

TEMPORAL AND SPATIAL VARIABILITY OF METAL DISTRIBUTIONS IN STATEN ISLAND
MARSH-CREEK SYSTEMS: DOES CONNECTIVITY TO THE ARTHUR KILL IMPACT
ANTHROPOGENIC ENRICHMENT, SEDIMENT QUALITY, AND TOXICITY POTENTIAL IN NY/NJ
THE MARSH HABITATS?

by

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Volume I

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ABSTRACT

TEMPORAL AND SPATIAL VARIABILITY OF METAL DISTRIBUTIONS IN STATEN ISLAND MARSH-CREEK SYSTEMS: DOES CONNECTIVITY TO THE ARTHUR KILL IMPACT ANTHROPOGENIC ENRICHMENT, SEDIMENT QUALITY, AND TOXICITY POTENTIAL IN NY/NJ HE MARSH HABITATS?

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The Arthur Kill is a polluted urban waterway situated between Staten Island, New York and New Jersey. It is unknown if this tidal strait serves as a significant source of trace metals to Staten Island marsh habitats, via redistribution and exchange, and thereby contributing to the substantial metal contamination found in sediments within these areas. Although loadings into the Arthur Kill have declined in recent years, the combination of historic impacts, modern point and non-point sources, and low flushing rates make this waterbody a sink for pollutants. Contaminated sediments are susceptible to remobilization via tidal action and shipping/dredging activities. Consequently, this may transport metals bound to suspended particles to neighboring areas, with subsequent uptake and toxicity to resident biota.

The primary goals of this dissertation research was to characterize spatial and temporal trends in sediment metal (Cd, Hg, Cu, and Zn) contamination in salt marshes adjoining the Arthur Kill; and examine the distribution and tidal transport of pollutants between the Arthur Kill and upland marsh habitats along the western shore of Staten Island, New York. Insight concerning temporal and spatial change within marsh habitats will aid in tracking success of current water quality initiatives targeting this severely impacted waterway. Research into the exchange of metals in polluted estuarine areas similar to this system is essential from a restoration standpoint and is a crucial step in gaining an overall understanding of metal transport and redistribution within this highly industrialized and ecologically important system.

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Chapter 1

Introduction

GENERAL INTRODUCTION

Historically, estuarine areas have acted as centers for industrial and urban development and consequently are known to be reservoirs for pollutants (Cundy, et al., 2003). Although anthropogenic discharges have declined, contemporary inputs as well as previous releases continue to threaten these areas, and thereby cause them to function as sinks of, and possible sources for, contaminated sediments (Hwang, et al., 2006; Balcolm, 2008). In polluted aquatic systems, sediments are an important repository of contaminants. When proximal to urban areas, estuaries are particularly vulnerable to the impacts of particulate reactive contaminants as slow currents, characteristic of some estuarine habitats (i.e. marsh-creek systems), promote the deposition of sediments (Tischler, 1998; Heyden, et al., 2004). Sediment deposition that is dominated by the attenuation of clean sediments can be a positive mechanism for reducing surface contamination over time by burying and containing pollutant-laden sediments (Weis, et al., 2005; EPA, 2008). Furthermore, within marsh areas tidal creeks act as conduits with the potential to exchange and distribute sediment-bound pollutants between upland marsh habitats and adjacent estuarine environments (Sanger, et al., 1999b).

Metals have been recognized as a specific concern in the protection and management of estuarine systems because of their potential toxicity. But elevated metal concentrations can also serve as a proxy for other toxic pollutants, signaling the presence of additional contaminants (Schropp, et al., 1988). Although natural attenuation can occur in the absence of active sources that contribute elevated metal loadings to marsh habitats, metals cannot be eliminated by

physical and biochemical processes at any depth. Non-degradable and persistent contaminants (e.g., metals) associated with fine-grained sediments threaten marsh habitats through a variety of processes that promote sediment resuspension and redistribution, and associated pollutants can be recycled within the ecosystem for many years following the cessation of previous inputs (Valiela, 1995; Hwang, 2006). The potential for continual release of contaminants from sediments put local biota at risk of possible exposure via direct uptake or through trophic transfer (Gillis, et al., 1995; Tischler, 1998; Hornberger, et al., 1999; Boorman, 1999; Hwang, 2006). However, evidence of natural attenuation, via source control or elimination, can buffer overlying waters and resident biota from diffusion and advection of pollutants from sediments and thereby reduce bioavailability and toxicity in upper sediment horizons, and limit remobilization of contaminated sediments and trophic transfer of pollutants (USEPA, 2008).

Dynamics of estuarine systems are difficult to fully understand because of a number of reasons. These include the non-linear behavior associated with fine grained sediment cohesion, biological modifications to the environment (bioturbation, plant stabilization) and physical-chemical interactions within sedimentary deposits (role of pollutants and organics in substrate stability) (Goodbred, et al. 2004). Accordingly, the complexity of estuarine systems makes it difficult to determine the effects of metals on these ecosystems. Knowledge of the physical and geochemical processes governing the transport and redistribution of metals in estuarine environments is critical to understanding metal bioavailability, toxicity and trophic transfer within these sensitive systems (Luoma, 1989).

Due to the interconnectedness and dynamic processes that occur within coastal environments, applied wetland research requires studying fundamental dynamics within both the marsh proper and the adjacent estuarine system. The majority of sediments delivered to the

marsh surface may be derived from resuspension of estuarine sediments or alternatively, runoff from within the catchment area. Estuarine sediments serve as reservoirs that provide temporary storage for new sediments, which may become remobilized and subsequently transported onto the marsh by a combination of waves, tides, and storms (Goodbred, et al., 2004). Thereby, estuarine sediments may serve as vectors for particle-reactive contaminants, just as tidal creeks may act as contaminant conduits to inland marsh environments (Suszkowski, et al., 2006).

STUDY AREA

The geographic context of this study is the center the New York Bight habitat study area, otherwise defined as the New York-New Jersey Harbor Estuary Core Area (NY/NJ HE). In general, this dissertation targeted tidal wetland systems that drain into open NY/NJ HE waterways that are located within different sub-regions of the Estuary, the Arthur Kill-Kill van Kull and Lower New York Bay, respectively (Fig. 1a). Specifically, this included three Staten Island marsh-creek study sites that are catchments within Arthur Kill or Raritan Bay watersheds (Fig 1b). Main Creek (MA) and Neck Creek (NC), which are located along the western shore of Staten Island, are adjacent subwatersheds of the Arthur Kill. In contrast, Lemon Creek (LC) is located within the eastern Raritan Bay subwatershed, Lemon Creek-Sandy Brook, and is situated along the southern shore (Fig 1b, Fig. 2).

Staten Island is surrounded by estuarine waterways; Raritan Bay to the east and south; Arthur Kill to the west; Kill Van Kull to the north and the Narrows (Hudson River) to the northeast. In total, 28,374 acres of estuarine waters have been ascribed to Staten Island (Richmond County), with the bulk of this acreage associated with Raritan Bay. The Island itself contains about 59 square miles of land mass and 18 miles of linear estuarine waters (National

Wetlands Inventory, USFWS, 1997). About 90 percent of Staten Island is now upland, characterized by mainly residential development (low and high intensity = 28% and 26%, respectively), upland forests (22%), and commercial/industrial/transportation development (10%), whereas, the remainder is classified as wetland or deepwater habitat. Altogether, wetlands occupy 9 percent of Richmond County. Vegetated wetlands are predominant, with approximately 2750 of 3407 Staten Island wetland acres inventoried.

The Fresh Kills Landfill Complex and William T. Davis Wildlife Refuge border Main Creek. Main Creek upland marsh and creek habitats are hydraulically-connected to the Arthur Kill Proper via Fresh Kills Creek. Main Creek and Neck Creek are parallel tidal wetland systems that extend from the Arthur Kill. Neck Creek is approximately 1.5 miles north of Main Creek and extends directly from the main channel of the Arthur Kill towards upland marsh habitat, covering 60-acres of land (OASIS NYC, 2011). In contrast, Lemon Creek is external to the Arthur Kill Complex and reaches in a northern direction from the Raritan Bay (Ward, 2002; Nichols, 2004).

Despite disparate geography, Main Creek, Neck Creek and Lemon Creek are tidal wetland systems that provide unique creek and upland marsh habitats and various essential ecosystem services, which are critical for sustenance and survival of many important benthic and threatened species (Bain, et al., 2006). All study sites have been recognized as habitats that are significant with respect to the NY/NJ Harbor Estuary Core Complex (USFWS, 1997) (Fig. 3a). Each study site represents a diversity of wetland habitat types, primarily tidal and non-tidal emergent salt, brackish, and fresh marshes, mudflats, ponds and creeks, dominated by cord

grasses (*Spartina alterniflora* and *S. patens*), spike grass (*Distichlis spicata*), marsh elder (*Iva frutescens*), common reed and cattail (*Typha latifolia*) (Fig. 3b.).

Wetlands are classified by their vegetation type or substrate (for non-vegetated areas), predicted water regime (hydrology), and other features. A variety of wetland types exist due to differences in soils, hydrology, water chemistry, vegetation, and other factors. Staten Island contains both tidal and non-tidal wetlands. Tidal wetlands (e.g., salt marshes and tidal mudflats) are lowlands along coastal embayments and tidal rivers. Most are flooded with brackish water by high tides, but a few are strictly freshwater wetlands whose water levels rise and fall with the tides. Staten Island's non-tidal wetlands (e.g., freshwater marshes, swamps, and vernal pools) occur beyond the reach of ocean-driven tides. They are found on flood-plains along streams (lotic wetlands), in the shallow water zone and along the margins of lakes (lentic wetlands), in ponds and along their shores, and in isolated depressions surrounded by upland (terrene wetlands). Some wetlands are formed on slopes where groundwater seeps out from below ground (terrene slope wetlands). Most wetlands are colonized by plants and are commonly called "marshes", "wet meadows", "swamps", and "bogs". Their periodic wetness or shallow water habitat distinguishes them from "deep water habitats" of lakes, rivers, and reservoirs.

The U.S. Fish and Wildlife Service classifies wetlands into five ecological systems: marine, estuarine, palustrine, lacustrine, and riverine (USFWS, 1997). In addition, wetland types are often named after their dominant plant species, such as common reed marsh, cattail marsh, red maple-sweet gum swamp, and alder swamp. Vegetated systems are commonly referred to as "salt marshes" (estuarine emergent wetlands), as they are dominated by halophytes. In contrast, non-vegetated estuarine wetlands include beaches, intertidal flats, and rocky shores along tidal rivers and coastal embayments (NYS DEC, 2009). Non-vegetated wetlands are periodically

exposed flats or shallow water areas along the shores of rivers, streams, ponds, and lakes. The majority of Staten Island's wetlands are vegetated, and either classified as estuarine wetlands or palustrine wetlands (NYS DEC, 2009). The three study sites focused on in this dissertation, Main Creek, Neck Creek and Lemon Creek, are examples of estuarine wetlands that are tidal, subjected to daily irregular inundation by salt water.

Estuarine wetlands are tidal marshes, mudflats, and sandy beaches associated with coastal embayments (e.g., Raritan Bay) and brackish rivers and streams. Estuarine wetlands may be further sub-divided, based on the frequency and duration of tidal inundation. Accordingly, low marsh areas are regularly flooded zones (inundated daily by tides), whereas high marsh areas are irregularly flooded zones (inundated less often than daily). The low marsh is characterized by the tall smooth cordgrass which grows to about 6 feet in these places. Vegetation of the high marsh is more varied with several dominant species including smooth cordgrass (short form less than 3 feet tall), salt grass, salt hay grass, and black grass (actually a rush), plus high-tide bush (especially in ditched marshes). Among the high marsh, depressions may be present, including pools or pannes (shallow flats). As expected, plant diversity in estuarine marshes typically increases along the upland border, with typical flora including stands of *Phragmites*, which can be found along the upper edges of all sites, and is common in stressed marsh areas, and/or in areas with restricted tidal flows (NYS DEC, 2009; Wollney and Johnson, 2010).

Arthur Kill

The study area includes the Arthur Kill along with the three salt marsh/creek habitats surrounding Staten Island. The Arthur Kill is an interstate tidal strait that stretches approximately thirteen miles in length and separates Richmond County in Staten Island, New York from Union and Middlesex Counties in New Jersey (Fig. 6a-b). This urban waterway is

bounded by densely populated areas and serves as the receiving water for effluents from many manufacturing and industrial facilities (Huntley, et al., 1995) (Fig. 5a-b, Fig. 7a-b). The Arthur Kill connects northern waterbodies, including the Kill van Kull and Newark Bay Complex, with the Raritan Bay and the Raritan River to the south (IEC, 1957). This waterway is important both economically and ecologically due to its connectivity (hydrological and biological) with waterways of the NY/NJ Harbor Estuary (NY/NJ HE).

The US Fish and Wildlife Service found that the Arthur Kill has an average flushing time of approximately two weeks (USFWS, 1997). The strait is flushed by dual tidal surges (Fig. 2) with an average semi-diurnal tidal range of 1.6 meters (5.3 feet). This lack of vigorous tidal flushing results in longer residence times, and thus longer transit times for contaminants (Butcher, et al., 1992). Previous studies have found that “slugs” of contaminated water move back and forth in the Arthur Kill with the ebb and flood of the tide, without major changes in the strength of pollutants (IEC, 1957). During flood tides Raritan Bay waters flow northerly into the Arthur Kill, and are primarily directed towards the lower end of the Newark Bay, with partial movement across the southern end of the Newark Bay easterly into the Kill van Kull. It follows that when the Raritan Bay is ebbing, the flow of waters in the Arthur Kill reverses to a southerly direction into the Raritan Bay, and some of the waters from the Newark Bay are drawn into the Arthur Kill (IEC, 1957; Lowe, et al., 2005).

In addition to slow flushing and long residence times, this waterway is further impaired by heavy shipping traffic (IEC, 1957; USFWS, 1997). The study area is part of the Port of New York and Jersey, which encompasses the extensive maritime facilities surrounding New York Harbor, and is categorized as the third busiest port in the nation (Caplow, et al., 2003). The Arthur Kill has been subjected to dredging activities, which have greatly altered its physical

features. This includes the region's network of salt marshes and overall wide and shallow estuarine environments that have been transformed into major shipping channels with bulkheads, and harbor traffic that has altered and eroded much of the shoreline (Vitaliano, et al., 2002; Caplow, et al., 2003).

Raritan Bay

The Raritan Bay is the westernmost portion of the Lower New York Bay Complex, extending west from Crookes Point on Staten Island, New York, to Point Comfort, New Jersey. The Bay is triangular in shape, with the apex of the triangle being the mouth of the Raritan River, the major source of freshwater input to Raritan Bay. A secondary source of significant volume contributes through the Arthur Kill, which carries water from Newark Bay and Upper New York Bay via the Kill Van Kull to Raritan Bay. The circulation pattern through Raritan Bay is counterclockwise, with water moving along the New Jersey shoreline toward the Bight. Flushing times are longer in this system than in other portions of the Hudson-Raritan estuary (USACE-NYD 1999).

Raritan Bay has extensive shoals and shallows cut by a network of navigation channels. The dredged navigation channels are 80 to 1,400 feet wide and are maintained to depths ranging from 10 to 35 feet – Mean Lower Low Water (MLLW). Outside the navigation channels, the bay has a mean depth of 22 feet and shoal depths are generally less than 20 feet. The mean tidal range is from 4.7 to 5.0 feet. The range of spring tides within the bay is 5.7 to 6.0 feet.

Water entering Raritan Bay carries a substantial amount of Sewage Treatment Plant (STP) effluent, and, consequently, is nutrient-rich. This, coupled with the Bay's relatively long flushing times and shallowness, provides ideal conditions for phytoplankton production. Shoreline

development ranges from heavily developed industrial complexes in the vicinity of Perth Amboy to areas of intertidal marshes, creeks, dunes, sand beaches, and remnant forests along the Bay's southern and western ends. The Staten Island shoreline includes beach, forest, pond, and wetland areas, as well as intertidal and subtidal mudflats that extend out to 0.25 miles (USACE-NYD 1999).

Marsh Study Sites

Study sites for this project include three salt marsh-creek systems surrounding Staten Island, New York: Main Creek (MA), Neck Creek (NC), and Lemon Creek (LC) (Fig. 3b and 4). Physiochemical measurements characterized by each of the three marsh-creek habitats, generally classified as estuarine vegetated wetlands, confirmed all study sites were oligohaline systems.

Neck Creek and Main Creek are located within the Arthur Kill proper and, to varying degrees, are impacted by a combination of sources related to past and present metal pollution. Neck Creek (NC) extends ~0.6 km south of Prall Island, which is situated in the northern of reach of the Arthur Kill, approximately 1.5 miles north of Fresh Kills landfill, along the western shore of Staten Island. The NY/NJ Harbor Estuary Program (HEP) Habitat Workgroup has developed watershed-based priorities for acquisition, protection, and restoration, and identifies Neck Creek as a tidal wetland for priority habitat acquisition and preservation (Habitat Work Group, 2001). This site (AK 13) is considered to be high priority because of its important ecological value to the NY/NJ Harbor Estuary, and therefore, the initiative aims to save and protect the remaining habitats surrounding the area (Suszkowski, et al., 2006; Habitat Work Group, 2001; Suszkowski, et al., 2006) (Fig. 1b). Surficial sediments at Neck Creek are contaminated (Cd, Cu, Pb and Zn) and chronologies (from cores collected in 2001) show a

subsurface peak followed by a modest recovery from a past contamination source (Appendix 2-B, 2-C; Hirschberg, 1996; Ward, 2002; Nichols, 2004).

The Main Creek (MA) marsh study site is connected to the Arthur Kill via Main Creek, which stems from Fresh Kills Creek and is surrounded (to some extent) by the Fresh Kills landfill, which covers nearly 1,100 hectares of former marshland, with almost 60 meters of solid waste, making it the largest landfill in North America (Clemants, et al., 2009). Main Creek, which is part of the William T. Davis Wildlife Refuge, is located due north of Richmond Creek, which is also a tributary of Fresh Kills Creek. Metal contamination in sediment from Main Creek appears to be consistent over time, and has been shown to exhibit similar pollutant trends with Richmond Creek. A constant source of heavy metal pollution appears to impact both marshes (Ward, 2002; Nichols, 2004). An obvious, though as of yet undetermined, source of contaminants to these sites would be the Fresh Kills Landfill.

Lemon Creek (LC) is located on the southeastern shore of Staten Island and is external to the Arthur Kill. Lemon Creek, which empties directly into Raritan Bay ~4 km north-east of the confluence between the Arthur Kill and the Raritan River, will serve as a regional reference marsh. The value of a regional reference site is that it will provide sediment core and particulate metal data from a site not directly impacted by the Arthur Kill. This will facilitate comparisons between study sites, and will help to assess if connectivity to the Arthur Kill or site-specific inputs are major sources of metal contaminants to study sites. This site is within the NY/NJ Harbor Estuary Program's (HEP) restoration site Lemon Creek (RB1) and is earmarked for a possible anadromous fish passage ladder project. Compared with sites within the Arthur Kill complex, Lemon Creek has been minimally impacted by metal contamination, although current sources of pollution may include urban runoff, marina activities, and the remediation of a dental

tool manufacturing facility near the creek (Ward, 2002; Nichols, 2004). The Lemon Creek flows through Lemon Creek Park which is regarded as one of the largest and most pristine salt marshes in Staten Island, which provides spawning and nursery grounds for a variety of fish and shellfish species, and a habitat for many migratory birds, including one of the only purple martin bird colonies in New York City (NYC Dept. Parks, 2007).

The Arthur Kill complex consists of four major habitat categories: colonial wading bird breeding sites or heronries; water bird foraging areas; freshwater marshes and wooded swamps; and upland forests. In addition to three island heronies (Shooters Island, Prall's Island and Isle of Meadows), Neck Creek Marsh, Fresh Kills, Main and Richmond Creeks are considered among the main foraging areas along the western shore of Staten Island.

Furthermore, the NY/NJ Harbor Estuary Program (HEP) Habitat Workgroup, which has developed watershed-based priorities for acquisition, protection and restoration, and the United States Army Corps of Engineers, have identified Neck Creek as a tidal wetland for priority habitat acquisition and preservation (NY/NJ HEP Habitat Work Group, 2001; USACE, 2010). Neck Creek, classified as "AK 13" or Comprehensive Restoration Plan (CRP) 17, is highly prioritized due to its importance and ecological value to the NY/NJ Harbor Estuary.

Accordingly, initiatives aim to save and protect the remaining habitats surrounding Neck Creek (Suszkowski, et al., 2006; NY/NJ HEP Habitat Work Group, 2001; Suszkowski, et al., 2006). Lemon Creek is also included as a NY/NJ Harbor Estuary Program (HEP) restoration site (RB1) and a Comprehensive Restoration Plan site (CRP 109). The site covers 10 acres of land that is currently owned by New York City Department of Parks and Recreation (NYCDPR) and National Park Service (NPS) (Open Accessible Space Information System (OASIS NYC, 2011).

United States Fish and Wildlife Service states that although many marshes around Staten Island are severely disturbed or degraded, Lemon Creek is one of the few undisturbed tidal wetlands, and the only undisturbed area that remains along the south shore of Staten Island (USFWS, 1992).

Land-use and anthropogenic impacts

Coastal areas along the Arthur Kill have been developed for industrial, commercial, and residential land uses, leaving the waterway susceptible to a variety of anthropogenic sources (point and non-point) of metal pollutants (Figs 7a-c). Many industrial and municipal facilities, including paint and chemical manufacturing industries, port facilities, petroleum refineries, metal scrap yards, wood treatment plants, and wastewater treatment facilities border the Arthur Kill's shores (Figs. 5a-b) (Huntley, et al., 1995).

The Arthur Kill study sites are surrounded by industrial areas that are interspersed with residential communities, which results in large amounts of wastes being brought into treatment plants from both industrial land-uses, commercial and residential land uses (Figs.7a-c, Figs.8-8a). Wastewater originating from these areas is processed locally and discharged directly or indirectly into the Arthur Kill. Improvements in the treatment of wastewater and industrial effluents emptying into these receiving waters has improved the quality of Arthur Kill sediments and surface waters, however concentrations of trace metals within sediments remain elevated (Vitaliano, et al., 2002). In addition, an obvious, though as of yet undetermined, source of contaminants to these study sites would be the Fresh Kills Landfill located along the western shore of Staten Island, and the closed Brookfield Landfill located in the central western portion of Staten Island (east of Fresh Kills Landfill) (Ward, 2002; Nichols, 2004) (Fig 5).

The Brookfield Avenue Landfill was originally designated as Sections 10 and 11 of the Fresh Kills Landfill, where it accepted municipal solid waste from 1966 until 1980, but reportedly industrial and hazardous wastes were illegally dumped at the landfill during the period from 1974 through 1980 (ATSDR, 1999). The Agency for Toxic Substances and Disease Registry (ATSDR) has identified the site as an "indeterminate public health hazard," meaning judgment regarding the degree of health hazard cannot be made because information critical to such a decision is lacking. This conclusion was drawn after the agency was petitioned to investigate health concerns of residents living near the Brookfield Avenue Landfill and to determine any link between reproductive health problems and cancers in neighboring areas, and potential contamination of air, groundwater and surface waters attributable to the landfill (ATSDR, 1999; ATSDR, 2010). The New York State Department of Environmental Conservation (NYSDEC) has classified the site as a Class 2 inactive hazardous waste disposal site (Fig 5a-b).

Contamination in Study Reach

Many studies have been conducted in close proximity to the Arthur Kill, including the Hudson River, New York Bight, Raritan River, and Newark Bay, however many of the natural, physical and biological processes contributing to contamination in these areas are not entirely understood. Characterizations of Arthur Kill sediment and water quality have been included in research on the Newark Bay Estuary and New York/New Jersey (NY/NJ) Harbor Estuary (HE) (Gillis, 1995; Levinton, et al., 2006). The New York/New Jersey Harbor Estuary is considered one of the most polluted, environmentally degraded systems in the United States (Mueller, et al., 1982; Olsen, et al., 1984; Huntley, et al., 1995). The Arthur Kill is identified as one of New York Harbor's "inner waterways," that contain some of the most toxic sediments and waters,

with respect to PCBs, dioxins, PAHs, and heavy metals, in the NY/NJ Harbor Estuary (Caplow, et al., 2003; Steinberg, et al., 2004). Newark Bay estuarine sediments have been assessed for sediment toxicity by assaying samples for contaminants, including DDT, DDD, and DDE (Gillis, et al., 1995). Several waterways of the Newark Bay Estuary have exhibited either decreased or constant levels of these compounds, however, elevated concentrations (among the highest in the Estuary) were found in recently deposited sediments in the upper and lower reaches of the Arthur Kill. These findings suggested that the potential for adverse effects to biota appears to be the greatest in the Arthur Kill (Gillis, et al., 1995).

Concern regarding sediment associated contaminants of this interstate waterway has been identified in research targeting the NY/NJ HE (Crawford, et al., 1995; Dimou, et al., 2006). Toxicity within the New York/New Jersey Harbor Estuary has been largely associated with high concentrations of degradable toxins like PCB and dioxins, however, these estuarine sediments are also considered to be among the nation's most heavily contaminated with non-degradable metal pollutants (Bopp, et al., 2006). Surveys conducted in 1991 examined the spatial extent of sediment toxicity in estuaries across the United States, and ranked several sites within the Hudson and Raritan estuaries among the most toxic in the nation (Long, et al., 1996; Weis, et al., 2006). Mercury (Hg) is considered a pollutant of primary concern in the Harbor Estuary, due to continued discharges from both point sources and atmospheric deposition, which result in concentrations that exceed enforceable standards (NY/NJ HEP, 1996; Balcolm, et al., 2008). Both cadmium (Cd) and copper (Cu) have also been identified as chemicals of concern to the NY/NJ Harbor Estuary, as they exceed unenforceable criteria and are predicted to exceed enforceable criteria, respectively (NY/NJ HEP, 1996).

Many sites within these estuaries have been found to exceed toxicity benchmark values set for Hg and other contaminants in both sediment and biota (Wolfe, et al., 1996; Balcolm, et al., 2008). Evaluation of sediment quality in the Hudson/Raritan Estuary through sediment and toxicity tests revealed that fifty percent of sites studies (in 1991 surveys) had at least one contaminant that exceeded Long and Morgan's ER-M values (Long, et al., 1991; Adams, et al., 1998; Weis, et al., 2006). Comparison of Cd, Hg, and Pb concentrations in Arthur Kill sediments with benchmark sediment quality criteria and toxicity guideline values have suggested that these sediments contain metals at levels that may pose a significant threat to aquatic life (Bonnevie, et al., 1992). Increasing efforts to broaden knowledge of sediment chronologies throughout the estuary have facilitated the characterization of major sources of trace metals to the Arthur Kill, such as smelting operations at a National Lead site (Chillrud, 1996; Bopp, et al., 2006).

Dredging activities can cause resuspension of estuarine sediments and subsequent mobilization of exchangeable metals trapped within sediment (Audry, et al., 2006). Nonpoint sources and benthic remobilization from contaminated sediments are important sources for some toxic heavy metals to the Hudson River estuary (Sanudo-Wilhelmy, et al., 1999). For instance, remobilization of mercury deposits that have accumulated over the past century within Hudson estuarine sediments, defined as "legacy Hg", continue to serve as a source of contamination to the ecosystem (Fitzgerald, et al., 2003; Balcolm, et al., 2008).

Few studies have focused specifically on the Arthur Kill, and little is known about the relationship between this tidal strait and adjacent marsh habitats. However, sediment in the Arthur Kill and adjoining salt marshes and creeks have been shown to be contaminated with a variety of pollutants (e.g., Cd, Cu, Hg) and biota residing in this area have shown a variety of

adverse effects (Wolfe, et al., 1996; Ward, 2002; Wallace, et al., 2003; Nichols, 2004; Ward, 2002). Additionally, the presence of oil refineries and associated pollutants (e.g., PAHs) in the Arthur Kill further threaten local ecosystems (Huntley, et al., 1995). Although loadings into the Arthur Kill have declined in recent years, the combination of historic impacts and contemporary inputs (point and non-point sources) allow this waterbody to act as a sink for pollutants. Low flushing rates and increased residence times, characteristic of the Arthur Kill, exacerbate the problem by promoting the deposition of contaminant-laden particles (Huntley, et al., 1995; Chant, 2005). Along with a suite of biogeochemical processes, contaminated sediments within the Arthur Kill are susceptible to remobilization due to heavy shipping traffic, dredging and tidal action. The Arthur Kill may therefore be an important active source of metal pollutants to Staten Island marsh habitats (and associated biota) if resuspended contaminant-laden sediment from the Arthur Kill is transported to adjacent areas (Luoma, 1989; Hornberger, et al., 1999; Audry, et al., 2006).

Urbanized coastal regions remain vulnerable to anthropogenic stressors that ultimately contribute to the alteration and loss of estuarine habitats via associated input and accumulation of pollutants, such as metal contaminants (Kennish, 2002). Although conditions within the NY/NJ Harbor Estuary have shown vast improvement, certain areas, including the Arthur Kill, are still impaired by historic as well as contemporary contaminant loadings (Gillis, et al., 1995; Sanudo-Wilhelmy, et al., 1999; Gillis, et al., 2004).

Previous research has established that the Arthur Kill is a polluted urban waterway that functions as a reservoir (sink and a potential source) of toxic pollutants (Thomann, 1989; Gillis, et al., 1995; Huntley, et al., 1995; Sanudo-Wilhelmy, 1999; Steinberg, et al., 2004). Observed metal contamination within the marshes is presumed to be the result of various contributions

from historic and present-day anthropogenic activities. Prior studies have noted that some marshes along the Arthur Kill have exhibited evidence of recovery via natural attenuation, while others appear to have a relatively consistent level of elevated concentrations resulting from unidentified sources (Ward, 2002; Nichols, 2004). It is plausible that the Arthur Kill may serve as a source of contaminants as sediments within the main channel of the Arthur Kill can become remobilized via tidal action and shipping/dredging activities, and these contaminant-laden suspended sediments may be redistributed to marsh habitats. Resident biota may either feed directly upon these suspended particles or indirectly once they become part of the bed load. Associated contaminants would then be available for possible bioaccumulation and trophic transfer (Luoma, 1989; Hornberger, et al., 1999; Seebaugh, et al., 2005; Audry, et al., 2006).

Suspended particulate matter is integral in the geochemical cycling of metals in aquatic systems. However, little is known about suspended particulate metal concentrations and fluxes in conduits that connect the Arthur Kill to marsh habitats. It is unknown if contaminated sediments within the Arthur Kill are remobilized by tidal action/dredging activities, and are being advected to adjacent areas. Insight into the transport of metals bound to suspended particulate matter/sediment will provide information regarding the physical and geochemical processes governing the redistribution of metals within the water column and marsh bed sediments that are tidally influenced by the Arthur Kill.

Research into tidally mediated resuspension and redeposition of contaminated sediments in a polluted estuarine system, such as the Arthur Kill, is essential from a habitat restoration standpoint. Identification of important factors that contribute to metal contamination in marsh areas can support a more sustainable development of wetland ecosystems, and are integral in the assessment of the conditions where wetland creation is suitable (Du Laing, 2008). Many areas

bordering the Arthur Kill are slated for restoration and remediation and the successes of these efforts may be compromised by the environmental quality of the Arthur Kill. If sites are remediated and subsequently become re-contaminated via a local source, like the Arthur Kill, these efforts may be both inefficient and ineffective, resulting in the loss of time and resources. Site assessment of contaminants and an understanding of the exchange of contaminants between the Arthur Kill and associated marsh habitats would be a useful management tool in prioritizing, as well as setting target criteria for restoration initiatives within the NY/NJ Harbor Estuary.

BACKGROUND

Classification of Trace Metals

Trace metals are elements that may serve as nutrients, however at high enough concentrations they may become toxic. Metal ions have been categorized into three groups, type A, type B, or borderline, based upon their inherent chemical properties (Ahrland, et al., 1958). Equilibrium constants for the formation of metal-ligand complexes have been utilized for classification purposes, where, type A metals generally seek out oxygen donors, type B metals react with nitrogen and sulfur donor ligands and borderline metal ions react with all categories of ligands (Ahrland, et al., 1958; Batley, 1989). Type A metal cations include: alkali metal cations Li^+ to Cs^+ , alkaline earth metal cations: Be^{2+} to Ba^{2+} , lighter transition metal cations in higher oxidation states: Ti^{4+} , Cr^{3+} , Fe^{3+} , Co^{3+} , and the proton, H^+ . Type B metals include heavier transition metal cations in lower oxidation states: Cu^+ , Ag^+ , Cd^{2+} , Hg^+ , Ni^{2+} , Pd^{2+} , Pt^{2+} (Ahrland, et al. 1958).

In estuarine systems metals are transported both in solution and on particle surfaces, where sorption processes are largely governed by the nature of the particle (i.e. inorganic or

biogenic) (Huthnance, et al., 1993). Generally, type A metals are geochemically reactive and form positively charged ions that react with negatively charged ions, like oxygen and suspended particles, and subsequently become retained in estuarine sediments. Alternatively, type B metals differ in that they are more biochemically active, and have propensity to form organic complexes that make them stable for transport through estuarine systems (Church and Scudlark, 1998). Borderline metals represent an intermediate class that do not have a preference for bonding to a specific type of donor atom and can react with all types of ligands (O_2^- , S^- , N^-) (Arhland, et al., 1958; Nieboer, et al., 1980; Batley, 1989). However, borderline ions can exhibit type A (i.e. Ni^{2+} , and Zn^{2+}) or type B (i.e. Cu^{2+} , Cd^{2+} , Pb^{2+}) character (Batley, 1989).

Metals are also classified based upon their role in biological functioning of organisms (Boevski, et al., 2007). Several trace metals, including iron (Fe), manganese (Mn), copper (Cu), cobalt (Co), zinc (Zn), calcium (Ca), selenium (Se), molybdenum (Mo), vanadium (V), strontium (Sr), are required for life processes, however, any element that reaches excessive levels can be detrimental and become toxic (Batley, 1989; Kennish, 1992; Church, et al., 1998; Boevski, et al., 2007). Non-essential metals, including cadmium (Cd), mercury (Hg), lead (Pb), chromium (Cr), arsenic (As), antimony (Sb), nickel (Ni), and silver (Ag), become toxic at certain concentrations and are of particular concern in surface waters (Kennish, 1992; Church, et al., 1998; Boevski, et al., 2007). In terms of toxicity, type B metal ions have a broad range of toxicity mechanisms and are considered to be the most toxic, followed by borderline metals (Batley, 1989; Shaw, et al., 2004).

Point and Non-Point Sources of Metals

Pathways of trace metals inputs are associated with natural and anthropogenic sources; however the natural cycling of metals into the environment is often exacerbated by human

activities. Both point and non-point sources contribute to metal contamination. Point sources that discharge metal pollutants into receiving waters include municipal and industrial wastewater treatment plants, stormwater outfalls and combined sewer overflows. Non-point sources contribute metals via atmospheric fallout on coastal waters, runoff from land, and leachate from mining, petrochemical and oil refineries, construction, and landfills (Hare, 1992; Helgen, et al., 1996; Herut, et al., 1997; Rozan, et al., 2001; Weis, et al., 2006).

Although anthropogenic inputs are often the primary source of certain metals, weathering and geochemical inputs also allow metals to enter the aquatic environment (de Groot, 1995). Delivery of trace metals to estuarine environments involves physical means, including aeolian and fluvial processes, and tidal energy and currents (Herut, et al., 1997; Church, et al., 1998). Natural pathways that contribute to metal releases include the chemical and physical breakdown of igneous and metamorphic rock and soil aggregates through weathering and erosion processes, decomposition of plant or animal detritus, precipitation or atmospheric decomposition of airborne particles from volcanic activity and from forest fires (Kennish, 1992). When leached from soils, metals can become mobilized by forming soluble complexes with organic molecules and other ligands. Metals become adsorbed by particulate material and associated organic matter debris and are transported to surface and groundwaters. Changing environmental conditions can cause metals to be released from the sediment; contaminants accumulate in local sediment profiles and erosion may re-release them into the environment (Andrews, et al., 2004).

Anthropogenic activities have altered the distribution and flux of many metals through the environment. Metal loads have been augmented above background levels, and thereby have obscured the natural range of metals in the environment (Valiela, 1995; Bopp, et al., 2006). This can be attributed to increased emissions from both non-point and point sources, which have

altered the forms and physical states in which metals occur in the environment. Since the onset of industrialization, associated discharges have quickly introduced increased metal loads into estuarine environments. Subsequently, receiving waters have become reservoirs for pollutants, acting as sinks and sources for fine, contaminated sediments (Cundy, et al., 2003; Hwang, et al., 2006).

Input loads of heavy metal pollutants may also result from land runoff. Frequently, high concentrations of metals are found within sediments in areas associated with urban and industrial land-uses, which are not attributed to discrete discharges (Suszkowski, et al., 2006). Stormwater runoff is recognized as a significant source of metal contamination to surface waters and sediments (Rice et al., 2002). Such non-point source pollution is difficult to control, especially when derived from a variety of locations. Any one input may contain a low concentration of contaminants but may be continual or combined with other sources, consequentially resulting in substantial accumulation.

Rivers and estuaries can serve as important sources of metals to coastal marine environments because within these systems there is a natural flux of heavy metals. However, in many estuaries, this process has been accentuated by anthropogenic inputs (Feng, et al., 1998; Masson, et al., 2006; Censi, et al., 2006; Qiao, et al., 2007). Industrial effluents and waste sludges substantially contribute to point source metal loadings (Connell, et al., 1984). Salt marshes are often vulnerable to heavy metals when they serve as the receiving waters for effluents, including treated sewage. Wastewater treatment technology and regulations have improved drastically since the end of the 1800s, when the main objective was to construct municipal primary treatment facilities that could physically remove floating solids and debris, in an effort to reduce contaminant concentrations that entered receiving urban waterways

(Stoddard, et al., 2002). In the late 1930s water pollution control plants were constructed in both New Jersey and New York to treat wastewater effluents (O'Connor, et al., 1972). Initially these facilities were built for primary treatment, but over time wastewater treatment plants have been constructed and designed for secondary and tertiary treatment. Today a variety of physical, biological, and chemical processes are employed in order better adhere to more stringent water quality requirements.

Wastewater treatment processes continue to improve the quality of effluents, however, wastewater outfalls and combined sewer overflows remain as major point sources of metals from metabolic wastes, corrosion of water pipes, and consumer products (Brosnan, et al., 2006). Since the passage of the Clean Water Acts secondary treatment processes and more stringent regulations have vastly improved the quality of wastewater effluents entering into receiving waters, however, despite reductions in point-source discharges, metal contamination still persists in estuarine systems, in part because of previous loadings captured within sediments (Sanudo-Wilhelmy, et al., 1999; Balcolm, et al.; 2008), and non-point sources continue to contribute metals to receiving waters and marsh habitats (Rose, et al., 2007). This necessitates monitoring and identification of geochemical signals in these areas, which can prove useful in the identification of input sources and understanding of metal transport to receiving waters and marshes (Masson, et al., 2006).

Decreased sediment and water quality in estuarine areas is often attributable to anthropogenic activities including coastal development for residential and commercial use, and port infrastructure initiatives (Schaffelke, et al., 2005). Metal concentrations in contaminated sediments can vary from site to site depending on the type and duration of anthropogenic activities in the area. A major factor governing metal distribution in estuaries is variability and

proximity to pollutant sources (Bopp, et al., 2006; Long, et al., 2006). It has been found that the highest values of metals in water and sediment occur in areas influenced by various pollution sources such as harbors, and sewage and industrial drains; the lowest concentrations were observed far from any pollution source (El-Moselhy, et al., 2004).

Contaminant loadings in marshes within urbanized estuaries can be excessive because of the impact of numerous point and non-point sources of metal pollution, including industrial discharges, wastewater effluents, tidal exchange, polluted rivers, stormwater outfalls, and combined sewer overflows, atmospheric input and urban runoff. The multiplicity of these contributory sources complicates the identification and the magnitude of individual sources, and subsequent transport, distribution and fate (Rozan, et al. 2001).

