Sediment fluxes and exchange between an urban salt marsh and Long Island Sound

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Abstract

Salt marshes provide a broad range of valuable ecological services. In urban settings these services are magnified in importance, as marshes are typically smaller, serve more concentrated human populations, and face more dramatic anthropogenic pressures. Unfortunately, our knowledge of material exchange between marshes and coastal waters is limited, particularly in urban areas. Tidal flux studies offer a means of understanding how marshes interact with coastal waters and how they affect water quality in the coastal zone.

The present study reports high resolution data on fluxes of water, salt, and sediment to and from an urban salt marsh in Norwalk, CT. This work focuses on short-term sediment dynamics, and the role of storm events in sediment transport. Field-based measurements of precipitation, water velocity, salinity, and turbidity were collected continuously for two months. Uncertainties in the data are evaluated and compared with other flux studies. The feasibility of estimating particulate material fluxes based on these data benefits from low spatial variability of suspended sediment in the water column. A net influx of sediment was observed over the course of the study, but the system is characterized by large, short-term variations in sediment transport. Only a small fraction of the imported sediment appears to be deposited on the marsh surface.

Moving towards an assessment of minor constituent fluxes, this project began optimizing a method for measuring trace metals in sea water, to be deployed in 2012. Experiments using chelating resin columns have highlighted the challenges of analyzing trace metals in seawater. This preliminary work has clarified essential methodological details such as the volume of eluent required to displace metals sorbed to the resin, and the necessity of purifying reagents.

Introduction

Salt marshes are dynamic inter-tidal environments, where marine and terrestrial systems interact. Marshes are often considered buffers or sinks for nutrient-laden waters, in recognition of the high denitrification rates in marshes (Reddy and DeLaune, 2008). But research into the magnitude and direction of exchange for many materials is still poorly understood. Marsh-estuary fluxes first gained attention in the 1960s as John Teal and Eugene Odum hypothesized that organic matter originating in salt marshes is exported to coastal waters, where it subsidizes estuarine food webs (Odum, 1968; Teal, 1962). There have been many subsequent efforts to understand the direction and magnitude of material fluxes, as well as the underlying mechanisms driving differences

between systems (Childers et al., 2002; Nixon, 1980; Odum, 2002; Stevenson et al., 1988).

Traditionally, even studies of abundant, easily measured constituents have been challenging. The effort and expense necessary to obtain accurate flow and concentration data has limited researchers to studying a limited number of tides in all but a few cases (e.g., Jordan and Correll, 1991; Suk et al., 1999). Selective sampling regimes are accompanied by problematic tendencies, such as the exclusion of storm events in favor of more common conditions. It should not be surprising, therefore, that flux studies have yielded disparate results. Without considering the full variability inherent in tidal systems it is difficult to draw general conclusions about material exchange. Interpreting disparate results is also made more challenging, since differences related to methodological and experimental conditions cannot be easily separated from those due to underlying processes.

Sediment is among the most abundant materials tidally exchanged in salt marshes. Sediment accretion and belowground production are the main processes that enable marshes to adjust to changing sea levels (Redfield, 1972; Reed, 1995). The availability and deposition of sediment are therefore critical for marsh stability (Kirwan et al., 2010). The clear implication, hardly necessary to state explicitly, is that marshes are depositional zones for sediment. While this is generally true on longer time scales (10-100 yr), it is not clear whether marshes also reliably trap sediment on shorter time scales, such as individual tidal cycles.

Observed differences between systems in the sign and magnitude of total suspended sediment (TSS) fluxes have been linked to variation in geography, climate, animal activity, and asymmetries in the timing and magnitude of peak current velocities (Boon III, 1975; Childers et al., 2002; Stevenson et al., 1985; Stevenson et al., 1988). Boon and Byrne (1981) extended the work of Groen (1967) to propose a model emphasizing the primacy of basin morphology in affecting peak velocity asymmetries. They suggested that open embayments tend to have higher flood tide velocities, whereas systems with a high proportion of vegetated marsh experience more intense velocities during ebb tides. The shift is driven by a changing relationship between water level and flooded basin area.

As a consequence of relying on a small number of tides, studies of sediment fluxes have tended to exclude storms and exceptional high tides, and are even poorly suited to capture medium-scale variations associated with lunar and seasonal cycles. Seasonal differences in particular can change the direction of sediment fluxes (Dame et al., 1986). Unfortunately, studies utilizing continuous sampling regimes may rely on acid preservation of samples, eliminating the possibility of distinguishing particulate and dissolved material (e.g., Jordan and Correll, 1991). Of those studies that have captured storm effects on particulate transport, the effect has been to augment both import (Dankers et al., 1984) and export (Stevenson et al., 1985) of sediment in different systems, with a tendency to be consistent within a system.

