between the sediments and the particulate matter.

Moreover, there were no significant differences in mean $\delta^{34}\text{S}_{\text{VCDT}}$ between the suspended sediments collected at harbor buoys within (stations B and C) and outside (stations A, D, and E) of mooring fields ($p = 0.68$), with $\delta^{34}\text{S}$ means of 11.76‰ and 13.00‰ respectively. The $\delta^{34}\text{S}_{\text{VCDT}}$ results strongly indicate that suspended particulates in Salem Harbor are not dominated by resuspended bottom

sediments, however the relative depletion of $\delta^{34}\text{S}_{\text{VCDT}}$ SPM values observed suggest that some mixing of surface sediments into the SPM pool is likely. .

If tidal currents were resuspending bottom sediments then there should be a periodicity to such events, with resuspension occurring on the maximum flood and ebb tides (~6.2 hours). Spectral analysis of the tidal data collected in Salem Harbor returned expected lunar periodic components 12.4 hours (M_2), and 23.9 hours (K_1), as well as the half tide peak (6.1 hours) and a higher frequency peak at 4.1 hours (Fig. 2). Spectral analyses of the turbidity time series do not show clear and significant peaks at the tidal periods (highlighted with gray in Fig. 2). Buoys A, B, D, and E do not have any significant periods in this zone. Although Buoy C's spectral plot has components above the 99% significance line in the lower frequency portion of the tidal range, the lack of clear spectral peaks suggests that this portion of the analysis is driven by noise, and that the AR(1) background assumption (Mann and Lees, 1996) is not a perfect fit for this time series. Since evidence is lacking of appropriate tidal spectral peaks in the turbidity records, tidal currents are eliminated as a resuspension mechanism for bottom sediments.

4.4.2 Hypothesis 2: Precipitation and Runoff

No correlation was found between daily mean turbidity and daily mean precipitation at any of the study sites ($p > 0.05$ for each buoy site). Presumably, precipitation events of a certain intensity may be more likely to trigger elevated turbidities (Masselink et al., 2011), but insufficient meteorological data resolution were available to determine the threshold for Salem Harbor.

To further assess the relationship, salinity was used as a proxy for freshwater inputs to Salem Harbor, presuming that freshwater inputs would be associated with a decrease in salinity and, under the conditions of this hypothesis, a corresponding increase in turbidity. A χ^2 test of independence between all increases and decreases in salinity and turbidity recorded at all five buoys (defined as increase or decrease of salinity or turbidity compared to the reading taken 15 minutes prior) showed that increases in turbidity sometimes coincided with decreases in salinity (Table 5). The adjusted residuals of this analysis indicate a

general tendency for turbidity to relate to salinity in the expected way: turbidity rises more frequently when water in the harbor gets fresher and falls more frequently when the water gets saltier.

Overall, there were approximately 3% more coinciding increases in turbidity with decreases in salinity than increases in turbidity with increases in salinity. Moreover, there were 6% more increases in turbidity with decrease of salinity than there were decreases of turbidity with decrease of salinity. These results indirectly support the hypothesis that precipitation and increased runoff to the harbor are sometimes associated with increased turbidities, but the extent to which precipitation accounts for the full frequency of turbidity events remains elusive.

The geochemical signature of particulate matter in the harbor did not support the hypothesis that storm water or river flow are primarily responsible for turbidity since clear separation was observed between freshwater input particulates and marine particulate matter in the $\delta^{13}\text{C}_{\text{VPDB}}$ and $\text{C}_{\text{org}}:\text{N}$ biplot (Fig. 6). A two-sample Welch's T-test indicated that the mean $\delta^{13}\text{C}_{\text{VPDB}}$ values of riverine and storm water particulate matter differed significantly ($t = -25.73$; $p = 1.07 \times 10^{-63}$) from marine samples (-30.17‰ , and -23.48‰ , respectively) (Fig. 6). If turbid conditions were driven primarily by increases in particulate matter from the watershed, one would expect to observe the terrestrial $\delta^{13}\text{C}_{\text{VPDB}}$ signal translated to the particulate matter in the harbor. Specific events appear to occasionally flush allochthonous matter into the harbor, however, as evidenced by a minority of samples with depleted $\delta^{13}\text{C}_{\text{VPDB}}$ values (Fig. 6) and some samples with elevated POC and $\text{C}_{\text{org}}:\text{S}$ values (Fig. 5). These anomalous samples are consistent with the salinity data that suggest occasional influence of allochthonous matter on SPM in the harbor.