Anthropogenic Metals: Cd, Cu, Hg

Since metals are commonly found in urbanized estuarine areas primarily from long-term accumulation from background sources, point source releases, and non-point sources (i.e. runoff), the identification of individual metal concentrations and loading trends can be useful in characterizing contaminant sources (Fletcher, et al., 1994; Emmerson, et al., 1997; Stout, et al., 2001; USEPA, 2008). Metal contamination in marshes is often directly linked to industrial activities, because marsh areas frequently serve as the receiving environments for related discharges (Marcovecchio, et al., 2001). For example, mining and ore treatment facilities have been responsible for contributing polymetallic pollution, primarily Cd, Zn, Cu, Pb, Hg, to many estuarine systems (Masson, et al., 2006). The extent of contamination by individual metal species in marsh sediment has been found to be dependent upon the nature of the site-specific inputs. For example, the enrichment of industrially derived metals, such as Cd, is often prevalent in sites adjacent to urban areas (Fletcher, et al., 1994). Zinc is also associated with urbanize

watersheds, and elevated concentrations of this metal is often associated with traffic and automotive tire wear (Rose, et al., 2007). It has been demonstrated that increased levels of metals, particularly Pb, Zn, Cd and Cu, result from discharges associated anthropogenic activities (Emmerson, et al., 1997). Along with additional metals, like Hg, these metals can be identified as anthropogenic trace metals, because they are commonly associated with urban and industrial sources, and are found at significantly higher concentrations in areas located in industrial/urban watersheds compared with suburban and forested watersheds (Sanger, et al., 1999).

Cadmium (Cd) is a transition metal that is classified as a non-essential metal, as it serves no biological role, and can be toxic even at low concentrations (Weis, et al., 2006). Naturally, cadmium is found in zinc, lead and copper ores, as well as within coal and other fossil fuels, and shales. Cadmium is a known carcinogen that is highly persistent within the environment. The potential for cadmium to have ecotoxicological impacts is based on its ability to become concentrated and bioaccumulate in biota (Masson, et al., 2006). Cadmium is mainly used in batteries and plasticizers. Sources are mainly attributed to zinc, copper, and lead smelting activities, and landfill leaching. Sediment adsorption/desorption processes are directly related to pH; adsorption of cadmium to sediments increases under alkaline conditions, and cadmium is desorbed as conditions become acidic (USEPA, 2008). This dependency may explain the tendency for cadmium to be more mobile in the environment, compared with other metals (Cobelo-Garcia, et al., 2005).

Unlike cadmium, copper is an essential metal that at low levels is a micronutrient necessary for carrying out biological functions. However, both metals become toxic when reaching certain levels. Long and Morgan's "effects range–median" (ER–M), the concentration found to cause negative effects to biota in 50% of studies, are commonly used as benchmarks for

assessing toxicity. Respective values for Cd and Cu in sediment have been established at 9.6 µg Cd/g and 270 µg Cu/g (Long, et al., 1991). Copper is an abundant, naturally occurring trace element found in both the earth's crust and surface waters. Human activities that are contributory sources of copper inputs to estuarine environments include mining industries, electrical equipment manufacturing, and municipal discharges (USEPA, 2008).

Mercury is classified as a non-essential metal that can be found within the environment as: elemental mercury, the form in which it is part of the earth's natural geochemistry; inorganic mercury, in mercuric salts; and organic mercury, in which it is present as methylmercury compounds (Landrigan, et al., 2006). Anthropogenic sources of mercury, including coal-burning plants and manufacturing activities, have augmented mercury levels within in the environment. Mercury is a persistent, bioaccumulative, toxic compound that in the inorganic form can be methylated by microorganisms into a highly bioavailable organic form that enters the environment and can be biomagnified up food chains (Baird, 1999; Bjerregaard, et al., 2007). It has been found that sublethal or chronic exposure to this metal can adversely impact growth, reproduction, behavior, metabolism, blood chemistry, and other crucial physiological functions (Eisler, 1987).

Metal accumulation and contamination in marsh sediments is dictated by sources contributions, but also by the ability of substrates to bind and release metals (Du Laing, et al., 2008). Complex processes that occur within estuarine systems are integral in dictating the transport, flux and fate of metals in coastal environments (Monbet, 2004). The distribution of metals through estuaries is controlled by dynamic sedimentological and geochemical processes that occur at river-estuary and salt marsh sediment interfaces, including precipitation, adsorption/desorption reactions, flocculation/aggregation, and settling/sedimentation (Benoit, et

al., 1994; Williamson, et al., 1996; Herut, et al., 1997; Censi, et al., 2006). Along with estuarine circulation, particle deposition and resuspension, these complex physicochemical and hydrological processes control residence times and predictions of fate and transport of particulate bound metals (Williamson, et al., 1996; Feng, et al., 2002; Butler, et al., 2008).

Metal Sediment Chemistry

Generally, the metals that represent the naturally occurring fraction in estuarine sediments are non-labile, as they are tightly bound within the crystalline structure of the sediment minerals, often as aluminosilicates (Schropp, et al., 1988). On the other hand, metals originating from anthropogenic-related activities are often loosely bound to sediments, and are therefore, readily released by a variety of chemical and biological-mediated processes (Blasco, et al., 2000). The distribution of metals within sediment is dependent upon a number of factors including the hydrological regime, sediment types, presence of vegetation, redox potential and organic matter content. In addition, metals may be present in a variety of different physical and chemical forms, namely as separate-phase solids, soil-adsorbed species, colloidal solution, soluble complexed species or ionic solutes (Connell, et al., 1984; Sandrin, et al., 2003).

The physical and chemical states of metals and retention in sediment are affected by environmental conditions such as pH, and ionic strength of the water phase, and are further affected by sediment properties that include cation exchange capacity, redox conditions, chloride content, clay type and content, and organic matter content (Sandrin, et al., 2003; Du Laing, et al., 2008). Natural particles are typically composed of organic material, including organisms and/or their degradation products, clay minerals, calcium carbonate, iron oxides and manganese oxides. These components of particulate matter are all involved in the binding of metal ions, but they can

differ in the types and numbers of functional groups on their surfaces and in the affinity of these surface groups for metal ions (Ahrland, et al., 1958; Batley, 1989; Sandrin, et al., 2003).

In addition to sediment properties, water chemistry conditions determine the type and stability of metal sorption and precipitation, and are also responsible for controlling rates of adsorption and desorption of metals onto and off of sediments; adsorption removes the metal from the water column and stores it with the sediments/particulate matter, and desorption allows metals to re-enter the water column (Connell, et al., 1984; Du Laing, 2008). Important properties like salinity, pH and redox potential control the remobilization and release of heavy metals from sediments. For example, it has been demonstrated that concentrations of both Type A and Type B metals bound to suspended sediments decreased as salinity increased (Church, et al., 1998).

Elevated salinity can increase competition between cations and metals for binding sites, and metals are subsequently released into the water column. In addition to the inverse relationship between salinity and particulate-associated trace metals, such as cadmium, copper, and zinc, it has also been found that partitioning of these metals onto suspended particulate matter is positively correlated with increases in particulate organic carbon (Kuwabara, et al., 1989). Metals may also be desorbed from sediments with decreases in redox potential, because this changes the composition of metal complexes (Connell, et al., 1984; Poikane, et al., 2005). Acidification also results in the remobilization of metals from surface sediment, increasing the transport of many metals to surface waters. A decrease in pH allows for mobilization of metals from sediments, as a result of greater competition between metals and hydrogen ions for binding sites, and also, because metal-carbonate complexes may be dissolved (Connell et al., 1984; Lead, et al., 1998; Wallstedt, et al., 2003).

Natural Metal Concentrations

When analyzing sediments from any location it can be expected that metals will be detected in samples, as many are naturally occurring in the Earth's crust. Therefore, a critical aspect in understanding and addressing the potential consequences of metal pollution is to determine the natural component versus anthropogenic contribution of metals in sediments is considered (Schropp, et al., 1988). Researchers use metal concentrations from external, unexposed sites or trace metals in the world shale average as standards to represent natural metal concentrations (Wedepohl, et. al, 1971; Tomlinson, et al., 1980; Gurrierri, et al., 1998; Ray, et al., 2006). Comparisons that use this background sediment approach help to assess if metal levels are within the range that can be associated with natural processes that cycle metals, or above these concentrations and, therefore, attributable to anthropogenic contributions (Hwang, et al., 2006). In an effort to put metal concentrations into context, in terms of contamination levels, observed concentrations in field sediments can be compared to background sediment concentration levels. The metal concentration data is divided by a baseline concentration found in literature, otherwise known as the background concentration (Tomlinson, et al., 1980; Angulo, et al., 1996). Trace metal averages found in world shale and Hudson sediment served as proxies for the background concentration values.

Sediment and Water Quality and Toxicity Guidelines

The majority of metals introduced into a system become associated with sediments and therefore, it has been found that sediment-bound metal loads are generally responsible for the majority of metal transport and have the potential to adversely affect aquatic health on a long-term basis (Sanudo-Wilhelmy, et al., 1999). Site specific knowledge of water quality provides a useful context to assess the environmental integrity of an ecosystem. However, even when water

quality guidelines are met, this single approach may fail to account for poor sediment quality that adversely affects exposed biota (Gurrieri, et al., 1998). Assessment of metal contamination and potential for toxicity to sediment dwelling organisms can be accomplished by evaluating metal concentration values in recovered sediments with respect to sediment quality guidelines and toxicity indices (Spencer, et al., 2002; Caeiro, et al., 2005; Okweye, et al., 2007; Priju, et al., 2007).

The environmental importance of essential metals illustrates that chemical speciation influences the extent of metal toxicity (Ackay, et al., 2002). Estuarine environments serve as important sinks of type A metals, based upon their tendency to become enriched and sequestered in sediments, and significant sources of type B metals, because of their affinity to form organic complexes that prove to be stable for transport. However, the extent to which these metals approach toxic levels is the main determinant as to whether or not they pose a threat to marsh ecosystems (Church, 1989).

The metals identified in this study, Cd, Cu, Zn and Hg were chosen because of their toxic implications at levels that exceed background/and or thresholds for environmental function, and because amplified levels resulting from anthropogenic activities had previously been identified and detected within the study reach.

Bioavailability

Degraded sediment and water quality affects tidal wetland communities through deterioration of water clarity and marine habitat loss (Schaffelke, et al., 2005). In addition, pollutants such as trace metals have the potential to cause risks to biota when certain concentrations are exceeded (Church and Scudlark, 1998). The complexity of estuarine systems complicates the determination of adverse effects of metals in these environments. It is critical to

understand factors that influence availability and exposure to potentially toxic metals in contaminated ecosystems (Bentivenga, et al., 2004). The adsorbed anthropogenic metal fractions are more loosely bound, and may be more available to estuarine biota and may be released to the water column in altered forms when sediments are subject to biochemical and physical processes (Schropp, et al., 1988; Blasco, et al., 2000). Therefore, it is important to consider biogeochemical parameters and reactions of metals in water, and, also, to consider concentrations of metals in suspended matter and sediments in order to estimate metal bioavailability (Luoma, 1989).

Bioavailability is an important determinant of the extent of toxicity of sediments (Di Toro, et al., 1990; Hansen, et al., 1996; Bentivenga, et al., 2004). Sediments are basic environmental components that supply nutrients to ecosystems, and ingestion of sediment and uptake from particles in solution may both be important pathways of metal bioaccumulation (Luoma, 1989; Akcay, et al., 2003). Complexation processes and particle chemistry partition and cycle metals between dissolved and particulate phases, and thus influence metal fate and bioavailability (Censi, et al., 2006). Sediment properties are responsible for metal accumulation, because they determine the type and stability of metal sorption and precipitation, which are linked to metal mobility, bioavailability, and ultimately their potential toxicity (Du Laing, 2008). Sediment characteristics and parameters that affect bioavailability of metals include cation exchange capacity, total organic carbon, iron and manganese oxides, and amount of sulfides for metal binding (Bentivenga, et al. 2004).

Marsh environments are highly productive ecosystems that serve as nursery and feeding grounds for a variety of species. Sediments contaminated with metals may affect both benthos and organisms higher in the food chain via biomagnification (Weis, et al., 2005). Aquatic biota

have developed varied mechanisms for dealing with exposure to both essential and toxic metals, and the rate of uptake and storage capability is largely dependent on the organism and metal contaminant (Bjerregard, et al., 2007). It has been found that phytoplankton and zooplankton are able to rapidly assimilate available metals because of their high surface area to volume ratio, while the ability of fish and invertebrates to adsorb metals is variable based on the physical and chemical characteristics of the metal (Kennish, 1992). However, sediment deposit feeders (e.g., clams, crabs and worms) are most vulnerable to exposure, through direct uptake or through trophic transfer, because these organisms selectively feed on the finer grained sediments, which often contain the majority of metal contamination (Tischler, 1998; Hornberger, et al., 1999).

Radionuclide Dating

When assessing temporal and spatial contaminant trends in marsh environments radiometric dating of sediment cores provides useful chronological information and a context in which to evaluate variations among pollutant concentrations (Feng, et al., 1996; Chillrud, et al. 1996). Utilizing radionuclides to provide a depositional timeframe for contaminants is useful in order to classify past versus present sources of contamination (Bonnevie, 1993). Although long-term monitoring is the ideal approach for measuring temporal changes in pollutant loadings and environmental quality of an ecosystem, radiodating and metal analysis of sediment cores serves as a suitable alternative (Geyh, et al., 1990; Clark, et al., 1997; USGS 2004). Determining the distribution of radioisotopes within sediment cores can establish a geochronological record of sediment and sediment-associated contaminant deposition and burial by estimating age and/or rate of sediment accumulation based upon decay properties or half-life (Bopp, et al., 1982; Bopp, et al., 1993; Bopp, et al., 1998; USGS, 2004; Weis, et al., 2005;). Radioisotope tracers serve as temporal markers, or chronometers, which, in addition to yielding information on deposition and

temporal variations of pollutants, can reveal sediment mixing at depth (Bloom, et al. 1987; Koide, et al., 1997; Mastioff, et al., 2002; USEPA, 2008).

Natural radioisotopes, including ^7Be and ^{210}Pb , adsorb to suspended particulates in the atmosphere, and are thereby supplied and sorbed onto surfaces of estuarine sediments (Feng, et al., 1996; Cheevaporn, et al., 1996). Artificial radioisotopes, including ^{137}Cs , have a similar affinity for adsorbing to particle surfaces, as observed in natural radioactive isotopes, and both can be effective radiochemical tracers that impart useful temporal and spatial information regarding sediment core depositional profiles (Mastioff, et al., 2002; Weis, et al., 2005; USEPA, 2008). Within the water column radionuclides also act non-conservatively, where they strongly adsorb to suspended particulate matter and the transport and residence times of radioisotopes parallel the exchange and movement of particulates and associated contaminants through marsh systems (Olsen, et al., 1986; Ritchie, et al., 1990; Zuo and Eisma, 1993; Hong, et al., 1999; Chai, et al., 2004). It follows that the partitioning of radioisotopes between dissolved and particulate phases are also greatly influenced by the dynamics of the coastal environment (Zuo and Eisma, 1993; Chai, et al., 2004).

By assuming uniformity in the atmospheric input of natural radioisotopes, distributions in sediments can provide information on localized conditions and depositional environments. In tidal marshes, radionuclide dating techniques have been successfully applied in geochronological studies that aim to evaluate depositional history (Bopp, Krishnaswamy et al., 1971; Krishnaswamy, et al., 1978; Church, et al., 1981; Evans, et al., 1981; Johnson, et al., 1982; Stevenson, et al., 1986; Edgington, et al., 1991; Peller, et al., 1996; Robideau, 1997; Benoit, et al., 1999; Rozan, et al., 1999; Kerfoot and Robbins, 1999; Masque, et al., 2002; Weis, et al., 2005; Bopp, et al., 2006; Kivia, et al., 2006). In order for radiodating to be an effective strategy

for deriving age and depositional timing of core horizons it is essential that sediments are uniform in terms of particle size distribution (USEPA, 2008). A variety of radioisotopes have proven useful in determining approximate date of sediment (Church, et al., 1981; Olsen, et al., 1984; Church, et al., 1998). The useful application of radioisotopes as tracers for short and long-term variations and the relative timescale of information that can be derived from radiodating surveys are dependent on the type of radionuclide and based upon differences in source function and half-life (Feng, et al., 1996). Each radioisotope follows its own decay series, where the unstable radioactive parent isotope decays exponentially into any number of radiogenic daughter isotopes, until reaching a stable isotopic form. This process is element specific, yet clearly defined by rates of decay and half-lives of unstable isotopes, which enables the dating of sediment associated with the radiochemical tracer employed in analysis (Hancock, et al., 2000).

The short half life of ^7Be ($t_{1/2}=53$ days) is useful in assessing recent ($<1\text{yr}$) deposition of particles and associated pollutants, which allows for this radionuclide to indicate short-term variations of sediments and particle-reactive contaminants (Feng, et al., 2002; Bopp, et al., 2006). ^7Be is a radioisotope that is produced naturally by cosmic ray bombardment of atmospheric nitrogen and oxygen, and is delivered from the atmosphere to Earth via precipitation. The reactive nature of beryllium causes this element to quickly and strongly associate with sediments (Geyh, et al., 1990; Clark, et al., 1997; USGS, 2004). Thus, ^7Be is an effective radiochemical tracer for dating sediments that have recently been deposited (Geyh, et al., 1990; Clark, et al., 1997; USGS, 2004; Bopp, et al., 2006).

Consequently, detection of significant ^7Be activities in marsh sediments typically occur in the top sediment layers of a core (Bopp, et al., 1993). Besides signaling that these sediments have been deposited within a year of collection, the vertical penetration of ^7Be activities were

indicative of the depth of sediment mixing zone. Accordingly, subsequent to water column exchange, recently deposited material are actively subject to sediment mixing processes and particle-reactive deposits (i.e. radionuclides and contaminants) may adsorb to sediment surfaces (Bacon, et al., 1976; Bopp, et al., 1993; Sarin et al., 1994; Feng, et al., 1996; Rozan, et al., 1999; Boisson et al., 2001; Chai, et al., 2004; Bopp, et al., 2006). Surface sediments typically comprise the mixing zone, which is characterized as a constant source and sink of sediments and bound metals to the system, as they continually exchange metals with ambient water above, yet this zone can extend below the surficial sediment layer (Rozan, et al., 1999). It follows that detectable activities in bottom sediment sections within a core can indicate extensive sediment mixing (Olsen, et al., 1986).

Therefore, downcore distributions of short-lived natural radionuclides in sediments can reveal variability in localized environments caused by biogeochemical processes that govern the transport and fate of suspended particulate matter; and can infer spatial variations of contaminants within an ecosystem because like metals, radioisotopes have particle-reactive properties that allow them to quickly sorb and transport with suspended particulates (Bruland, 1974; Cochran and Aller 1979; Olsen et al. 1986, Dibb et al. 1989, Provini et al. 1989, Feng, et al., 1996).

Another natural radioisotope, ^{210}Pb (half life 22.3 y), is useful as a tracer for long-term variations because of its relatively short half-life and affinity for fine-grained particles (Cochran et al. 1993, Huntley, et al., 1995; Feng, et al., 1996). Several radioactive decay processes occur before natural ^{210}Pb deposits are released to surface sediments. ^{210}Pb is a radioactive element that is part of the ^{238}U family, or decay series, which very slowly decays into ^{234}U ($t_{1/2}=248,000$ years), and subsequently ^{230}Th ($t_{1/2}=80,000$ years) which then decays to the radium isotope ^{226}Ra

($t_{1/2}=1622$ years). Radioactive ^{226}Ra decays to yield the inert gas ^{222}Rn , which, subsequently, decays ($t_{1/2}=\text{of } 3.83$ days) through a series of short-lived isotopes to ^{210}Pb ($t_{1/2}=22.26$ yrs) (Appleby, et al., 1983).

Atmospheric deposition via dry fallout or precipitation is the main source of ^{210}Pb fallout to sediments in estuarine systems; however, additional point and non-point sources also release ^{210}Pb into the system, which include rivers, tributaries, and runoff in the delivery process (Krishnaswamy, et al., 1978). It is important to recognize that within estuarine sediments the total inventory of ^{210}Pb activities are comprised of “supported” ^{210}Pb , from the radioactive decay of ^{226}Ra , which yields ^{210}Pb that is in equilibrium and not associated with recent atmospheric deposition, and “unsupported” or “excess” ^{210}Pb , derived from radioactive decay of atmospheric ^{222}Rn , which produces “ ^{210}Pb that is not in equilibrium (Wan, et al., 2005). The atmospheric deposition of ^{210}Pb is deposited at a constant rate that is linked to the volatilization rate of ^{222}Rn , and is referred to as “unsupported” ^{210}Pb (Huntley et al. 1994). This highly particle-reactive isotope has a five to ten day residence time in the atmosphere before reaching surface waters via atmospheric dry fallout or precipitation, and subsequently, rapidly scavenged from the water column and adsorbed onto sediments as “unsupported” ^{210}Pb (Krishnaswani et al. 1978, USGS, Geyh et al. 1990). In analysis total ^{210}Pb activities are observed, however, both supported and unsupported ^{210}Pb activities must be differentiated within the total ^{210}Pb inventory, and ultimately the latter component is utilized in sediment age dating (Huntley et al. 1994, Feng et al. 1996). Excess (unsupported) ^{210}Pb is determined by:

$$^{210}\text{Pb}_{\text{unsupported}} = ^{210}\text{Pb}_{\text{total}} - ^{210}\text{Pb}_{\text{supported}} \quad (\text{Eq.1})$$

The analysis of unsupported ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) activities as a function of depth, which takes into account the integrated activity and the differential activity within a core, has advanced from analysis of ice cores, lake sediments and is now widely applied to coastal sediments (Goldberg, 1963; Koide, et al., 1972; Krishnaswamy, et al., 1978; Joshi, et al., 1991). Radiodating techniques rely on the notion that the flux of atmospheric $^{210}\text{Pb}_{\text{xs}}$ activities and specific activities of ^{210}Pb deposited onto the marsh sediments is constant through time (steady state), and subsequently, sedimentation occurs at a generally constant rate, and is the dominant process compared to any post-depositional biological or physical mixing (Appleby, et al., 1983). Additional assumptions regarding ^{210}Pb deposition are that ^{210}Pb is removed quickly from the atmosphere and sequestered in sediments, ^{210}Pb is immobile, and is not desorbed nor does it migrate vertically and is independent of depth (Pennington, et al., 1976; Feng, et al., 1996; Noller, 2000).

Dating techniques are fundamentally based upon the radioactive decay of $^{210}\text{Pb}_{\text{xs}}$ activities, where ^{210}Pb activities in sediments decrease exponentially with respect to time (depth) in accordance with its half-life, and therefore, sediment-rate relationships can be derived (Appleby, et al., 1983; Wan, et al., 2005). Measurements of downcore $^{210}\text{Pb}_{\text{xs}}$ distributions allow for ages to be assigned to sediment sections based upon the established decay rate of ^{210}Pb (Appleby, et al., 1992; Lee, et al., 2001). Sediments can be age-dated and/or accumulation rates can be derived from a general decay equation (Eq. 2): (Goldberg, 1963; Robbins, et al., 1975; Krishnaswamy, et al., 1978; Joshi, et al., 1991; Ivanovich, et al., 1992; Church, et al., 2006). Ultimately, this equation can be expressed to provide a calculation of the age of a specific sediment interval at depth as described in equation 3 (Eq. 3) (Faure, 1986; Ivanovich, et al., 1992; Huntley, et al., 1994; Faure, 1986).

$$A_{(h)} = A_o e^{-\lambda t} \quad (\text{Eq. 2})$$

$$t_h = 1 / \lambda * \log(A_o / A_h) \quad (\text{Eq. 3})$$

where:

A_o = $^{210}\text{Pb}_{\text{xs}}$ measured in surface sediment section (present)

$A_{(h)}$ = activity of $^{210}\text{Pb}_{\text{xs}}$ at depth h

λ = ^{210}Pb radioactive decay constant

t_h = age of sample (yr)

A number of dating models and mathematical formulations have been developed that help establish age-depth relationships and thereby derive sedimentation rates (Joshi, et al., 1991; Wan, et al., 2005). The basic age equation has been extended to further interpret ^{210}Pb profiles, integrating a variety of parameters that attempt to take into account physical processes and dynamics of environmental settings, including: compaction, nutrient cycling, and diagenesis, that affect ^{210}Pb geochronologies (Appleby, et al., 1978; Krishnaswamy, et al., 1978; Appleby, et al., 1983; Joshi, et al., 1991; Sonke, et al., 2003). Although conceptual models can estimate sedimentation rates, additional assumptions may be required, including a constant sedimentation rate for the entire length of the core. It is necessary to recognize that accretion rates of sediments may be less variable in sheltered areas like marshes however; localized sedimentation rates are spatially variable based upon water flows and morphology within estuarine systems (Fox, et al., 1999). Therefore, the application of models can yield oversimplified estimates and conclusions that rely too heavily on the use of one radionuclide indicator without applying supporting temporal information (Pennington, et al., 1976; Krishnaswamy, et al., 1978; Appleby, et al., 1983; Bopp, personal communication). For the purpose of this study, which is to provide a

depositional context for sediments at marsh locations, it was deemed more appropriate to draw conclusions based upon consistency with a variety of temporal radiodating indicators (Bopp, personal communication).

In addition to natural ^{210}Pb , artificial ^{137}Cs fallout rates are widely used and documented to establish chronologies, age-date sediments, and estimate accretion rates (Huntley, et al., 1994; Bopp, et al., 2006; Kumar, et al., 2007). Regardless of the radiometric dating technique or procedure that is employed, it is important to account for the variability that exists within sediment cores by substantiating data by an ancillary method; often, ^{137}Cs activity profiles are used in conjunction with ^{210}Pb distribution chronologies to corroborate/confirm sediment dates (Smith, et al., 2001; Arnaud, et al., 2006). ^{137}Cs ($t_{1/2}=30.3$ years) is a thermonuclear byproduct of atmospheric testing of nuclear weapons which began around 1954, though peak fallout occurred between 1963 and 1964 (Olsen, et al., 1981; Huntley, et al., 1994; Bopp, et al., 1996; Clark, et al., 1997; Weis, et al., 2005; Church, et al., 2006; Bopp, et al., 2006). In geochronological studies these two dates, 1954 and 1963, serve as discrete time markers that represent the onset and maximum of ^{137}Cs production and deposition, respectively. Therefore, this radioisotope is an advantageous temporal indicator/tracer for estimating sedimentation rates and identifying sediments that were deposited before or after the 1960s (Clark, et al., 1997; Magar, 2001; Bopp, et al., 2006; USEPA, 2008). In the absence of sediment mixing, no ^{137}Cs activity would be measurable in sediment layers that were deposited before 1954, and significant levels would correlate with these fallout dates, while vertical distributions in sediment profiles would ideally decrease after peak fallout delivery which occurred from 1963-64 (Huntley, et al., 1994; Wan, et al., 2005).

Analyzing sediment cores for radionuclides and trace metals allows for the construction of contaminant chronologies, which enables an assessment of temporal contamination trends. (Bopp, et al., 1993; Mil-Homens, et al., 2008). Measurements of ^{210}Pb and ^{137}Cs activity have been useful in establishing vertical accretion rates that can be correlated with depth profiles of metal concentrations, thereby providing a time-integrated record of historical metal inputs (Callaway, et al., 1998; Lee et al., 2001; Fuller, et al., 1999; Bopp, et al., 2006). Interpretations of radionuclide chronologies may not only allow for temporal trends to be reconstructed, but for contemporary and historical inputs of metal contaminants to be compared (Bopp, et al. 1993; Cundy, et al., 2003; Bopp, et al., 2006). Subsequent research will pair dating information with contaminant concentrations of sediment core sections in order to evaluate trends in contaminant deposition and attenuation, and identify recovery from past sources or degradation from new or existing sources (Bopp, et al., 1993; Weis, et al., 2005).

STUDY APPROACH

Sediment enrichment results from both natural and anthropogenic contributions. Although metals are present naturally in the environment, excessive amounts of metals enter the environment from anthropogenic sources (Kabir, et al., 2010). It is expected that, compared with sediments in suburban or rural environments, urban marsh sediments receive greater metal loads from surrounding watersheds (Thornton, 1991). Contaminant loadings within urbanized estuaries can be excessive because of the impact of numerous point and non-point sources. Likewise, decreased sediment quality in urbanized estuaries is often attributable to anthropogenic activities including coastal development for residential and commercial use, and port infrastructure initiatives (Schaffelke, et al., 2005). Furthermore, the greater contamination associated with

urban sediments often results from sustained and intermittent pollutant contributions derived from past and present sources (Franco, 2005).

In general, notable pathways in which metal pollutants reach surface waters and cycle through coastal ecosystems include industrial and municipal facilities, land runoff, atmospheric deposition, erosion and weathering (Hare, 1992; Helgen, et al. 1996; Herut, et al. 1997; Rozan, et al., 2001; Weis, et al 2006; Harikumar, et al., 2009). Accordingly, urbanized coastal regions remain vulnerable to anthropogenic stressors that ultimately contribute to the alteration and loss of estuarine habitats via associated inputs and accumulation of persistent contaminants (i.e. metals) (Kennish, 2002).

Increased regulation and treatment advances targeting anthropogenic effluents have enhanced the environmental integrity of estuaries nationwide (Jones, et al., 1997; Bopp, et al. 2006). However, characterizations of region-wide progress may over-generalize and misrepresent the condition of individual waterways within these systems. For instance, overall sediment and water quality improvements reported in the New York/New Jersey Harbor Estuary (NY/NJ HE) can misconstrue the progress of certain areas, such as where contemporary deposits remain active repositories of toxic chemicals, and the effects of these contaminated sediments on ecological function and human use are significant (Bonnevie, 1994; NY/NJ HEP 1996; HREP 1996; Bain, et al., 2006; USACE HRE, 2010).

In particular, the Arthur Kill remains severely impaired by legacy and contemporary contaminant loadings (Steinberg, et al., 2004). Ecosystems along the Arthur Kill have long been vulnerable to deleterious impacts of various industrial and manufacturing facilities sited along this urban waterway (Huntley, et al., 1995). Currently, many of these operations have been

marginalized, displaced or no longer exist, which has consequently reduced anthropogenic metal loadings and minimized residual impacts from point sources. However, contaminant-laden sediments within the Arthur Kill complex may remain a threat to neighboring ecosystems (Vitaliano, et al., 2002).

Study Objectives

The primary goal of this project is to characterize large and small-scale spatial and temporal distributions and variability in sediment metal (Cd, Hg, Cu and Zn) contamination in salt marshes adjoining the Arthur Kill and the Raritan Bay. Additional goals are to 1) estimate the flux of contaminants between the Arthur Kill and salt marsh habitats and 2) to compare acquired data sets (sediment and water quality) with relevant benchmarks and guidelines. Specific objectives are to: 1) Examine spatial trends in surface sediment metal contamination to determine if connectivity to the Arthur Kill or site-specific inputs are the major source of contaminants to each study site; 2) Examine temporal trends in sediment metal contamination to determine site-specific contamination histories/chronologies; 3) Characterize tidal exchange of suspended sediment metals between the Arthur Kill and adjoining creeks to estimate net advective flux for subsample of metal contaminants. Datasets will provide concentrations on a suite of metals, however a subset of these metals (Cd, Hg, Cu, and Zn) have been selected because of their potential toxicity and because they have been identified as contaminants of concern to the NY/NJ Harbor Estuary (Kennish, 1992; NY/NJ Harbor Estuary Program 1996; Church, et al., 1998; CARP, 2010,

This dissertation will use a weight of evidence (WOE) approach to establish an assessment framework in which to evaluate sediment quality throughout the study area, in terms of magnitude of anthropogenic enrichment and potential toxicity of metal-contaminated sediments. Geochemical analysis of sediment cores and surface sediments collected along longitudinal transects will evaluate vertical and lateral (Cd, Hg, Cu, and Zn) distribution patterns in order to identify intra-marsh fluctuations, and characterize site-specific temporal and spatial variability of metal enrichment and contamination levels. Evaluation of metal within overlying ambient waters will enhance characterization of site-specific conditions, and provides a useful means context to comparatively assess marsh study sites. Furthermore, this facet was integral in order to account for the dynamic setting of marsh-creek systems, specifically the cyclic deposition and resuspension of particle-reactive metals among the water column and biologically active marsh bed surface layers.

Via examination of metal contamination within a variety of ecologically-relevant environmental media (at depth or in surface deposits, and suspended particulates within the water column), on a variety of spatial and temporal scales, this study will provide insight concerning the distribution of Cd, Hg, Cu, and Zn within three critical Staten Island marsh-creek habitats, and examine variability of anthropogenic metal enrichment, contamination and potential toxicity over time in marshes in the reach of Arthur Kill and Raritan Bay watersheds, extending longitudinally along the western and southern shore of Staten Island, New York. Beyond individual objectives of each research component, an important element of this dissertation was to evaluate and synthesize acquired datasets compiled over the past decade in order to establish a comprehensive spatial and temporal context to characterize localized vs. regional factors affecting geographic gradients with respect to anthropogenic enrichment and contamination.

Multiple lines of evidence will be provided by each of the research components to investigate the role of natural disturbances and anthropogenic stressors (including terrestrial loadings and or advective tidal exchange of contaminants), among marsh habitats in Arthur Kill and Raritan Bay watersheds.

Below is a listing of general *Hypotheses (H1-H3)* that were tested through the course of this dissertation:

(H1) – Study sites exhibit site-specific temporal sediment metal contamination;

(H2) – Study sites exhibit site-specific spatial sediment metal contamination;

(H3) – Study sites exhibit site-specific tidally mediated net advective flux of metals with the Arthur Kill.

Below is a listing of specific *Approaches (A1-A3)* that were used to test the respective hypotheses, listed above. All of these *Approaches* rely on the use of metal-specific instrumentation, including inductively coupled plasma-atomic emission spectrometry (ICP-AES) (for Cd, Cu and Zn) and flow injection mercury analyzer (for Hg).

(A1) – Sediment cores were collected at all study sites and chronologies of Cd, Hg, Cu and Zn were determined. These newly acquired datasets were compared with previous (~2000) site-specific metal chronology data (Nichols, 2004; Bopp, 2006).

(A2) – Surficial sediments collected from spatial gradients at primary study sites were assessed for concentrations of Cd, Hg, Cu and Zn and compared among Staten Island study sites (Weis et al. 2005).

(A3) – Lateral movement/scalar transport of particle-bound metal fluxes (Cd, Cu, Zn, and Hg) within the water column of each study sites was examined. Sampling was conducted from roadway bridges above creek conduits over two complete tidal cycles (once

at neap tide and once at spring tide). Concentrations of particle-bound metals were determined in conjunction with a variety of other hydrodynamic (i.e., flow rates, depth and width of water column, etc.) and physicochemical parameters. Contaminant fluxes on incoming and outgoing tides were compared to determine the net direction and magnitude of metal exchange between the Arthur Kill and the upland marsh habitat over an average tidal cycle (Sokal, et al., 1996; Hazen and Kneip, 1980; Lion and Leckie, 1982; Mackie, et al., 2006).

SIGNIFICANCE

Previous research has established that the Arthur Kill is a polluted urban waterway that functions as a sink for toxic pollutants (Huntley, et al., 1995; Gillis, et al., 1995; Steinberg, et al., 2004; CARP, 2010). Although conditions within the NY/NJ HE have shown vast improvement, certain areas, including the Arthur Kill, are still impaired by historic as well as contemporary contaminant loadings (Huntley, et al., 1995; Sanudo-Wilhelmy, et al., 1999; Steinberg, et al., 2004). Sediments within the main channel of the Arthur Kill can become remobilized via tidal action and shipping/dredging activities, and these contaminant-laden suspended sediments may be redistributed to marsh habitats. Resident biota may either feed directly upon these suspended particles or indirectly once they become part of the bed load. Associated contaminants would then be available for possible bioaccumulation and trophic transfer (Hornberger, et al., 1999; Seebaugh, et al., 2005; Audry, et al., 2006).

The significance of this project aligns closely with a variety of management goals being pursued within the area. For example, habitat acquisition and restoration of ecologically

important areas that are threatened by pollution and development is a major focus of the NY/NJ Harbor Estuary Program (HEP) and many sites along the Arthur Kill are slated for such efforts (NY/NJ HEP, 2008; USACE, 2010; NY/NJ HEP CCMP, 2010; NY/NJ HEP, 2010).

Furthermore, information concerning sediment metal loadings within marsh habitats would be important data to supplement the HEP's Contaminant Assessment Reduction Program (CARP) and is a critical step in gaining an overall understanding of the transport and redistribution dynamics of contaminants within this ecologically important and sensitive system.

An assessment of current conditions (in terms of anthropogenic metal enrichment, sediment contamination, and potential for toxicity) will aid in tracking the success of efforts to protect local waterways from metal contamination. Furthermore, understanding the exchange of metals between the heavily-polluted Arthur Kill and neighboring habitats, as set forth in this research, will provide useful information to programs that monitor ecosystem health, assess the vulnerability of ecologically-important species, and design, implement, and assess the success of site remediation and ecological restoration.

Research into tidally mediated resuspension and redeposition of contaminated sediments in a polluted estuarine system, such as the Arthur Kill, is essential from a habitat restoration standpoint. Many areas bordering the Arthur Kill are slated for restoration and remediation and the successes of these efforts may be compromised by the environmental quality of the Arthur Kill. If sites are remediated and subsequently become re-contaminated via a local source, like the Arthur Kill, these efforts may be both inefficient and ineffective, resulting in the loss of time/resources. Site assessment of contaminants and an understanding of the exchange of contaminants between the Arthur Kill and associated marsh habitats would be a useful

management tool in prioritizing, as well as setting target criteria for restoration initiatives within the NY/NJ HE.

Large and small-scale metal concentration datasets obtained from chemical analysis of depth and surface samples collected from Main Creek, Neck Creek and Lemon Creek provided a comprehensive spatial and temporal context/framework to examine the current condition of sediment and habitat quality throughout the study area. Although toxicity tests/assays were beyond the scope of the study, an aggregate of reference values (i.e. background and contamination indices) proved useful for characterizing the extent of anthropogenic contamination, metal pollution loads and potential toxicity of sediments at each site. Metal concentrations in cores and surface sediments were evaluated in terms of sediment quality and toxicity benchmarks to assess human-induced impacts and ecological implications that may affect marsh habitats over the extent of the study area. This study will provide additional data of finer spatial resolution necessary to help evaluate the progress of various regional efforts for long-term contaminant reduction of sediments in NY/NJ Harbor and adjoining waters (HydroQual, 2001; CARP, 2010; USACE HRE, 2010).



Figure 1-1a Study sites within Arthur Kill and Raritan Bay watersheds with respect to eight planning regions of the Hudson-Raritan study area. (Figure adapted from *Hudson-Raritan Estuary Comprehensive Restoration Plan* draft 2009.

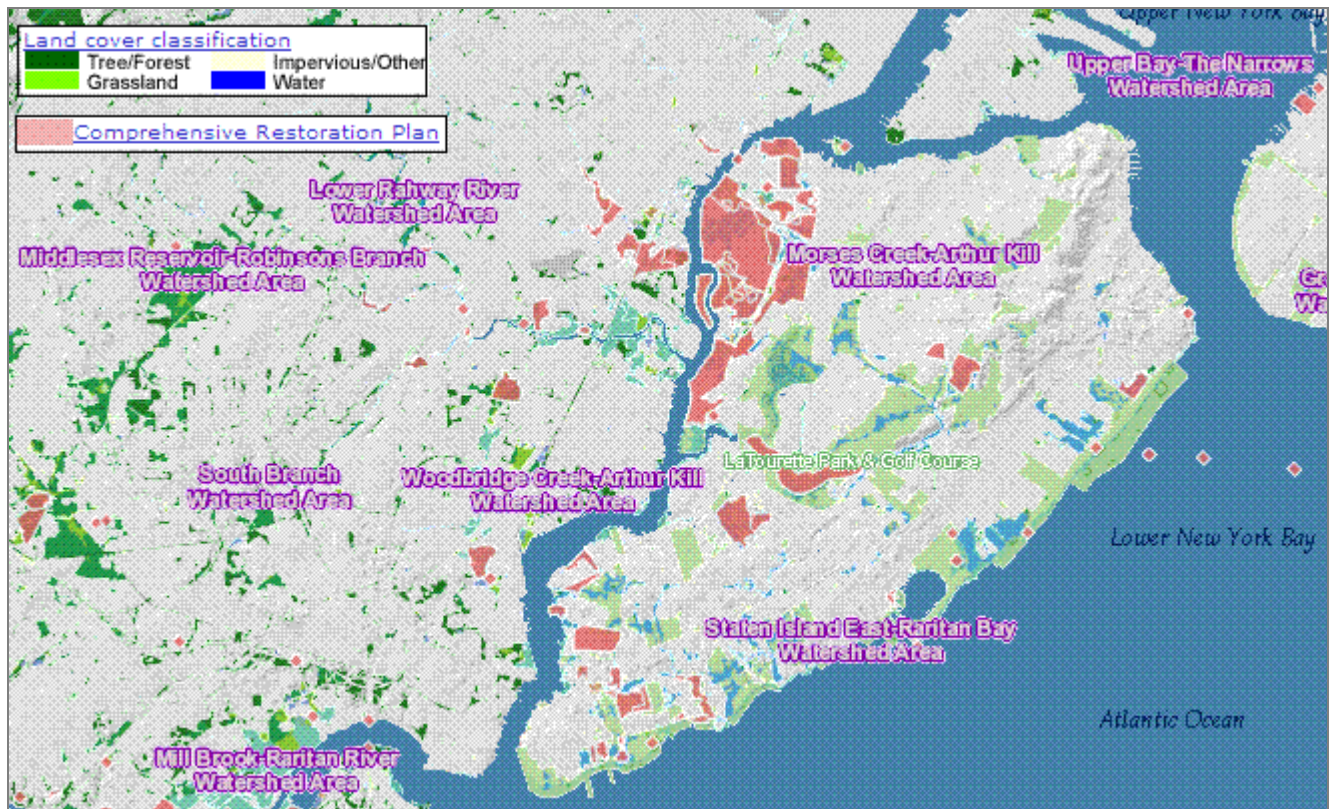


Figure. 1-1b New York- New Jersey Harbor Estuary (NY/NJ HE) watershed areas and comprehensive restoration plan (CCMP) sites. (Figure created from <http://oasis.nyc> 2011).