The challenges described above are even more pronounced for trace constituents such as metals. There has been only one major study of short-term trace metal fluxes between marshes and coastal waters (Cu, Zn, Fe; Pellenbarg and Church, 1979). The metals studied showed export, consistent with suspended particulate matter

(SPM) transport, though the three tidal cycles studied leave ample room for uncertainty in extrapolating the observed trends.

The present study takes advantage of two recent technological advances which make it possible to overcome many of the limitations described above. The availability of high precision acoustic Doppler current profilers (ADCPs) has made accurate, continuous flow data obtainable (e.g., Bouchez et al., 2011), though this technology has not yet been applied in salt marsh flux studies reported in the literature. A second development, autosamplers and continuous dataloggers, has enabled high-frequency monitoring of constituent concentrations, either directly or indirectly through proxies. These advances suggest that it is now possible to obtain flux estimates that are comprehensive, high-resolution, and accurate.

This project examines tidal fluxes of sediment, exploring the following hypotheses:

- (1) Storms provide important pulses of inorganic sediment into the marsh
- (2) On time scales of individual tides, marshes can serve as both sinks and sources of sediments and sediment-borne pollutants

Additionally, this project began optimizing a method for trace metal analysis in seawater. Measurement of dissolved and particulate metal fluxes offer a means of extending the work reported here to materials that are of concern for human and environmental health.

Methods

Research site

Salt marshes in LIS are attractive for tidal flux studies. Many marshes along the coast have formed in flooded embayments with small watersheds. Coastal development has proceeded in a way that has often limited marsh-estuary tidal exchange to a single connection, often under a bridge or through a remnant tide gate. These narrow inlets can be ideal for the use of ADCPs because the relationship between water column depth and channel cross-sectional area can be readily quantified, a major challenge in systems with wide, heterogenous channels or where exchange occurs over expanses of vegetated area (Dame et al., 1986; Poulin et al., 2009).

Harborview marsh (Fig. 1) in Norwalk, CT is a 10 ha marsh, with 4.4 vegetated hectares, of which 1.1 ha is high marsh. A primarily residential upland zone (12 ha) contributes to the marsh through storm drains that discharge into the creeks. There is only a negligible natural upland watershed.

Instrumentation

Flood- and ebb-tide water discharge was measured continuously using an acoustic Doppler flow meter (YSI Sontek Argonaut-SW[®]) deployed in the creek's thalweg. The meter was positioned such that positive values reflect flooding tides. Water discharge was calculated by multiplying velocity data, averaged from measurements in up to ten vertical cells, by the cross-sectional area of the creek

inundated at the recorded depth. The Argonaut was calibrated by the manufacturer. Argonaut depth measurements have an accuracy of $\pm 0.1\%$, ± 0.3 cm and velocity readings have an accuracy of $\pm 1\%$, ± 0.5 cm·s⁻¹.

А YSI 6920 multiparameter sonde was deployed nearby with sensors for turbidity (optical; accurate to ±0.3 NTU or 2%), pressure, dissolved temperature, O_2 (non-optical), pH. and conductivity. Turbidity was converted to suspended sediment concentration using site-specific correlation а (described below). The sonde was initially calibrated in the laboratory, but subsequent calibrations were performed in the field. Minimal deviations observed were between calibrations. Data were



Figure 1. Harborview marsh in Norwalk, CT. Sampling plots and instruments are indicated.

downloaded and instruments were cleared of biofouling every 1-2 weeks. Both instruments recorded data at 15 minute intervals over the course of the study. Finally, an Onset precipitation gage was deployed from September 24th to October 31st. The gage recorded precipitation at 5 minute intervals in 1 mm increments.

Fluxes of water, salt, and sediment were calculated for each tidal cycle as the difference between summed incremental discharges over flood- and ebb-tides. This can be represented by Equation (1):

$$\Delta S_{TC} = \sum_{t=0}^{1} Q_t C_t - \sum_{t=1}^{2} Q_t C_t$$
 (1)

where

 ΔS_{TC} = Material flux over a tidal cycle (e.g., mg) Q_t = Discharge rate at time t (m⁻³·sec⁻¹) C_t = Material concentration (e.g., mg·m⁻³) at time t t = time in tidal cycle (0 and 2 = low tides and 1 = high tide, such that a flood tide occurs from t=0 to t=1, and an ebb tide from t=1 to t=2)

Testing heterogeneity

The deployed instruments measure velocity and turbidity at a single location in the creek. A well-mixed stream is essential to minimize uncertainty in extrapolations based on these data. Two experiments were conducted to examine heterogeneity in velocity and turbidity at the creek mouth.