4.4.3 Hypothesis 3: Phytoplankton

There was no direct linear correlation between recorded turbidities and chlorophyll concentrations, either measured with secchi depth or nephelometry (using the buoy probes). The lack of correlation may have been related to the small chlorophyll sample size ($n=26$), or perhaps to analytical underestimation due to storage conditions as discussed in section 2.4.1. However, summer days had larger percentages of turbidity events than did days during the other seasons (Fig. 4B). A one-way

ANOVA of daily percentage of turbidity events against season revealed significant differences ($p = 0.0028$) and a Tukey's Honest Significance Test showed significant differences between spring and summer ($p = 0.014$) and summer and fall ($p = 0.001$). Turbidity events display the greatest magnitudes in summer (Fig. 4). A one-way ANOVA of mean daily turbidity magnitude against season indicated significantly different magnitudes between seasons ($p = 0.0093$); a Tukey's Honest Significance Test indicated significant differences between mean daily turbidity magnitudes during the spring and summer and summer and winter ($p = 0.034$ and $=0.019$, respectively). These results both support the notion that turbidity events differ seasonally, and that there are more turbidity events and events of greater magnitude during the summer. Summer months also coincide with the highest chlorophyll values from the 1997 sampling season (Chase et al., 2002) and C biomass, both indicators of seasonal plankton activity (Fig. 4A). Further, there was a significant and positive correlation between POC and $\delta^{13}\text{C}_{\text{VPDB}}$ ($r = 0.67$; $p = 2.71 \times 10^{-14}$). This correlation demonstrates that when POC increases, $\delta^{13}\text{C}_{\text{VPDB}}$ becomes more enriched, consistent with a marine phytoplankton signal (Fig. 6).

A number of geochemical parameters support the interpretation that phytoplankton have a dominant role in the SPM causing turbidity in Salem Harbor. First, the majority of $\delta^{13}\text{C}_{\text{VPDB}}$ and $\text{C}_{\text{org}}:\text{N}$ data are consistent with phytoplankton (Fig. 6). A two-sample Welch's T-test indicated that the mean $\delta^{13}\text{C}_{\text{VPDB}}$ values of marine SPM and terrigenous sources (storm water and river water SPM) differed significantly ($t = -25.73$; $p = 1.07 \times 10^{-63}$), with marine samples representing higher mean ^{13}C isotope enrichment than river/storm water samples (-23.48‰ and -30.17‰ , respectively). Second, POC and $\text{C}_{\text{org}}:\text{S}$ data support the interpretation that the majority of samples are consistent with a phytoplankton signature. These data also show storm water and surface sediments as possible solutions, however the $\delta^{13}\text{C}_{\text{VPDB}}$ data negate storm water as a dominant forcing of SPM (Fig. 6). POC:Chlorophyll *a* values (Table 3 and Fig. 3) are not conclusive, however values center just below the threshold of 200 for phytoplankton (Savoye et al., 2003) suggesting that plankton are a contributing factor to SPM.