Figure 1-2. Staten Island Subwatersheds. Lemon Creek is located within Lemon/Creek Sandy Brook watershed and is among the various watersheds (green borders), which are retrofitted as part of the Staten Island Bluebelt system for stormwater control.

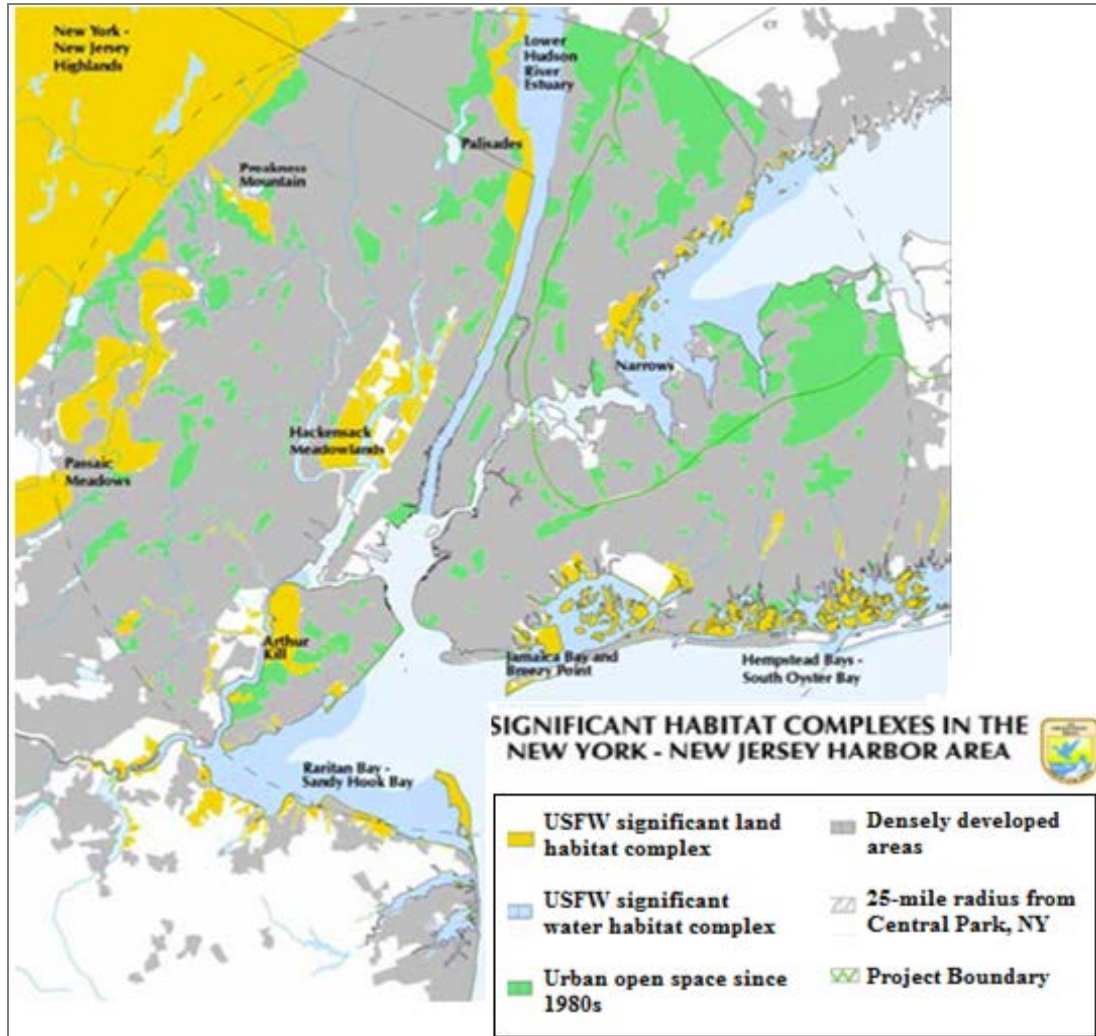


Figure 1- 3a. Significant habitats of the New York Bight Watershed within the NY/NJ Harbor (NFWS 2007, USACE 2009).

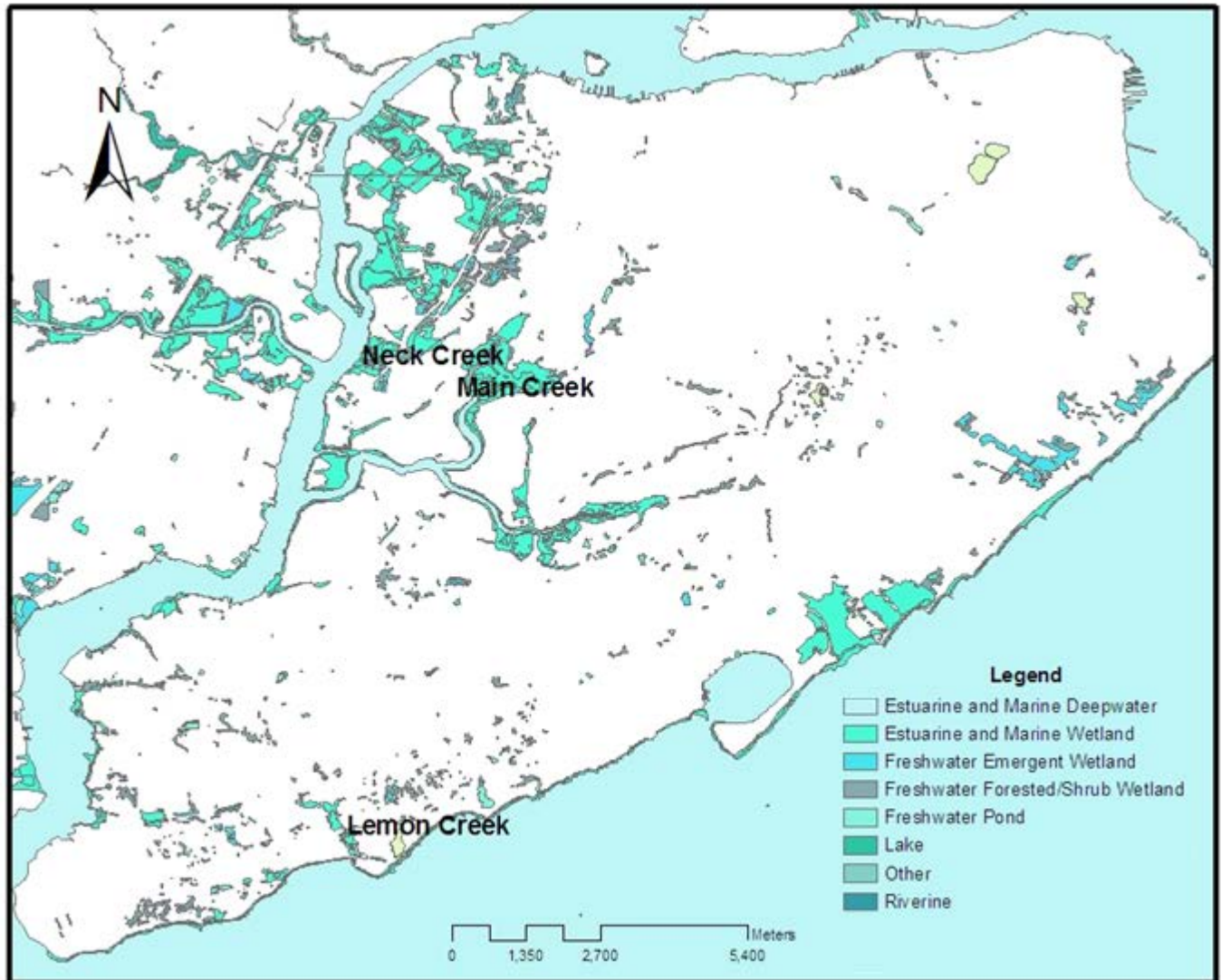


Figure 1-3b. Wetland types associated with Staten Island marsh study sites: Neck Creek (NC), Main Creek (MA), and Lemon Creek (LC).

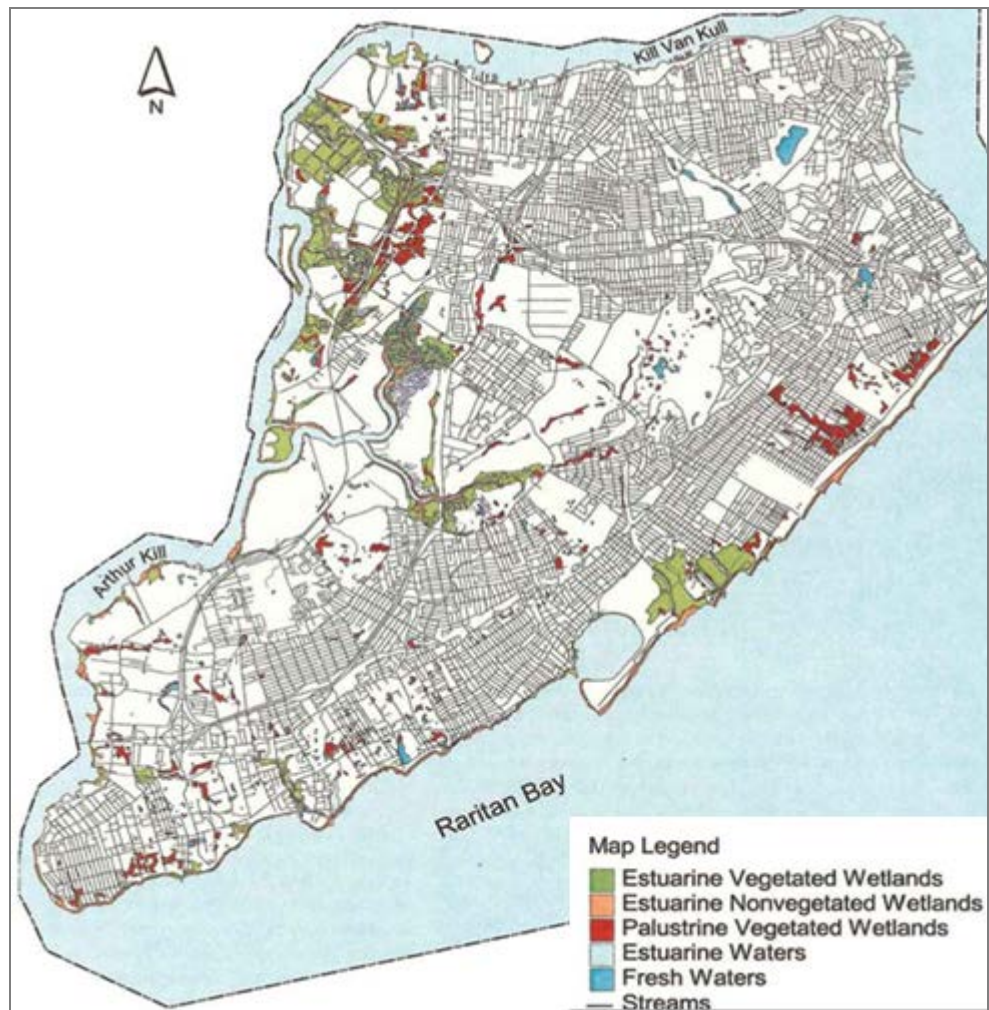


Figure 1-3c. Wetland environments throughout Staten Island.



Figure 1-4. The Arthur Kill and Staten Island Marsh study sites: Neck Creek (NC), Main Creek (MA), and Lemon Creek (LC)

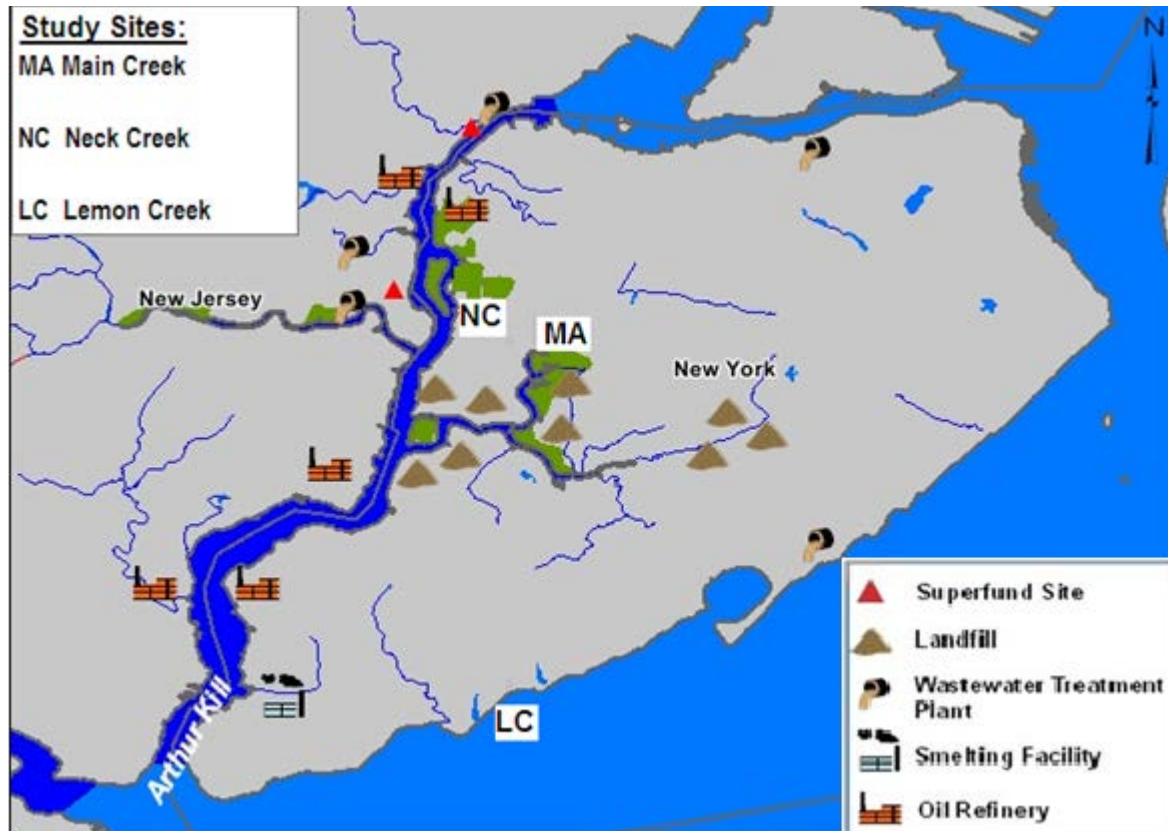


Figure 1-5a. Waterways and point sources surrounding the Arthur Kill and marsh study sites.

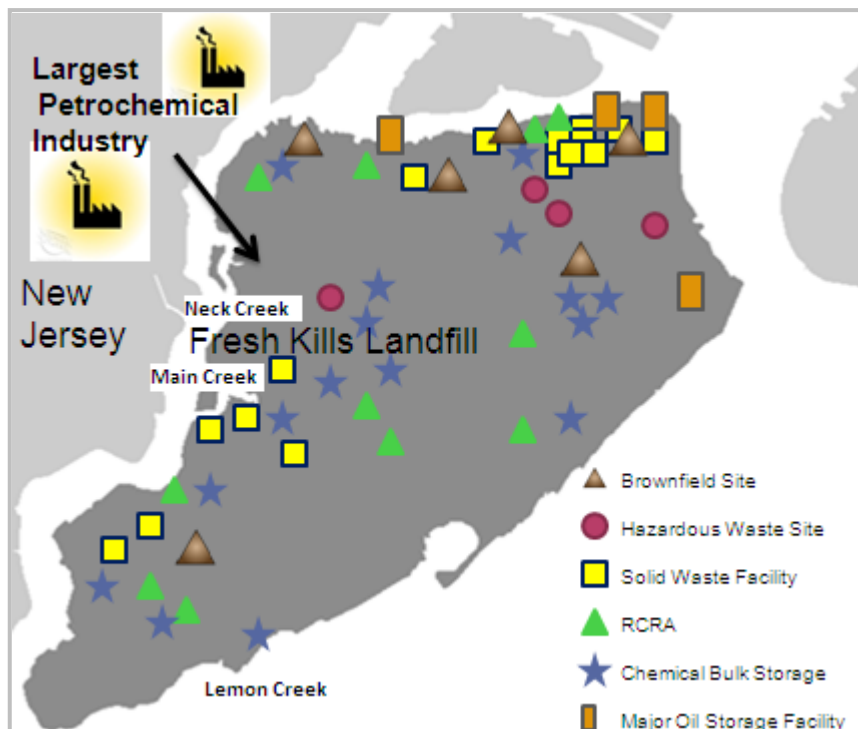


Figure 1-5b. Staten Island Contamination Sites. Staten Island study sites are downwind from the world's largest petrochemical industry. Sites within the Arthur Kill Complex (Main Creek and Neck Creek) are also adjacent to various solid waste and chemical bulk storage facilities.

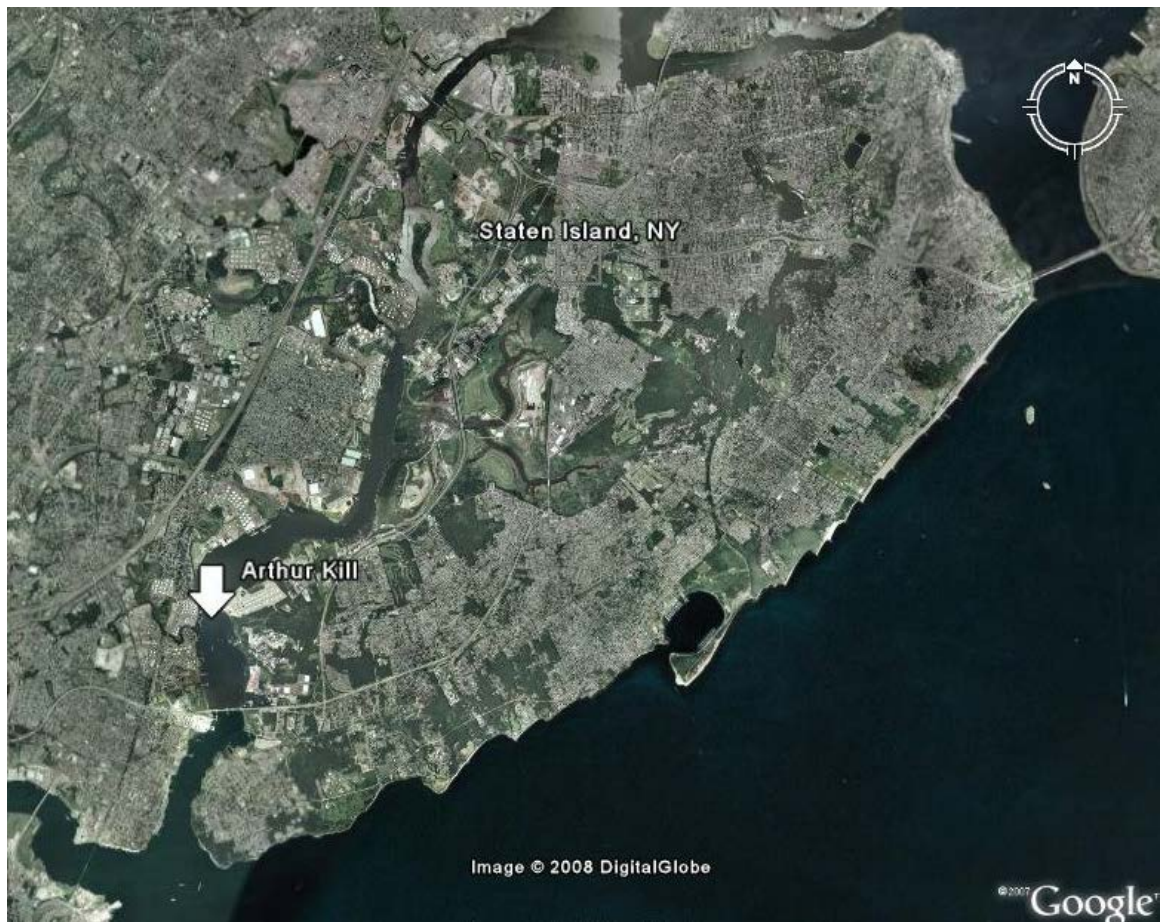


Figure 1-6a. Arthur Kill and surrounding area.

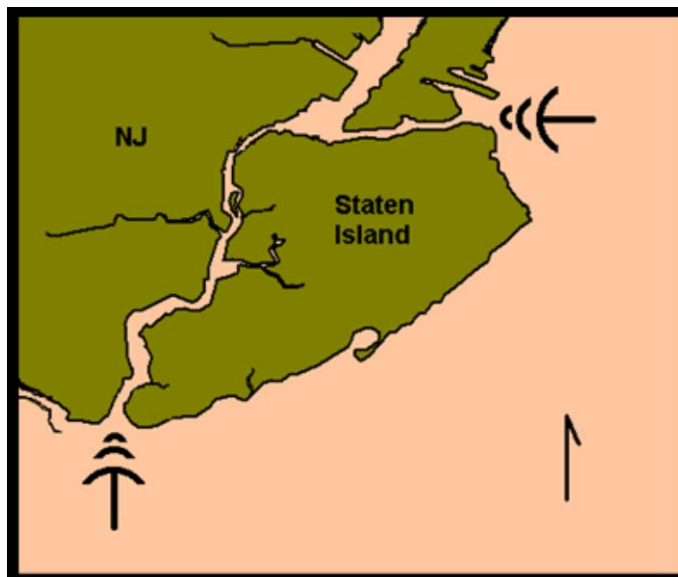


Figure 1-6b Dual tidal surges and the Arthur Kill

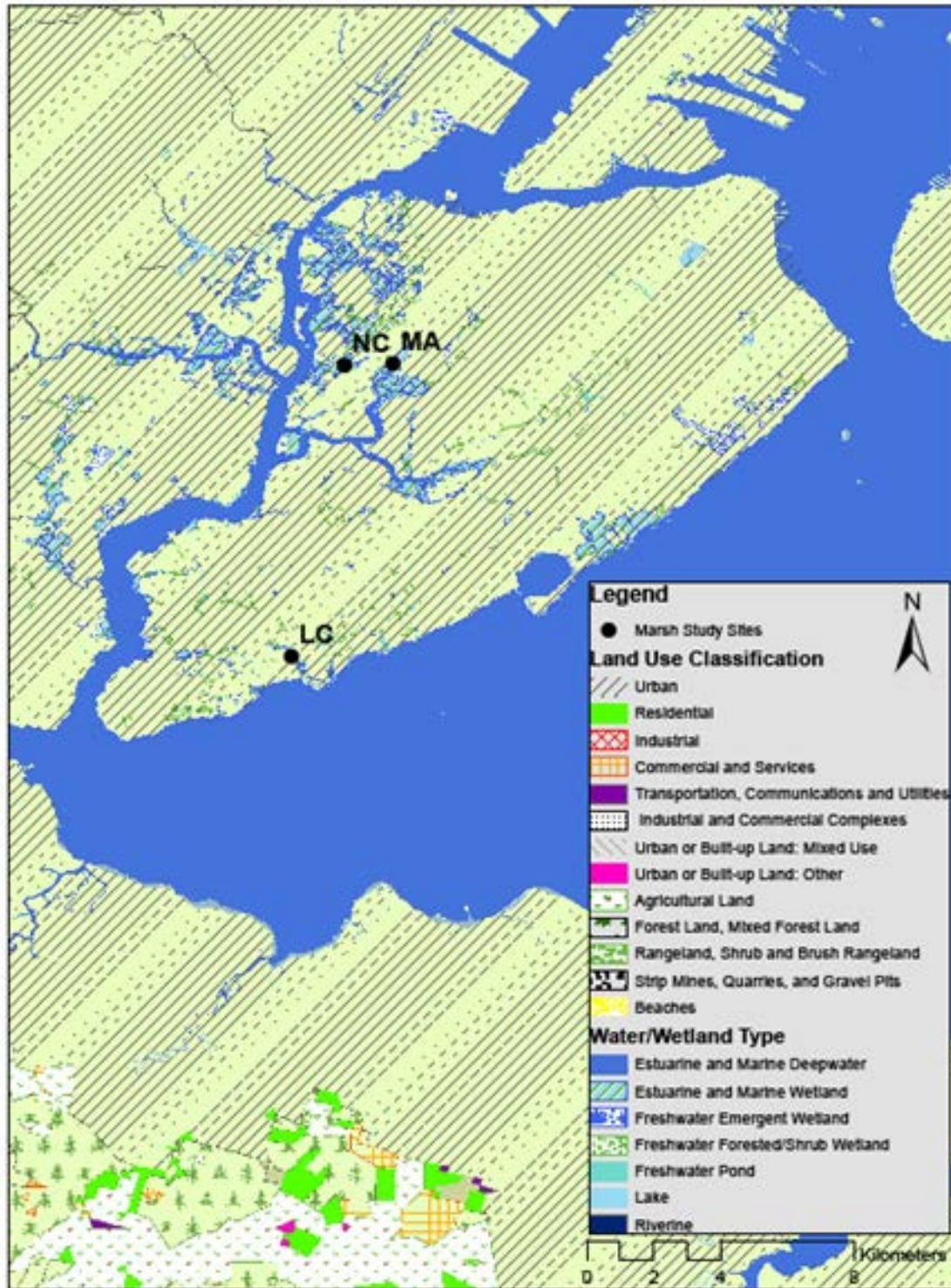


Figure 1-7 Staten Island urban land-use classification. In general, all study sites are characterized as urban and/or considered built-up land of mixed land uses.
(Map created from GIS shapefiles obtained from NOAA Mid-Atlantic land-use datasets).

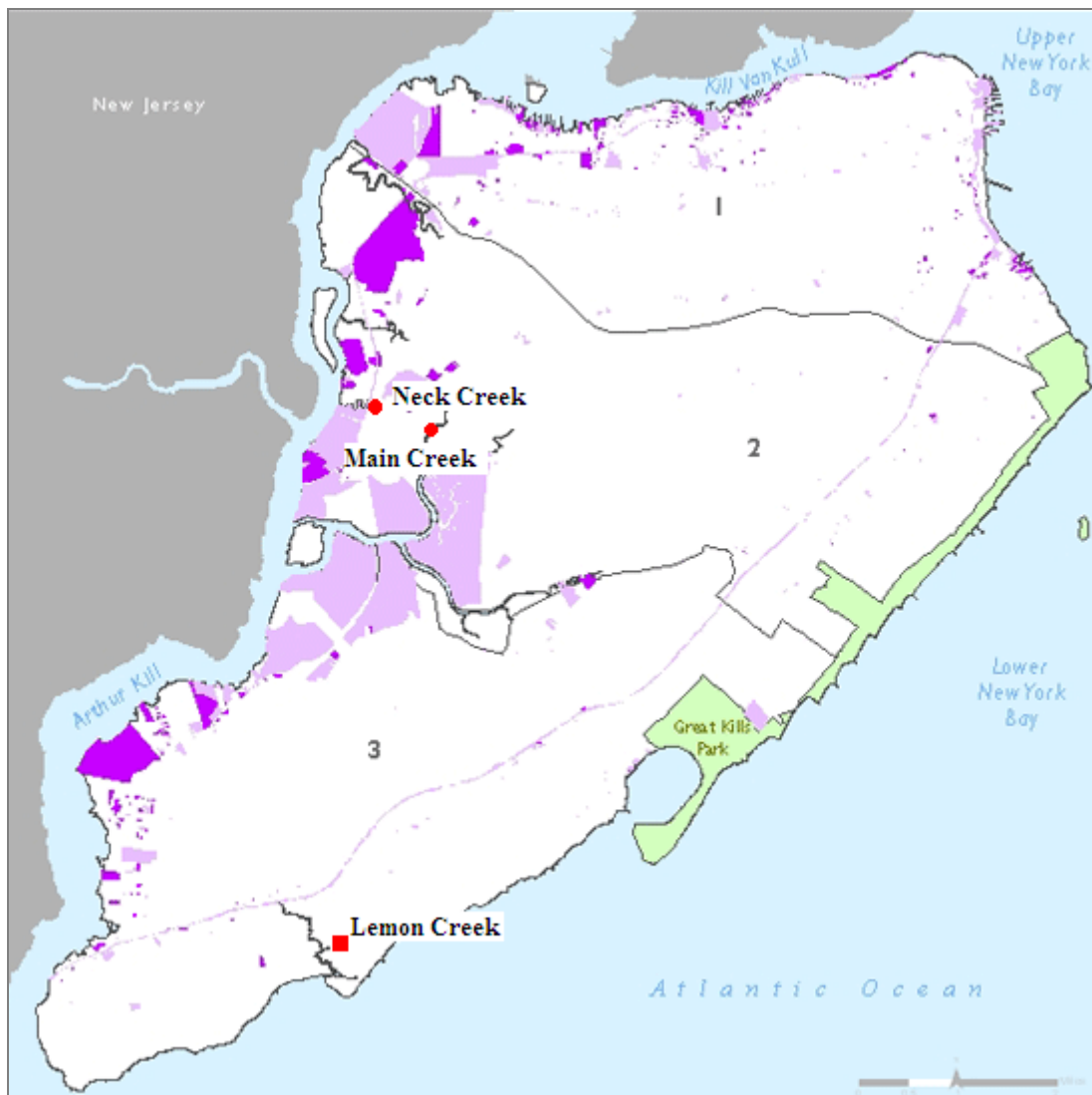


Figure 1-7a. Staten Island Industrial land-use areas. At a finer resolution scale, a greater concentration of industrial land-use is apparent in areas proximal to Arthur Kill sites vs. Lemon Creek. (GIS files obtained from PLUTO NYC Department of Planning).

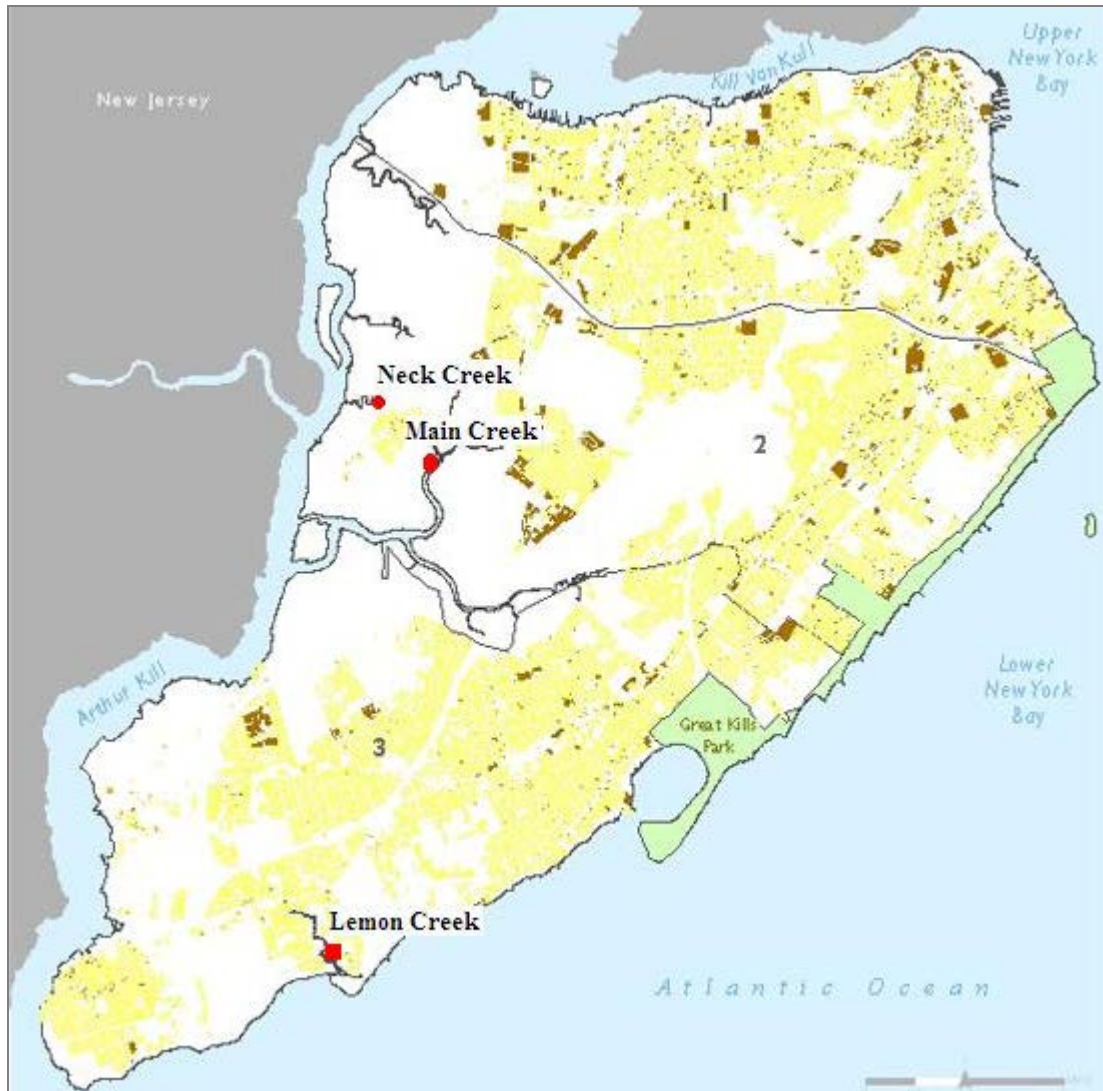


Figure 1-7b. Staten Island residential land-use map. Greater residential land-use surrounding Lemon Creek vs. Arthur Kill sites. (GIS files obtained from PLUTO NYC Department of Planning).

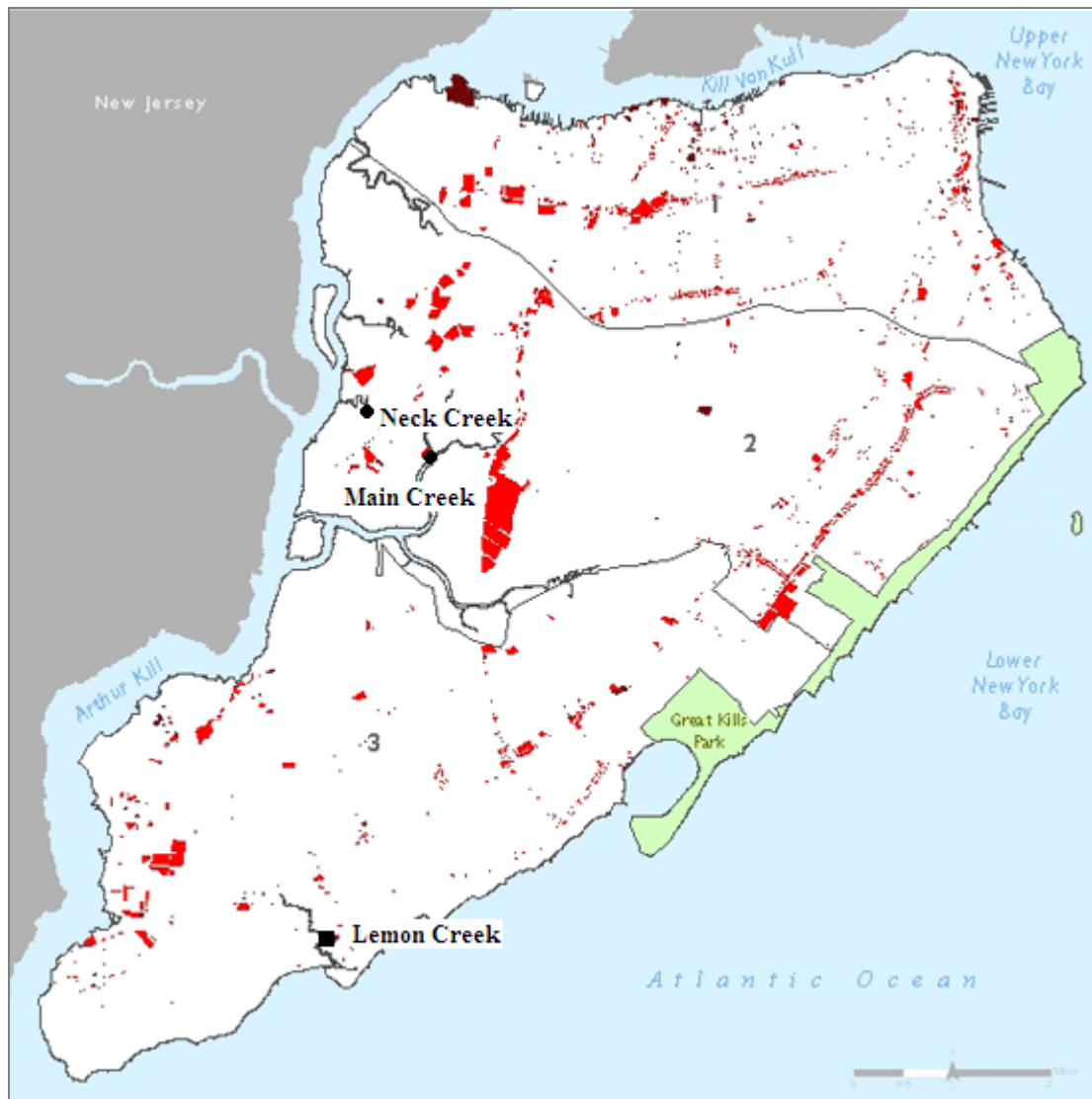


Figure 1-7c. Staten Island commercial land-use map. Greater commercial land-use activities concentrated in the vicinity of the Arthur Kill sites (Main Creek and Neck Creek) vs. Lemon Creek. (GIS files obtained from PLUTO NYC Department of Planning).