In the first experiment, turbidities were measured at locations distributed across the depth and width of the creek, as well as temporal spacing over the course of tidal cycles. Depending on water depth and creek width, up to three vertical positions were sampled (0.2*depth, 0.6d, and 0.8d), and up to six lateral positions. In total, thirteen such cross-sections were measured.

In a second experiment, velocity disparities were examined in a similar manner. This was more difficult, because of the lack of a bridge or structure to stabilize the velocity measurements at higher depths and flow rates. Canoes and kayaks were used, and a rope tied across the channel assisted in stabilizing the measurements, but some additional variability was likely introduced by the experimental conditions. Eight velocity cross-sections were measured.

TSS concentrations

TSS cannot be measured continuously, but can be estimated from turbidity data if a strong relationship exists between the two parameters. To establish this relationship, grab samples were taken from just below the water surface in the creek thalweg using a telescoping Nasco[®] swing sampler. Turbidity was measured on replicate samples using a LaMotte 2020 turbidimeter (accuracy: ±0.05 NTU or 2%). Grab samples were chilled and precisely measured volumes were filtered in the laboratory on pre-washed, preweighed fiberglass filters. Filters were dried to constant weight at 105°C, re-weighed, and combusted at 500°C for 8 hours to determine organic content. Suspended sediment concentrations were calculated by dividing three quantities by the volume of water filtered; the dry mass of sediment, the ash-free mass (inorganic suspended sediment), and the difference between the two (organic suspended sediment).

Aqueous metals

Measuring trace metals in seawater faces dual challenges of seeking target analytes present at extremely low concentrations (μ g/L or lower) and in the presence of a matrix rich in dissolved ions. This creates a tension between the desire to dilute the sample and reduce matrix interferences, and the need to pre-concentrate to enhance the target analyte concentrations. Chelating resins are capable of strongly sorbing metals and excluding much of the seawater matrix, satisfying both of these objectives.

In this study, Chelex-100 resin was used to optimize analysis of metals in seawater (following Gueguen et al., 2001). Columns were constructed of plunger-less syringes with a frit at the base and a Luerlock valve attached to regulate flow. Columns were filled with 2.5 cm³ of Chelex after soaking in 2.5M HNO₃ overnight. For conditioning, the columns were eluted with 30 mL of 2.5M HNO₃ and 30 mL DI water. Chelex was converted to the NH_4^+ form by elution with 2 mL 2M NH_4OH , followed by 30 mL of DI water to rinse any remnant NH_4OH , followed by final rinses with 5 mL each of 1M NH_4OAc and DI water. All steps utilized a flow rate of 1 mL·min⁻¹.

After samples (60 mL) were loaded onto the column, the seawater matrix was removed by eluting with 10 mL DI water and 20 mL 1M NH₄OAc. A final elution with 25 mL 2M HNO₃ displaced trace metals from the Chelex. Standard solutions (1 and 10 μ g/L), acidified estuarine standard reference material (CASS-5), Long Island Sound seawater samples (spiked and unspiked), and several blanks were run using this method. Analysis was conducted on a Perkin-Elmer ICP-MS using a Meinhard spray chamber.

Aqueous metals work utilized strict clean techniques in the lab, including the use of a class-100 clean room and extensive acid cleaning of all materials contacting samples. Reagents that were not Seastar grade were purified with Chelex prior to use (a blank experiment was conducted to test the necessity of this step). When this method is field-ready, it will be applied in combination with rigorous quality assurance and quality control measures for field sampling (Ahlers et al., 1990; Benoit, 1994).

Additional measurements

Six benchmarks were installed around the perimeter of the marsh in May 2011 (Fig. 1). Their locations were measured in the National Geodetic Vertical Datum (NGVD 29) using a TopCon HiPer Lite RTK-GPS. Tide heights were measured at these benchmarks four times with duplicate tide sticks (stakes coated with a washable indicator). Tidal datums at Harborview were estimated using the modeled high tides derived from the correlation between local high tides and those recorded by NOAA in Bridgeport. High tides were modeled at Harborview for the period 1 Jan 2008 to 31 July 2011. Using these modeled high tides, mean higher-high tide (MHHT), and mean high water (MHW) are, respectively, 0.238 m and 0.118 m above Harborview's benchmark 1. MHW was calculated for Bridgeport using the same restricted time period, producing an estimate 0.075 m above the established epoch (1983-2001).