4.4.4 Hypothesis 4: Sewage Effluent

Particulate matter from the effluent had $\delta^{15}\text{N}_{\text{AIR}}$ values of $-0.19 \pm 0.56\text{‰}$ (Table 4). These depleted nitrogen isotope values are atypical for common anthropogenic enrichment of ^{15}N found from animal (human) waste (McClelland and Valiela, 1998). They are consistent, however, with $\delta^{15}\text{N}_{\text{AIR}}$ data reported from sewage effluent resulting from secondary wastewater treatment. For instance, Rhode Island's Bucklin Point and Field's Point WWTFs had effluent $\delta^{15}\text{N}_{\text{AIR}}$ values of $-2.12 \pm 0.28\text{‰}$ and $-1.37 \pm 0.38\text{‰}$, respectively (King et al., 2008). Further, particulate matter of secondary effluent from the Massachusetts Water Resources Authority Deer Island WWTF were 0.0 to $+1.9\text{‰}$ in 1994, and -0.9 to $+3.6\text{‰}$ in 1995 (Butler et al., 1997). The SESD effluent $\delta^{15}\text{N}_{\text{AIR}}$ was more depleted than the mean particulate matter from the buoys sites ($5.03\text{‰} \pm 6.49\text{‰}$) (Fig. 7). The difference in $\delta^{15}\text{N}_{\text{AIR}}$ between SESD effluent and the harbor's particulate matter indicates that sewage effluent is not the direct cause for turbidity in Salem Harbor.

Although sewage effluent is not the direct cause of turbidity, we note that $\delta^{15}\text{N}_{\text{AIR}}$ of POM in Salem Harbor is lower than the expected coastal marine plankton signal of 8.5‰ (Peterson and Howarth, 1987), although it is within the broad range of 3 – 18‰ proposed by Sharp (2006). The more depleted $\delta^{15}\text{N}_{\text{AIR}}$ signal in Salem Harbor suggests that the depleted $\delta^{15}\text{N}_{\text{AIR}}$ from the effluent is mixed into the SPM pool, however the magnitude of influence is difficult to determine without a better constraint on the phytoplankton $\delta^{15}\text{N}_{\text{AIR}}$ signature in Salem Sound. In Narragansett Bay, King et al. (2008) observed such an effect in $\delta^{15}\text{N}_{\text{AIR}}$ values and demonstrated a $\delta^{15}\text{N}_{\text{AIR}}$ gradient in particulate matter and sediment in samples from proximal (depleted $\delta^{15}\text{N}_{\text{AIR}}$) to distal (more enriched $\delta^{15}\text{N}_{\text{AIR}}$) locations relative to point-source WWTFs.

4.5 Turbidity Causes in Salem Harbor

The results of this study have demonstrated that the source of SPM in Salem Harbor is complex, and that SPM has multiple origins. The majority of data constrain the *dominant* causal factor of turbidity in Salem Harbor to phytoplankton, based primarily on geochemical proxies, the timing of elevated turbidity, and the timing of elevated C biomass. It is evident, however, that at times other factors

influence SPM, including the resuspension of surface sediments (likely dominated in mooring locations of harbor during spring and summer) and the influx of allochthonous material from the watershed (primarily at river mouth locations of harbor in summer).

Regarding phytoplankton, the source of the requisite nutrient loading in Salem Harbor has not been established and is likely to be diffuse. Infiltration of raw sewage into groundwater is unlikely, given the general absence of septic systems and prevalence of bedrock throughout Salem and Marblehead. However, sewage may still account for nutrient inputs to the harbor. Recent monitoring efforts in Salem have already uncovered numerous degraded or incorrectly installed sewage pipes. The diffuse comingling of sewage with storm water may be a more likely means by which anthropogenic nitrogen makes its way to the Harbor. In addition, nutrient loading may be sourced to effluent from SESD WWTF. It is interesting to note, however, that the apparent increase in turbidity since the mid-1990s coincides with the initiation of secondary treatment at SESD in 1998, which would be expected to decrease nutrient loading to Salem Sound.

Since nitrogen loading to the harbor is diffuse (non-point), arbitrarily measured concentration values may not be meaningful unto themselves, though variations may certainly be worth examining spatially and temporally. Nevertheless, using concurrent and frequent measurement of total bioavailable nitrogen in conjunction with total suspended solids, temperature, salinity, and chlorophyll *a* concentrations can only develop a strong empirical model of the interactions between nitrogen eutrophication and phytoplankton biomass in Salem Harbor. A dynamic model of harbor eutrophication would allow prediction of meteorological and/or seasonal conditions under which the effects of nutrients might be most pronounced. This knowledge would facilitate targeted mitigation efforts if and when continued anthropogenic eutrophication is deemed to account for significant habitat quality issues in Salem Harbor.