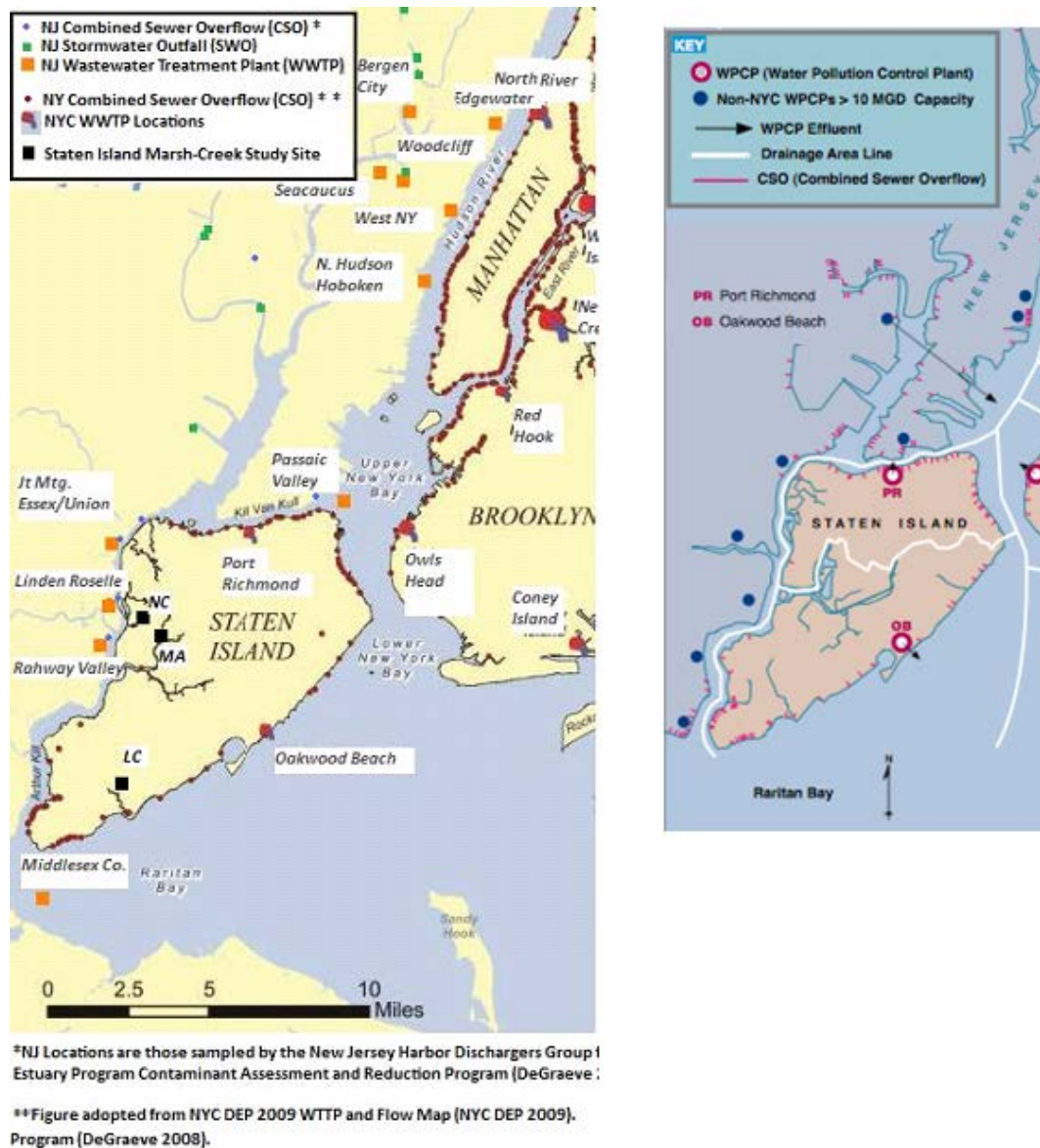


Figure 1-8. New York City Department of Environmental Protection (NYC DEP) and New Jersey Department of Environmental Protection (NJ DEP) Wastewater Treatment plant locations in the vicinity of Staten Island.

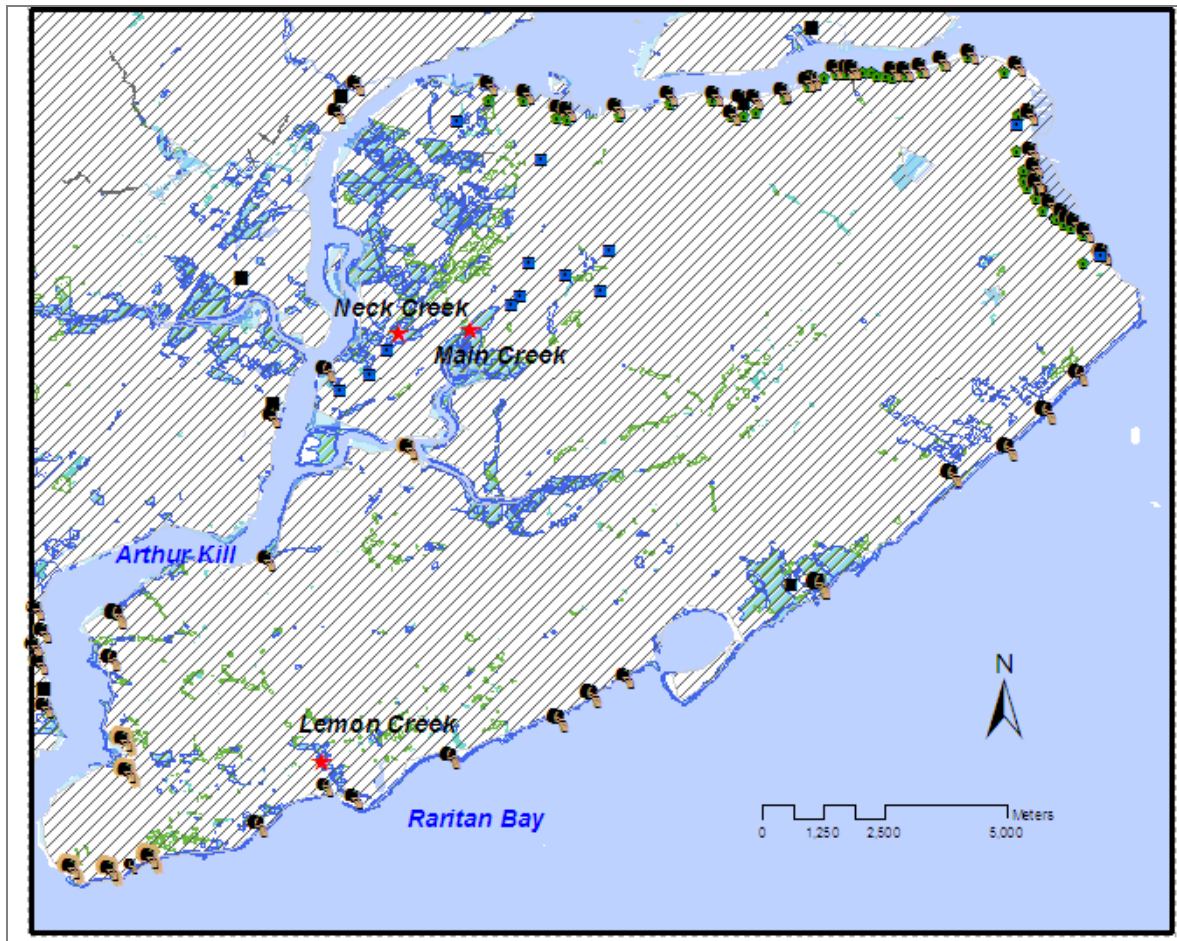


Figure 1-8a. New York City Department of Environmental Protection (NYC DEP) and New Jersey Department of Environmental Protection (NJ DEP) combined sewer overflow discharge points and separate stormwater outfalls surrounding Staten Island.

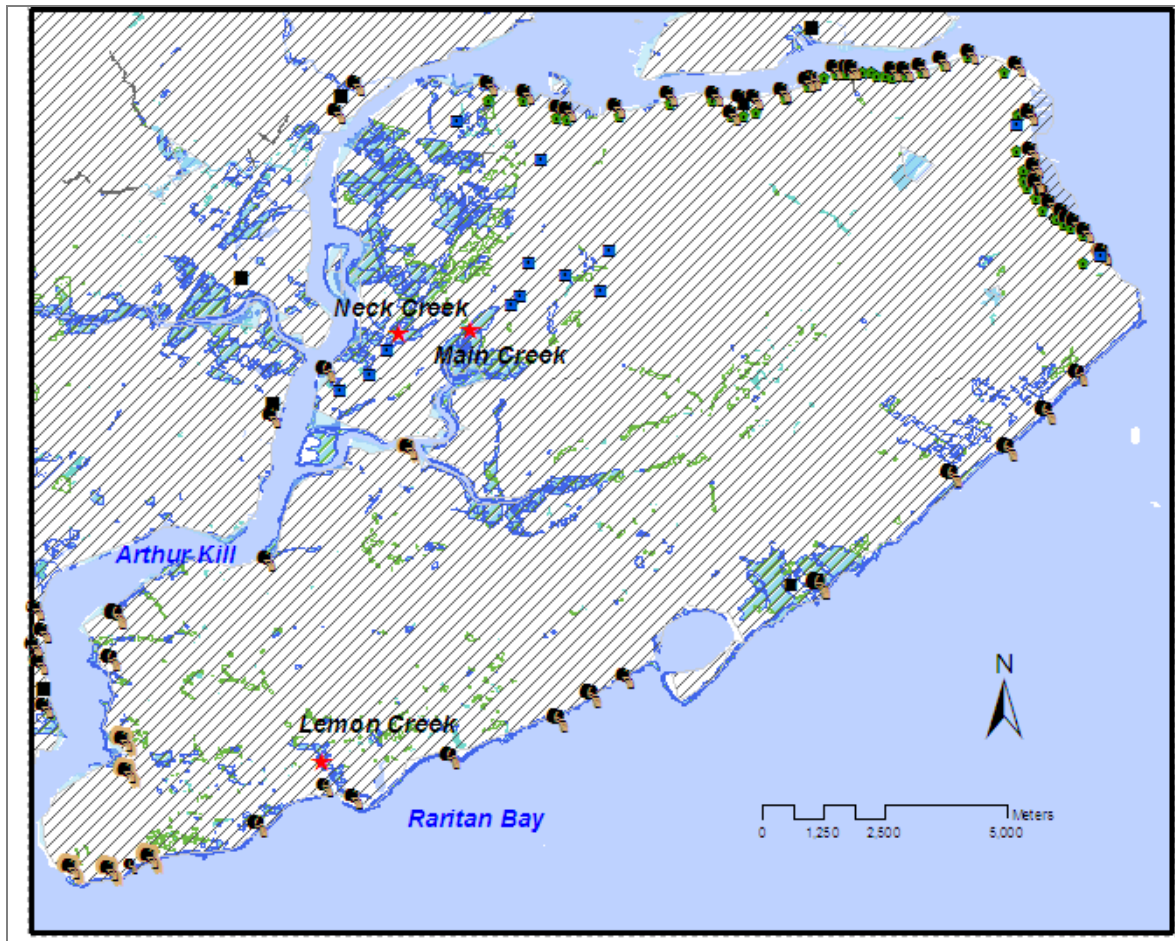


Figure 1-8a. New York City Department of Environmental Protection (NYC DEP) and New Jersey Department of Environmental Protection (NJ DEP) combined sewer overflow discharge points and separate stormwater outfalls surrounding Staten Island.

Chapter 2

Marsh Sediment Chronologies: Downcore Radionuclide and Metal Distributions

INTRODUCTION

Since the onset of industrial and urban development, humans have left behind a legacy of point sources and pervasive non-point sources that have subjected coastal ecosystems to increased metal loadings. The persistence of metals and their tendency to accumulate in marsh sediments enables past inputs to remain a threat to contemporary ecosystems. The impact of metal pollutants from historical activities combined with present-day sources and anthropogenic stressors ultimately contributes to habitat alteration and loss (Kennish, 2002).

When assessing temporal and spatial contaminant trends in marsh environments, radiometric dating of sediment cores provides useful chronological information and a context in which to evaluate variations in pollutant concentrations (Feng, et al., 1996; Chillrud, et al., 1996). Radioisotopes adsorb to suspended particulates in the atmosphere, and are thereby supplied to and bound with surfaces of estuarine sediments (Cheevaporn, et al., 1996, Feng et al., 1996). Particle-reactive properties give both natural and anthropogenic radioisotopes an affinity to quickly sorb to and transport with suspended particulates, which makes them effective radiochemical tracers that can impart useful information regarding depositional processes that have occurred in an area (Mastioff, et al., 2002; Weis et al., 2005; USEPA, 2008). Biogeochemical processes govern the transport and fate of suspended particulate matter in salt marsh systems (Cochran, et al., 1979; Feng, et al., 1996). Accordingly, observed differences of short-lived radionuclide distributions within sediments can reveal variability in localized

environments, which can subsequently infer spatial variations of contaminants within an ecosystem (Bruland, et al., 1974; Olsen, et al., 1986; Dibb, et al., 1989; Provini, et al., 1989).

Radioisotopes, including ^{40}K , ^7Be , ^{210}Pb and ^{137}Cs , have proven useful in providing information about local conditions and depositional environments but, also, in the determination of approximate sediment age (Church, et al., 1981; Olsen, et al., 1984; Church, et al., 1998). The practical application and the relative timescale of information that can be derived from radiodating surveys are largely dependent on the type of radionuclide (Koide, et al. 1997; Mastioff, et al., 2002). Based upon differences in source function and half-life, specific radioisotopes can be used as chronometers for detecting long-term environmental variations or as short-term tracers for identifying sediment mixing depth (Bloom, et al., 1987; Feng, et al., 1996; USEPA, 2008).

Salt marshes provide an ideal setting for geochronological studies that aim to identify enrichments in anthropogenic inputs of trace metals because of the of tendencies for such sheltered environments to accumulate sediment and associated contaminants in horizons over time (Weis, et al., 2005; Strong, et al., 2008; Mil-Homens, et al., 2008). Although long-term monitoring is the ideal approach for measuring temporal changes in pollutant loadings and environmental quality of an ecosystem, sediment coring combined with radiodating and elemental analysis serves as a suitable alternative (Geyh, et al., 1990; Clark, et al., 1997). Collectively applying metal and radioisotope methodologies to sediment cores supersedes the use of sediment traps or real-time discrete sampling methods when assessing long-term contamination trends (Strong, et al., 2008). This integrative approach can provide information and suggest evidence of temporal variability regarding the environmental conditions in accreted sediments (Strong, et al., 2008).

Radiometric techniques provide a depositional context for accumulated contaminants that is useful in order to classify past versus present sources of contamination (Bonnevie, 1993). Based upon estimation of age and/or rate of sediment accumulation from decay properties or half-life, the distribution of radioisotopes within sediment cores can provide a geochronological record of sediment and sediment-associated contaminant deposition and burial (Bopp, et al., 1982; Bopp, et al., 1998; Weis, et al., 2005). Simultaneously analyzing sediment cores for radionuclides and metal concentrations allows for the construction of contaminant chronologies, which enables assessment of temporal and spatial variations of metal contamination within marsh systems (Bopp, et al., 1993; Cundy, et al., 2003; Bopp, et al., 2006; Mil-Homens, et al., 2008). Sediment profiles also allow contemporary and historical inputs of metal contaminants to be compared (Bopp, et al., 1993; Cundy, et al., 2003). Coring studies have been widely used to characterize pollutant loadings that may be attributable to current sources or prior impacts/sources of metal contaminants (Hornberger, et al., 1999; Sutherland, et al., 2002; Cundy, et al., 2003). Pairing radiodating and trace metal analyses permits evaluation and assessment of temporal contamination to identify if trends are indicative of metal burial and attenuation, and thereby suggest recovery from past sources, or degradation from new or existing sources (Bonnevie 1993; Bopp, et al., 1993; Weis, et al., 2005).

Salt marshes along the Arthur Kill have long been vulnerable to the impacts of metal pollutants that are consequent of effluents from the many industrial and manufacturing facilities that have occupied the shores of this urban waterway (Huntley, et al., 1995). Regulations and improvements in the treatment of anthropogenic effluents emptying into these receiving waters has improved the quality of Arthur Kill sediments and surface waters, however polluted sediments remain a threat to the ecosystem (Vitaliano, et al., 2002). Recent studies have found

elevated metal concentrations in sediments from marsh systems along the western shore of Staten Island, New York (Ward, 2002; Nichols, 2004). Although the contributory sources of this contamination are unknown, these sites both exhibited consistent metal contamination, indicative of continuous impact (Ward, 2002; Nichols, 2004). Baseline metal data within these marshes suggest that the observed pollution may be attributable to various contributions from historic and present-day anthropogenic activities. However, since both sites tidally exchange water with the Arthur Kill, it is plausible that advection of metal pollutants from the Arthur Kill may also serve as a predominant source.

The main objective of this study was to establish the depositional context of sediments in Staten Island marshes to provide a framework for evaluation of temporal variations and pollutant trends described by downcore metal concentration profiles. Specific objectives were to apply multiple radiodating techniques to sediment cores in order to interpret the depositional environment identifiable with the study marshes and to determine if sites demonstrate spatial heterogeneity, which could thereby suggest spatial variability throughout the study area, with respect to metal concentrations. In addition, radionuclide activity distributions were determined to emphasize spatial and temporal sediment dynamics and differentiate recent deposits for characterization of contemporary pollution throughout the study area. Collective determinations of radionuclides and metal concentrations will provide a depth-integrated record of marsh contamination, which will describe metal contents within successively older sediments and establish a timeframe for observable metal trends. Evaluation of metal chronologies will help identify and characterize site-specific pollutant trends; and if marsh contamination exemplified recovery from a former source via natural attenuation; consistent impacts from a long-term existing source; or recent environmental releases linked to new metal sources. This approach

will also aid in tracking success of current water quality initiatives targeting this severely impacted estuarine system.

METHODS

Study Sites

Monitoring activities consisted of sediment core collection, in triplicate, from three Staten Island, New York marsh locations: Main Creek (40°35'53.13"N; 74°10'32.62"W), Neck Creek (40°35'51.24"N; 74°11'19.56"W), and Lemon Creek (40°31'8.94"N; 74°12'10.98"W). Main Creek (MA) and Neck Creek (NC) are located along the western shore of Staten Island and tidally exchange water with the Arthur Kill (AK). Lemon Creek (LC) is situated on the southern shore of Staten Island and is tidally influenced by the Raritan Bay and serves as an external site (see Fig.1 and chapter one for detailed site descriptions).

Selection of study sites was based upon previous trace metal studies conducted within these Staten Island marsh systems. Baseline sediment data (2001) demonstrated these marshes exhibited site-specific metal contamination that was attributable to either known point sources or general regional contamination. Prior coring studies concluded the latter explanation, regional pollution, contributed to the elevated metal concentrations identified in marshes along the western shore of Staten Island, including Main Creek and Neck Creek, which served as targeted locations for the current study (see Chapter 1 for detailed site descriptions) (Appendix 2-A; Ward, 2002).

Both sites tidally exchange water with the Arthur Kill: Main Creek shares a border with the Fresh Kills landfill and connects to the Arthur Kill via the Fresh Kills creek; Neck Creek is north of Main Creek and directly flows from its upland marsh habitat to the Arthur Kill.

Previous research found Main Creek and Neck Creek were considerably more polluted than Lemon Creek (Ward, 2002; Nichols, 2004). Datasets and metal profiles for the Arthur Kill sites showed consistent, elevated metal concentrations throughout the cores, which were indicative of continuous deleterious impacts to the marsh habitats (Ward, 2002; Nichols, 2004).

Prior coring results established that sediment metal (Cu and Zn) concentrations at Lemon Creek were near background levels, which might be expected as the site is considered the most pristine of all salt marshes on Staten Island (Appendix A; Ward, 2002; Nichols, 2004; NYC Dept. Parks, 2007). However, Lemon Creek was primarily included in the study design because it is located on the southeastern shore of Staten Island. Therefore, this marsh system drains into Raritan Bay and the Arthur Kill does not directly influence this site. Thereby, Lemon Creek served as a regional reference site because its externality provided radionuclide and metal data from sediment cores outside the Arthur Kill Proper, which can facilitate comparisons between study sites, and help assess if connectivity to the Arthur Kill or site-specific inputs are major sources of metal contaminants to study sites.

Field sampling

During low tide, sediment cores were collected from exposed mudflats on the banks alongside each creek using 22.5 cm (2.5 cm in diameter) nitric (HNO₃) acid-washed cores. At each coring location, the plastic cores were gently inserted until they reached downward to a depth of 21 cm; the submerged ends were manually capped at this depth. Once extruded, the top of the sediment cores were capped and placed into a bucket until the samples were transferred to the laboratory. Subsequently, sediment cores were stored in a -20°C freezer until processing and analysis (USEPA, 2001; Weis, et al., 2005).

Sediment core processing for radionuclide and metal analysis

In order to limit biases from differences in particle size distributions, fine-grained fractions of sediments core samples were distinguished prior to radionuclide and metal analysis. Samples were also differentiated by particle size because isotopes and metals mainly adsorb to fine-grained sediments and benthic biota feed upon them (Gurrieri, et al., 1998; Cundy, et al., 2001; USEPA, 2008). Three sediment cores (20 cm) from each site (MA, NC and LC) were thawed and sliced lengthwise, to extrude individual cores in one piece, and subsequently, sliced downcore at 2 cm intervals. To minimize cross contamination the inner sediments from the center of each core section, which came into the least contact with sampling and processing materials, were wet-sieved with NANOpure[®] water. Sediments from each core section were wet sieved with a nylon mesh screen (74µm), in order to recover the fine-grained fraction, and dried (60°C) to a constant weight to compensate for grain size effect (Hornberger, et al., 1999). After drying, the fine-grained sediments were placed in separate mortars and homogenized while ground to a fine powder with a pestle. Subsequently, one core from each site was prepared for radionuclide analysis (see: Radionuclide analysis, below). Approximately 4.0g (rounded to 5 decimal places) of dried fine-grained sediment from each depth interval was packed into a gamma counting vial (4 cc volume Wheaton Omnivial[®]). For trace metal analysis, approximately 0.5g aliquots (rounded to 5 decimal places) of each site's 10 core sections were placed into a 22 ml glass scintillation vial (see section 2.5).

Radionuclide analysis

The radionuclides, ⁴⁰K, ⁷Be, ²¹⁰Pb, ¹³⁷Cs, selected for analysis serve as effective chronometers, which can provide dating information to establish a depositional timeframe for the

collected sediment cores. One core replicate from each marsh location (MA, NC, LC) was dated radiometrically to establish a depositional timeframe for accreted sediment horizons. Fine-grained sediment samples were analyzed for radioactive isotopes via established techniques for gamma spectrometry (Bopp, et al., 1998; Chillrud, et al., 1999). Gamma counting vials containing packed sediment samples (see: Sediment core processing, above) were sent to the Gamma Counting Laboratory of Rensselaer Polytechnic Institute for measurement of ^{40}K , ^7Be , ^{137}Cs , and ^{210}Pb activities. Counting vials were placed into the well of an intrinsic Ge detector (ORTEC GWL-120). Samples were counted for a minimum of 8 hours or up to approximately 24 hours, to achieve acceptable precision (Bopp, personal communication). Reported activities of all radioisotopes analyzed were decay-corrected to the date of core collection (August, 2007) and values were reported with $\pm \sigma$ uncertainties based on counting statistics.

Laboratory quality assurance practices included the use of blanks and calibration standards for verification of instrumentation accuracy, precision, and efficiency. Initial and continuing calibration standards, which were run every twenty samples, included NBS standard sediment (River Sediment NBS 4350B), a liquid NBS standard (NBS 4953-C) that was used to prepare spiked sediments, and secondary standards, which were prepared at the Lamont-Doherty Earth Observatory and calibrated to NBS standards. Specific standards included certified reference material supplied by the National Institute of Meteorology, Beijing, China (River sediment GBW 08304a), and a secondary standard (LGP) analyzed for total ^{210}Pb by alpha spectrometry at the Lamont-Doherty Earth Observatory were additional standards which were incorporated. Additional laboratory QA/QC procedures included the counting of blanks. Concentrations of ^7Be and ^{137}Cs activities were reported in picocuries per kilogram ($\text{pCi}\cdot\text{kg}^{-1}$),

while ^{210}Pb activities were reported in units of decay per minute per gram ($\text{dpm}\cdot\text{g}^{-1}$). Sample results were reported with ± 1 standard deviation (σ) based on counting statistics.

Multiple radionuclides served as temporal markers in order to best characterize the temporal context of sediment deposition. Plotting distributions of radioisotope activity versus core depth depicted radionuclide concentration profiles. ^{40}K activities were used as a proxy for stable K content, and thereby distributions provided a measure of homogeneity within the cores. Detection of significant ^7Be activities ($\pm 2\sigma$) helped evaluate metal inputs associated with recent sediment deposition, defined here as sediments deposited within 1 year. The short half life of ^7Be ($t_{1/2}=53$ days) was used to assess short-term ($<1\text{yr}$) deposition of particles and associated pollutants, which allows for this radionuclide to indicate short-term variations of sediments and particle-reactive contaminants and/or mixing when detected at depth (Feng, et al., 2002; Bopp, et al., 2006).

Distributions of ^{210}Pb and ^{137}Cs activities established sediment chronologies on a decennial timescale and were measured to estimate vertical accretion rates (Huntley, et al., 1994; Lee, et al., 2001; Kumar, et al., 2007). Evaluation of the decay of excess ^{210}Pb (unsupported) activity helped further assess sediment ages at depth. Prior to ^{210}Pb analysis, the daughters of ^{222}Rn grew into secular equilibrium in sealed counting tubes for 20 days for the determination of supported ^{210}Pb levels. However, it was necessary to count samples in the upper core sections as soon as possible to optimize the detection of short-lived ^7Be activities. Therefore, it was necessary to estimate the supported ^{210}Pb activities in the uppermost core sections from the value measured in the samples immediately below. Excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) activities were calculated by subtracting the supported ^{210}Pb component from the inventory of

total ^{210}Pb , which is expressed in the equation below (Eq. 1) (Huntley, et al., 1994; Feng, et al., 1996).

$$^{210}\text{Pb}_{\text{xs}} = ^{210}\text{Pb}_{\text{total}} - ^{210}\text{Pb}_{\text{supported}} \quad (\text{Eq. 1})$$

The radioactive decay of $^{210}\text{Pb}_{\text{xs}}$ activities, where ^{210}Pb activities in sediments decrease exponentially with respect to time (depth) in accordance with its half-life, derived sediment-rate relationships (Appleby, et al., 1983; Wan, et al., 2005). Cores were age-dated using a general decay equation; as described in Eq. 2, this equation can be expressed for the calculation of core age (Goldberg, 1963; Krishnaswamy, et al., 1978; Ivanovich, et al., 1992).

$$t_h = 1/\lambda \cdot \log(A_0/A_h) \quad (\text{Eq. 2})$$

where:

t_h = age of sample (yr)

λ = ^{210}Pb radioactive decay constant

A_0 = $^{210}\text{Pb}_{\text{xs}}$ measured in surface sediment section (present)

A_h = activity of $^{210}\text{Pb}_{\text{xs}}$ at depth h

Vertical profiles of ^{137}Cs activities were used to corroborate information derived from ^7Be and ^{210}Pb dating (Smith, et al., 2001; Arnaud, et al., 2006). ^{137}Cs ($t_{1/2}=30.3$ years) is a thermonuclear byproduct of atmospheric testing of nuclear weapons which began around 1954, though peak fallout occurred between 1963 and 1964 (Olsen, et al., 1981; Huntley, et al., 1994; Bopp, et al., 2006). In geochronological studies evidence of peaks in downcore ^{137}Cs activities serve as discrete time markers that represent the onset and maximum of ^{137}Cs production and deposition, respectively (Rozan, et al., 1999; Feng, et al., 2002; Bopp, et al., 2006). In the

absence of sediment mixing, no ^{137}Cs activity would be measurable in sediment layers deposited before 1954, and significant levels would correlate with these fallout dates, while up-core vertical distributions in sediment profiles would ideally decrease after a 1963-64 peak (Huntley, et al., 1994; Wan, et al., 2005).

Metal analysis

Fine-grained sediments from each core section were prepared for analysis of near-total trace metal content (Cd, Cu, Zn) as described in section 2.3. Samples were processed further using standard techniques, which included digestion with trace metal grade nitric acid (HNO_3), resuspension with 2% HNO_3 , filtration, and analysis using Perkin Elmer Optima 3300XL Inductively Coupled Plasma Argon Emission Spectrophotometer (ICP-AES) (Luoma, et al., 1981; Hornberger, et al., 1999; Andrews, et al., 2004). A near-total hot HNO_3 reflux metal digestion method was initiated with the addition of 10ml of concentrated trace metal grade nitric acid to each scintillation vial containing 0.5g of fine-grained sediment recovered from each core. The vials were loosely capped, and placed in a fume hood to sit overnight at room temperature. Subsequently, resuspension of the sediment acid slurry was achieved by gently agitating the vials by hand, the caps were removed and replaced by reflux bulbs and lastly, vials were placed inside a fume hood on top of a hotplate and heated to approximately 150°C . The samples refluxed until the digestion was complete (approximately 7 days), at which time the reflux bulbs were carefully removed and samples were allowed to evaporate to dryness. In preparation for ICPAES analysis, dried samples were reconstituted to 10 mls with 2% HNO_3 (trace metal grade), filtered through $0.45\ \mu\text{m}$ Millipore[®] filters, and collected in acid washed autosampler tubes.

ICPAES assays yielded metal concentration datasets for a suite of elements. However, a subset of these metals (Cd, Cu, Zn) were selected because of their potential toxicity and because

they have been identified as contaminants of concern to the NY/NJ Harbor Estuary (Kennish, 1992; Church, et al., 1998; NY/NJ HEP, 1996). ICAPES instrumentation was calibrated according to normal operating procedures after correction for peak interferences in the samples' digest matrix.

Laboratory quality assurance practices included acid-washing all sample collection and processing materials with 10% HCl and rinsing with NANOpure[®] water before use, and the creation and application of procedural blanks. After initial calibration of the ICAPES, continual calibration standards along with two internal quality control standards (ERA and SPEX 1 ppm reference standard) were analyzed every 12 samples to ensure consistent performance of the instrument. Accuracy and precision of metal analysis were further verified by checking with certified estuarine sediment reference material ("Standard Reference Material[®] 1646a" from the National Institute of Standards and Technology) which yielded metal concentrations in agreement with the reported values (95% confidence level). All analyzed samples yielded concentrations above the instrument's minimum detection limits (MDLs), which are calculated and confirmed routinely.

To put sediment metal concentration results into context, and to account for the inherent level of metals that are naturally present in the Earth's crust, Cd, Cu, and Zn concentrations from uncontaminated regional sediments served as background values (Tomlinson, et al., 1980; Gurrierri, et al., 1998; Ray, et al., 2006). The regional metal concentrations used to determine the extent of metal enrichment in sediment core samples were $0.11 \mu\text{g Cd}\cdot\text{g}^{-1}$, $14 \mu\text{g Cu}\cdot\text{g}^{-1}$, and $81 \mu\text{g Zn}\cdot\text{g}^{-1}$ (Hirschberg, et al., 1996) (Table 3). The formula used to identify the enrichment factor (EF) for a specific metal species is expressed below (Alexander, et al., 1993; Valette-Silver, 1993; Hornberger, et al., 1999; Strong, et al., 2008):

$$EF = C_o / C_b \quad (\text{Eq. 3})$$

where:

C_o = metal concentration observed in core section o

C_b = background/baseline metal concentration (Hirschberg, et al, 1996)

Sediment concentration datasets were graphically represented (using SigmaPlot 8.0), with respect to depth, to construct metal chronologies. This approach profiled Cd, Cu, and Zn concentrations in surface, and successively older, sediments from each marsh site. Thereby, results acquired from analysis of each sediment core section provided a record of temporal contamination for each site.

RESULTS

Radionuclide analysis of marsh sediment cores

Measurements of radionuclide activities revealed variations in isotope distributions both spatially (from coring locations) and temporally (within sediment cores) (Table 1). Interpretations of sediment chronologies were based on the activities of multiple radionuclides in vertical distribution profiles. Radioisotope depth profiles were developed by plotting activity distributions versus sediment core depth. Radionuclide profiles representing ^{40}K , ^7Be , $^{210}\text{Pb}_{\text{xs}}$, and ^{137}Cs activities at each marsh location are shown in Figures 2-4.

Cores did not reveal any evidence of large burrows that could have potentially distorted stratification of the sediment record. Downcore profiles from all three sites: Main Creek (MA), Neck Creek (NC), Lemon Creek (LC), exhibited no major variations in ^{40}K activities (Fig 2). Values of ^{40}K activity varied between 12-13.9 pCi·g⁻¹, 14-16.1 pCi·g⁻¹, and 14.1-16.2 pCi·g⁻¹ at Main Creek, Neck Creek and Lemon Creek, respectively.

Downcore distributions of ^7Be and ^{137}Cs in Main Creek, Neck Creek and Lemon Creek sediments are shown in Figs. 3a-c. ^7Be activities detected in the top horizon of the Neck Creek sediment core measured $1454 \text{ pCi}\cdot\text{kg}^{-1}$, while detectable ^7Be at Main Creek and Lemon Creek were nearly double, ranging from $3254\text{-}2177 \text{ pCi}\cdot\text{kg}^{-1}$ and $2504\text{-}2221 \text{ pCi}\cdot\text{kg}^{-1}$, respectively. Accordingly, significant ^7Be values, defined as activities greater than 2σ above the counting uncertainty, were only present in the uppermost core section (0-2 cm) at Neck Creek, while ^7Be activities were detectable in the upper two sediment core sections (0-2cm and 2-4 cm) at both Main Creek and Lemon Creek.

At all marsh sites, vertical distributions of ^{137}Cs were consistent with ^7Be data, and the ^{137}Cs activity does not show a significant increase with depth toward a mid 1960s peak (Figs. 3a-3c). Measurements of ^{137}Cs activities were comparable among the sites, though the differences in vertical distributions were apparent. Detectable ^{137}Cs was measured throughout the lengths of Main Creek and Lemon Creek cores. Surface and bottom activities varied from $104\text{-}119 \text{ pCi}\cdot\text{kg}^{-1}$ at Main Creek, and ranged from $133\text{-}128 \text{ pCi}\cdot\text{kg}^{-1}$ at LC. However, no detectable ^{137}Cs activities extended below the 6 cm interval in the Neck Creek profile; above this depth ^{137}Cs activities increased from $84 \text{ pCi}\cdot\text{kg}^{-1}\text{-}108 \text{ pCi}\cdot\text{kg}^{-1}$ at the top of the core.

Distributions of ^{210}Pb activities observed in the sediment chronologies were analogous to the trends seen in the plots of ^{137}Cs activities at each site (Figs. 4a-c). Generally, $^{210}\text{Pb}_{\text{xs}}$ decreased with depth, although vertical profiles revealed fluctuations and deviations from an ideal exponential decay curve, and activities were scattered and detected at low levels. At both Main Creek and Lemon Creek, $^{210}\text{Pb}_{\text{ex}}$ activities were detectable throughout the cores with little to no gradient. Main Creek and Lemon Creek $^{210}\text{Pb}_{\text{ex}}$ ranged from $6.3\text{-}3.83 \text{ dpm}\cdot\text{g}^{-1}$ and 4.52-

1.56 dpm·g⁻¹, respectively. Neck Creek ²¹⁰Pb_{xs} was only detectable in the upper two core sections, and varied from 3.42-2.54 dpm·g⁻¹. Within sediment depths greater than 4 cm Neck Creek and Lemon Creek ²¹⁰Pb_{xs} measurements fell below or approached supported ²¹⁰Pb activities, which signaled ²¹⁰Pb that was not attributable to natural fallout.

Trace metal analysis of sediment cores

Sediment core metal concentrations and enrichment factors

Sediment samples were analyzed for Cd, Cu and Zn at successive 2 cm intervals for the length of all cores collected from marsh study locations. Relative to Lemon Creek sediments, trace metal concentrations for all elements were higher in sediments from sites adjacent to the Arthur Kill [Main Creek and Neck Creek]. Mean metal concentrations ($\pm \sigma$), standard error (SE), and ranges (minimum to maximum) in $\mu\text{g}\cdot\text{g}^{-1}$ are reported in Tables 2a-c. Levels of Cd, Cu, and Zn reported in uncontaminated sediments within the vicinity of the study area have measured 0.11 $\mu\text{g}\cdot\text{g}^{-1}$, 14 $\mu\text{g}\cdot\text{g}^{-1}$, 81 $\mu\text{g}\cdot\text{g}^{-1}$, respectively (Hirschberg, et al., 1996) (Table 3). These values served as proxies for background metal concentrations for calculating the enrichment factor (EF) of core sediments. All sediment core samples yielded metal concentrations that appreciably exceeded these regional background levels, regardless of site or depth. The EFs summarized in Table 4 reflect the high ratio of observed, compared with background, metal concentrations throughout the cores

An average of the metal concentrations found in each sediment core sub-sample, which represented the 10 depth intervals, determined the mean Cd, Cu, and Zn values within the entire core. For each site, the core mean for each element helped calculate respective EF values, which served as both a pollution assessment measure and means for site comparisons. Overall, it was apparent that Main Creek sediments had the highest EFs for Cd and Zn. Observed Cd

concentrations at Main Creek were 59 times higher than background levels, and Zn values were 4 times greater than background. Neck Creek sediments showed the greatest Cu enrichment, followed by Main Creek (36 and 21 times higher than background, respectively). Lemon Creek core sediments were the least contaminated among all the sites. Nevertheless, average values of pollutant concentrations at Lemon Creek were notably greater than background levels: Cd, Cu, and Zn enrichment corresponded to levels that were 14, 11, and 2 times higher than background concentrations for the same metals.

Metal enrichment in recently deposited sediments

As described in section 3.1, the most recent sediments were defined as those deposited within 1 year, which correlated to core sections where presence of significant ^7Be activities was established (see section 3.1 and Table 1). Identification of recently deposited sediments extended through the 2-4 cm interval of Main Creek and Lemon Creek cores, but was limited to the surface compartment (0-2cm) of Neck Creek cores. Accordingly, an average of the Cd, Cu, and Zn concentrations detected in the upper two sections of Main Creek and Lemon Creek cores represented the concentration of the same metals in the sediments characterized as most recently deposited.

Recent sediments from each site generally had lower or comparable metal concentrations, as compared to the values found in the deeper core sections (Table 2). However, the EF values characterized for recent sediments were on the same scale as the EFs representing the entire core (Table 4). With respect to modern sediments, the enrichment factor of Cd at Main Creek was 4.7 times Lemon Creek, and was greater than Neck Creek by a factor of three. While Neck Creek had the highest enrichment of Cu, the contamination of recently deposited sediments was only slightly greater than like sediments at Main Creek, but two-fold Cu levels observed at Lemon

Creek. Main Creek exhibited the greatest Zn EF, although the magnitude was comparable to Neck Creek.

Recent Main Creek deposits (0-4 cm) demonstrated levels of Cd, Cu, and Zn that were on similar scales of contamination to metal concentrations observed in the oldest sediments (18-20 cm).

Compared with the Main Creek core mean values, Cd and Cu concentrations were slightly lower in recent sediments. However, the enrichment ratios determined for recent sediments, which showed Cd, Cu, and Zn concentrations were 55, 20, and 4 times greater than background respectively, were nearly equivalent to EFs measured for the full extent of the Main Creek cores.

Like Main Creek, comparisons between pollutant loads in recent (0-4 cm) versus bottom (18-20 cm) Lemon Creek core sediments showed either little variance or reflected minor improvement, which was demonstrated by slightly lower levels of Cd and Cu, and equivalent Zn concentrations. Accordingly, recent Lemon Creek deposits were comparable to average concentration values that represented the cores as a whole. The degree of Cu and Zn enrichment in recent Lemon Creek sediments was equivalent to EFs calculated for the length of the core; Cu exceeded background levels by 11 times and the enrichment factor of Zn showed it was twice background. Enrichment of Cd in sediments deposited within a year of collection measured 12 times higher than background levels, which was slightly lower than the whole core ratio (14 times background) that evaluated Cd enrichment in all core intervals.

Minimum metal concentration values were detected in either recent Neck Creek sediments, which were limited to the uppermost layer (0-2 cm), or within the bottom-most horizon (18-20 cm). Accordingly, the lowest Cd and Cu enrichment occurred in the upper core

sections of Neck Creek cores, while Zn levels were slightly higher in recent sediments than concentrations measured in the bottom core sediments. Recent Neck Creek sediments also had Cd and Cu concentrations that were substantially less than the whole core average Cd and Cu values. Recent Neck Creek sediments contained levels of Cd and Cu that corresponded to 19 and 22 times background, whereas assessment of all core sections determined core mean Cd and Cu concentrations that were greater than background by factors of 30 and 36, respectively.

Downcore metal profiles: Main Creek

Metal concentration data corresponding to each sediment core section was represented by depth via contaminant profiles, which were constructed for each element (Cd, Cu, Zn) at all coring locations (Main Creek, Neck Creek and Lemon Creek) (Figs. 5-7). Main Creek metal concentration data yielded vertical contamination profiles that were generally consistency in Cd, Cu, and Zn values, irrespective of sub-surface peaks evident in the deep and mid-core horizons (Figs. 5a-c). Contamination was evident throughout the entire extent of the cores, which exhibited episodic subsurface peaks and analogous pollutant trends for all metals. Metal concentrations within sediments decreased towards the surface, with mean levels of Cd, Cu, and Zn ranging from $6.6\text{--}5.6\ \mu\text{g}\cdot\text{g}^{-1}$, $310.8\text{--}254.6\ \mu\text{g}\cdot\text{g}^{-1}$, and $339.8\text{--}291.1\ \mu\text{g}\cdot\text{g}^{-1}$, respectively. EF values in all Main Creek horizons were comparable, the ranges were limited and demonstrated minor variation with depth. EFs for Cd, Cu, and Zn remained relatively constant over the length of the core, ranging from: $51.1\text{--}69.5\ \mu\text{g}\cdot\text{g}^{-1}$, $18.2\text{--}23.9\ \mu\text{g}\cdot\text{g}^{-1}$, and $3.6\text{--}4.2\ \mu\text{g}\cdot\text{g}^{-1}$, respectively.