The Harborview benchmarks were also used in surveying vegetation and mud flat elevations. A reflectorless TopCon 3203-NW total station was used to survey mud flats without disturbance. Tide sticks were used to determine elevations of vegetation zones along three transects into the marsh (Fig. 1). No significant differences in relative elevations were detected following a comparison between benchmarks measured using tide stakes, RTK, and the total station.

Several additional measurements were also taken along the three transects. Sediment traps, composed of washed 0.45 μ m micropore filters secured onto upsidedown petri dish platforms, were deployed in duplicate at each of the three high and low marsh plots in Figure 1. Sediment traps were deployed in mid-July and replaced after 90 days. Upon retrieval, traps were dried to constant weight at 70°C.

Net aboveground primary productivity (NAPP) was sampled in low and high marsh plots using the peak standing crop method. Aboveground biomass was harvested from 400 cm² quadrats during the peak of the growing season. This method excludes material decomposed or exported prior to measurement. Aboveground biomass was cleaned with DI water and separated by species. For each species, the number of culms was counted and the lengths of the longest three culms were measured. Biomass was then dried to constant weight at 70°C.



Figure 2. A typical turbidity cross-section (#4). Values are nephelometric turbidity units.

Results

Assessing creek heterogeneity

Turbidity and velocity cross-section data are presented in Appendix 1 (Table A1). On average, coefficients of variation were 18% for turbidity samples. Replicate turbidity samples from repeatedly sampling the same point have coefficients of variation (CV) averaging 5%, while replicate subsamples taken from a single grab sample have an average CV of 4%, greater than the stated uncertainty of the turbidimeter, and a likely component in the cross-sectional variability. Another possible source of variation is temporal; the time span over which samples were taken varied depending on the width and depth, but at times was 30 minutes or more per cross-section.

For cross-sections with sufficient sample sizes in different depth and width positions, ANOVAs were performed using Tukey's multiple comparison post-hoc test, to

similarity between assess lateral and vertical positions. Figure illustrates 2 the sampling regime and shows data from a typical turbidity cross-section. Three of turbiditv thirteen crosssections showed statistically significant lateral differences. and in one case significant vertical differences were observed.

Turbidity data from these cross-sections made it possible to also compare turbidities at the creek mouth to those recorded by the YSI sonde, at a fixed sub-tidal location 3-4 meters away.



Figure 3. Empirical relationships between turbidity and inorganic, organic, and total suspended sediment at Harborview marsh.

Variability exists in this relationship, especially at higher turbidities. The correlation relating turbidities at the two locations is very strong (p > 0.01; n = 11) with a coefficient of 1.5. Modeling data below 40 NTU separately retains significance and has a coefficient of 1.3.

Velocity data showed greater variation than the turbidity data (mean CV: 40%). This is due to three main factors. Low values, such as those reported here for velocity, inescapably have high coefficients of variation. A second component of the variability is related to the difficulty in stabilizing the wading rod, as described above. Although this variation is difficult to quantify and account for, it is encouraging that velocities



Figure 4. Net flux of water (panel A), salt (panel B), sediment (panel C), and precipitation (panel D). Positive values, shown in blue, reflect net import to the marsh over a tidal cycle; negative values are export.

measured by hand correspond well with the range recorded by the Argonaut. Finally, variation appears to be mainly driven by slow-flow zones within 1-2 m of the creek banks where frictional effects are greatest. The bulk of the creek remains a zone of relatively homogenous velocity.

While TSS concentrations are the most relevant parameter for measuring sediment fluxes, they are not continuously measurable. Turbidity may be used as a proxy, but this relies on a strong correlation between turbidity and TSS. Figure 3 shows that this relationship is very strong for total, inorganic, and organic sediment concentrations. This curve will continue to be populated by data gathered year-round to further strengthen and extend the range of values covered.



Tide height relative to local MHW (cm)

Figure 5. Relationship between tide height and proportional flux disparities (net flux/influx) of water (A), salt (B), and sediment (C). Blue points and regression lines indicate tides with precipitation events; gray lines and open circles indicate tides without rainfall.