4.6 Applicability to Other Locations

This study has focused on Salem Harbor and the results clearly demonstrate the dominant role of phytoplankton activity in water column turbidity as well as more minor influences of sediment resuspension and allochthonous inputs. The approach that we used, and the results presented, will be applicable to other coastal locations that have observed turbidity issues. In particular, the isotopic and other geochemical analyses were able to elucidate source information on the particulate matter that complemented the turbidity monitoring time series.

Although our approach required more field time than automated water quality loggers, we were able to utilize the assistance of local volunteers and university students to assist in the collection of water samples to be filtered. This approach allowed us to more easily obtain a temporally and spatially diverse range of samples to analyze. As stable isotope mass spectrometers become more cost effective and available, the isotopic analyses presented are relatively accessible to most organization, through either university partnerships or commercial facilities.

The large role of marine phytoplankton as a source of particulate matter in the water and sediments of Salem Harbor is different from a number of other coastal areas. For instance, in the Gironde Estuary, France, 98% of particulate organic matter was found to be of terrestrial source (Savoye et al., 2012). Additionally, large fluxes of terrestrial organic matter have been observed in the coastal waters of the Gulf of Mexico (Goñi et al., 1997) and the Andaman Sea (Ramaswamy et al., 2008). In each of these cases, the high fluxes of terrigenous organic matter can be attributed to large fluvial inputs to the regions. Salem Harbor, on the other hand, has relatively low average freshwater inflow, much of which is from SESD outfall, and as a result represents a coastal system that behaves differently from classic estuarine systems. In addition, the local geology of thin glacial drift and exposed bedrock, combined with a large percentage of impervious urban surfaces, further limits the supply of sediments from the watershed. Such location-specific differences highlight the influences of local effects such as freshwater fluxes, geology, land use, geography, nutrient loading, and food web dynamics. This further confirms the applicability of a multi-faceted approach to constrain the dominant factors in a specific location. As such, we recommend that coastal studies related to phytoplankton variability and turbidity follow a holistic approach that takes

into account influences such as those listed above in addition to the typical water column properties and general fluvial input.

The large carbon biomass in Salem Harbor implies relatively frequent blooms (Carstensen et al., 2015). In other coastal systems such biomass has been found most prevalently in regions of strong anthropogenic influence (Bužancic et al., 2016; Lugoli et al., 2012), presumably due to nutrient loading. In still other systems allochthonous DOC has been shown to be an important forcing is structuring estuarine ecosystems (Hitchcock and Mitrovic, 2013). Although many responses of phytoplankton communities to anthropogenic and natural forcings are site specific, generally anthropogenic development has been found to be a driver of coastal production (Reed et al., 2016). In Salem Harbor, we observed a dominance of phytoplankton with regard to SPM provenance. Since the harbor is relatively highly developed, it is likely that coastal production and community structure have been altered over past centuries. The importance of phytoplankton in this system underscores the need to better understand phytoplankton communities and their relationships to turbidity, nutrient loading, and development stresses. The dynamics of phytoplankton community structure and biodiversity are beyond the scope of this paper, however it is a logical next step in this field area and other similar coastal embayments.

The study underscores the importance of better understanding the balance of different mechanisms in affecting coastal turbidity. In this particular case study, state agencies are interested in determining the most effective strategy for abatement of turbidity in Salem Harbor. Although the data reveal a situation more complex than a simple unimodal system, the identification of one source of SPM as the dominant forcing (*i.e.* phytoplankton) allows local agencies to target the most pressing situation first in order to maximize benefit to the system.