Overall, Main Creek sediment chronologies showed agreement amongst all metals studied; Cd, Cu and Zn minima and maxima were mainly evident at corresponding depths. Minimum concentrations for Cd, Cu and Zn were identified at the surface (0-2 cm), in Main Creek sediment samples ($5.62\ \mu\text{g}\cdot\text{g}^{-1}$, $254.6\ \mu\text{g}\cdot\text{g}^{-1}$, $291.1\ \mu\text{g}\cdot\text{g}^{-1}$, respectively). In comparison,

the highest concentrations were $7.65 \mu\text{g}\cdot\text{g}^{-1}$ for Cd, and $333 \mu\text{g}\cdot\text{g}^{-1}$ for Cu, which were observed at 4-6 cm. Zn measured $338 \mu\text{g}\cdot\text{g}^{-1}$ at 4-6 cm, which was comparable to the Zn maximum, $340 \mu\text{g}\cdot\text{g}^{-1}$, reached at 12-14 cm. Cd and Cu levels were also elevated in this mid-core section ($6.64 \mu\text{g}\cdot\text{g}^{-1}$ and $311 \mu\text{g}\cdot\text{g}^{-1}$), which was reflected by the subsurface peaks at 12-14 cm (Fig. 5).

Downcore metal profiles: Neck Creek

Like Main Creek downcore profiles, elevated concentrations of Cd, Cu, and Zn were detected in Neck Creek core sediments. However, Neck Creek pollutant chronologies exhibited metal-specific trends that demonstrated less correlation between elements than was observed in Main Creek metal profiles (Figs. 6a-c). Subsurface concentration peaks and subsequent declines were apparent mid-core and within the deep horizons above the bottom layer. Metal concentration data from all Neck Creek cores established maximum Cu and Zn concentrations at 14-16 cm, where sediments measured $838.6 \mu\text{g Cu}\cdot\text{g}^{-1}$ and $440.1 \mu\text{g Zn}\cdot\text{g}^{-1}$. However, assessment of downcore Cd concentrations suggested maximum levels of this element were evident in the horizon below. Therefore, the core profile for Cd depicted its maxima peak at 16-18 cm, where the element measured $5.55 \mu\text{g}\cdot\text{g}^{-1}$, as compared to $4.43 \mu\text{g}\cdot\text{g}^{-1}$, which was determined for sediments from the 14-16 cm compartment. However, the lower Cd mean at 14-16 cm may be a result of the wider range of Cd values found at this interval, compared with the higher, smaller concentration range observed for 16-18 cm sediments. From these maxima, all profiles exhibited intermittent fluctuations, but demonstrated a general trend of decreasing pollutant levels towards the surface. Surface sediments showed attenuation of Cd and Cu with lower concentrations of these metals at 0-2 cm than detected in the bottom core sediments (18-20 cm) (Figs. 6a,b). From its mid-core maximum Zn also showed recovery; surface concentrations

were not restored to values lower than observed at the base of the core, however, a comparable degree of Zn enrichment was attained at 0-2 cm (Fig 6c).

Determinations of surface Cd, Cu and Zn concentrations corresponded to $2.06 \mu\text{g}\cdot\text{g}^{-1}$, $314.56 \mu\text{g}\cdot\text{g}^{-1}$, and $235.89 \mu\text{g}\cdot\text{g}^{-1}$, compared to the $4.33 \mu\text{g}\cdot\text{g}^{-1}$ of Cd, $339.46 \mu\text{g}\cdot\text{g}^{-1}$ of Cu and $176.21 \mu\text{g}\cdot\text{g}^{-1}$ of Zn found in the bottom core sediments. Neck Creek pollutant chronologies revealed mean Cu and Zn surface concentrations that approached levels comparable to the bottom-most sediments, while at the surface (0-2 cm), Cd measured half the concentration detected in the bottom sediments (18-20 cm).

Although metal chronologies showed prominent peaks in the lower core sections, less apparent, episodic oscillations were seen mid-core, as exemplified by data from the 6-8 cm depth where the upper range of Cd reached $4.84 \mu\text{g}\cdot\text{g}^{-1}$ and Zn levels measured between 229.11 - $274.33 \mu\text{g}\cdot\text{g}^{-1}$. Zn concentration data revealed little disparity in between sediment core sections and demonstrated that Zn levels were consistent throughout the Neck Creek cores as evidenced by the narrow range between minimum and maximum that ranged from 176.21 - $290.43 \mu\text{g}\cdot\text{g}^{-1}$. In contrast, Cd and Cu profiles appeared more disparate, which is emphasized by the less consistent and larger reach of Cd and Cu concentration values, which corresponded to 5.55 - $1.82 \mu\text{g}\cdot\text{g}^{-1}$ and 691.47 - $303.85 \mu\text{g}\cdot\text{g}^{-1}$.

Downcore metal profiles: Lemon Creek

Collectively, downcore metal concentrations in Lemon Creek sediments were consistent (Figs. 7a-c). Amid generally steady vertical profiles, concentrations of Cd, Cu and Zn fluctuated slightly between sediment core horizons. However, the degree that Cd, Cu, and Zn

concentrations fluctuated throughout the cores was negligible and did not affect the consistent downcore enrichment trends demonstrated by all metals.

Altogether, the minor variations observed in Cd, Cu, and Zn chronologies were evident as disparate subsurface peaks, however, vertical Cu and Zn variations paralleled each other (Figs 7b,c). The Cd profile (Fig. 7a) deviated from the similar patterns identified in the Cu and Zn cores. Accordingly, contrasting subsurface peaks demonstrating increased Cd enrichment did not coincide with peaks showing elevated Cu and Zn levels. Thereby, the depth each element reached its maximum concentration within the contaminant profile was metal-specific. The 14-16 cm layer had the greatest levels of Cd ($2.44 \mu\text{g}\cdot\text{g}^{-1}$), while Cu and Zn concentrations were the highest in the bottom sediments (18-20 cm), at $195.02 \mu\text{g}\cdot\text{g}^{-1}$ and $218.03 \mu\text{g}\cdot\text{g}^{-1}$, respectively.

All metals declined to minimum concentrations at 4-6 cm, where Cd ranged from 0.83- $1.17 \mu\text{g}\cdot\text{g}^{-1}$, Cu levels were between 91.39- $170.75 \mu\text{g}\cdot\text{g}^{-1}$, and Zn decreased to 123.09- $196.28 \mu\text{g}\cdot\text{g}^{-1}$. Accreted sediments within the 2-4 cm section were more contaminated, as evidenced by EFs for Cd, Cu, and Zn that increased from: 8.91 to 12, 8.48 to 11.21, and 1.86 to 2.38, respectively. Concentrations of all metals declined in the uppermost core section (0-2 cm). However, these recent deposits still showed Cu and Zn that corresponded to 11 and 2 times greater than background levels, while the EF for Cd, 11.5, was slightly lower than the value (14 times background) that evaluated the whole core by taking into account all core intervals. Levels of all metals were lower, but comparable, in the surface and bottom sediments of Lemon Creek core profiles. Ranges of EFs for Cd, Cu, and Zn detected in the top and bottom core intervals corresponded to 10.91-15.55, 10.03-13.93, and 2.10-2.69 (Table 4).

DISCUSSION

Subsequent to the Clean Water Acts of the 1970s, pollution control programs implemented regulations that were more stringent in an effort to minimize contaminants permitted in commercial and municipal discharges emptying into receiving waterways nationwide. In addition, legislative action has driven technological advancements, which has improved anthropogenic effluents, and thereby reduced point source contamination (Sanudo-Wilhelmy, et al., 1999; Stoddard, et al., 2002; Brosnan, et al., 2006). However, elevated levels of all metals studied (Cd, Cu, and Zn) remain prevalent in environments proximal to urban areas and have been specifically identified within the study reach (Steinberg, et al., 1994; Gillis, et al., 1995; Marcovecchio, et al., 2001; Vitaliano, et al., 2002; Gillis, et al., 2009). Although the overall environmental quality of urban waterways, and more specifically areas of the New York/New Jersey Harbor Estuary (NY/NJ HE), have consequently improved, the Arthur Kill remains impaired by both historical and contemporary contaminant loadings (NOAA, 1995; Steinberg, et al., 2004).

Prior coring studies, conducted within the same marsh-creek systems used in this study, found elevated metal concentrations in Arthur Kill marsh habitats, which were attributable to numerous contributions from past and present-day anthropogenic activities (Appendix C; Ward, 2002; Nichols, 2004). Land-use largely affects the environmental condition of adjacent watersheds (Hare, 1992; Helgen, et al., 1996; Herut, et al., 1997; Weis, et al., 2006;). Historically, wetlands around Staten Island have served as receiving environments for anthropogenic metal loadings related to industry and commerce (USFWS, 1997; Vokral, et al., 2003; see Chapter 1 for more information). With time, the combined impact of urbanization and suburbanization has altered natural ecosystems and adversely affected the water and sediment

quality of the study area (Blanchard, et al., 2001). Concern regarding sediment-associated contaminants within this interstate waterway has been identified in research priorities targeting the NY/NJ HE (Crawford, et al., 1995; Dimou, et al., 2006).

Although human-induced changes have disrupted the interconnected natural system that once characterized the coastal environments and habitats along the Arthur Kill, geographic and hydrologic linkages still exist between and among marsh sites (Blanchard, et al., 2001). Specifically, the diurnal tidal flow associated with Main Creek and Neck Creek represents a hydrologic linkage that connects upland marsh habitats and the Arthur Kill. Consequently, tidal exchange may also expose these sites to the consistently poor water quality and legacy contamination characterized by the Arthur Kill, which has resulted from impacts such as metal-contaminated effluents associated with the multiplicity of industrial and manufacturing facilities that have monopolized the shores of this major urban shipping channel (Huntley, et al., 1995).

Today, many of the industries previously sited near the marsh-creek systems studied have been marginalized, displaced, or no longer exist. Accordingly, reduced metal loadings from these point sources have occurred, but residual impacts remain (Chillrud, et al., 1996; Nichols, 2004; Perez, et al., 2004). This trend has occurred throughout Staten Island, including a land-use shift near Lemon Creek where, prior to the relocation of a former dental tool manufacturing operation in the early 1970s, this site could have exposed marsh sediments to metal contaminants. Within the last decade, trace metal studies analyzed cores within the Lemon Creek system and determined that sediments were either not markedly affected or have recently recovered to levels similar to background concentrations (Appendix C; Ward, 2002; Nichols, 2004). Conversely, baseline metal data collected from the Arthur Kill sites demonstrated regular

enrichment within Main Creek and Neck Creek sediments (Appendix C; Ward, 2002; Nichols, 2004).

Nevertheless, results from this current study determined that sediments from all marshes exhibited variable metal enrichment. Observable contamination extended from the oldest horizons and persisted through the most recent deposits, which indicated that current impacts, related to new or long-standing sources, continue to threaten ecosystems throughout the study area (Gillis, et al., 1995; Vitaliano, et al., 2002; Steinberg, et al., 2004; Strong, et al., 2008).

Before ascribing new sources or identifying past loadings, proper assessment of metal concentrations and pollutant trends required further understanding of the influence of site-specific biogeochemical processes that ultimately control the depositional contexts particular to each marsh-creek system. Interpretations of radioisotope activity measurements within sediment cores can establish temporal and spatial patterns concerning sediment movement within estuarine systems (Fox, et al., 1999). Radiometric analysis of sediment cores provides useful chronological information and a context to identify site-specific processes and discern variations among pollutant concentrations (Feng, et al., 1996; Chillrud, et al., 1996). Thereby, this technique is integral for the evaluation of contaminant trends within marsh environments.

Pollutant chronologies described site-specific metal distributions, which provided a means to compare temporal trends and characterize interspatial variations between marsh systems (Hornberger, et al., 1999; Cundy, et al., 2003; Weis, et al., 2005;). Paired radionuclide dating and trace metal analyses helped to examine degradation from new or existing sources. This geochronology technique, also termed Monitored Natural Recovery (MNR), is an acceptable sediment management alternative in remediation initiatives, which is used to analyze

recovery over time via natural attenuation (USEPA, 2008; Harikumar, et al., 2009;). This approach effectively evaluates temporal and spatial contamination demonstrated by the study marshes, but may also help initial assessments of the efficacy of environmental initiatives intended to improve this severely impacted estuarine system. Evaluation of sediment core profiles from all study locations established that observable differences and temporal variations occurred between and among sites with respect to radionuclide activities and metal contaminants.

Radionuclide analysis of sediment cores

Sediments recovered throughout the study area were mainly comprised of silt and clays, which served as a favorable fine-grained matrix for radionuclide dating (Geyh., et al., 1990; Bopp, et al., 1993). Intertidal marsh flats are appropriate settings for employing radionuclide dating methods and conducting trace metal studies because in these environments the accretion of sediments can establish a relatively complete sedimentary record (Orson, et al., 1992; Delaware River Basin Commission, 2010). Conversely, these areas may not always be suitable for ^{210}Pb radiodating because of characteristically low levels of $^{210}\text{Pb}_{\text{ex}}$ surface activities (Orson, et al., 1992; Weis, et al., 2005).

In general, inherent counting uncertainties can further complicate the interpretation of radionuclide data. Consequently, it is most effective to combine results from several radioisotope activity measurements rather than rely on a singular radionuclide method (Bopp, et al., 2006). However, discrepancies can become apparent when comparing interpretations derived from multiple radionuclides. These may be attributed to the isotope's behavior or degradation within the sediment column including post-depositional migration, episodic erosion, diagenesis and variations in supply rates of ^{210}Pb that are ignored by the assumption of a constant

supply rate (Appleby, 2000; Strong, et al., 2008). In order to best decipher the depositional context of the cores recovered from each marsh location, it was necessary and most appropriate to draw conclusions based upon consistencies among a suite of temporal radiodating indicators (Bopp, personal communication).

Radionuclide activity distributions

No major variations in ^{40}K activities, an indicator of stable K content, suggested that sediments were generally homogenous in composition throughout the length of all cores. The detected consistency among ^{40}K values substantiated field observations and further supported ancillary methods implemented to identify fine-grained sediment core fractions. Furthermore, cores did not reveal any evidence of large burrows, which could have potentially distorted stratification of the sediment record.

As observed in other estuarine field settings within the region, the low $^{210}\text{Pb}_{\text{ex}}$ surface activities found within the Staten Island marsh sediments limited its application and challenged the effectiveness of the ^{210}Pb radionuclide technique (Weis, et al., 2005). In theory, vertical profiles displaying $^{210}\text{Pb}_{\text{ex}}$ activity versus depth yield an exponentially decreasing curve. However, as illustrated in the chronologies derived in this study, deviations from the ideal vertical profile can occur, which may have resulted from a number of contributory variables (Geyh, et al., 1990; Holmes, 1998). Explanatory factors include seasonal differences, organic content variations of particulates, changing deposition and erosion rates, which can be associated with natural processes and exacerbated by anthropogenic activities (Wan, et al., 2005).

Despite minor subsurface fluctuations, surface measurements of ^{137}Cs activities were comparable among the sites, though differences in vertical distributions were apparent. ^{137}Cs and $^{210}\text{Pb}_{\text{xs}}$ activity profiles were consistent with each other and plots generally exhibited

analogous trends at all sites. Activities of ^{137}Cs and $^{210}\text{Pb}_{\text{xs}}$ were detectable throughout the length of the Main Creek and Lemon Creek cores. Conversely, within Neck Creek sediment horizons, the activities of all radionuclides analyzed were either undetectable or insignificant at depths below the 4-6 cm interval.

The unexpected Neck Creek radionuclide profiles suggest core sediments were influenced by an erosional event or sediment reworking, as evidenced by a possible dredge boundary between 4 and 6 cm. This finding is a likely consequence of human-induced disruption to the system, which may have resulted from infrastructure development activities that occurred within the Neck Creek watershed a few years prior to coring at the site. Increased sediment loads related to construction repairs to a train trestle, which transverses Neck Creek downstream of the core collection location (~200 m), may have influenced upstream dynamics.

^7Be analysis of sediments provided additional insight into the spatial and temporal dynamics associated with the marsh locations. The depth of significant ^7Be activities within sediment cores identified the extent of sediment mixing zones for each study site (Bacon, et al., 1976; Chai, et al., 2004). The rapid, continual exchange of metals between surface sediments and the ambient water above indicates that this layer characteristically serves as a constant source and sink of metals. Although the surficial horizon typically constitutes the sediment mixing zone that acts as a reservoir which contributes and cycles sediments and bound metals to the system, the mixing zone can also often involve additional layers and extend below surficial deposits (Rozan, et al., 1999). Accordingly, detection of measurable ^7Be activities in bottom core sediments indicates extensive sediment mixing (Olsen, et al., 1986).

Differences in the distribution of the short-lived natural radionuclide, ^7Be , within core sediments also revealed heterogeneity in the localized environments of marsh study sites.

As encountered in most marsh systems, significant ^7Be activities were detectable in the top layers of the sediment cores, which indicated vertical mixing of newly deposited particulates and coupled metal contaminants was limited to the upper core sections (Bopp, et al., 1993). Analysis of ^7Be data suggested vertical mixing was restricted to the top core section (0-2 cm) at NC and confined to the upper two core horizons (0-2 cm and 2-4 cm) at Main Creek and Lemon Creek. Therefore, this implies sediment mixing dynamics do not appreciably affect distributions at depths beyond a few centimeters (Bopp, et al., 1993).

Based on the geographic proximity and the mutual hydrologic link with the Arthur Kill, it was projected that Main Creek and Neck Creek cores would depict similar site dynamics that collectively contrasted with the external reference site, Lemon Creek. However, comparisons between the Arthur Kill marsh locations showed observable differences, which implied the two adjacent areas have very different rates of sediment deposition and erosion. Apparent radionuclide variations existed over the geographic extent of the study area. In conjunction with large-scale variability, observable differences may have also been apparent on an even smaller spatial scale; present both between, but also within, sites along longitudinal gradients (Aalto, et al., 2005; Weis, et al., 2005). However, distribution profiles displayed evidence that demonstrates site specific, disparate processes control and affect the localized conditions of the marshes.

Sediment core dating

^7Be analysis of sediments supplemented other radionuclide dating techniques by yielding dating information on more recent timescales, as compared with ^{137}Cs and ^{210}Pb (Feng, et al., 1998; Bopp, et al., 2006;). Although ^7Be techniques are not suitable for determination of accumulation rates for whole sediment cores, this type of radiometric analysis helped identify short-term variations and recent accumulation patterns within the study sites, with respect to sediments and cohesive particle-reactive contaminants (Feng, et al., 2004; Bopp, et al., 2006).

Apart from distinguishing the extent of sediment mixing zones within cores, detection of significant ^7Be activities also characterized core sediments deposited within a year of field collection (Bacon, et al., 1976; Chai, et al., 2004). The confinement of ^7Be to the uppermost core section at NC (0-2 cm) and the penetration of significant activities through the upper 4 cm at Main Creek and Lemon Creek, suggested that sediments and associated contaminants in these sediment sections were deposited within a year of collection (August 2007). Therefore, this established that subsequent to water column exchange, where radionuclides and contaminants adsorb to sediment surfaces, these sediments were recently deposited (Bopp, et al., 1993; Sarin, et al., 1994; Boisson, et al., 2001).

For all sites, low measurable $^{210}\text{Pb}_{\text{xs}}$ activities in the surface sections of all study sites limited its application as a primary dating indicator (Weis, et al., 2005). Interpretations based on downcore $^{210}\text{Pb}_{\text{xs}}$ data were particularly challenging at Neck Creek because the high particle flux environment notably diluted $^{210}\text{Pb}_{\text{xs}}$ activities and $^{210}\text{Pb}_{\text{xs}}$ was only measurable in the upper two core intervals. Although ^{137}Cs can be an appropriate tracer for estimation of sedimentation rates, this was also not practicable in any of the constructed chronologies.

At all marsh sites, vertical distributions of ^{137}Cs were consistent with the rapid rate of net accumulation indicated by the ^7Be data, and the ^{137}Cs activity does not show a significant increase with depth toward a mid 1960s peak. The absence of ^{137}Cs maxima, associated with either 1954 (which signals the approximate date of the beginning of a detectable signal from global fallout) or 1963 (the maximum fallout year that the radionuclide was released into the atmosphere), indicated that the length of the cores was not adequate to capture evidence of either of these time markers.

By identifying all recovered sediments from each coring location that were deposited within the past few decades, and not earlier than the 1960s, ^{137}Cs proved to be the most advantageous decadal temporal indicator. However, low surface $^{210}\text{Pb}_{\text{xs}}$ and inadequate ^{137}Cs activity distributions, which were constrained by the timeframe captured by the length of collected cores, affected the utility of these radiometric dating methods (Bopp, et al., 2006). These limitations prevented the calculation of accurate vertical accretion rates, which were necessary for correlation with contaminant profiles and for the establishment of a complete time-integrated record of historical metal inputs (Callaway, et al., 1998; Fuller, et al., 1999; Lee, et al., 2001).

Although interpretations of ^{137}Cs and $^{210}\text{Pb}_{\text{xs}}$ chronologies failed to yield estimation of sedimentation rates, which would have enabled comparison of a time-marker technique with a natural decay dating method, radioisotope profiles can still provide approximate timing of sediment core deposition (Arnaud, et al., 2006). While it was not feasible to estimate the specific rate of accumulation at marsh study locations, the applied methods tentatively age-dated the sediments and determined that all core sub-samples were less than a few decades old. Interpretation of the Main Creek profile indicated that the entire length represented less than a

decade of deposition. First-order analysis of the LC $^{210}\text{Pb}_{\text{ex}}$ data, infers that the bottom of the core possibly dates back as much as 30 years (~ 1.4 half-lives). However, the low surface activity and inconsistent decline with depth, demonstrated by the Lemon Creek $^{210}\text{Pb}_{\text{ex}}$ profile, can challenge the defensibility of this interpretation. Therefore, it is also feasible that the entire length of the Lemon Creek core only represents net accumulation on an order of five years.

Collectively, the application of multiple radionuclide techniques provided useful dating information for identification of the temporal context of the cores collected from each site, which emphasized the distinctive localized environmental settings of the study marshes. Given that the tidal influence of the Raritan Bay supplemented the various, inherent biogeochemical processes that control the transport and fate of suspended particulates within marsh systems, the externality of Lemon Creek projected a disparate environmental context when compared with Arthur Kill sites (Bruland, et al., 1974; Provini, et al., 1989). ^{137}Cs , $^{210}\text{Pb}_{\text{xs}}$ and ^7Be analyses confirmed the unique depositional dynamics and environmental conditions at Lemon Creek but also, revealed variability and inconsistencies in Main Creek and Neck Creek cores (Feng, et al., 1996; Olsen, et al., 1986). Thereby, this demonstrates that sediment transport, fate and deposition dynamics were marsh-dependent, regardless of their connectivity to the Arthur Kill or location within the study area. Accordingly, the premise that both metals and radioisotopes similarly exhibit particle-reactive properties, inferred trace metal data would also portray site-specific contaminant distribution patterns (Cochran, et al., 1979; Dibb, et al., 1989; Weis, et al., 2001;).

Metal analysis of sediment cores

Altogether, interpretations from radionuclide analysis of sediment cores substantiated that unique depositional processes and dynamics were identifiable with each marsh, which, in part played a role in the site-specific metal contamination demonstrated by sediment cores respective

to each marsh (Feng, et al., 1996). Determinations of enrichment factors (EFs) emphasized the inter-spatial variability of metal pollutants within the study area and allowed for comparisons between coring locations. A range of ratios were calculated from marsh core subsamples; all of which reflected high enrichment factors that represented the cores in their entirety. The demonstrably high Cd, Cu and Zn enrichment factors determined for all sites were indicative of anthropogenic metal inputs, which have intensified the concentrations inherently found within regional sediments (Bopp, et al., 1996; Hirschberg, et al., 1996).

When referenced to the other coring locations, Main Creek cores were the most severely polluted with Cd and Zn. The Cd levels at Main Creek were substantially higher than the other coring locations; the mean Cd EF for Main Creek cores was double Neck Creek and threefold the value determined for Lemon Creek. Although Main Creek had the greatest mean Zn EF, the magnitude was not appreciably higher than Neck Creek. Conversely, Cu enrichment was only slightly higher at Neck Creek, comparable to Main Creek core sediments, but more than double the Cu EF value for Lemon Creek sediments.

Combining ^7Be and trace metal analysis permitted assessment of contemporary marsh sediment quality (Olsen, et al., 1996). Recent deposits collected from all marshes exhibited obvious metal enrichment and accordingly, these contaminant-laden sediments facilitated the cyclical movement and exchange of metals throughout the study area (Cundy, et al., 2003). Thereby, sediments within the upper 4 cm at Main Creek and Lemon Creek and sediments in the Neck Creek surficial horizon functioned as sinks, but also, active sources of metal pollutants, which can further impair and deteriorate nearby habitats (Hornberger, et al., 1999; Strong, et al., 2008).

Pairing ^7Be with Cd, Cu and Zn data allowed for evaluation of study sites with respect to full-core assessments and current pollution levels (Weis, et al., 2005). In comparison with enrichment characterization using core mean metal concentrations, recent deposits showed decreased metal pollution at the Arthur Kill marsh sites, and a similar scale of contamination at the external site, Lemon Creek. Furthermore, recent Main Creek and Neck Creek sediments exhibited the lowest metal concentrations of all core sub-samples, while the lowest metal contents in Lemon Creek cores were detectable in the layer immediately below recent sediments. Nevertheless, recent and full-core evaluations showed agreement, in terms of the order in which sites ranked, according to pollution magnitude.

Temporal variability and trends

Assessments of radionuclide distributions projected site-dependent temporal variability, with respect to particle-reactive metals. The slight downcore metal fluctuations demonstrated by all marsh cores may be a result of numerous variables pertaining to the localized environmental conditions particular to each coring site. Seasonal variations and/or increased organic content of sediments, which can result from either soil erosion or the dynamic delivery processes that transfer particulate organic matter from the water column to the bed sediments, may account for the more distinct downcore metal concentration variations (Wan, et al., 2005). Additional explanatory factors may include changing erosion and deposition rates associated with natural processes or exacerbated by development activities, accordingly, periods of high erosion and deposition rates could correlate to evident subsurface peaks within sediment core profiles (USFWS, 1997; Wan, et al., 2005).

In general, sediment cores for all sites reflected steady contamination with depth or displayed defined temporal variation exemplified by subsurface peaks. On a finer scale, further

evaluation of metal profiles revealed all sites demonstrated at least minor temporal variability. Accordingly, trace metal analysis confirmed that the homogeneity of downcore metal distributions and the extent of temporal pollution varied spatially amongst marshes in the study area. Furthermore, intra-site comparisons of metal chronologies established that altogether elements generally adhered to one principal trend. General assessment of downcore metal concentrations revealed identifiable trends, which suggested that sites exhibit temporal sediment contamination characterized by either consistency, or recovery and attenuation of metal pollutants.

Main Creek

Minor fluctuations at depth and declining concentrations in the upper core horizons reflected slight temporal variability within individual Main Creek metal chronologies. Assessment of the temporal distribution of metal loads in Main Creek chronologies showed comparable contaminant patterns, which were reinforced by the agreement of vertical Cd, Cu and Zn variations and the coupled detection of minimum and maximum values for each element. Overall, Main Creek Cd, Cu, and Zn profiles exhibited a primary trend indicative of consistent downcore metal contamination. Negligible downcore differences in metal concentrations and consequently, consistent EF values determined for each horizon, indicated continuous sediment contamination. The narrow concentration ranges measured in core sub-samples emphasized the uniformity in Main Creek sediment cores.

Neck Creek

Vertical profiles representing Neck Creek sediment core data revealed substantial contamination throughout the cores. Although Neck Creek sediments were metal-enriched at every depth, concentration levels were highest in the deeper core sections. Interpretations of radionuclide activity distributions identified the site's high particle flux environment, which

predicted the variability demonstrated by downcore metal concentrations. Neck Creek concentration profiles characterized the greatest degree of overall temporal variability of pollutants in the study area. Concentrations fluctuated to varying degrees, as per metal, throughout the length of the cores and Neck Creek cores revealed differences in terms of the magnitude of individual metal loadings.

Among all sites, Neck Creek cores demonstrated the least uniformity concerning the interrelationships between metals throughout time. For example, the Cd profile appeared to reflect a departure from the corresponding patterns and depths of contaminant peaks exhibited by the Cu and Zn profiles. The level of contaminants, determined by triplicate analysis of Neck Creek cores, also yielded wider ranges for individual elements. Mean concentrations of Cu and Zn showed maximum elevations coincided at equal depths, while the highest mean value of Cd was detected within older sediments. However, the greatest upper range of all metals corresponded to the same deep subsurface core section. Regardless of such discrepancies, overall, Neck Creek contaminant variability showed general agreement with respect to depth.

The marked differences in downcore metal concentrations and greater disparities among individual metal profiles contrasted with the appreciably consistent temporal contaminant trends illustrated by the Main Creek and Lemon Creek. However, all metals conformed to a broader trend of attenuation in which metal concentrations measured in the surface layers were restored to levels that were comparable to the bottom sediments.

Lemon Creek

Although metal contents throughout Lemon Creek cores were relatively low in comparison to Main Creek and Neck Creek cores, concentrations detected at all depths exceeded

background levels. Sediment cores were characterized by steady downcore enrichment of all metals with lesser, disparate subsurface Cd, Cu, and Zn peaks. Assessment of Lemon Creek sediment sections established that, like radionuclide distributions, metals analyzed were clearly interrelated downcore. Slight increases in contaminant levels were observable regularly throughout the length of the cores; peaks at the deep, mid and upper core sections reflected subsurface enrichment of all metals. However, profiles depicted higher mean concentrations within the oldest sediments, and maximum values of all elements peaked at depths below midcore horizons.

Like Main Creek, Lemon Creek profiles exhibited generally constant enrichment of all metals in conjunction with slight temporal variations. However, initial comparative evaluation of Lemon Creek contaminants suggested more pronounced disagreement than observed in Main Creek profiles. Further assessment found the most evident dissimilarities between metals recovered from Lemon Creek profiles could be accounted for by the larger metal concentrations ranges detected from the analysis of replicate sediment core samples, which yielded standard deviations that were among the greatest calculated for all horizons. Throughout the span of Lemon Creek cores, Cu and Zn patterns were parallel; however, contrasting Cd peaks displayed elevated levels that deviated from the congruent Cu and Zn profiles. Consequently, the depth of maximum contamination was metal-specific.

All Lemon Creek metal profiles showed greater concurrence in the upper core sections. Levels of all metals were lower, but comparable, within the top versus bottom sediments of Lemon Creek core profiles. Collectively, all metals declined to minimum concentrations at 4-6 cm. Sediments deposited above this layer exhibited decreased environmental quality as evidenced by the greater quantity of metal pollutants measured. Subsequently, the declined

concentrations of all metals associated with sediments in the uppermost section of Lemon Creek cores (0-2 cm) exhibited improvement at the surface. Although concentrations of all metals fluctuated slightly at depth, pollutants associated with Lemon Creek sediments showed an overall trend of consistency with respect to downcore contamination.

Comparison with metal concentrations in sediment cores from 2001

Main Creek and Neck Creek profiles were similar to previous coring studies that involved metal analysis of sediments collected in 2001. Compared to sediments from the external site, the 2001 results found that Arthur Kill marshes had demonstrably higher metal concentrations, which revealed consistent pollutant loading patterns. In agreement with the 2001 assessment, results from this study established that Main Creek chronologies clearly demonstrated steady metal enrichment. However, Neck Creek contaminant chronologies demonstrated a comparable scale of contamination, but reflected slightly greater temporal variability than projected. However, it can be expected that disparities not only occur over the extent of the study area but, also, within the study sites (Aalto, et al., 2005; Weis, et al., 2005). Therefore, spatial variability within the marshes may account for any inconsistencies with baseline data that were recognized. Nevertheless, it was likely that the greater extent of temporal variability depicted by Neck Creek core profiles resulted from the site's high particle flux environment.

The lower temporal contamination observed in Lemon Creek profiles, aligned with prior studies that were proximal to the coring area (Ward, 2002; Nichols, 2004). However, it is noteworthy that Lemon Creek metal concentrations were higher than projected by prior studies, which observed Cu and Zn at levels comparable to background (Appendix A; Ward, 2002; Nichols, 2004). In contrast, the current study found that, with respect to the concentration ranges

of all metals analyzed, even the minimum metal values measured in Lemon Creek cores were markedly higher than background concentrations.

Overall, downcore metal concentrations exhibited site-specific temporal trends that were either consistent or characterized by intermittent fluctuations with moderate recovery; pollutant patterns in Main Creek and Lemon Creek cores demonstrated enriched, mainly steady concentrations despite minor variations throughout the core profiles, while Neck Creek exhibited prominent contaminant elevations at depth. The prevalence of metal-enriched sediments and site-dependent temporal variability throughout the study area implied that, besides individual site dynamics and depositional environments, supplementary factors influenced the extent of contamination and trends associated with each marsh.

Metal geochronologies

Coupling radionuclide and trace metal data derived contaminant chronologies to differentiate current and past metal inputs and, in effect, helped recognize new sources or implicate existing sources. Although, core length limited the temporal scale of the constructed metal chronologies, which, in turn challenged objectives to precisely age-date sediments, general radionuclide interpretations suggested cores from all sites accumulated within the past few decades (Bopp, et al., 2006). Therefore, chronologies depicted contaminant progressions associated with a timeframe subsequent to the heyday of regional industry and manufacturing activities (Chillrud, et al., 1996). However, the geochronological approach utilized in this study effectively describes metal deposition on a more contemporary time-scale (Chillrud, et al., 1996).

Metal chronologies respective to all study sites clearly exhibited demonstrable interrelationships between metals, which extended for the length of most cores and further linked

temporal contamination at each site to anthropogenic activities (Fletcher, et al., 1998; Feng, 1998). When pollution is markedly associated with an individual metal species, the nature of the site-specific input affecting the contaminated site can help identify the source (Fletcher, et al., 1998). Conversely, the contamination characterized by all marshes did not demonstrate predominance by a singular metal species or display temporal pollution defined by a particular element. However, the corresponding peaks evident in many of the metal chronologies, which often occurred at multiple depths, implicated the same enrichment source (Sanger, et al., 1998; Mil-Homens, et al., 2008). This can signify the introduction of metals from a new human-related source. However, subsurface peaks could also reveal a site's distinctive depositional environment, which can influence sediment contaminant profiles and depict degradation associated with metal inputs from an existing or prior source (Gillis, et al., 1995; Strong, et al., 2008).

A variety of anthropogenic activities have been linked to impairment to the entire region encompassing the study area, which implicates land-use largely affected the extent of temporal metal contamination and influenced the site-specific pollutant trends characterized by marsh sediment chronologies (Gillis, et al., 1995; Steinberg, et al., 2004). Although the geochronologies established the burial of heavily contaminated sediments directly associated with historical regional point sources, all marshes exhibited obvious metal contamination (Weis, et al., 2005; Balcolm, et al., 2008). Metal loadings from point sources continue to impact the NY/NJ HE as a whole however, it is likely that the pollution displayed by metal chronologies is largely a result of anthropogenic non-point source contributions (Fitzgerald, et al., 2001; Suszkowski, et al., 2006; Balcolm, et al., 2008). Any combination of regional non-point sources, including atmospheric deposition, storm water runoff, landfill leachate, and indirect discharges

associated with construction, petrochemical and oil refineries have the potential to increase metal loads in marsh sediments (Herut, et al., 1997; USFWS, 1997; Rozan, et al., 2001; Rice, et al., 2002; Weis, et al., 2006;). To varying degrees, marshes showed evidence of regular impacts and in some cases, metal chronologies may reflect new sources or remobilization of contaminated sediments.

Main Creek

The analogous peaks apparent in the Main Creek core profiles could signify previous metal loading events, followed by removal or control of the source accountable for the increased contaminant inputs and finally, deposition of cleaner sediments. However, considering the minor extent that Main Creek metal profiles fluctuated, it may be more plausible that the peaks were indicative of past disturbance of metal-contaminated sediments deposited near the coring location . In general, the subtle temporal differences in metal concentrations suggested an active, continuous pollutant source helped sustain the persistent metal enrichment identified in Main Creek cores. This observation aligns with previous coring studies within the Main Creek system, which concluded a constant source of trace metals appeared to consistently impact sediments within the marsh habitat (Appendix C; Ward, 2002; Nichols, 2004). Potential terrestrial sources particular to Main Creek include the Freshkills Landfill. However, the effect of leachate on the Main Creek drainage area and upstream habitats remains undetermined (Helgen, et al., 1996; ATSDR, 1999).

Neck Creek

The subsurface peaks characterized in the deep horizons above the bottom layer and at mid-core in Neck Creek chronologies signified augmented contamination, but also suggested the release of metal pollutants from a former source. The successive decreased metal

concentrations observed in overlying sediments indicated improvement with accretion. Decreased contaminant levels in core sediments above the concentration maxima indicated removal or control of the contributory source of increased metal inputs. Thereby, the minimized impact allowed for deposition and accumulation of less polluted sediments.

Both remobilization and contemporary sources may account for the greater variation reflected in Neck Creek contaminant chronologies, which tended to be more prominent than the underlying trend of steady enrichment that prior coring within the system projected (Ward, 2002; Nichols, 2004). Discrepancies with previous metal chronologies could indicate a local disturbance, which resulted in the remobilization and transport of previously deposited metal-laden sediments. Subsequent to erosional processes, contaminant-laden sediments may have cycled through the marsh-creek system, where they were resuspended, deposited, and eventually buried (Andrews, et al., 2004).

The sustained decline apparent towards the surface was indicative of recovery from a past metal loading event, however, as suggested by the radionuclide interpretations, obvious subsurface elevations may also largely be attributed to the evident sediment reworking or erosion. The irregular Neck Creek metal chronologies and unexpected radionuclide profiles may implicate that anthropogenic activities, rather than natural processes, simultaneously influenced the depositional environment and affected sediment quality (Wan, et al., 2005). As stated earlier, it is possible that infrastructure initiatives, which occurred a few years prior to coring at Neck Creek, introduced metals to the system and/or exacerbated erosion or reworking of contaminated watershed sediments. In addition, runoff and non-point source pollution, associated with the extensive development of Arthur Kill watersheds for industrial, residential and municipal land use, may be primarily responsible for metal loadings derived from terrestrial sources, which, in

some measure, contribute to present-day contamination within Neck Creek and Main Creek sediments.

Lemon Creek

Mitigation efforts after past pollutant incidences, which allowed for attenuation via accretion of less polluted sediments, may be one explanation for the subtle, episodic contaminant pulses and successive recoveries observable in the deep, mid and upper Lemon Creek core sections. However, it is more likely that a combination of releases from non-point sources and remobilization of contaminated sediments caused the minor variances identified in the Lemon Creek chronologies (Andrews, et al., 2004). The mainly consistent, comparatively low, concentrations of all metals identified in Lemon Creek chronologies, is not readily linked to a specific point source or a particular anthropogenic activity; but rather, this trend was indicative of a steady input of metals.

Potential metal sources of pollution within the vicinity of Lemon Creek may include marina activities and the remediation of a former dental tool manufacturing facility. In addition, localized areas within the Lemon Creek watershed have been susceptible to flooding, erosion and degraded water quality, which has generally caused deleterious impacts to marshes on the South Shore of Staten Island (Vokral, et al., 2001). Lemon Creek banks serve as storm water receiving areas, therefore runoff and/or erosion of contaminated sediments may regularly contribute metals to the marsh flats (Rice, et al., 2002; Wan, et al., 2005).