Parameter trends and material fluxes

Based on depth data recorded at the YSI sonde, Harborview marsh has a 2.5 m spring tide range. The creek mouth is semi-trapezoidal and manual measurements show that the creek ranges from ~0.5 m wide at spring low tides to 30 m at extreme high tides. Tides at the site are slightly flood-dominated, with average maximum velocities on flood and ebb tides of 57 cm \cdot s⁻¹ and 52 cm \cdot s⁻¹, as recorded by the Argonaut. This velocity differential is less extreme than at other sites, where velocities can differ by upwards of 35% (Ganju et al., 2005). The average tidal prism at the creek mouth is $7.5 \cdot 10^5$ m³.

Parameters tended to varv systematically over the course of a tidal cycle. Velocity on flood and ebb tides consistently peaked within ~2.5 hours of low tide during both neap and spring tides. Salinity was around 25 ‰ until near low tide, when it would decline to ~21 ‰. The salinity signal during storm events was very clear, especially on the ebb tide. pH is similarly tied to tidal trends, with a decline from 8 to ~6.5 on ebb tides, possibly showing the effects of decomposition. Turbidity was generally low for most of the tidal cycle, but increases, sometimes dramatically, near low tide.

Figure 4 shows the balance between tidal import and export of water, salts, and sediment. Net water import occurred during 90% of the 114 tides measured (Fig. 4A). Average net inflow was 3,200 m³ per tidal cycle (TC), with a typical flow disparity of

approximately 4.3% of the average flood tide volume. The proportion of water that is unaccounted for in this study is lower than in other flux studies (Dankers et al., 1984; Ganju et al., 2005).

It is likely that a number of factors, both real and artificial, contribute to this bias. In the former category are unrecorded water losses due to evapotranspiration, incomplete drainage from marsh peat, and migration as groundwater. Artificial bias includes, for example, lateral flow variability and difficulties in measuring water stage in a wave-influenced environment. Distinguishing between real and artificial sources of bias is important, since biases resulting from the hydrologic processes noted above would not affect sediment fluxes.

The relationship between proportional flow disparity and tide height is insignificant (Fig. 5A), even when accounting for the effects of precipitation events. This time period appears to have been a period of higher than average tides, with 72% of tides extending above MHW.

Salt and sediment budgets were more tightly balanced than the water flows. Salt fluxes (Fig. 4B) were slightly positive, with an average 1.4 Mg of salt imported with each tidal cycle, equal to 0.1% of the average mass influx. Sediment fluxes also show average import of 118 kg TC⁻¹, 2.8% of mean gross influx. Neither parameter has a statistically significant relationship with high tide height (Fig. 5B/C), indicating that tide levels are not important in governing import/export tendencies. Separately modeling tides influenced by rainfall does not improve the relationships for water or salt flux disparities. Sediment fluxes, however, do show a stronger relationship with tide height when looking only at rainfall-affected (Fig. 5C). Although this relationship remains insignificant (p = 0.12), higher tides associated with rainfall events appear to yield slightly greater sediment import into the marsh.

Ancillary data

Three transects were established in the marsh, extending from the upland edge to the creek (Fig. 1). Sediment traps were deployed along these transects for approximately 90 days from mid-July to mid-September. Over this period, sedimentation rates averaged 0.16 and 0.43 g·m⁻²·d⁻¹ in the low and high marsh zones, respectively. These rates are similar to sedimentation rates measured at two nearby marshes over the same period, but significantly lower than sedimentation in central Long Island Sound marshes (Hill, unpublished data).

Geochemistry cores collected from the site for a separate study provide independent estimates of sediment accumulation. sediment Averaging accumulation rates modeled three bv techniques suggests best estimates of 2.19 ± 0.02 $q \cdot m^{-2} \cdot d^{-1}$ in the low marsh, and 2.06 \pm 0.24 g·m⁻²·d⁻¹ in the high marsh (Hill, unpublished data). Of



Figure 6. Culm density (panel A) and NAPP (panel B) at Harborview marsh.

course, sedimentation estimates from sediment cores reflect 50-100 year averages, whereas sediment traps are more apt to reflect fine-scale variations in sediment deposition.