5. Conclusions

This study successfully used a combination of water quality monitoring, geochemical, and meteorological data to constrain the provenance of SPM in a coastal embayment. Specifically, we

identified that the source of SPM causing elevated turbidity in Salem Harbor is of multiple origins, and that of the four potential sources of suspended particulates in Salem Harbor, the weight of evidence demonstrates that phytoplankton are the dominant forcing. Geochemical investigation of particulates suspended in the water column indicated that resuspension of sedimentary particulates is not the dominant source of elevated turbidities, especially given that there appears to be no difference in $\delta^{34}\text{S}_{\text{VCDT}}$ between suspended particulate samples collected within and outside of the harbor's mooring fields. However, proxy data clearly show that occasionally surface sediments are resuspended, likely associated with summer boat mooring activity. Allochthonous sediments flushed from the watershed through storm water runoff and river flow was not substantiated as a dominant source of suspended particulate matter, though there does seem to be an association between precipitation and turbidity when salinity was used as a proxy for freshwater inputs, potentially due to nutrient loading from the watershed and/or WWTF. Potential mixing of allochthonous matter was observed mostly at river mouth locations during summer months. Finally, there is some evidence that SPM in SSTF effluent may mix into the SPM pool, however we were unable to quantify the magnitude of this effect without local phytoplankton $\delta^{15}\text{N}_{\text{AIR}}$ data. Our combined approach utilizing monitoring buoys, isotopic analysis, and meteorological data was successful in constraining the causes of turbid water in Salem Harbor, and this multi-faceted approach should be applicable to other coastal locations with turbidity issues.

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Figure Captions

Fig. 1. Map of Salem Harbor with sampling locations noted (see Table 1 for location details). Buoy locations include control site (A), mooring sites (B and C), and river mouth sites (D and E). Marine samples were taken at buoy locations as well as at shoreline locations Congress Street (CS) and Lead Mills (LM). Freshwater river samples were from Forest (n=2) and South Rivers and storm water outfalls at Palmer Cove (PC), Village Street (VS), and Stramski Park (SP). South Essex Sewerage District (SESD) effluent was sampled directly at the plant as labeled in the figure, and the effluent outfall pipe is located ~2.5km northeast of Salem Harbor. Weather data recorded at Salem State University (SSU).

Fig. 2. Spectral analysis of Salem Harbor tides (May 2012 – January 2014) and turbidity time series from monitoring buoys. Gray line represents the 99% confidence level with respect to AR(1) red noise background (Mann and Lees, 1996). Note significant peaks in tidal series at 23.9, 12.4, 6.1, and 4.1 hours highlighted by gray vertical box. Turbidity spectral analyses lack distinct significant spectral peaks corresponding with tidal cycles.

Fig. 3. Biplot of particulate organic carbon: Chlorophyll *a* ratios vs. the percentage of particulate organic carbon in suspended particulate matter. Box labeled “Phytoplankton” represents expected range of values for marine phytoplankton (Savoye et al., 2003; Veyssy et al., 1999).

Fig. 4. (A) Monthly carbon biomass data from Salem Harbor marine samples (this study), monthly chlorophyll *a* data from 1997 (Chase et al., 2002), and seasonal turbidity data, as the natural log of mean turbidity excesses of 15 NTU (this study), and (B) seasonal turbidity data plotted as proportion of a day where turbidity is > 15 NTU.

Fig. 5. Biplot of particulate organic carbon (POC) percentage of suspended particulate matter vs. $C_{org}:S$ ratio. Labeled boxes represent the ranges of samples from different particulate matter sources quantified in this study (Table 4), as well as values expected for marine phytoplankton from the literature (Berner and Raiswell, 1984;

Veyssy et al., 1999). Data points represent individual marine samples from Salem Harbor separated by location (symbol) and season (winter, spring, summer, fall are 100%, 80%, 60%, and 40% gray scale, respectively).

Fig. 6. Biplot of $\delta^{13}\text{C}_{\text{VPDB}}$ vs. $\text{C}_{\text{org}}:\text{N}$ ratio. Labeled boxes represent the ranges of samples from different particulate matter sources quantified in this study (Table 4), as well as values expected for marine phytoplankton from the literature (Meyers, 1994). Data points represent individual marine samples from Salem Harbor separated by location (symbol) and season (winter, spring, summer, fall are 100%, 80%, 60%, and 40% gray scale, respectively).

Fig. 7. Biplot of $\delta^{15}\text{N}_{\text{AIR}}$ vs. $\delta^{34}\text{S}_{\text{VCDT}}$. Labeled boxes represent the ranges of samples from different particulate matter sources quantified in this study (Table 4), as well as values expected for marine phytoplankton from the literature (Sharp, 2006). Data points represent individual marine samples from Salem Harbor separated by location (symbol) and season (winter, spring, summer, fall are 100%, 80%, 60%, and 40% gray scale, respectively).