Compared with sites bordering the Arthur Kill complex, it was apparent that Lemon Creek sediments contained notably lower levels of metal pollutants, regardless of the depth or age. The lower magnitude of metal concentrations observed in Lemon Creek metal chronologies

implied that this marsh-creek system has been the least impacted by past and present-day metal contaminant loadings; as would be expected by the description of the Lemon Creek watershed (see Chapter 1 for more information). Understanding that proximity to pollutant sources primarily controls spatial variability suggests geography and land-use played a role in the evident contrast in the degree of temporal contamination demonstrated by Lemon Creek profiles versus Arthur Kill marsh chronologies (Spencer, et al., 2002; Suszkowski, et al., 2006). Apart from the fewer contemporary or legacy sources of metals within the Lemon Creek drainage area, as compared with Arthur Kill watersheds, detachment from the Arthur Kill complex may also provide sufficient tidal flushing via the Raritan Bay and may have further minimized Lemon Creek temporal contamination.

Not only was there a considerable contrast in metal concentrations found in Lemon Creek sediments versus Main Creek and Neck Creek deposits, but it also appeared that there was an association between the latter two sites with respect to degree of contamination over time. The prolonged degradation of these sites implicated a common influence. Acknowledgment of past point sources within the Main Creek and Neck Creek watersheds can explain past metal enrichment, but recent pollutant trends demonstrated by Main Creek and Neck Creek cores suggested a predominant source affected both sites.

Specifically, in addition to any site-specific inputs to the creeks from terrestrial sources, the parallel adjacency to the Arthur Kill may have put these sites at risk of additional metal loadings. Although downcore concentration profiles derived for each site do not specifically characterize the considerable metal inputs from historical point sources, legacy contamination remains present within the Arthur Kill and adjacent watersheds (Gillis. et al.. 1995; Steinberg et al.. 2004; Gillis. et al., 2008). Furthermore, natural transport of watershed contaminants serves

as a major source of pollutants to regional waterways, sediments and biota (USFWS, 1997; Hwang, et al., 2006). Accordingly, connectivity with the Arthur Kill could have potentially subjected Main Creek and Neck Creek marsh habitats to advection of particle-bound contaminants via tidal transport. Thereby, the Arthur Kill may have served as a continual source of metal inputs and played an integral role in perpetually elevated metal contamination observed in Arthur Kill marsh-creek systems.

Although the Arthur Kill marsh sites similarly contrasted with Lemon Creek, in respect to the persisting degree of contamination, it was apparent Main Creek was more comparable with Lemon Creek in terms of their corresponding sediment mixing depths, parallel recent depositional characteristics and vertical pollutant patterns. Albeit on different scales, the limited variability of elevated contaminant values demonstrated a common trend of steady metal pollution in Main Creek and Lemon Creek profiles. The greater similarity between the two most distant sites, Main Creek and Lemon Creek, which are adjacent to the Arthur Kill and Raritan Bay, respectively, emphasized disparity between the Arthur Kill sites, Main Creek and Neck Creek. Therefore, although proximity and connectivity to the Arthur Kill may contribute to elevated contamination levels, it did not ultimately dictate analogous contaminant chronologies or trends. However, the contrasting radionuclide activity distributions and pollutant profiles at Main Creek and Neck Creek, indicated that site-specific depositional contexts and site-specific terrestrial inputs may have primarily influenced temporal variability and metal contaminant trends.

CONCLUSION

Results from this study found heterogeneity in terms of the depositional context of marshes within the study area, which both projected and influenced the site-specific vertical distributions of metal concentrations. Assessment of metal chronologies revealed metal trends that were site-specific and characterized by consistency or intermittent fluctuations with moderate recovery. Pollutant patterns in Main Creek and Lemon Creek cores demonstrated enriched, mainly steady concentrations despite minor variations throughout the core profiles, while Neck Creek exhibited prominent contaminant elevations at depth.

Although sites reflected variable degrees of recovery and short-term attenuation within contemporary sediments, the incessant contamination characterized by all marshes indicated that current impacts, related to new or long-standing sources, continue to threaten ecosystems throughout the study area (Gillis, et al., 1995; Vitaliano, et al., 2002; Steinberg, et al., 2004; Strong, et al., 2008). The context of the cores collected in this study challenges direct linkage to past industrial, commercial and manufacturing facilities, which, to the detriment of the region, operated in an era that pre-dated fundamental air and water pollution legislation. However, the geochronological approach utilized in this study effectively describes metal deposition on a more contemporary time-scale. Anthropogenic non-point source contributions, which are largely responsible for present-day water quality impairments, likely had a major effect on the spatial and temporal variability demonstrated by marsh sites and the overall environmental integrity of the study area (Suszkowski, et al., 2006; Rose, et al., 2007). Although metal loadings derived from non-point sources remain difficult to identify and control, land use activities associated with watersheds surrounding the study sites may have principally determined the scope of metal releases delivered to receiving marsh-creek systems (USFWS, 1997; Rice, et al., 2002).

Evaluation of Arthur Kill metal chronologies indicated that a predominant factor, either exposure to a continuous source of metals or a dynamic within these systems, prevented natural attenuation via steady accretion of cleaner sediments. The indeterminate impact of upstream versus downstream sources of metals needs further assessment. However, it is plausible that identification of dominant downstream metal contributions at Main Creek and Neck Creek could implicate the Arthur Kill as an active, ongoing source and explain the comparable magnitudes of some metals and steady enrichment demonstrated in marsh sediments.

In conclusion, distinct depositional environments and biogeochemical processes were major factors governing the transport and fate of marsh contaminants. Therefore, both localized environmental dynamics and site-specific anthropogenic contributions primarily determined sediment quality and controlled the metal trends identifiable with the study sites. Additional studies that assess spatial variability on a smaller spatial scale and monitor metal contamination within the study area are necessary for environmental quality assessments and protection. Further research will also aid in tracking success and the efficacy of current water quality initiatives that aim to improve this severely impacted estuarine system.

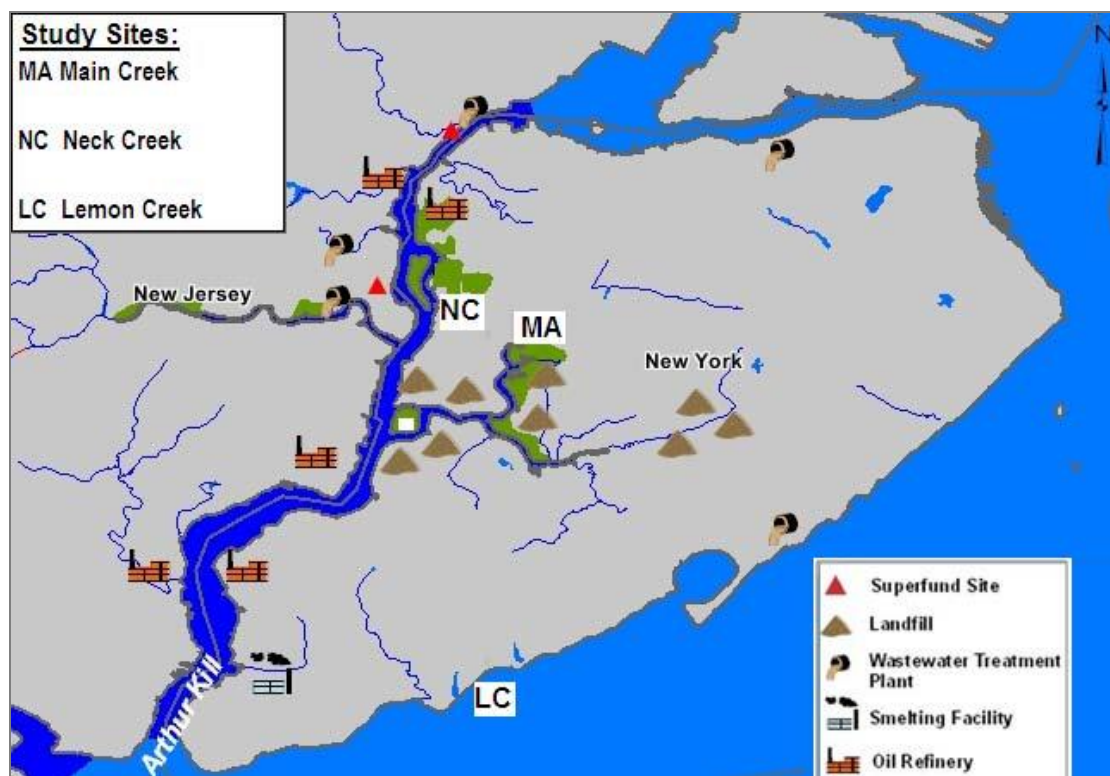


Figure 2-1. Staten Island marsh study sites. Map of study area and point sources of pollutant loadings surrounding Main Creek, Neck Creek, and Lemon Creek.

Table 2-1. Radionuclide activities (^{40}K , ^7Be , ^{137}Cs , and $^{210}\text{Pb}_{\text{xs}}$) in core subsamples from Main Creek (MA), Neck Creek (NC), and Lemon Creek (LC) marsh sites.

Core Site	Depth (cm)	K-40 ($\text{pCi}\cdot\text{g}^{-1}$)	1 σ	Be-7 ($\text{pCi}\cdot\text{kg}^{-1}$)	1 σ	Cs-137 ($\text{pCi}\cdot\text{kg}^{-1}$)	1 σ	$\Sigma\text{Pb-210}$ ($\text{dpm}\cdot\text{g}^{-1}$)	1 σ	Pb-210 _{sup} ($\text{dpm}\cdot\text{g}^{-1}$)	1 σ	Pb-210 _{xs} ($\text{dpm}\cdot\text{g}^{-1}$)	1 σ
MA	0-2	13.9	1.0	3254	728	104	30	8.20	0.68	1.95	0.12	6.30	0.70
	2-4	12.8	0.9	2177	650	127	28	9.07	0.68	1.95	0.12	7.18	0.70
	4-6	13.9	1.0	570	680	190	32	8.20	0.69	1.95	0.12	6.31	0.71
	8-10	13.0	0.9	-	-	127	29	8.49	0.69	1.95	0.12	6.63	0.71
	12-14	13.4	1.2	-	-	129	40	8.92	0.89	1.83	0.16	7.19	0.92
	14-16	13.9	1.0	-	-	132	34	7.79	0.75	1.66	0.13	6.22	0.77
	18-20	12.0	0.9	-	-	119	30	6.19	0.64	2.42	0.13	3.83	0.66
NC	0-2	14.0	1.0	1454	677	108	30	5.61	0.59	2.22	0.13	3.42	0.61
	2-4	15.0	1.0	608	588	144	28	4.73	0.52	2.22	0.13	2.54	0.54
	4-6	16.3	1.1	-	-	84	28	3.18	0.51	2.22	0.13	0.98	0.53
	6-8	15.1	1.2	-	-	11	36	1.93	0.66	2.14	0.16	-0.22	0.69
	8-10	15.3	1.4	-	-	39	43	2.52	0.77	2.91	0.21	-0.39	0.81
	12-14	16.1	1.2	-	-	11	33	3.18	0.59	2.25	0.15	0.95	0.62
LC	0-2	14.12	1.05	2504	953	133	36	6.26	0.63	1.78	0.11	4.52	0.65
	2-4	13.97	1.09	2221	944	118	38	4.94	0.87	1.78	0.11	3.19	0.88
	6-8	16.23	1.04	-	-	188	30	3.34	0.47	1.78	0.11	1.61	0.50
	10-12	14.30	1.33	-	-	225	52	4.51	0.85	1.56	0.18	3.05	0.90
	14-16	15.47	1.06	-	-	151	32	3.46	0.53	1.92	0.13	1.58	0.56
	18-20	15.42	1.05	-	-	128	32	3.17	0.53	1.66	0.12	1.56	0.57

¹Supported ^{210}Pb activities shown in bold estimated from measured value in the sample immediately below.

²Data shown in italics represent radionuclide activities with measurements that were not significant.

Table 2-1 (Abbreviated). Observed radionuclide activities (^{40}K , ^7Be , $^{210}\text{Pb}_{\text{xs}}$, and ^{137}Cs) from Main Creek (MA), Neck Creek (NC) and Lemon Creek (LC) marsh sites.

Core Site	Depth (cm)		K-40 (pCi·g ⁻¹)	1 σ		Be-7 ¹ (pCi·kg ⁻¹)	1 σ		Pb-210 _{xs} ¹ (dpm·g ⁻¹)	1 σ		Cs-137 (pCi·kg ⁻¹)	1 σ
MA	0-2		13.9	1.0		3254	728		6.30	0.70		104	30
	2-4		12.8	0.9		2177	650		7.18	0.70		127	28
	4-6		13.9	1.0		<i>570</i>	680		6.31	0.71		190	32
	8-10		13.0	0.9		-	-		6.63	0.71		127	29
	12-14		13.4	1.2		-	-		7.19	0.92		129	40
	14-16		13.9	1.0		-	-		6.22	0.77		132	34
	18-20		12.0	0.9		-	-		3.83	0.66		119	30
NC	0-2		14.0	1.0		1454	677		3.42	0.61		108	30
	2-4		15.0	1.0		608	588		2.54	0.54		144	28
	4-6		16.3	1.1		-	-		<i>0.98</i>	0.53		84	28
	6-8		15.1	1.2		-	-		<i>-0.22</i>	0.69		11	36
	8-10		15.3	1.4		-	-		<i>-0.39</i>	0.81		39	43
	12-14		16.1	1.2		-	-		<i>0.95</i>	0.62		11	33
LC	0-2		14.1	1.05		2504	953		4.52	0.65		133	36
	2-4		14	1.09		2221	944		3.19	0.88		118	38
	6-8		16.2	1.04		-	-		1.61	0.50		188	30
	10-12		14.3	1.33		-	-		3.05	0.90		225	52
	14-16		15.5	1.06		-	-		1.58	0.56		151	32
	18-20		15.4	1.05		-	-		1.56	0.57		128	32

¹Data shown in italics represent radionuclide activities with measurements that were not significant.

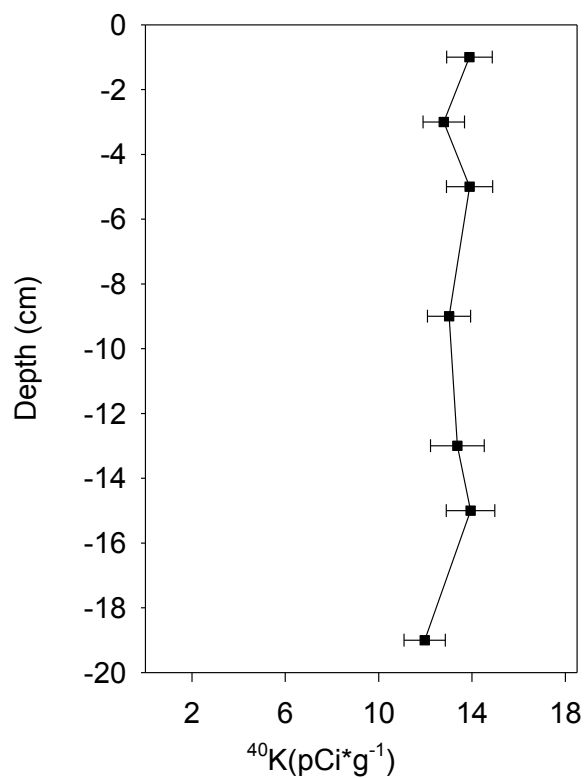


Figure 2a. Main Creek

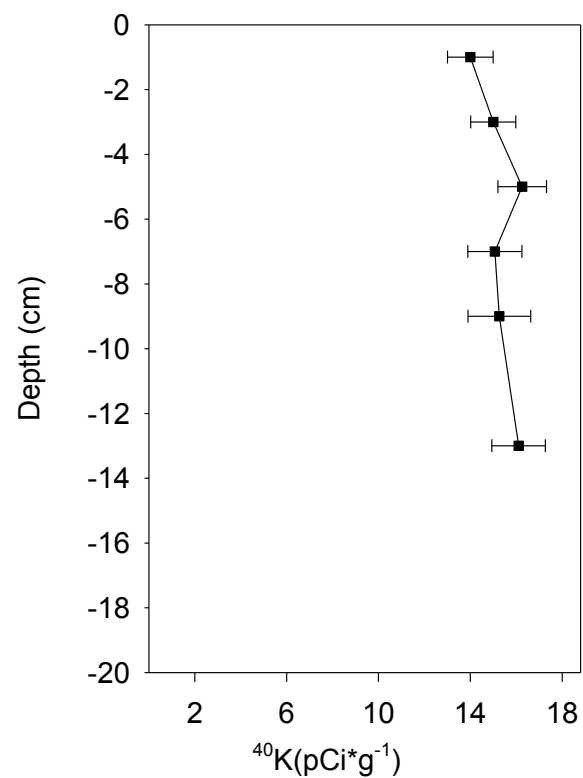


Figure 2b. Neck Creek

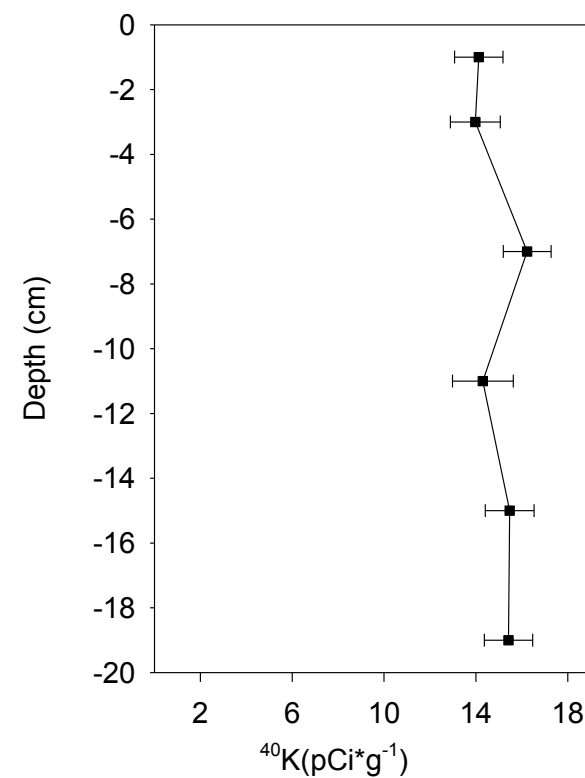


Figure 2c. Lemon Creek

Figure 2-2a-c. Vertical ^{40}K activity (■) distribution profiles from marsh coring study sites: Main Creek (2a), Neck Creek (2b), and Lemon Creek (2c) marsh sites. Error bars reflect ± 1 standard deviation (S.D.).

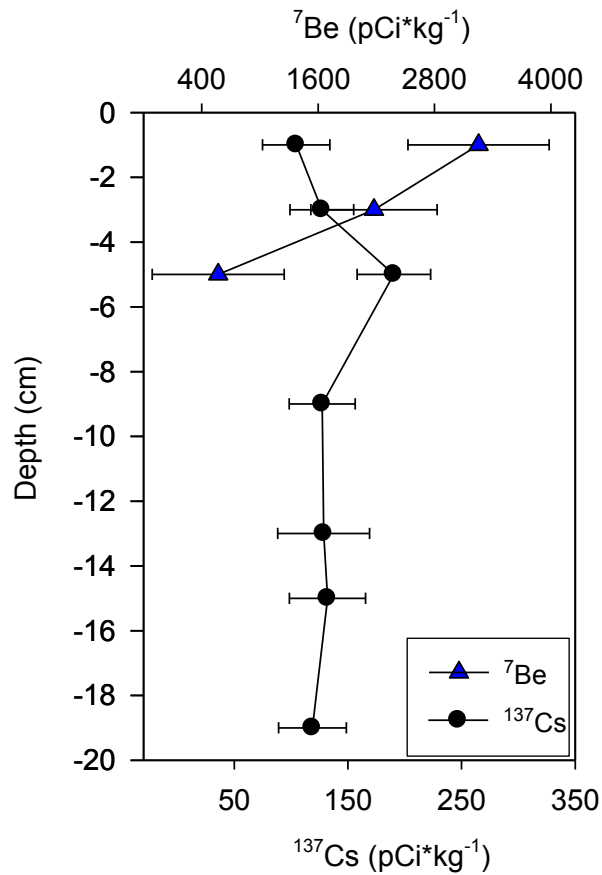


Figure 3a. Main Creek

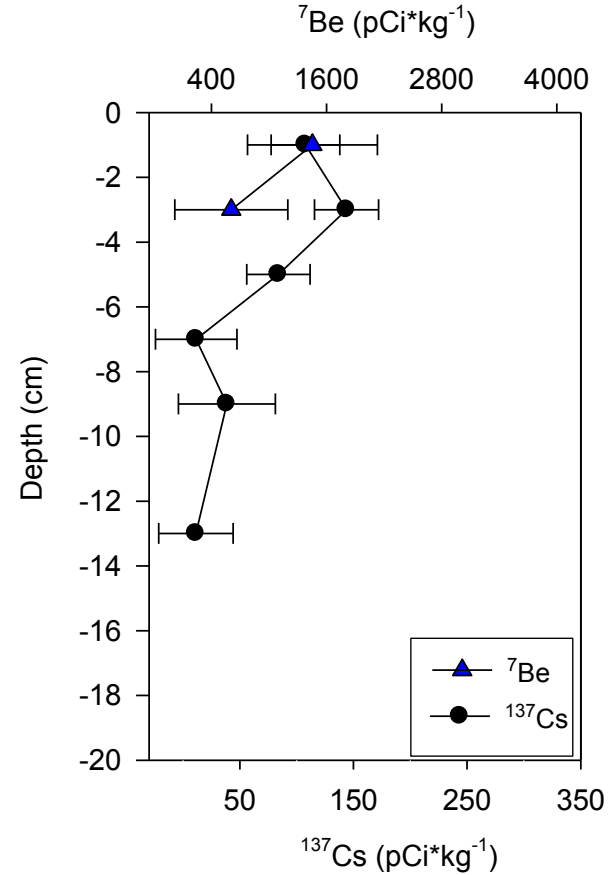


Figure 3b. Neck Creek

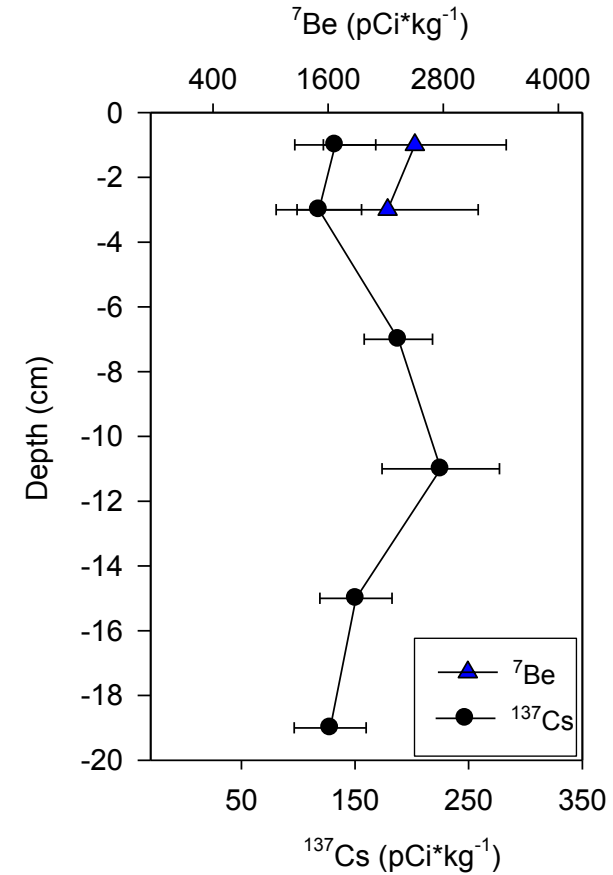


Figure 3c. Lemon Creek

Figure 2-3a-c. Vertical ^7Be (▲) and ^{137}Cs activity (●) distribution profiles from marsh coring study sites: Main Creek (3a), Neck Creek (3b), and Lemon Creek (3c) marsh sites. Error bars reflect ± 1 standard deviation (S.D.).

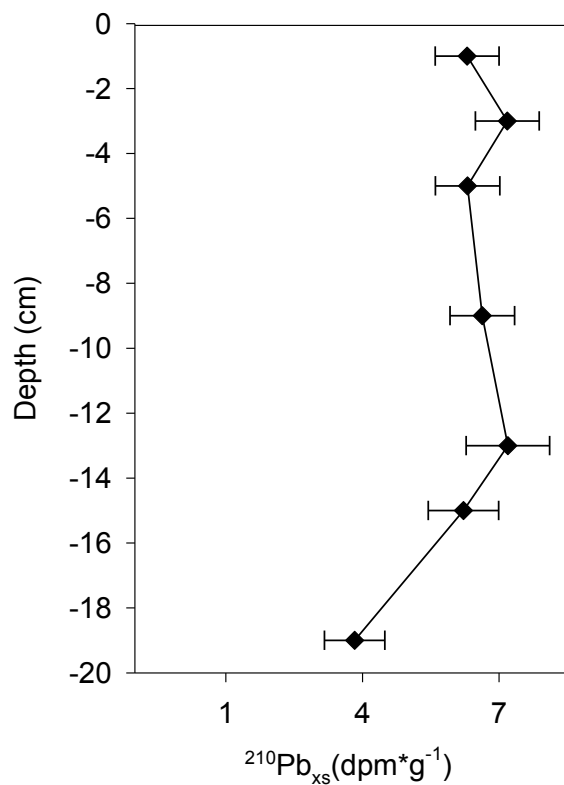


Figure 4a. Main Creek

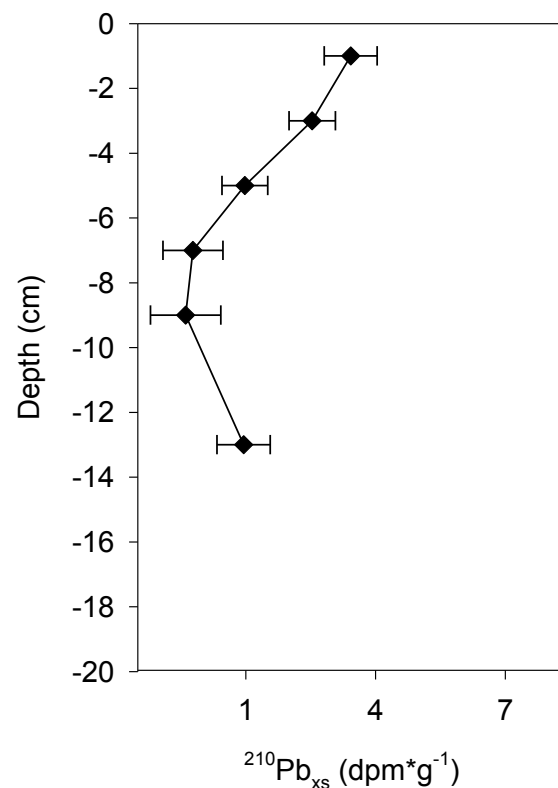


Figure 4b. Neck Creek

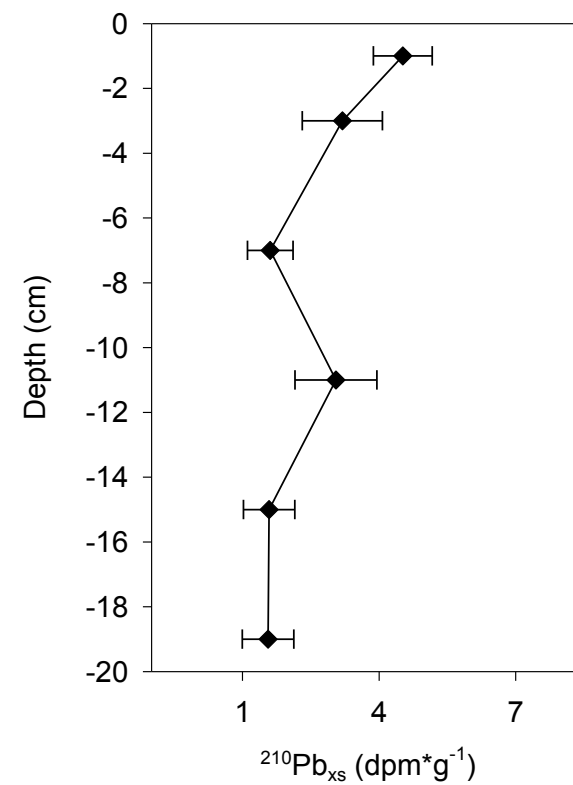


Figure 4c. Lemon Creek

Figure 2-4a-c. Vertical $^{210}\text{Pb}_{\text{xs}}$ activity (●) distribution profiles from marsh coring study sites: Main Creek (4a), Neck Creek (4b), and Lemon Creek (4c) marsh sites. Error bars reflect ± 1 standard deviation (S.D.).

Table 2-2a. Trace metal concentrations in Main Creek sediment cores (2007).

Main Creek	#	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)			Cu ($\mu\text{g}\cdot\text{g}^{-1}$)			Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
Depth	Samples	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE
0-2cm	n=9	5.08-6.27	5.62±0.61	0.35	250-265	255±9.04	5.22	280-301	291±10.4	5.98
2-4cm	n=9	5.95-7.27	6.43±0.74	0.43	282-315	301±17.2	9.91	303-346	322±22.0	12.7
4-6cm	n=9	6.51-8.83	7.65±1.16	0.67	326-342	333±7.69	4.44	312-365	337±27.0	15.4
6-8cm	n=9	6.70-7.00	6.85±0.15	0.08	310-361	332±26.5	15.3	320-371	339±30.2	17.4
8-10cm	n=9	6.06-7.51	6.68±0.74	0.43	294-331	317±20.0	11.5	307-361	331±27.0	15.6
10-12cm	n=9	5.55-7.37	6.28±0.97	0.56	263-302	278±20.9	12.0	298-328	317±16.6	9.60
12-14cm	n=9	6.28-7.20	6.64±0.49	0.28	299-334	311±20	11.4	321-375	340±30.5	17.5
14-16cm	n=9	5.99-7.13	6.41±0.62	0.36	269-294	279±13.6	7.82	299-319	306±11.6	6.72
16-18cm	n=9	5.75-6.91	6.22±0.61	0.35	261-280	267±10.8	6.22	291-325	305±18.0	10.4
18-20cm	n=9	5.83-6.50	6.27±0.38	0.22	238-314	267±41.0	23.7	267-352	302±43.9	25.3

Table lists Main Creek average (n=9) metal-specific concentrations reported per dry weight of sediment ($\mu\text{g}\cdot\text{g}^{-1}$), standard deviation ($\pm \sigma$), standard error (SE), and ranges (minimum to maximum). Dataset reflects mean metal concentrations (Cd, Cu, and Zn) from analysis of 3 sediment cores, each split into 10, 2cm intervals (from 0-20cm). At each 2 cm depth downcore, sediment sub-samples were processed in triplicate for replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to HNO_3 digestion (n=90).

¹**Bold** values represent recent sediments (deposited within 1 year of core collection), as determined by Be^7 analysis.

Table 2-2b. Trace metal concentrations in Neck Creek sediment cores (2007).

Neck Creek	#	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)				Cu ($\mu\text{g}\cdot\text{g}^{-1}$)				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
Depth	Samples	Range	Mean	SE		Range	Mean	SE		Range	Mean	SE
0-2cm	n=9	0.72-3.92	2.06±1.67	0.96		287-369	315±47.5	27.4		208-266	236±29.1	16.8
2-4cm	n=9	0.75-2.95	1.82±1.10	0.64		289-328	304±21.1	12.2		206-263	237±29.2	16.8
4-6cm	n=9	0.88-4.12	2.19±1.71	0.98		331-472	417±75.7	43.7		213-226	218±6.40	3.70
6-8cm	n=9	1.26-4.84	2.90±1.81	1.04		424-547	469±67.9	39.2		229-274	252±32.0	22.6
8-10cm	n=9	0.60-4.66	2.89±2.08	1.20		538-626	575±45.5	26.3		109-326	206±110	63.7
10-12cm	n=9	1.88-4.14	2.74±1.22	0.70		617-703	672±48.2	27.8		102-302	212±102	58.8
12-14cm	n=9	3.11-6.29	4.29±1.75	1.01		629-714	675±43.0	24.8		129-365	266±122	70.4
14-16cm	n=9	2.28-7.18	4.43±2.50	1.44		564-839	692±138	79.9		145-400	290±131	75.8
16-18cm	n=9	4.35-6.55	5.55±1.12	0.64		453-561	525±62.0	35.8		141-362	249±110	63.8
18-20cm	n=9	4.15-4.45	4.33±2.50	0.10		132-469	340±182	105		108-223	176±61.0	35.2

Table lists Neck Creek (2007) average (n=9) metal-specific concentrations reported per dry weight of sediment ($\mu\text{g}\cdot\text{g}^{-1}$), standard deviation ($\pm \sigma$), standard error (SE), and ranges (minimum to maximum). Dataset reflects mean metal concentrations (Cd, Cu, and Zn) from analysis of 3 sediment cores, each split into 10, 2cm intervals (from 0-20cm). At each 2 cm depth downcore, sediment sub-samples were processed in triplicate for replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to HNO_3 digestion (n=90).

¹**Bold** values represent recent sediments (deposited within 1 year of core collection), as determined by Be^7 analysis.

Table 2-2c. Trace metal concentrations in Lemon Creek sediment cores (2007).

Lemon Creek	# Samples	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)				Cu ($\mu\text{g}\cdot\text{g}^{-1}$)				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
Depth		Range	Mean	SE		Range	Mean	SE		Range	Mean	SE
0-2cm	n=9	0.92-1.47	1.20±0.27	0.16		101-193	141±47.5	27.4		1418-219	170±42.8	24.7
2-4cm	n=9	0.98-1.97	1.32±0.56	0.32		101-260	157±89.1	51.5		135-287	193±85.6	47.7
4-6cm	n=9	0.83-1.17	0.98±0.18	0.10		91.4-171	119±45.1	26.0		123-196	151±39.7	22.9
6-8cm	n=9	1.19-1.31	1.25±0.06	0.03		117-156	131±21.5	12.4		140-165	150±13.2	7.60
8-10cm	n=9	1.06-3.98	2.12±1.62	0.94		118-208	149±50.9	29.4		141-204	166±33.2	19.2
10-12cm	n=9	0.95-2.30	1.48±0.72	0.42		132-297	188±94.8	54.7		142-324	204±103	59.8
12-14cm	n=9	1.03-2.11	1.41±0.61	0.35		107-239	157±72.0	41.6		142-274	187±75.8	43.8
14-16cm	n=9	1.42-3.60	2.44±1.10	0.63		142-234	179±48.8	28.2		157-270	204±59.4	34.3
16-18cm	n=9	1.08-1.99	1.49±0.46	0.27		153-210	177±29.8	17.2		162-262	201±53.5	30.9
18-20cm	n=9	1.15-2.72	1.71±0.88	0.51		136-291	195±84.1	48.5		146-332	218±99.4	57.4

Table lists Lemon Creek average (n=9) metal-specific concentrations reported per dry weight of sediment ($\mu\text{g}\cdot\text{g}^{-1}$), standard deviation ($\pm \sigma$), standard error (SE), and ranges (minimum to maximum). Dataset reflects mean metal concentrations (Cd, Cu, and Zn) from analysis of 3 sediment cores, each split into 10, 2cm intervals (from 0-20cm). At each 2 cm depth downcore, sediment sub-samples were processed in triplicate for replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to HNO_3 digestion (n=90).

¹**Bold** values represent recent sediments (deposited within 1 year of core collection), as determined by Be^7 analysis.

Table 2-3. Regional background metal concentrations.

Metal	Background Concentration ($\mu\text{g}\cdot\text{g}^{-1}$)¹		Main Creek Core Mean ($\mu\text{g}\cdot\text{g}^{-1}$)²		Neck Creek Core Mean ($\mu\text{g}\cdot\text{g}^{-1}$)²		Lemon Creek Core Mean ($\mu\text{g}\cdot\text{g}^{-1}$)²
Cadmium	0.11		6.5		3.3		1.5
Copper	14		294		498		159
Zinc	81		319		234		184

¹Literature-based background concentration derived from Hudson River sediment data (Hirschberg et al. 1996). Site-specific mean Cd, Cu, and Zn concentrations from the average of downcore metal concentrations (n=90) from analysis of 3 sediment cores, each split into 10, 2cm intervals (from 0-20cm), and sub-sampled in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to HNO₃ digestion.

Table 2-4. Enrichment factors (EF=C_{observed}/C_{background}) within Main Creek, Neck Creek and Lemon Creek sediment cores.

Main Creek	Cd EF	Cu EF	Zn EF		Neck Creek	Cd EF	Cu EF	Zn EF		Lemon Creek	Cd EF	Cu EF	Zn EF
0-2cm	51.1	18.2	3.6		0-2cm	18.7	22.5	2.9		0-2cm	10.9	10.0	2.1
2-4cm	58.5	21.5	4.0		2-4cm	16.6	21.7	2.9		2-4cm	12.0	11.2	2.4
4-6cm	69.5	23.8	4.2		4-6cm	19.9	29.8	2.7		4-6cm	8.9	8.5	1.9
6-8cm	62.2	23.7	4.2		6-8cm	26.4	33.5	3.11		6-8cm	11.4	9.4	1.9
8-10cm	60.7	22.7	4.1		8-10cm	26.3	41.1	2.54		8-10cm	19.3	10.6	2.1
10-12cm	57.1	19.9	3.9		10-12cm	24.9	48.0	2.62		10-12cm	13.5	13.4	2.5
12-14cm	60.4	22.2	4.2		12-14cm	39.0	48.2	3.28		12-14cm	12.8	11.2	2.3
14-16cm	58.3	19.9	3.8		14-16cm	40.3	49.4	3.59		14-16cm	22.2	12.8	2.5
16-18cm	56.6	19.1	3.8		16-18cm	50.5	37.5	3.08		16-18cm	13.6	12.6	2.5
18-20cm	57.0	19.1	3.7		18-20cm	39.4	24.3	2.18		18-20cm	15.6	13.9	2.7
Core Mean (n=90)	59.1	21.0	3.9		Core Mean (n=90)	30.2	35.6	2.89		Core Mean (n=90)	14.0	11.4	2.3

¹Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996). Site-specific mean Cd, Cu, and Zn concentrations from the average of downcore metal concentrations (n=90) from analysis of 3 sediment cores, each split into 10, 2cm intervals (from 0-20cm), and sub-sampled in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to HNO₃ digestion.

***Bold** values represent recent sediments (deposited within 1 year of core collection).

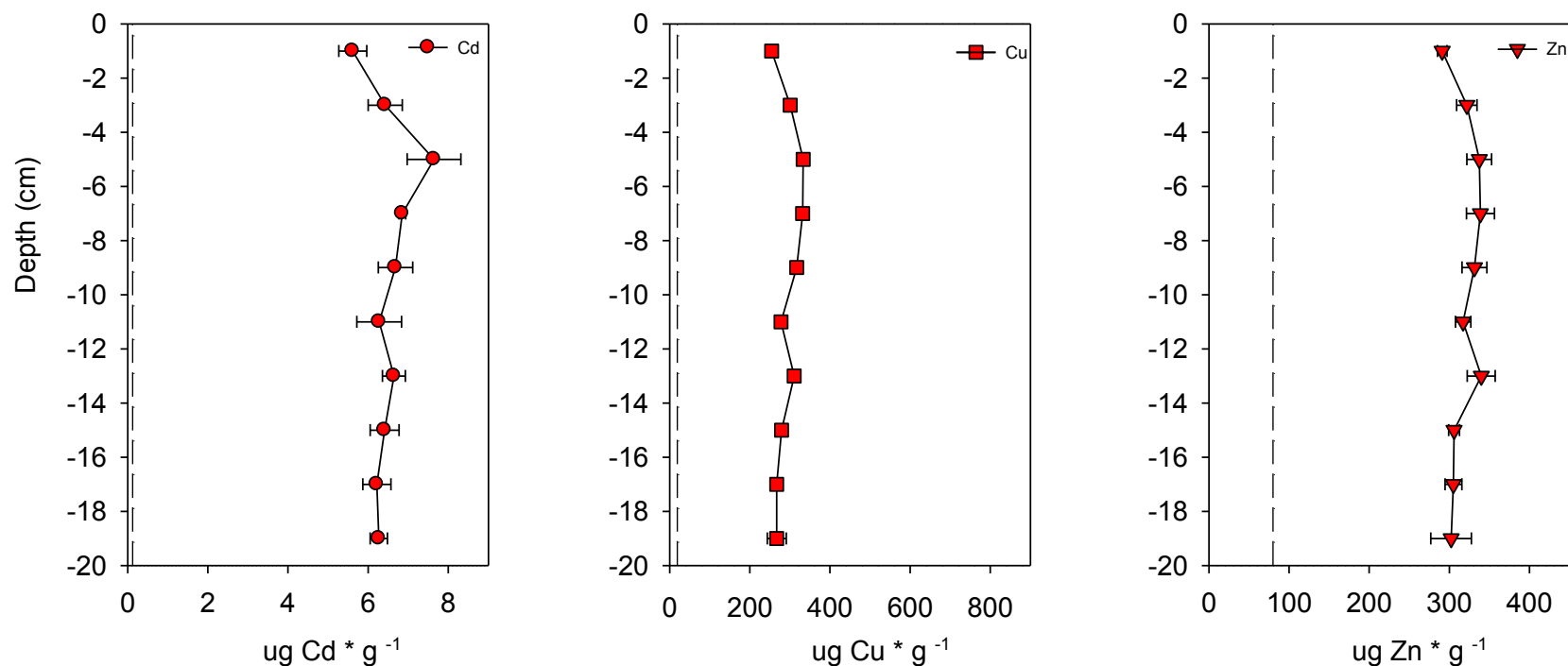


Figure 2-5. Main Creek downcore Cd, Cu, and Zn concentrations (2007) with respect to natural sediment background concentrations. Datapoints (Cd (●), Cu (■), and Zn (▼)) and respective error bars reflect the mean of average sediment sample concentrations ($n=3$) $\pm$ 1 standard error (S.E.) for respective depth intervals ($n=10$) from 0-20cm. Dashed lines represent metal-specific regional elemental background level derived from Hirschberg et al. 1996 and Bowen et al. 1979.