Multiplying sediment trap data by the area of high and low marsh estimates total sediment accumulation at 590 ±150 kg for the vegetated portion of the marsh over a 60 day period. This accounts for ~5% of the 13,500 kg of sediment estimated to have been imported over the course of the Argonaut deployment, a remarkable disparity. One likely contributing factor is that only 45% of the marsh is included in this estimate of sediment deposition. There is also much uncertainty regarding mud flat deposition/erosion dynamics, such that it cannot be ruled out that they are accumulating sediment more rapidly than the vegetated areas (although a 95% contribution is difficult to reconcile). Another possible explanation is that the sediment traps were deployed so as to be representative of their respective marsh classes on an areal basis, rather than a hydroperiod basis. It is possible that creekbank areas, though marginal in areal terms, may be rapidly accumulating sediment. This is likely to be the case, since creekbanks are lower elevation and contact water before sediment has been filtered out by vegetation.

NAPP, culm density, and culm length were measured in high and low marsh plots along three transects through the marsh (Fig. 6). Culm densities averaged 2,140 \pm 220 culms·m⁻² in the low marsh, and 7,760 \pm 770 culms·m⁻² in the high marsh. High marsh culms were both denser and longer than those in the low marsh, a pattern reproduced in NAPP data, which average 481 \pm 64 g dw·m⁻²·yr⁻¹ in the low marsh and 766 \pm 182 g dw·m⁻²·yr⁻¹ in the high marsh. Productivity rates at Harborview are comparable to those observed in other LIS marshes (Anisfeld and Hill, in press; Hill, unpublished data).

The main determinant of marsh plant distributions is physical stress, and primarily flooding stress (Lefor et al., 1987). Because of local variation in tidal range and hydroperiod between marshes, the same vertical elevation can be subject to very different inundation regimes. Comparing vegetation zones based on their elevations is

Species	Mean (SE)	Lower bound	Upper bound	Range (MHW; cm)	n	therefore meaningf
Mudflat transition	94% (5)	100%	75%	-82.7 to -19.4	3	paramete incorpora
Spartina alterniflora (med/tall)	70% (5)	100%	49%	-82.7 to 1.3	14	of hydr enable
S. alterniflora (short)	51% (2)	66%	41%	-11.2 to 6.9	15	comparis tide data
S. patens	47% (2)	56%	38%	-4.0 to 9.0	13	define the
Distichlis spicata	45% (3)	61%	29%	-7.6 to 16.8	12	between relative t
Phragmites australis	42% (1)	43%	41%	5.3 to 6.9	3	local frequency
Iva frutescens	32% (3)	35%	29%	11.9 to 16.8	2	percent that inun

meaningful than parameters that incorporate measures hydroperiod. То of these enable comparisons, modeled tide data were used to define the relationship between elevations relative to MHW and local inundation frequency the percent of high tides that inundate a given elevation. With this data. plant

less

Table 1. Inundation frequency (percentage of flooding high tides) and distributions relative to MHW for species found at Harborview.

distributions could be compared based on inundation frequency (Table 1).

Mean plant distributions show anticipated trends. Low marsh plants (short and tall form *Spartina alterniflora*) are found in areas inundated more frequently than high marsh plants (*S. patens* and *Distichlis spicata*), which are, in turn, wetted more frequently than upland transition species (*Phragmites australis* and *Iva frutescens*). Although some overlap is observed, this is consistent with similar studies (Lefor et al., 1987) and suggests that competition, historical contingency, and non-hydrological physical stress remain relevant to present-day species distributions.

	Ni-60	Cu-63	Cu-65	Zn-66	Zn-67	Zn-68	Ag-107	Cd-111	Cd-114	Pb-208
1 ppb recovery (%)	101%	61%	60%	114%	100%	110%	82%	68%	67%	100%
10 ppb recovery (%)	188%	149%	143%	104%	103%	100%	100%	82%	82%	73%
CASS-5 recovery (%)	442%	241%	161%	128%	128%	109%	1%	117%	230%	98%
NHH concentration										
(ug/L)	2.75	8.47	8.36	13.0	11.6	12.7	0.015	0.183	0.193	0.274
NHH 1 ppb spike										
recovery (%)	88%	170%	161%	176%	166%	144%	7%	77%	75%	81%
Blank with Chelexed										
reagents (ug/L)	0.036	0.016	0.015	0.511	0.446	0.675	0.011	0.003	0.001	0.005
Blank with unpurified										
reagents (ug/L)	0.097	0.145	0.136	0.495	0.429	0.743	0.008	0.003	0.012	0.025

Table 2. Recoveries from Chelex experiments.

Trace metal analysis

Trace metal recoveries from aqueous samples are presented in Table 2. These data were designed to answer three questions:

- (1) Is it necessary to purify reagents that are not Suprapure grade?
- (2) Are metals quantitatively retained by Chelex?
- (3) How much eluent is necessary to quantitatively displace metals from the resin?