Table Captions

Table 1: Description of sites and corresponding data from Salem Harbor, MA and its watershed.

Table 2: Date ranges of accepted turbidity data from buoy sensors. Turbidity data were considered acceptable up until biofouling began to artificially inflate turbidity readings: this phenomenon was identified by plotting turbidity against the number of days the sensor had been submerged. Data collected on days after which daily mean turbidities began an exponential increase and subsequently failed to fall back below a plausible maximum of 100 NTU were excluded from the analysis; the dates shown below reflect the date ranges included in the turbidity analysis.

Table 3: Water quality parameters measured at each of the monitoring buoy locations from 2012-2014. See Figure 1 and Table 1 for details on station locations.

Table 4: Geochemical data for hypothesized suspended sediment sources in this study. Data are used to constrain particulate matter source in Figures 5-7.

Table 5: Output of Pearson's Chi-Square test of independence for concurrent increases and decreases in turbidity and salinity from aggregated 15-minute buoy data collected in Salem Harbor from 2012 to 2014. The test results indicate a statistically significantly greater frequency of concurrent turbidity increase with salinity decrease.

Table 1

Table 1: Description of sites and corresponding data from Salem Harbor, MA and its watershed.

Site	Map label	Latitude	Longitude	Description	Category	Data collected
Salem Harbor A	A	42.52168	-70.86582	Buoy at harbor mouth between Naugus Head and Winter Island: estimated depth 10-12m	marine control	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$; buoy data: turbidity, salinity, temperature, conductivity.
Salem Harbor B	B	42.51345	-70.87407	Buoy in the east moorings: estimated depth 5-6m	marine mooring field	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$; buoy data: turbidity, salinity, temperature, conductivity.
Salem Harbor C	C	42.51608	-70.87800	Buoy in the west moorings: estimate depth 5-6m	marine mooring field	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$; buoy data: turbidity, salinity, temperature, conductivity.
Salem Harbor D	D	42.51612	-70.88430	Harbor buoy near South River mouth: estimated depth 3-4 m	marine river mouth	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$; buoy data: turbidity, salinity, temperature, conductivity.
Salem Harbor E	E	42.50285	-70.88042	Harbor buoy off of Forest River mouth: estimated depth 1-2 m	marine river mouth	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$; buoy data: turbidity, salinity, temperature, conductivity.
Forest River Friendship Bridge	FR	42.49241	-70.90195	Forest River site 2km upstream of Lead Mills site	river	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$
Forest River Upstream	FR	42.49302	-70.90443	Forest River site 2km upstream of Lead Mills site	river	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$
Palmer Cove	PC	42.51380	-70.88804	Shoreside at Palmer Cove	storm water	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$
South River	SR	42.51002	-70.90134	South River at the corner of Jefferson and Dove avenues, Salem	river	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$
Stramski Park	SP	42.51444	-70.86573	Stormwater outfall to Salem Harbor at Stramski Park, Marblehead	storm water	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$
Village Street	VS	42.50607	-70.87279	Stormwater outfall to Salem Harbor at Village Street, Marblehead.	storm water	suspended sediment/water samples: $\delta^{13}C_{VPDB}$, $\delta^{15}N_{AIR}$, $\delta^{34}S_{VCDT}$, $C_{org}:N$, $C_{org}:S$

Congress Street	CS	42.51920	-70.88938	Dock sample from the South River mouth off of Congress Street, Salem	marine shore	suspended sediment/water samples: $\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{15}\text{N}_{\text{AIR}}$, $\delta^{34}\text{S}_{\text{VCDT}}$, $\text{C}_{\text{org}}\text{:N}$, $\text{C}_{\text{org}}\text{:S}$
Lead Mills	LM	42.49733	-70.88628	Shore sample at Forest River mouth into Salem Harbor	marine shore	suspended sediment/water samples: $\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{15}\text{N}_{\text{AIR}}$, $\delta^{34}\text{S}_{\text{VCDT}}$, $\text{C}_{\text{org}}\text{:N}$, $\text{C}_{\text{org}}\text{:S}$
South Essex Sewerage District Effluent	SESD	42.52820	-70.52821	Effluent sample taken directly from the WWTF	effluent	suspended sediment/water samples: $\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{15}\text{N}_{\text{AIR}}$, $\delta^{34}\text{S}_{\text{VCDT}}$, $\text{C}_{\text{org}}\text{:N}$, $\text{C}_{\text{org}}\text{:S}$