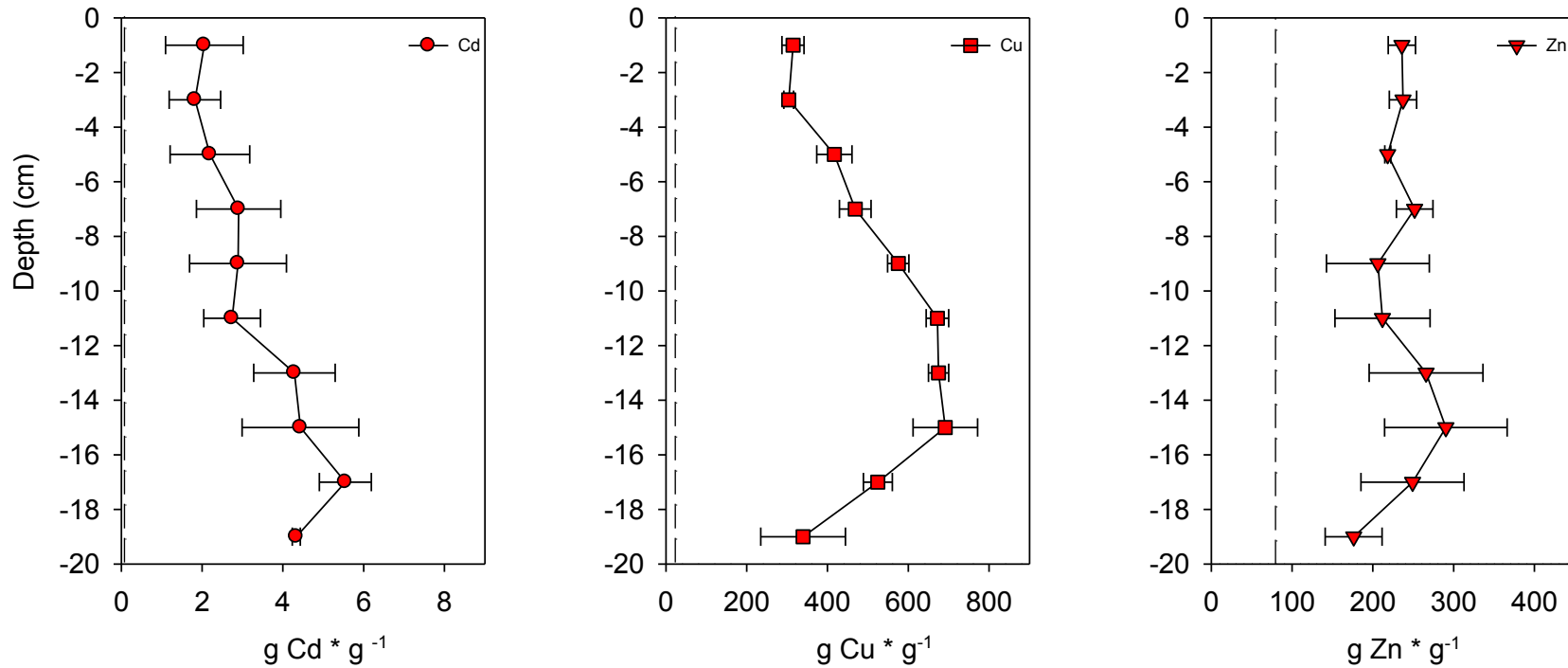


Figure 2-6. Neck Creek downcore Cd, Cu, and Zn concentrations (2007) with respect to natural sediment background concentrations. Datapoints (Cd (●), Cu (■), and Zn (▼)) and respective error bars reflect the mean of average sediment sample concentrations ($n=3$) $\pm$ 1 standard error (S.E.) for respective depth intervals ($n=10$) from 0-20cm. Dashed lines represent metal-specific regional elemental background level derived from Hirschberg et al. 1996 and Bowen et al. 1979.

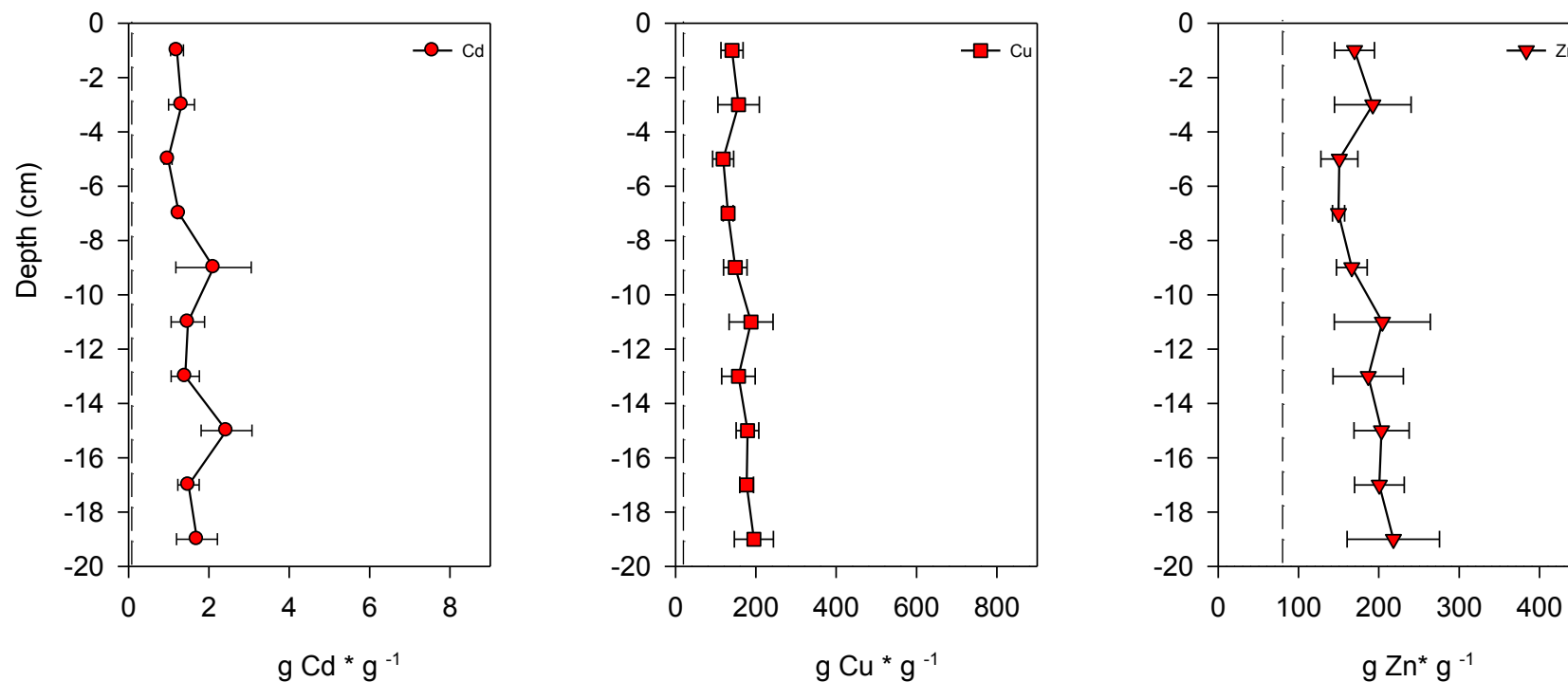
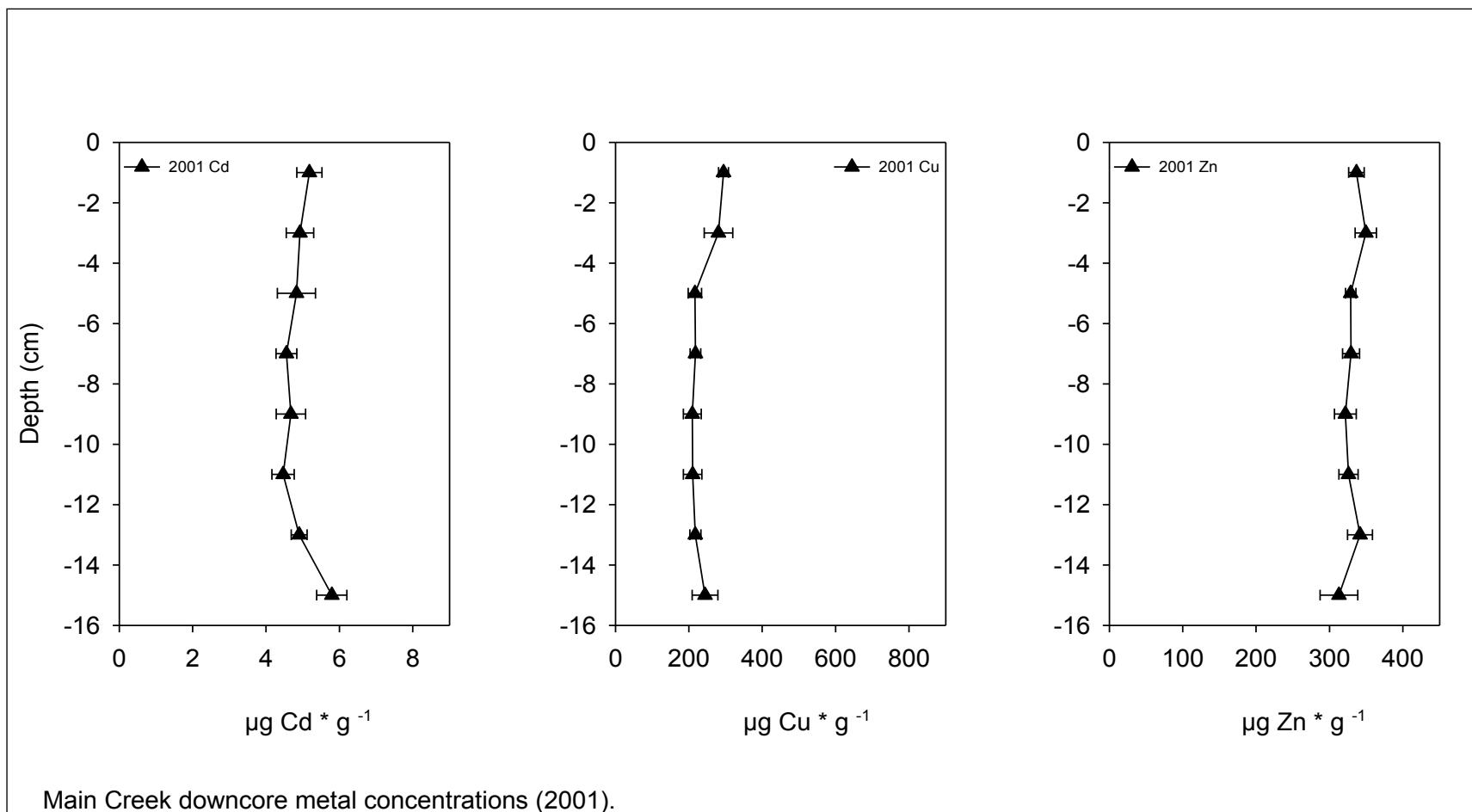
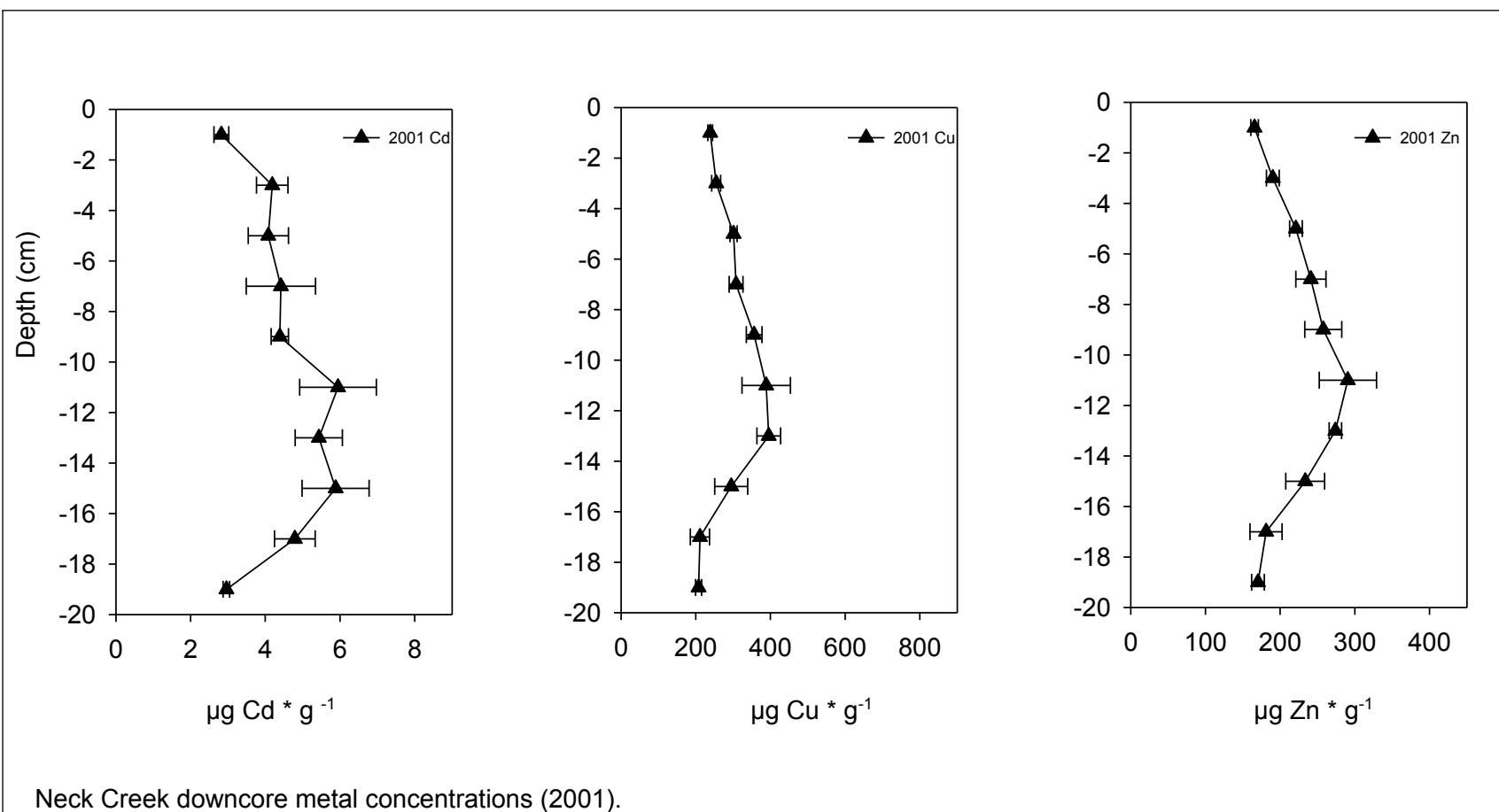


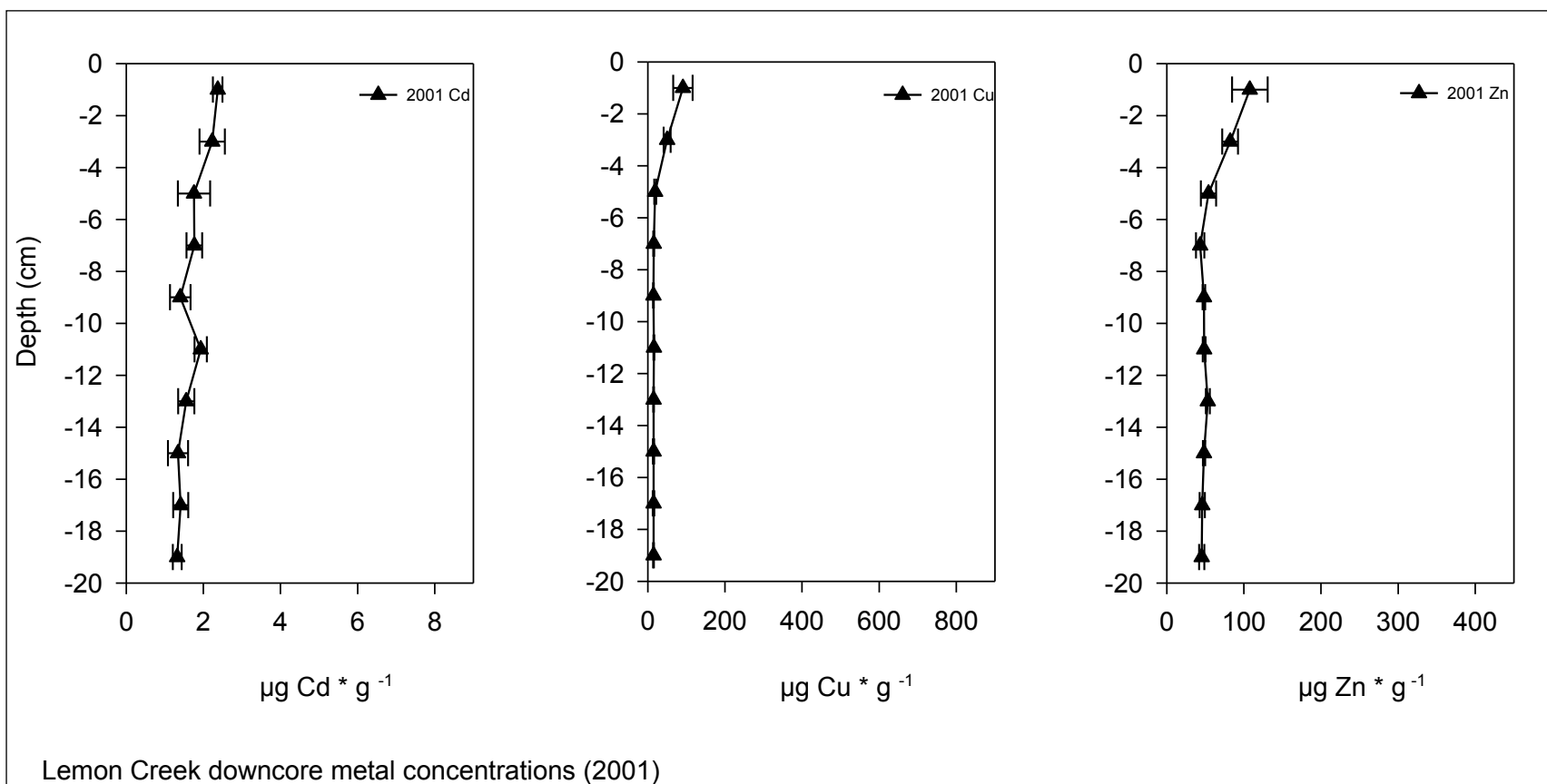
Figure 2-7. Lemon Creek downcore Cd, Cu, and Zn concentrations (2007) with respect to natural sediment background concentrations. Datapoints (Cd (●), Cu (■), and Zn (▼)) and respective error bars reflect the mean of average sediment sample concentrations ($n=3$) $\pm$ 1 standard error (S.E.) for respective depth intervals ($n=10$) from 0-20cm. Dashed lines represent metal-specific regional elemental background level derived from Hirschberg et al. 1996 and Bowen et al. 1979.

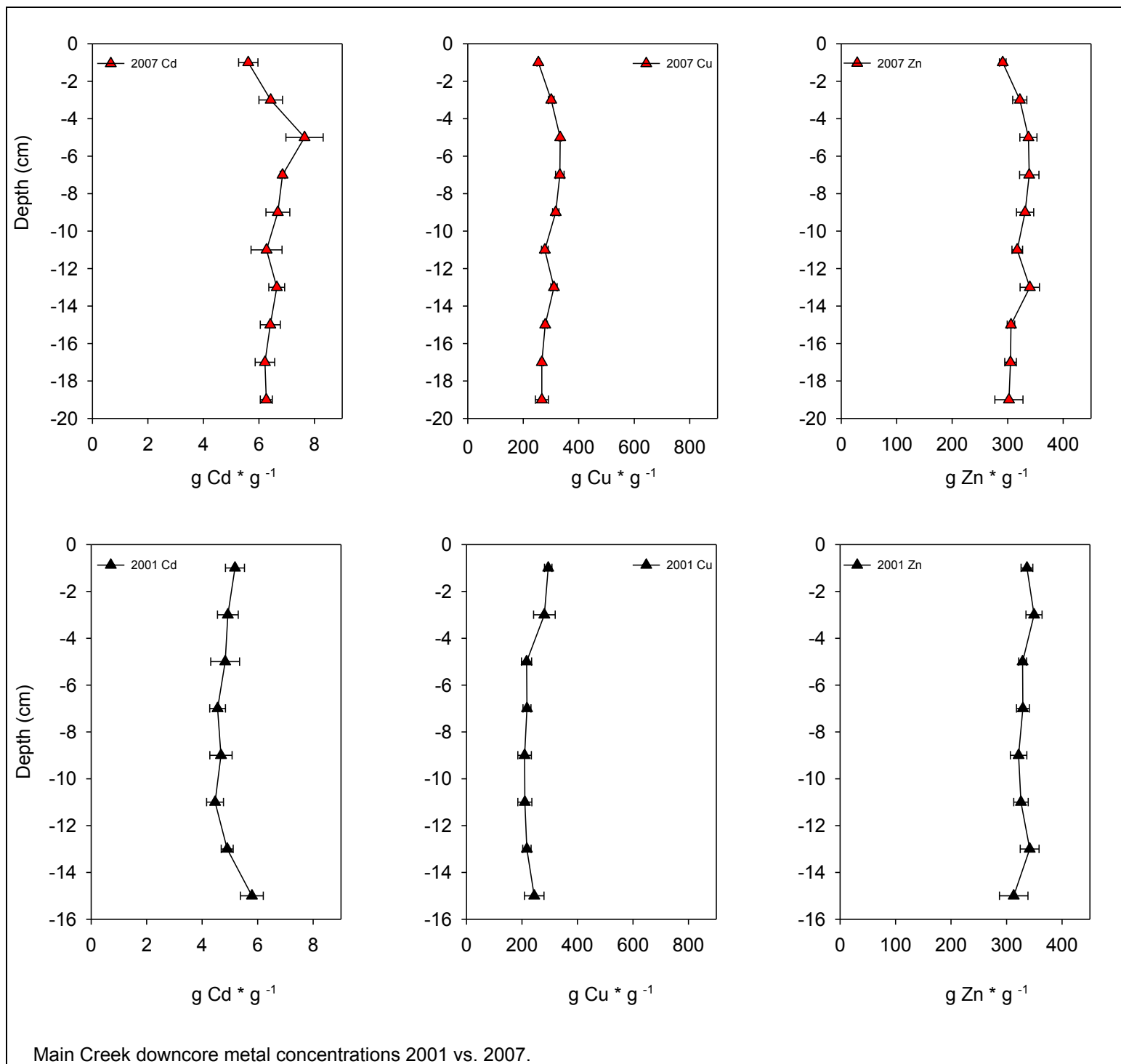
Appendix 2-A. Vertical metal (Cd, Cu, Zn) profiles from 2001 Main Creek, Neck Creek and Lemon Creek.

Appendix 2-A-1: Vertical metal (Cd, Cu, Zn) profiles from 2001 coring at Main Creek.

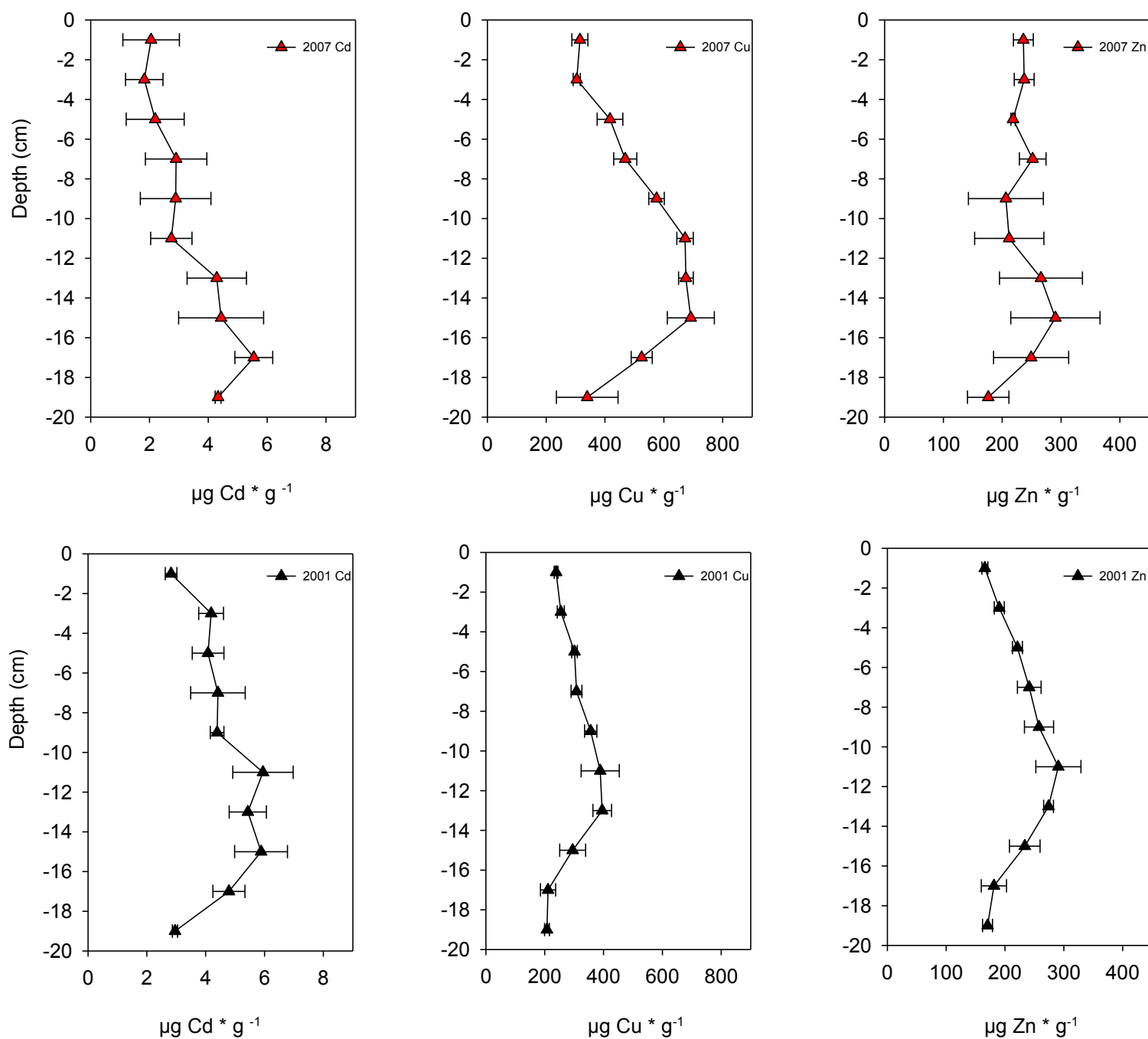


Appendix 2-A-2: Vertical metal (Cd, Cu, Zn) profiles from 2001 coring at Neck Creek.

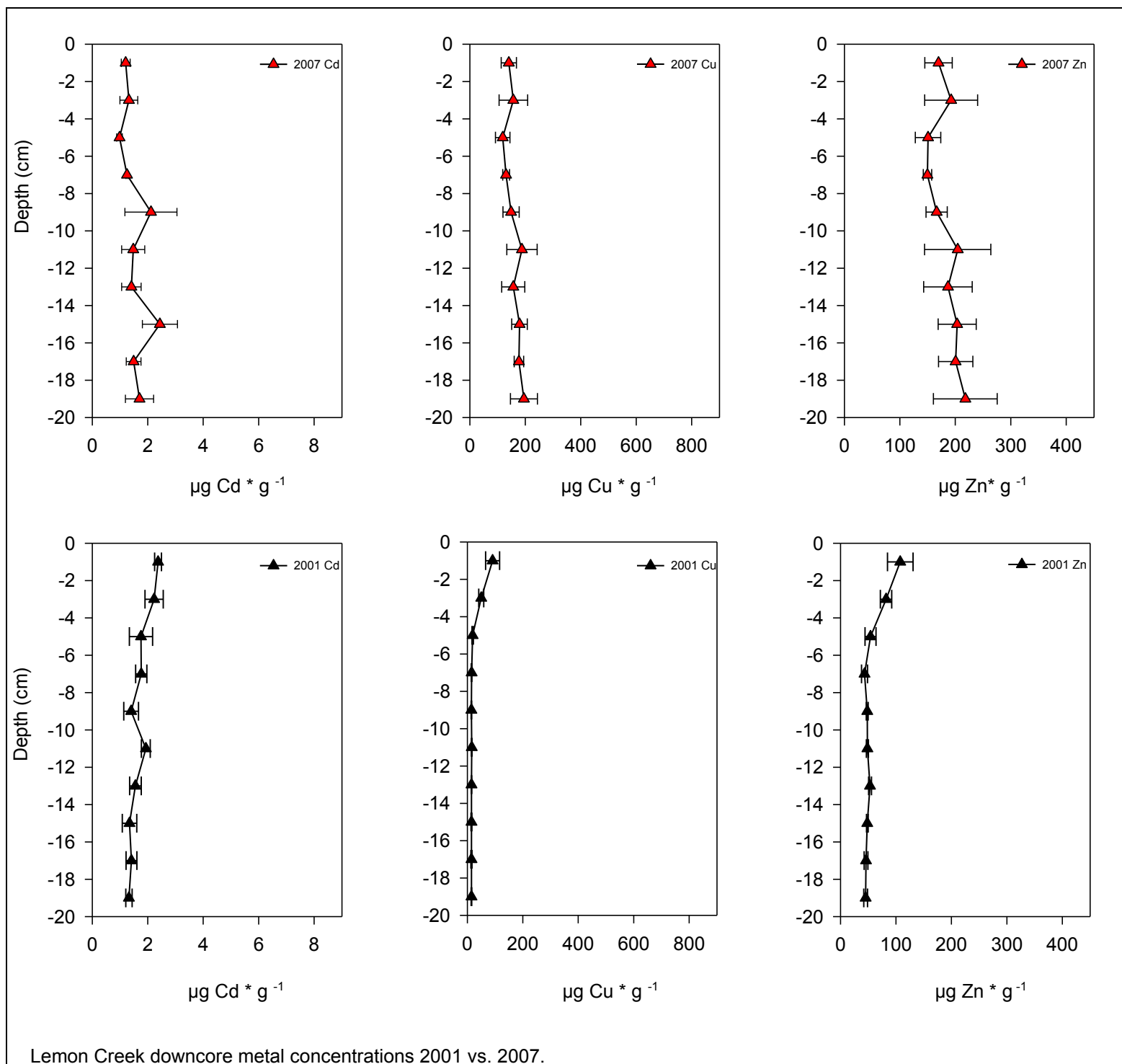
Appendix 2-A-3: Vertical metal (Cd, Cu, Zn) profiles from 2001 coring at Neck Creek.

Appendix 2-B. 2001 v. 2007 metal profiles from Main Creek, Neck Creek and Lemon Creek.**Appendix 2-B-3: 2001 v. 2007 metal profiles from Main Creek.**

Appendix 2-B-3: 2001 v. 2007 metal profiles from Neck Creek.



Neck Creek downcore metal concentrations 2001 vs. 2007.

Appendix 2-B-3: 2001 v. 2007 metal profiles from Lemon Creek.

[illegible]

Appendix 2-C. Trace metal concentrations in sediment cores recovered from marsh study sites in 2001.

Lemon Creek (2001)	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)				Cu ($\mu\text{g}\cdot\text{g}^{-1}$)				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
Depth	Range	Mean	SE		Range	Mean	SE		Range	Mean	SE
0-2cm	2.01-2.58	2.37±0.25	0.12		41.5-137	91.3±50.3	25.17		54.2-163	108±46.0	23.0
2-4cm	1.39-2.76	2.23±0.66	0.33		32.0-73.4	50.3±17.9	8.96		66.7-112	82.2±20.4	10.2
4-6cm	1.09-2.98	1.75±0.84	0.42		13.95-23.6	19.2±5.08	2.54		33.2-79.2	54.1±19.8	9.88
6-8cm	1.37-2.31	1.77±0.40	0.20		13.3-17.6	15.4±2.09	1.05		27.9-52.5	43.3±10.9	5.47
8-10cm	0.80-2.10	1.40±0.53	0.27		12.7-16.6	14.7±1.62	0.81		44.7-52.6	48.2±3.36	1.68
10-12cm	1.53-2.29	1.93±0.32	0.16		14.7-18.7	15.8±1.97	0.99		44.8-52.8	48.4±3.46	1.73
12-14cm	0.93-1.79	1.56±0.42	0.21		13.5-17.9	15.1±1.93	0.97		48.7-59.1	53.3±4.97	2.49
14-16cm	0.92-2.06	1.34±0.52	0.26		12.3-19.3	14.9±3.29	1.65		45.5-51.7	48.3±2.96	1.48
16-18cm	0.88-1.82	1.41±0.39	0.20		11.1-19.8	14.9±3.67	1.84		36.7-51.7	46.0±6.55	3.27
18-20cm	1.08-1.62	1.32±0.23	0.11		12.6-17.9	14.9±2.36	1.18		36.1-51.5	45.4±6.86	3.43

Chapter 3

Intra-marsh Distribution and Longitudinal Variations of Anthropogenic Metals in Marsh Sediments: Large and Small Scale Spatial Enrichment Patterns (Cd, Hg, Cu and Zn)

INTRODUCTION

A variety of natural and anthropogenic factors like geology, biological productivity, industrialization, changing land use patterns, development activities and urbanization regulate the metal load received by marsh sediments (Prasad, et al., 2006). Although metals are present naturally in the environment, excessive amounts of metals enter the environment from anthropogenic sources (Kabir, et al., 2001). The anthropogenic metal component in sediments may be derived from a variety of land uses and are generally defined as either point or nonpoint source loadings. It is expected that, compared with sediments in suburban or rural environments, urban marsh sediments receive greater metal loads from surrounding watersheds (Thornton, 1991). The greater contamination associated with urban sediments largely results from sustained and intermittent metal inputs via past and present sources (Franco, 2005).

Anthropogenic activities have introduced increased metal loads in estuarine environments, which have become reservoirs for pollutants; acting as sinks and sources for fine, contaminated sediments (Cundy, et al., 2003; Hwang, et al., 2006). Decreased sediment quality in estuarine areas is often attributable to coastal development for residential and commercial use as well as port infrastructure initiatives (Schaffelke, et al., 2005). Anthropogenic activities result in a variety of waste materials that pollute and potentially release metals in urban areas including building wastes, industries, road construction wastes and facilities, power stations, oil spills, organic and chemical waste spills, transportation systems, scrap yards and waste disposal sites

(Franco, 2005). Frequently, high metal concentrations found in sediments are proximal to areas associated with urban and industrial land-uses. However, the observed contamination is not directly attributable to discrete discharges, but rather to nonpoint source loadings (Suszkowski, et al., 2006).

Clean Water Act legislation has helped mitigate metal-contaminated effluents from industrial and commercial point sources, however, few measures prevent metal contributions from non-point sources (Bakan and Ozkoc, 2007). Contaminated waterways throughout the NY/NJ Harbor Estuary have benefited from the enactment of sewer ordinances and the national and state pollutant discharge elimination system (NPDES, SPDES) which requires industrial pretreatment and enforces effluent limitations of permitted dischargers. However, despite fewer unregulated contaminant loadings, receiving waters and critical marsh habitats are subject to pervasive non-point source loadings (Rose, et al., 2007). Therefore, this necessitates monitoring and identification of geochemical signals throughout each system, which can prove useful in the identification of input sources and better understanding of metal transport to receiving waters and marshes (Masson, et al., 2006).

Non-point source pollution is difficult to control, especially when derived from a variety of locations. Metals on impervious surfaces may accumulate in stormwater and enter surface waters via runoff discharged from surrounding watersheds. It is possible that diffuse sources can contain high metal concentrations and can be larger sources than direct discharges, as any one input may contain a low concentration of contaminants but may be continual or combined with other sources, consequentially resulting in substantial accumulation (Loska and Wiechula, 2002). Accordingly, stormwater runoff is recognized as a significant source of metals to surface waters and sediments (Rice, et al., 2002).

In general, major New York City point sources include discharges from wastewater treatment plants, combined sewer overflows (CSOs) and municipal storm sewer systems. Nonpoint source metal inputs are associated with industrial, commercial, municipal and residential land use activities. Nonpoint source contributions are mainly the consequence of urban stormwater runoff, but can also result from faulty infrastructure (i.e. sanitary sewer lines).

Identification of specific pollutant sources and tracking metal mobility is often technically challenging. The multiplicity of potential point and non-point sources and the combined effect of intermittent and/or consistent inputs, which may have resulted from past or present sources, makes this particularly complicated in Staten Island marsh systems (Loska and Wiechula, 2002). Although metal inputs attributable to certain sources (i.e. legacy contamination and CSOs) are difficult to monitor and trace because volumes and frequencies can vary, it is critical to consider potential impacts on receiving environments. Furthermore, with increasing Staten Island development initiatives, the natural ability of marshes to filter runoff and control stormwater have been compromised, making stormwater pollution an increasing threat to marsh ecosystems (Ward, 2002). Therefore, as receiving coastal environments for both local terrestrial inputs and redistributed estuarine contaminants, marsh-creek areas (including Main Creek, Neck Creek and Lemon Creek) may become increasingly vulnerable to metal loadings, eventually failing as effective buffers and becoming contaminant conduits (Sanger, et al., 1999b; Goodbred, 2004). Therefore, this necessitates monitoring and identification of geochemical signals throughout each system, which can prove useful in the identification of input sources and better understanding of metal transport to receiving waters and marshes (Masson, et al., 2006).

Previous work examined the vertical distribution of chemical constituents in sediment cores from Main Creek, Neck Creek, and Lemon Creek to characterize temporal pollution in

marshes throughout Staten Island. Metal and radionuclide analyses established that coring locations within all marshes acted as a sink for fine-grained particles and associated contaminants on a long (<10yrs.) and short-term (<1yr.) scale. For all sites, the levels of Cd, Cu and Zn found throughout the temporal extent of all sediment cores were indicative of anthropogenic pollution. Although metal concentrations and radionuclide activities were site-specific, all sites showed comparable levels of bottom and top sediment contamination. Higher radionuclide activities were identifiable in sediments that were recently (within a year) scavenged from the water column and deposited at Main Creek and Lemon Creek however, the latter site (LC) demonstrated comparatively lower metal pollution than the marshes that have a direct hydrological connection with the Arthur Kill (MA and NC). Therefore, sediment core analysis determined that unique depositional contexts, along with site-specific inputs, influenced the degree of metal enrichment and the contaminant trends characterized with the marsh-creek systems studied.

The comparable extent of temporal contamination demonstrated by the Arthur Kill sites indicated that, in addition to any site-specific sources, a continuous, unknown influence maintained the constantly high magnitudes of enrichment identifiable with these sites. Baseline metal data within these marshes suggests that the observed pollution may be attributable to various contributions from historic and present-day anthropogenic activities. It is plausible that tidal exchange with the Arthur Kill may also serve as an active, dominant source of metal pollutants, which contributed to greater scales of metal contamination than observed in marsh environments outside the Arthur Kill complex.