Blank samples were run through Chelex columns using reagents that had been previously cleaned, and without the pre-cleaning step. These blank data show that contamination resulting from purified reagents is in the low ng/L level for Ag, Cd, Cu, Pb, and Ni, but roughly 500 ng/L for Zn. Regent purification reduces contamination for all metals except Zn, Ag, and ¹¹¹Cd, which remained unaffected. Thus, the time consuming step of reagent purification is necessary to attain the ng/L accuracy required for some trace metals; question (1) above, must be answered affirmatively.

The 1 μ g/L standard offers an environmentally relevant concentration, whereas the 10 μ g/L standard give a better indication of whether the method recovers metals when they are relatively abundant. At 1 μ g/L, recoveries were problematic (>10% discrepancy) for Cu, Ag, and Cd. Recoveries at the 10 μ g/L concentration were unsatisfactory for Ni, Cu, Cd, and Pb.

Seawater-based samples offer a more difficult matrix in which to measure trace metals. The CASS-5 estuarine standard reference material had acceptable recoveries only for ⁶⁸Zn and Pb. A seawater sample taken from New Haven Harbor had low μ g/L concentrations of all metals except Pb, Ag, and Cd, which were present at the ng/L level. Spiking the New Haven Harbor sample with 1 μ g/L yielded recoveries that were within 20% for Ni and Pb, and within 25% for Cd, but otherwise problematic. Based on the very mixed recoveries for seawater and non-seawater samples, question (2) cannot be conclusively answered. More trials are required, with modified experimental procedures.

To determine how much eluent is necessary to displace the metals sorbed to Chelex resin, all samples shown in Table 1 were incrementally eluted from columns. In all cases except the un-spiked New Haven Harbor sample, the first 10 mL of eluent contains 80-90% of the total mass eluted. Recoveries from the first 16 mL of eluent contained 98% of the total mass. One exception to this is Ag, which has a more extended elution profile than other elements, particularly in seawater samples, where small but significant proportions of Ag (4-10% of the total) were still emerging from the column after 25 mL of eluent. This Ag phenomenon may have more to do with the poor trapping of seawater-borne Ag than inadequate elution; Ag recoveries were poor in seawater and eluent concentrations rapidly fell to pg/L levels. This may be because Ag reacts with the abundant Cl⁻ in seawater to form AgCl, a highly soluble compound. The monovalent charge on ionic Ag⁺ may also contribute by allowing Ag to be outcompeted for ion exchange sites on Chelex, which has a stronger affinity for divalent cations. More work remains to be done to optimize Ag recoveries, but elutions of 15-20 mL are sufficient to recover 99-100% of the trace metals retained on Chelex. This ratio makes for a 3-4x concentration factor.

Not shown in Table 2 are signal intensities for internal standards used in ICP-MS to correct concentrations. The internal standard used for Ni, Cu, and Zn appears to have significant matrix interferences due to a combination of the HNO₃ used to elute the column, and some remaining NH₄OAc that is rinsed out with the HNO₃. These compounds may be producing N₂O ($^{15}N^{14}N^{16}O$) and $^{13}CO_2$ during ionization, artificially increase the ^{45}Sc signal. Ni, Cu, and Zn are then adjusted upwards. Other internal standards used for Pb, Ag, and Cd do not show the same increase in signal intensity, suggesting that the increase is an artifact rather than a reflection of changing ionization conditions. Future work with more internal standards will explore the suitability of alternatives to Sc.

Community outreach

Results from this work have been presented to Harborview community members in several forums. Whenever possible, I also sought to use my research to address concerns of the community and encourage their engagement with the natural areas around them.

As example. the an Harborview community, like many others in low-lying coastal areas, experiences regular floodina. Several community members expressed concern wind that patterns were pushing water to the western edge of the marsh, raising tide levels and intensifying flooding on the western side of the marsh, although they lacked the equipment document necessary to the phenomenon. By setting up two water level loggers on either end of the marsh. I was able to document the relationship between high tides at the two locations (Fig. 7). This experience led to enriching discussions with community members, which helped advance their understanding of physical processes in the marsh and the nature of coastal flooding. For me, experiences such as this have exercises been valuable in communicating scientific principles and thought.



Figure 7. High tides as recorded at the creek mouth and western edge. Significant departures are mainly cases of lower tide levels at the western side of the marsh.