Table 2

Table 2: Date ranges of accepted turbidity data from buoy sensors. Turbidity data were considered acceptable up until biofouling began to artificially inflate turbidity readings: this phenomenon was identified by plotting turbidity against the number of days the sensor had been submerged. Data collected on days after which daily mean turbidities began an exponential increase and subsequently failed to fall back below a plausible maximum of 100 NTU were excluded from the analysis; the dates shown below reflect the date ranges included in the turbidity analysis.

Buoy	Start	End	Buoy	Start	End	Buoy	Start	End
A	5/17/2012	6/5/2012	C	5/7/2012	5/17/2012	E	6/21/2012	7/31/2012
	6/11/2012	6/24/2012		5/17/2012	6/11/2012		8/10/2012	8/30/2012
	8/10/2012	9/3/2012		6/11/2012	7/19/2012		12/14/2012	1/22/2013
	11/26/2012	12/10/2012		8/10/2012	9/9/2012		1/28/2013	2/26/2013
	12/14/2012	12/27/2012		11/26/2012	12/11/2012		5/6/2013	5/24/2013
	1/28/2013	3/7/2013		12/14/2012	12/27/2012		6/4/2013	6/15/2013
	4/1/2013	4/14/2013		1/28/2013	2/13/2013		7/16/2013	8/19/2013
	5/6/2013	5/20/2013		7/22/2013	8/10/2013		8/27/2013	9/25/2013
	6/4/2013	6/16/2013		8/27/2013	11/18/2013		7/11/2014	8/2/2014
	7/16/2013	7/28/2013		6/4/2014	6/25/2014		8/26/2014	10/4/2014
B	5/7/2012	5/17/2012	D	5/7/2012	5/17/2012	E	6/21/2012	7/31/2012
	5/17/2012	6/11/2012		5/17/2012	5/31/2012		8/10/2012	8/30/2012
	6/11/2012	7/10/2012		6/21/2012	7/23/2012		12/14/2012	1/22/2013
	11/26/2012	12/11/2012		11/26/2012	12/11/2012		1/28/2013	2/26/2013
	12/14/2012	1/27/2013		12/14/2012	1/23/2013		5/6/2013	5/24/2013
	1/28/2013	2/10/2013		12/14/2012	12/30/2012		6/4/2013	6/15/2013
	4/1/2013	4/19/2013		1/28/2013	2/13/2013		7/16/2013	8/19/2013
	5/6/2013	5/24/2013		4/1/2013	4/27/2013		8/27/2013	9/25/2013
	6/4/2013	6/14/2013		5/6/2013	7/2/2013		7/11/2014	8/2/2014
	7/16/2013	10/1/2013		10/21/2013	11/11/2013		8/26/2014	10/4/2014
	10/21/2013	11/10/2013		7/11/2014	8/19/2014			
				8/26/2014	10/4/2014			

Table 3

Table 3: Water quality parameters measured at each of the monitoring buoy locations from 2012-2014. See Figure 1 and Table 1 for details on station locations.

Station	Temperature (°C)	Salinity (psu)	Turbidity (NTU)	Chlorophyll <i>a</i> (µg/l)	SPM (mg/l)	POC (%)	POC:Chl <i>a</i>
A	16.4 ± 3.9	29.1 ± 1.7	40.9 ± 95.5	3.4 ± 1.1	13.2 ± 5.2	2.7 ± 1.8	179.6 ± 65.8
B	13.2 ± 6.1	29.9 ± 1.5	20.1 ± 327.2	3.5 ± 1.0	11.4 ± 4.5	3.4 ± 2.4	204.5 ± 66.1
C	15.3 ± 5.2	30.3 ± 1.5	11.0 ± 38.4	4.4 ± 1.1	13.9 ± 12.6	4.0 ± 2.0	173.0 ± 76.0
D	13.3 ± 5.6	30.0 ± 1.2	297 ± 900.8	2.8 ± 0.5	12.1 ± 5.5	4.6 ± 3.8	165.5 ± 33.2
E	14.8 ± 6.8	29.3 ± 3.4	59.4 ± 283.4	3.8 ± 0.9	13.0 ± 5.6	5.0 ± 3.5	256.2 ± 155.8

Table 4

Table 4: Geochemical data for hypothesized suspended sediment sources in this study. Data are used to constrain particulate matter source in Figures 5-7.

	Surface Sediments					River Inflows					Storm Water					SESD Effluent				
	N	Mean	Min	Max	Std. dev.	N	Mean	Min	Max	Std. dev.	N	Mean	Min	Max	Std. dev.	N	Mean	Min	Max	Std. dev.
$\delta^{13}\text{C}_{\text{VPDB}}/\text{‰}$	48	-21.28	-26.34	-13.48	2.07	78	-30.71	-37.31	-24.81	1.87	23	-28.45	-31.85	-24.94	1.60	2	-23.92	-23.93	-23.90	0.02
$\delta^{15}\text{N}_{\text{AIR}}/\text{‰}$	47	+5.47	-3.79	+8.12	1.74	80	+4.72	-7.48	+11.11	2.68	17	+0.25	-4.27	+9.08	3.12	2	-0.19	-0.58	+0.21	0.56
$\delta^{34}\text{S}_{\text{VCDT}}/\text{‰}$	47	-17.13	-23.04	-5.08	3.20	59	+11.16	-21.11	+40.26	12.05	15	+18.61	+0.14	+54.13	18.52	2	+7.24	+6.98	+7.49	0.36
%C _{org}	48	3.7	0.3	7.3	3.2	79	18.2	3.4	47.3	7.4	22	23.7	1.0	90.4	25.1	2	31.6	27.8	35.4	5.4
%N	47	0.3	0.1	0.5	0.1	80	2.4	.4	9.2	1.6	22	3.8	0.1	21.4	12.0	2	5.7	5.2	6.3	0.8
%S	49	0.9	0.2	1.7	0.3	78	2.4	.4	6.8	1.5	22	12.4	0.3	44.1	12.0	2	1.3	1.2	1.3	0.1
C _{org} /N	46	13.2	9.3	21.5	3.0	79	8.6	2.5	20.2	3.4	22	7.5	2.2	14.0	3.9	2	5.5	5.4	5.6	0.2
C _{org} /S	48	4.3	2.1	8.5	1.4	78	10.8	2.6	49.3	8.4	22	2.2	0.4	5.9	1.2	2	24.6	22.8	26.4	2.6
POC	N/A	N/A	N/A	N/A	N/A	79	1.5	0.4	12.2	1.8	21	0.3	0.1	0.9	0.2	2	1.7	1.7	1.8	0.1
SPM	N/A	N/A	N/A	N/A	N/A	80	16.8	1.3	303.0	41.4	22	6.0	0.2	63.2	13.3	2	9.3	7.2	11.5	3.0

Table 5

Table 5: Output of Pearson’s Chi-Square test of independence for concurrent increases and decreases in turbidity and salinity from aggregated 15-minute buoy data collected in Salem Harbor from 2012 to 2014. The test results indicate a statistically significantly greater frequency of concurrent turbidity increase with salinity decrease.

<i>raw counts</i>	salinity increase	salinity decrease
turbidity increase	25158	25847
turbidity decrease	25001	24324
df = 1	p= 1.614e-05***	X-squared = 18.598
<i>std. (adjusted) residuals</i>	salinity increase	salinity decrease
turbidity increase	-4.312532	4.312532
turbidity decrease	4.312532	-4.312532

Figure 1

Figure 2
[Click here to download Figure: Turb_Fig2.pdf](#)