Conclusion

Salt marshes are typically conceived of as depositional environments, or sinks for sediment. This study examined sediment transport dynamics over multiple temporal and spatial scales within a Norwalk, CT, salt marsh. The data I present show that the sediment budget of this marsh is complex. Approximately 4 Mg of sediment moves in and out of the marsh with each tidal cycle. The ecosystem is characterized by a dramatic level of flashiness, oscillating between net influxes and net effluxes of sediment. The balance of this dynamism, at least over the study period considered here, is a slight net import. These data are consistent with literature suggesting that flood-dominated systems are net sediment importers, and also with the notion that marshes with low vegetative cover are prone to import material. More broadly, these data reinforce the concept of salt marshes as pulse-based ecosystems (Odum et al., 1995) by demonstrating the magnitude and variability of inputs.

Storm events are important pulses for tidal systems. Storms raise tides and stir up sediment, but can also wash sediment out of the marsh. In the case of Harborview it appears that storms are primarily a source of sediment. While this differs from the effect of storms in other systems (Stevenson et al., 1985), there is an overarching consistency in that storm effects seem to be a reflection of the flood- or ebb-dominated nature of the site in question. That is, in flood-dominated systems, the tendency for sediment import is enhanced by storms, whereas in ebb-dominated marshes, storms magnify the natural tendency for net sediment export.

Storms have the potential to be particularly severe in an urban context. Urban marshes are often fragmented, with human barriers (roads, houses) obstructing the natural process of inland migration that accompanies sea level rise (Donnelly and Bertness, 2001). This is certainly the case for Harborview marsh, which has anthropogenic structures lining the entirety of its upland margin. Vertical accretion is therefore essential for the long-term viability of urban salt marshes. If storms were an erosive force, it would not portend well for marshes such as Harborview.

The data presented here also contribute to an understanding of how spatial and temporal scales affect sediment budgets. Comparing tidal flux data with sedimentation rates on the marsh platform suggests that sediment dynamics at the ecosystem level appear dramatically different from a consideration limited to vegetated portions of the marsh. Only a small portion of the sediment imported to this system is deposited on the marsh surface. The sediment dynamics of mud flats appear to be an important source of uncertainty in this marsh's sediment budget.

In addition to looking in more depth at mud flat sediment dynamics, future research will expand the flux work to include trace metal measurements. Method optimization continues for the analysis of dissolved metals. The use of chelating resins holds promise for concentrating dissolved metals while also eliminating the seawater matrix. The industrial legacy of western Long Island Sound and the demonstrated importance of this marsh as a sink for sediments suggest that the marsh is likely a sink for sediment borne pollutants, although dissolved fluxes may differ since distinct processes affect the two forms.

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Appendix I: Supplemental information

Table 1 shows data from TSS and velocity cross-sections conducted to understand variation in turbidity and velocity in the creek. Samples from all vertical and lateral positions were pooled to calculate means, standard deviations, and coefficients of variation.

Cross-	No.	TIN	Depth	TSS (mean;	TSS	TSS	Velocity	Velocity	Velocity
section	samples	lide	(m)	NTU)	(sd)	(CV)	(mean, m/s)	(sd)	(CV)
1	3	Flood	0.8	9.9	1.91	0.19			
2	4	Ebb	0.8	15.05	0.81	0.05			
3	4	Ebb	0.5	15.27	2.89	0.19			
4	9	Ebb	0.8	39.38	3.77	0.1			
5	7	Ebb	0.5	92.54	19.67	0.21			
6	27	Ebb	0.5		•		0.1	0.06	0.57
7	9	Ebb	0.7				0.19	0.05	0.26
8	13	Flood	0.9		• (0.27	0.09	0.31
9	9	Flood	1.1		•		0.58	0.13	0.22
10	9	Flood	1.4		•		0.67	0.26	0.39
11	14	Flood	2.1				0.33	0.19	0.58
	5 (TSS););							
12	14 (vel)	Flood	0.26	61.2	16.67	0.27	0.33	0.16	0.49
12	8 (TSS););							
15	12 (vel)	Flood	0.76	14.34	2.69	0.19	0.64	0.27	0.43
14	13	Flood	1.9	7.54	1.27	0.17		-	
15	19	Flood	2.4	4.61	0.59	0.13			
16	19	Ebb	2.8	4.64	0.58	0.13			
17	19	Ebb	2.5	4.57	0.58	0.13			
18	18	Ebb	1.3	10.93	5.57	0.51			
19	10	Ebb	0.43	38.55	1.35	0.04			

Table A1. Turbidity and velocity cross-section data.

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