Overall, temporal assessments of Main Creek, Neck Creek and Lemon Creek cores established large-scale spatial contamination and site-specific degrees of recovery and

attenuation, though recent deposits remained enriched with metals. However, discrete differences may exist not only between, but also within, marsh systems (Aalto, et al., 2005; Weis, et al., 2005). Accordingly, evaluation of small-scale variations in terms of metal concentrations is necessary not only to characterize site-specific contamination, but to understand the significance of large-scale temporal and geographic variations (i.e. different sampling events and study locations) (Aalto, et al., 2005; Thursby, et al., 2000).

Evaluation of Main Creek, Neck Creek and Lemon Creek cores demonstrated the sediments acted as a repository of metals. However, geochemical analyses focused on cores collected from particular marsh flat locations; targeting sites that were previously sampled and/or exhibited optima conditions for reconstructing sediment chronologies (slow-currents, fine-grained sediments dominated by silt and clay fractions) (Bopp, et al., 2006). Thereby, site-specific characterizations of intra-spatial metal distributions were limited to the spatial extent examined within each study site

Accordingly, much remained unknown in terms of the spatial distribution of particle-reactive contaminants throughout the areal reach of each marsh study site. Considering the short-distance heterogeneity of net particle-deposition rates recognized throughout the NY/NJ Harbor Complex (Bopp, et al., 1982) it was unclear to what extent any small-scale spatial variations influenced the evident large-scale patterns of inter-marsh variability demonstrated by prior marsh assessments (Olsen, et al., 1978; Feng, et al., 1978; Gibbs, et al., 1994; Bopp, et al., 2006).

Therefore, the overall goal of this research component was to characterize spatial distribution pollutant trends on a variety of scales. The first aspect examined was metal

concentrations in sediments along a longitudinal transect at Main Creek, Neck Creek and Lemon Creek in order to characterize site-specific surficial contamination and small-scale distribution trends. A comparative assessment of study sites with respect to the extent of metal enrichment observed in surface sediments sought to discern large-scale pollution gradients. To fulfill these objectives, site-specific spatial and temporal datasets described metal enrichment throughout the study area. A secondary objective was to consider intra-marsh variability that characterized surficial enrichment gradients that were indicative of terrigenous enrichment and suggestive of (inland or downstream) localized metal sources or remobilization of metal contaminated sediments from the surrounding catchment area or estuarine inputs.

METHODS

Study sites

Prior coring studies (2001) provided the basis for the design of the current study (see Chapter 1 for map and detailed site descriptions) (Appendix A; Ward, 2002). These studies suggested that Staten Island marshes exhibited variable degrees of metal contamination and established that pollution at particular study sites was attributable to known point sources. Conversely, unknown sources contributed to the consistent sediment contamination identified within marshes along the Arthur Kill (Appendix A; Ward, 2002). This included Main Creek (MA) and Neck Creek (NC), which served as targeted locations for the current study (see Chapter 1 for detailed site descriptions). A companion coring study (2007) confirmed these marsh systems demonstrated similar extents of contamination that was indicative of an unidentified, continuous impact which sustained the consistently high magnitudes of enrichment (see Chapter 2 for more information).

Main Creek and Neck Creek are located along the western shore of Staten Island, New York and tidally exchange water with the Arthur Kill (AK) (see Chapter 1 for detailed site descriptions). Main Creek shares a border with the Fresh Kills landfill and connects to the Arthur Kill via the Fresh Kills Creek. Neck Creek is north of Main Creek and directly flows from its upland marsh habitat to the Arthur Kill. Assessments of baseline coring data from these marsh-creek systems have concluded that sediments recovered from Main Creek and Neck Creek exhibited substantially greater metal contamination, as compared with Lemon Creek (LC), a site external to the Arthur Kill complex (Ward, 2002; Nichols, 2004).

The Lemon Creek marsh system was primarily included in the study design because of its location on the southeastern shore of Staten Island. Lemon Creek tidally exchanges water with the Raritan Bay and provided metal concentration data from marsh sediments not directly influenced by the Arthur Kill. Lemon Creek served as an external site to help evaluate if the comparatively elevated magnitude of metal enrichment observed in Main Creek and Neck Creek sediments could be a result of the Arthur Kill or site-specific terrestrial sources.

Field Sampling

The sampling schema called for collection of surface sediments along a longitudinal transect within the tidal portion of each study site. At low tide, sediments at similar depths were "skimmed" off the surface of exposed mudflats at locations along the creek banks, which were upstream and downstream of where sediment cores were previously recovered (see Chapter 2). To span the greatest extent of each marsh-creek system as feasible, samples were consecutively collected at six equidistant points (~100-200 m apart). For all sites, surface sediments were collected from six sampling points (A-F); transect sampling site A was the most downstream location and set up as close as possible toward the Arthur Kill (MA and NC) or Raritan Bay

(LC), while location F was situated the farthest upstream and near the upland area of each marsh-creek system (Figure 1).

Transects extended from a downstream intertidal mudflat and proceeded inland, in an easterly direction at Main Creek and Neck Creek (away from the Arthur Kill) and northerly at Lemon Creek (away from the Raritan Bay), toward the upland marsh habitat. Transect sampling locations were numbered accordingly, as depicted on Figs. 1-3.

To prevent contamination, all instruments and storage containers were new or acid-washed prior to use in the field and laboratory. Subsequent to collection, samples were stored in sealed containers and transported to the laboratory. Prior to processing and analysis, sediment cores were stored in a -20°C freezer in accordance EPA guidelines (USEPA, 2001; Weis, et al., 2005).

Sediment Processing

Frozen surface sediment samples collected from transect locations within each site (MA, NC, and LC) were removed from the sub-zero freezer and slightly thawed in the laboratory at room temperature. Subsequently, samples were split; one portion was processed and analyzed for Cd, Cu, and Zn and the other separately processed and analyzed for Hg. To compensate for grain size effect, all samples were wet sieved using 74µm nylon mesh screens. This technique limited biases from differences in particle size distributions and allowed for identification of the fine-grained sediment fraction, to which metals tend to adsorb and benthic biota feed upon (Gurrieri, et al, 1998; Cundy, et al., 2001; USEPA, 2008). The sieved samples were oven-dried for 24-48 hours at ~60°C to achieve a constant weight, placed in a mortar, homogenized, ground to a fine powder with a pestle and transferred into acid-washed scintillation vials (Hornberger, et

al., 1999). Six aliquots of the fine-grained sediment from each sample were weighed to approximately 0.5 g dry sediment (rounded to 5 decimal places) for Cd, Cu, Zn, and Hg analysis.

Metal Analysis

Cd, Cu, Zn Analysis

Three replicates of fine-grained sediment from each respective transect sampling location were put into 22 ml glass scintillation vials for near-total trace metal content (Cd, Cu, Zn, Hg) using standard techniques. Detection methods for Cd, Cu and Zn included digestion with trace metal grade nitric acid (HNO₃), resuspension with 2% nitric acid, filtration and analysis with a Perkin Elmer Optima 3300XL Inductively Coupled Argon Plasma Emission Spectrophotometer (ICAPES) (Hornberger, et al., 1999; Andrews, et al., 2004; Luoma, et al., 1981). The near-total hot nitric acid reflux metal digestion procedure was initiated with the addition of 10ml of concentrated trace metal grade nitric acid to each scintillation vial containing 0.5g of fine-grained sediment recovered from each core. Vials were loosely capped and placed in a fume hood to sit overnight at room temperature. Subsequently, the vials were gently agitated by hand to resuspend the sediment acid slurry; reflux bulbs replaced the caps and vials were placed on a hot plate in a fume hood at approximately 150°C. Samples refluxed for approximately 7 days until the samples were clear; at which time the reflux bulbs were carefully removed allowing the samples to evaporate to dryness. Dried samples were reconstituted with 2% trace metal grade nitric acid, filtered through 0.45 µm Millipore[®] filters and collected in acid washed autosampler tubes in preparation for analysis by ICPAES.

ICAPES calibration involved normal operating procedures after correction for peak interferences in the samples' digest matrix. The high sensitivity, precision and accuracy of the ICPAES allows for determination of low levels of trace elements and therefore was an

appropriate method for detection of Cd, Cu, and Zn (Boevski, et al., 2007). Datasets provided concentrations of a suite of metals however, a subset of elements (Cd, Cu, Zn) were selected because of their potential toxicity and because they have been identified as contaminants of regional concern (Kennish, 1992; NY/NJ HEP, 1996; Church, et al., 1998).

Hg Analysis

After weighing three replicates from each surface sediment sample, the 0.5 g aliquots were transferred into 250 ml acid-washed digestion bottles containing 100 ml reagent grade NANOpure water for total mercury (Hg-T) analysis. Accordingly, samples were digested using standard techniques, which included digestion with a combination of (2:1) concentrated nitric (HNO_3) and sulfuric (H_2SO_4) acids and with a PerkinElmer flow injection mercury analyzer (FIMS-100). The Hg-T digestion procedure was initiated with the addition of 10 ml of concentrated trace metal grade (HNO_3) and 5 ml of concentrated trace metal grade H_2SO_4 to each sample digestion bottle containing 100mL of reagent water (NANOpure[®]) and 0.5g of fine-grained sediment recovered. Samples were digested in diluted potassium permanganate (KMnO_4) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) solutions, oxidized and heated for 2 hours at 95°C in a covered water bath (USEPA, 1991; Cole, et al., 2001; McIntosh, et al., 2004). After cooling to room temperature, samples were oxidized with the addition of sodium chloride-hydroxylamine chloride ($[\text{NaCl}(\text{NH}_2\text{OH})\text{HCl}]$) to reduce excess KMnO_4 . Samples were transferred to acid washed autosampler tubes in preparation for analysis. Following instrument calibration, Hg-T content was determined via the cold-vapor atomic absorption spectrophotometric method (CVAS) outlined by Hatch and Ott (1968); stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) reduced mercury within sample digests to elemental mercury.

Laboratory quality assurance practices included the creation and application of procedural blanks and acid-washing all sample collection and processing materials with 10% HCl before use for Cd, Cu, Zn analysis and rinsing with NANOpure[®] water; a greater concentration, 20% HCl, was used before processing samples for Hg. After initial calibration of the ICAPES and FIMS-100, continual calibration standards and internal quality control standards (ERA and SPEX 1 ppm reference standards) were analyzed every 10-12 samples to ensure consistent performance of the instruments. Further verification of metal analysis accuracy and precision included certified estuarine sediment and soil reference materials (“Standard Reference Material[®] 1646a” from the National Institute of Standards and Technology, Metals in Soils” from Environmental Resource Associates [ERA]), which yielded metal concentrations in agreement with the reported values (95% confidence level).

Determinations of Cd, Cu, Zn and Hg within sediments collected along each transect were used to construct lateral concentration profiles for each marsh study site to illustrate intra-marsh metal distributions and determine the extent of site-specific surficial contamination. Metal loads within consecutive sediment samples were evaluated with respect to successive distance upstream to assess small-scale variability and determine site-specific enrichment trends (Weis, et al., 2005).

Calculating Enrichment and Contamination Factors

In order to provide a context to assess the degree of contamination demonstrated by marsh sediments, acquired datasets were evaluated in terms of natural background metal concentrations (Schropp, et al., 1988; Hwang, et al., 2006). The sediment enrichment factor (EF) of each element studied was based on comparison with regional background values derived from uncontaminated sediments previously collected within the vicinity of the study area (O'Reilly

Wiese, 1995). The literature-based values used to represent background levels are as follows: $.11\mu\text{g Cd}\cdot\text{g}^{-1}$, $0.18\mu\text{g Hg}\cdot\text{g}^{-1}$, $14\mu\text{g Cu}\cdot\text{g}^{-1}$, and $81\mu\text{g Zn}\cdot\text{g}^{-1}$ (Hirschberg, et al., 1996; Bowen, et al., 1979) (Table 1). Accordingly, the enrichment factor (EF) of each metal was determined by the ratio of the reported concentration against the element's local background concentration (Alexander, et al., 1993; Valette-Silver, 1993; Hornberger, et al., 1999; Strong, et al., 2008).

The EF is expressed below as:

$$\text{EF} = C_o / C_r \quad \text{Equation 1.}$$

where:

C_o = metal concentration observed in sediment sample

C_r = regional background metal concentration

The extent to which sediment samples varied from these reference values served to comparatively assess the extent of contamination throughout the study area and characterize spatial variability within sites (Wedepohl, et. al., 1971; Gurrierri, et al., 1998; Tomlinson, et al., 1980; Ray, et al., 2006).

Statistical Analysis

Data were analyzed using the software Statistica version 7 (2005). Linear regression analysis was used to: (1) compare sediment concentrations among intra-marsh sampling locations, and (2) to understand the relationship between marsh surface sediment metal concentration ($\mu\text{g}\cdot\text{g dry wt}^{-1}$) and inland distance (from confluence with open waters of the NY/NJ HE (i.e. Arthur Kill and Raritan Bay).

To identify (1) among-site small-scale spatial differences or co-occurrence of metal-specific surficial sediment contents and intra-marsh anthropogenic enrichment trends, (2) determine

inter-spatial variability of site-specific levels of anthropogenic metals, and (3) discern large-scale geographic gradients in marsh sediment enrichment.

Linear regression analysis was used to produce an equation that predicted the how much the variance of the dependent variable (metal concentration) was driven by the independent variable, or distance from the open NY/NJ HE waterway, in which each tidal wetland system drained into s the independent variables. This equation had the form:

$$Y = m1X1 + b$$

Equation 2.

The Y term represented sediment concentration (or the dependent variable) predicted, whereas, $X1, X2, etc.$ are the independent variables (inland distance); $m1, m2$ and so on are the coefficients or multipliers that describe the size of the effect the independent variables (distance) are having on the dependent variable Y , (metal-specific surface sediment concentration); b is the value Y is predicted to have when all the independent variables are equal to zero (y-intercept).

Accordingly, concentration prediction equations were used to determine intra-marsh variance, spatial trends and/or co-occurrence of surface metal distributions along lateral transects spanning the wadable reach of MA, NC, and LC. Surface sediments were collected during low-tide conditions from exposed marsh flats at 6 stations within each study site and analyzed for Cd, Hg, Cu, and Zn. The intent of this field sampling design was to consider small-scale, or among-site differences extending inland toward the upland marsh habitat.

RESULTS

Large-scale spatial distribution of metals in surface sediments

Metal concentrations and ranges detected in Main Creek, Neck Creek and Lemon Creek sediments are shown in Table 2. Over the whole study area, Main Creek sediments had the highest mean concentrations of all reported metals: $3.46 \mu\text{g Cd}\cdot\text{g}^{-1}$, $1.26 \mu\text{g Hg}\cdot\text{g}^{-1}$, $214.46 \mu\text{g Cu}\cdot\text{g}^{-1}$, and $240.04 \mu\text{g Zn}\cdot\text{g}^{-1}$. Average concentrations of Cd, Hg, and Cu with respect to marsh sites is in the order of $\text{LC} < \text{NC} < \text{MA}$. Mean Cd concentrations measured at Neck Creek and Lemon Creek were $1.90 \mu\text{g}\cdot\text{g}^{-1}$ and $1.61 \mu\text{g}\cdot\text{g}^{-1}$, respectively. The mean Hg concentration in Neck Creek sediments, $1.14 \mu\text{g}\cdot\text{g}^{-1}$, was comparable to Main Creek values but, significantly higher than the $0.24 \mu\text{g Hg}\cdot\text{g}^{-1}$ measured in Lemon Creek samples. The mean Cu value for Neck Creek was $175 \mu\text{g}\cdot\text{g}^{-1}$ compared with $129.95 \mu\text{g Cu}\cdot\text{g}^{-1}$ at Lemon Creek. The lowest average Zn value, $157 \mu\text{g}\cdot\text{g}^{-1}$, was exhibited by Neck Creek sediments, however this value was similar to $176. \mu\text{g}\cdot\text{g}^{-1}$ reported for Lemon Creek.

Study area/large-scale contamination assessment: background comparisons, EFs

At all three marsh sites studied, mean Cd, Hg, Cu and Zn concentrations were greater than background values of these metals (Table 3; Figure 5). Although average Hg in Lemon Creek surface sediments was the most similar to the background (0.24 versus 0.18, respectively), mean surface concentrations significantly exceeded regional baseline levels for all metals studied (all p values < 0.00 ; LC Hg p value = 0.009).

Average metal-specific enrichment factors respective to each marsh studied are displayed in Table 4. Cd enrichment showed the greatest variability between sites; Cd levels were up to 32 times background at Main Creek, which was nearly two-fold the levels of Lemon Creek. Zinc enrichment factors were the most consistent among marshes. Mean surface Zn concentrations

exceeded background concentrations by a factor of 3 at Main Creek and up to a factor of 2 at both Neck Creek and Lemon Creek.

Hg concentrations in Main Creek and Neck Creek samples were up to 5 times greater than Lemon Creek samples and exceeded regional background levels by factors of 7 and 6, respectively. Cu concentrations were also significantly greater than Lemon Creek and varied between 15 and 13 times higher than background, at Main Creek and Neck Creek, respectively.

Small-scale spatial distribution of metals in surface sediments

Metal concentrations in Main Creek surface sediments

Metal analysis of all Main Creek surface sediment samples yielded concentration ranges of: 1.28-5.24 $\mu\text{g Cd}\cdot\text{g}^{-1}$, 0.03-2.52 $\mu\text{g Hg}\cdot\text{g}^{-1}$, 41.2-371 $\mu\text{g Cu}\cdot\text{g}^{-1}$, and 117-322 $\mu\text{g Zn}\cdot\text{g}^{-1}$ (Table 5). The lateral variation of all metals is shown in Fig. 6. Small-scale differences in average Cd concentrations were in the sequence $E < F < D < B < A < C$, as shown in Fig. 7a. Accordingly, the greatest mean Cd value reached 5.04 $\mu\text{g}\cdot\text{g}^{-1}$ at location C. However, similar values were reported for A and B (4.93 $\mu\text{g}\cdot\text{g}^{-1}$ and 4.04 $\mu\text{g}\cdot\text{g}^{-1}$, respectively). The lowest Cd value, 1.30 $\mu\text{g}\cdot\text{g}^{-1}$, was observed in sediments from E, although a comparable level was reported at F, which measured 1.62 $\mu\text{g}\cdot\text{g}^{-1}$.

Average Hg concentrations followed the order $F < E < D < C < B < A$. The longitudinal variation of Hg is shown in Fig 7b. The maximum Hg concentration, 2.44 $\mu\text{g}\cdot\text{g}^{-1}$, was achieved in samples from both A and B. Conversely, the lowest concentrations were detectable at locations F and E, 0.03 $\mu\text{g}\cdot\text{g}^{-1}$ and 0.04 $\mu\text{g}\cdot\text{g}^{-1}$, successively.

With respect to transect location Cu concentrations varied in the sequence $B < A < C < F < E < D$ and ranged from 352.5 $\mu\text{g}\cdot\text{g}^{-1}$ to 44.76 $\mu\text{g}\cdot\text{g}^{-1}$ (Fig.7c) The spatial variation of average

Zn concentrations were in the order $B < A < E < F < D < C$. The variation of Zn laterally is shown in Fig. 7d; the maximum Zn value reached $288.93 \mu\text{g}\cdot\text{g}^{-1}$ and the minimum level reported was $119.44 \mu\text{g}\cdot\text{g}^{-1}$.

Background comparisons; lateral variation of Enrichment Factors and small-scale spatial contamination trends at Main Creek

To variable degrees, Main Creek sediment samples demonstrated enrichment above background levels for all metals studied, as indicated by Table 6. The lateral variation of Main Creek EFs for Cd, Hg, Cu, and Zn is illustrated by Figure 8. The lowest Cd and Hg EFs were associated with location E (11.82 and 0.19, respectively), but were comparable to the low Cd and Hg sediment enrichment levels at F. Conversely, the lowest Cu and Zn EFs were found at B (3.20 and 1.47 greater than background, respectively), followed by A. The Cd and Zn EFs peaked in the mid-transect at C, reaching 45.8, 3.98 respectively. Values comparable to the maximum Cu EF, which ranged from 25.2-23.5 times background, were observed at locations D, E, F. Conversely, the greatest Hg EFs were found at the inland in locations A, B, C where Hg levels reached between 13.6-13.2 times higher than background. Sediment samples collected from locations A-C were the most enriched with Cd, while samples from locations D-F demonstrated the greatest enrichment by Cu.

Metal concentrations in Neck Creek surface sediments

The metal concentrations and ranges for Neck Creek surface sediment metal concentrations are shown in Table 2. Although detectable concentrations in all Neck Creek surface sediments varied from $0.82\text{-}2.76 \mu\text{g Cd}\cdot\text{g}^{-1}$, $0.63\text{-}1.59 \mu\text{g Hg}\cdot\text{g}^{-1}$, $60.9\text{-}249 \mu\text{g Cu}\cdot\text{g}^{-1}$, and $71\text{-}184.7 \mu\text{g Zn}\cdot\text{g}^{-1}$, the mean concentrations of all metals studied exceeded regional background values (Table 5). The order in which transect locations ranked, in terms of Cd, Hg, Cu, and Zn

concentrations, depended on the metal. The mean surface Cd concentrations, with respect to transect location, followed the order $C < E < B < D < A < F$ and ranged from $1.45 \mu\text{g} \cdot \text{g}^{-1}$ to $2.41 \mu\text{g} \cdot \text{g}^{-1}$ (Fig. 10a). Average Hg concentrations varied from 1.55 to $0.64 \mu\text{g} \cdot \text{g}^{-1}$ and were in the sequence $D < C < E < A < B < F$ (Fig 10b). Detectable Cu levels ranged from $100.19 \mu\text{g} \cdot \text{g}^{-1}$ to $248.62 \mu\text{g} \cdot \text{g}^{-1}$ (Fig. 10c). Surface sediment concentrations varied according to the following sequence: $C < D < B < A < E < F$. Neck Creek surface sediments demonstrated limited variability in terms of Zn content (Fig 10d). The minimum Zn concentration was observed at $105 \mu\text{g} \cdot \text{g}^{-1}$ within location C, but according to the order $C < B < D < E < A < F$, reached a maximum level of $185 \mu\text{g} \cdot \text{g}^{-1}$.

Background comparisons; lateral variation of EFs and small-scale spatial contamination trends at Neck Creek

Neck Creek surface sediments demonstrated significant but variable degrees of Cd, Hg, Cu and Zn enrichment (Table 3.2). The spatial variation of the EFs determined for each metal studied in Neck Creek surface sediments are depicted in Figure . Regardless of location along the longitudinal gradient, all samples showed the greatest sediment enrichment with respect to Cd, and successively less by Cu, Hg, and Zn. However, the spatial distribution of metal-specific EFs showed parallel enrichment trends. For all metals, the minimum EFs aligned with samples from mid-transect locations and the maximum EFs occurred at the most inland sampling location, as indicated by Figure 11. In terms of transect location, patterns were analogous; the spatial variation of the EFs determined for each metal, with respect to location show similar distribution patterns. The lowest EFs for Cd, Cu, and Zn were determined for transect location A as 13.18, 7.16, and 1.30, respectively, while the lowest Hg EF was observed at location D,

measuring 3.55. The greatest EF for all elements were demonstrated in samples from F, reaching 21.9, 8.63, 17.8, and 2.28 for Cd, Hg, Cu, and Zn, respectively.

Metal concentrations in Lemon Creek surface sediments

Metal values reported in Lemon Creek surface sediments ranged from 1.36-2.08 $\mu\text{g Cd}\cdot\text{g}^{-1}$, 0.06-0.35 $\mu\text{g Hg}\cdot\text{g}^{-1}$, 101-162 $\mu\text{g Cu}\cdot\text{g}^{-1}$, and 158-228 $\mu\text{g Zn}\cdot\text{g}^{-1}$ (Table 2). Mean Cd, Hg, Cu, and Zn concentrations demonstrated minor variability along the Lemon Creek surface sediment transect (Fig 12.). The spatial variation of average Cd concentrations were in the sequence $C < D < B < E < A < F$, as shown in Fig 13a. However, comparable Cd values were detected in Lemon Creek transect samples, ranging from 1.99 to 1.37 $\mu\text{g}\cdot\text{g}^{-1}$ at locations F and C, respectively. Average Hg concentrations varied from 0.34-0.07 $\mu\text{g}\cdot\text{g}^{-1}$ and followed the order $A < B < C < D < E < F$. Apart from the minimum value observed at location A, transect sampling locations exhibited generally similar mean Hg values.

Although the spatial variation of average Cu concentrations were in the sequence $E < F < C < B < A < D$, Cu values detected in Lemon Creek sediments were generally comparable (Fig. 13b). The lateral variation of Cd is shown in Fig.13a. The greatest difference in Cd was observed between locations D and E, where the maximum and minimum concentrations consecutively measured 151 $\mu\text{g}\cdot\text{g}^{-1}$ and 111 $\mu\text{g}\cdot\text{g}^{-1}$. The spatial variation of average Zn concentrations were in the sequence $C < B < D < F < E < A$ as shown in Fig. 13d. The lowest Zn value, 161 $\mu\text{g}\cdot\text{g}^{-1}$, was detected in samples from location C, whereas the greatest Zn concentration reached 191.07 $\mu\text{g}\cdot\text{g}^{-1}$ at location A .

Background comparisons; lateral variation of EFs and small-scale spatial contamination trends at Lemon Creek

Hg and Zn show similar distribution patterns, which characterized consistent sediment enrichment (Fig. 14). Cd and Zn EFs demonstrated more variable spatial trends, with respect to location though limited. The lowest EFs for Cd and Zn were detectable in sediments at C, reaching respective values of 12.47 and 1.99. Comparatively, the maximum EF for Cd was determined in samples from location F (18.12 times greater than background). The greatest Zn EF was observable at A, which reached a level 2.36 times higher than Zn background values. Hg EFs were ranged from 0.37 to 1.91 at A and E, respectively. The Cu EF profile shows a slight peak at D, where values were greater than background by a factor of 10.8. Conversely, the minimum Cu EF was associated with sediment from transect location D, which reflected concentrations that exceeded background by a factor of 7.94. Spatial comparison of sediments collected from downstream and upstream areas showed subtle differences with respect to metal enrichment. However, EFs were mainly similar for most metals, regardless of location along the Lemon Creek transect. Collectively, the relatively consistent enrichment levels failed to characterize a substantial pollution gradient, but demonstrated steady surficial contamination at Lemon Creek.

DISCUSSION

Temporal assessments of Main Creek, Neck Creek, and Lemon Creek cores established large-scale spatial contamination and site-specific degrees of recovery and attenuation, though recent deposits remained enriched with metals. Therefore, respective marsh sediments may continue to act as metal repositories. However, given that prior elemental analyses focused on a specified area within each system, much remained unknown in terms of the spatial distribution of metals over the areal extent of Main Creek, Neck Creek, and Lemon Creek. Furthermore, it was

unclear to what extent small-scale spatial variations contributed to the large-scale variability demonstrated by prior marsh assessments (Feng, et al., 1998). Accordingly, the present study accounted for small-scale spatial variations of metals to better characterize the extent of contamination in Main Creek, Neck Creek, and Lemon Creek surface sediments.

This research component first examined Cd, Hg, Cu, and Zn concentrations in sediments along longitudinal transects within each marsh system to characterize surficial distributions and sediment enrichment in upstream and downstream areas of prior Main Creek, Neck Creek , and Lemon Creek coring locations. Collectively, comparative assessment of site-specific sediment enrichment provided a comprehensive context to identify and evaluate large-scale spatial variability and trends. Thereby, this approach helped to discern the affect that small-scale variations of metals in Main Creek, Neck Creek and Lemon Creek marsh sediments have on broader pollution gradients for a greater understanding of spatial and temporal contamination throughout the study area (Ray, et al., 1995; Feng, et al, 1998). Furthermore, an examination of lateral variations of Cd, Hg, Cu, and Zn enrichment identified the affect of natural and/or anthropogenic factors and thereby, determined if surficial contamination at Main Creek, Neck Creek , and Lemon Creek is a consequence of enhanced deposition from localized inputs and marsh dynamics or, conversely, attributable to a prevalent source of pollutants (Aalto, et al., 2005). Site-specific spatial distributions and pollutant patterns were also evaluated at Main Creek, Neck Creek and Lemon Creek to further assess the impact of upstream versus downstream metal sources within each marsh-creek system. Specific objectives were to examine if connectivity to the Arthur Kill or site-specific terrestrial sources affect small and large-scale spatial variability of metals and the extent of anthropogenic pollution throughout the study area.

Large-scale spatial assessment of metals in surface sediments

Comparison of average surface metal concentrations in marsh transects

Marshes surrounding Staten Island demonstrated large-scale spatial variability in terms of the distribution of metals in surface sediments. Analysis of sediments at similar depths permitted comparisons between the marshes studied (ref). Average total metal concentrations in Main Creek and Lemon Creek sediments decreased in the sequence $\text{Zn} > \text{Cu} > \text{Cd} > \text{Hg}$. In contrast, the mean Cu value was greatest in Neck Creek sediments, though comparable to the mean Zn concentration ($174.9 \mu\text{g Cu}\cdot\text{g}^{-1}$ and $156.7 \mu\text{g Zn}\cdot\text{g}^{-1}$).

Compared with previous discrete surface samples collected from each marsh system, mean sediment concentrations from Main Creek and Neck Creek transects were mainly lower, whereas total metal values at Lemon Creek were slightly higher or comparable (Feng, et al, 1998). Nevertheless, the present study demonstrates that considerably different metal concentrations remain apparent throughout the study area; the greatest mean metal concentrations were observable at Main Creek, Neck Creek and Lemon Creek, consecutively. Although Main Creek consistently ranked the highest in terms of all metals studied, only the mean value for Cd ($3.46 \mu\text{g}\cdot\text{g}^{-1}$) was significantly greater than Neck Creek and Lemon Creek values ($1.9 \mu\text{g}\cdot\text{g}^{-1}$ and $1.61 \mu\text{g}\cdot\text{g}^{-1}$, respectively).

Assessment of metal enrichment by comparison with regional background concentrations

In this study, regional uncontaminated sediments served as a proxy for metals inherently present in the Earth's crust (Gurrierri, et al., 1998; Tomlinson, et al., 1980; Ray, et al., 2006). Comparatively, surface sediments from all study marshes contained average metal concentrations that exceeded local data used to represent background sediment values. Accordingly, this background sediment approach determined that the mean surface levels of Cd, Hg, Cu and Zn detected at Main Creek, Neck Creek and Lemon Creek were above the range that

could be associated with natural processes that cycle metals (Hwang, et al., 2006). Therefore, anthropogenic contamination was evident in marsh surface sediments throughout the study area. However, the extent to which reported elements were higher than regional background concentrations depended on the metal species and marsh system.

An examination of marsh-specific metal concentrations with respect to background determined enrichment factors helped describe the severity and type of metal contamination throughout the study area. Therefore, the magnitude that Main Creek, Neck Creek and Lemon Creek sediment samples exceeded background concentrations served as a measure to characterize large-scale spatial trends (Wedepohl, et. al., 1971; Tomlinson, et al., 1980; Gurrierri, et al., 1998; Ray, et al., 2006;). In general, an increasing order of surface enrichment was observed ($LC < NC < MA$) for most metals studied in Staten Island marsh sediments. Furthermore, except for Zn, marsh sediments from the western margin of the study area (NC and MA) demonstrated significantly greater anthropogenic metal contamination than sediments analyzed from the southern shore (LC). Although Lemon Creek exhibited metal concentrations that were generally the closest to the local background values and thereby the least affected by anthropogenic contributions, the significantly greater levels of Cd, Hg, Cu, and Zn characterized by all marsh study sites, in comparison with background concentrations, confirmed the widespread impact of anthropogenic pollution sources (Hwang, et al., 2006).

The degree of Cd enrichment showed the greatest variability over the entire study area; reaching up to 32 times background at Main Creek, which was nearly two-fold the levels of Lemon Creek. Conversely, the level of Zn enrichment observed within the study marshes varied the least. However, Zn values exceeded background concentrations by a factor of 3 at Main Creek, and up to a factor of 2 at both Neck Creek and Lemon Creek. In contrast to the

consistent Zn enrichment trend, Hg concentrations in Main Creek and Neck Creek samples were up to 5 times greater than observed in Lemon Creek samples and exceeded regional background levels by factors of 7 and 6, respectively. The comparable magnitudes of Cu demonstrated by Main Creek and Neck Creek surface sediments, which reached levels up to 15 times higher than background, were also significantly greater than levels detected in Lemon Creek surface sediments.

Large-scale spatial variability and study area anthropogenic pollution gradient

Overall, in addition to describing large-scale spatial differences and identifying the anthropogenic component of metals observed in surface sediments, site-specific enrichment factors also emphasized similarities among the marshes that border the Arthur Kill. Specifically, although enrichment factors were highly variable (both between, but also within certain sites like MA on small and large scales) throughout the study area, the comparable levels of Hg, Cu, and Zn in Main Creek and Neck Creek sediments established that in comparison with Lemon Creek, marshes along western shore of Staten Island demonstrated considerably greater magnitudes of most metals. The lower extent of metal contamination exhibited by Lemon Creek surface sediments aligns with observations based on prior coring studies within the same marsh-creek systems (Chapter.2). Accordingly, on both spatial and temporal scales, comparative pollution assessments at Main Creek, Neck Creek and Lemon Creek were consistent; large-scale distribution patterns and enrichment trends revealed a pollution gradient over the extent of the study area (AK sites > LC).

Small-scale spatial assessment

Site-specific assessments of average Cd, Hg, Cu, and Zn in the Staten Island marshes studied established that anthropogenic pollution is present on a broad scale. In addition, comparison of metal enrichment in Main Creek, Neck Creek and Lemon Creek sediments confirmed a large-scale gradient defines surficial contamination throughout the study area. Albeit to different extents, depending on marsh and element studied, lateral Cd, Hg, Cu, and Zn distributions demonstrated spatial variability of metal contents/accumulation and pollution loads is present on small spatial scales as well.

Examination of metal accumulation in surface sediments collected from different locations along longitudinal transects at Main Creek, Neck Creek and Lemon Creek helped to assess the probable influence of both natural and anthropogenic factors within each marsh to further describe the magnitude and type of anthropogenic contamination and identify site-specific and regional impacts. Furthermore, evaluation of small-scale variability of Cd, Hg, Cu, and Zn helped characterize spatial (landward-seaward) contaminant trends to compare upstream and downstream areas to consider site-specific marsh dynamics, recognize localized sources and further understand terrestrial/estuarine influences on metal transport and fate within each system.

Longitudinal distribution of metals in Main Creek surface sediments

Main Creek exhibited the most complicated lateral metal distributions. Concentrations of all metals (Cd, Hg, Cu, and Zn) studied in the six Main Creek surface sediment samples exhibited high spatial variability. Overall, Main Creek surface sediments demonstrated inconsistent, metal-specific distribution patterns. Of all the elements studied, Zn concentrations showed the most uniformity, which is consistent with both temporal and broad-scale spatial patterns. Nevertheless, lateral metal profiles revealed highly variable Cd, Hg, Cu, and Zn concentrations in Main Creek surface sediments and established that metal loads at downstream

and upstream sites were distinctly different. Compared with Main Creek surface sediments from the upstream location, the extent of Cd and Hg contamination in downstream sediments was demonstrably greater (3 and 70 times greater, respectively). Conversely, Zn and Cu concentrations were predominately lower in downstream samples. Compared to downstream sediments (recovered from MA transect locations A and B), Cu and Zn concentrations were consistent (ranging from 323.05-329.2 $\mu\text{g Cu}\cdot\text{g}^{-1}$ and 250.45-267.32 $\mu\text{g Zn}\cdot\text{g}^{-1}$) and greater (Cu 5:1, Zn 1.7:1) in upstream sediments (E and F).

Although variable degrees of enrichment were obvious along the Main Creek spatial gradient, it is noteworthy that Cd, Cu, and Zn were present at levels that exceeded regional background values, regardless of location. In comparison with Hg background levels, substantially higher Hg values (13.6-13.2 greater than regional background levels) were limited to samples from the locations most proximal to the Arthur Kill; sediments east of the mid-transect location (~5200m) dropped lower than regional Hg background. Therefore, evaluation of the metal-specific EFs indicated that apart from the two most eastward sites, all transect locations were contaminated with Cd, Hg, Cu, and Zn. Although the greatest magnitude of Cd, Cu, and Zn occurred in mid-transect samples, maximum Cu and Zn EFs were comparable with upstream sediments, which were 25.2-23.5 and 4-3.1 fold Cu and Zn background values, respectively. Nonetheless, the obvious Cd, Hg, Cu and Zn enrichment observed laterally throughout Main Creek confirms surface sediments are subject to anthropogenic contributions from upstream and downstream metal sources.

In general, the relationship between distance upstream and EF described two small-scale spatial trends that characterized Main Creek surficial contamination. Spatially, Cd and Hg

demonstrated similar distribution/enrichment patterns that contrasted with the trends illustrated by Cu and Zn. With respect distance from the Arthur Kill, proximal sediments exhibited considerably greater Cd and Hg EFs and substantially lower Cu and Zn EFs than were determined at the eastward (inland) transect locations. Accordingly, concentrations of certain metals (Cu and Zn) show a relatively inverse relationship with marsh surface inundation (distance upstream). Alternatively, Cd and Hg show a relatively opposite pollutant pattern (Wood, et al., 2005).

The greater magnitude of Cd and Hg in downstream sediments suggests an active source contributes metal-specific loadings; which consequently elevated surficial enrichment. Location B is immediately beneath a roadway overpass. However, Cu and Zn are more commonly associated with street runoff than Cd and Hg. It may be possible that the least inundated sediments are accumulating higher levels of certain metals from tidal exchange with the Arthur Kill or localized inland terrestrial source. This may imply that tidal inundation causes dilution of Cu (and to a lesser degree Zn) enriched sediments within the water column.

The apparent difference in metal enrichment observed in samples A-C versus D-F primarily defined the inconsistency recognized between the analogous Cd and Hg trends and Zn distribution trends. However, limited similarities among all metals were observable at Main Creek. In particular, all metals were relatively steady between E-F. Furthermore, Cd, Cu and Zn levels fluctuated to variable degrees from A-C which, in part, may be explained by the comparatively smaller distance between A and B (100m) than measured between all other locations (200m).

Overall, the greatest metal load was determined at mid-transect location C, which is largely attributable to the concurrent maximum EFs for Cd and Zn. Peak Cd and Zn pollution exceeded background by factors of 45.8 and 4, respectively, and Hg reached levels that were comparable to the maximum value (13.2 times higher than background values) at C.

Depending on location within the system, surface sediments were more enriched with Cd or Cu than any other element studied. Lateral metal profiles indicated a transition occurred mid-transect where the decreasing eastward trend of Cd and increasing westward trend of Cu converged. Accordingly, at greater distances from the Arthur Kill lower EFs were determined for Cd than Cu. Therefore, Cd dominated Main Creek surficial contamination in sediments from downstream through mid transect sites (44.8-35.0 times background), but sediments from the upland marsh habitat (E-F) exhibited a greater degree of Cu pollution (23.1-23.5 greater than background). The evident intramarsh variations in anthropogenic metal enrichment levels, reflected by site-specific EFs and relative contribution to the inconsistent surficial pollutant loads demonstrated throughout this marsh-creek system, may be due to metal-specific inputs derived from localized watershed sources..

The evident spatial disparities established episodic degrees of metal pollution at Main Creek also indicates that complex biogeochemical processes, in combination with site-specific loadings from multiple sources, were likely major factors for the distinct small-scale variations and complicated areal contamination, which characterized Main Creek. Thereby, variable depositional dynamics may influence the fate and transport of metal loadings, which are possibly related to the dual impact of local terrestrial and estuarine inputs and likewise, may explain the

analogous Cd and Hg trends and account for the comparatively, inverse relationship/opposite pattern depicted by the lateral distributions of Cu and Zn.

Longitudinal distribution of metals in Neck Creek surface sediments

The distribution of metals in Neck Creek surface sediments showed less variability than characterized at Main Creek. Lateral Cd, Hg, Cu, and Zn profiles show similar distribution trends in which all metals fluctuated in accordance with each other. The maximum value of all metals ($2.41 \mu\text{g Cd} \cdot \text{g}^{-1}$, $1.55 \mu\text{g Hg} \cdot \text{g}^{-1}$, $248.62 \mu\text{g Cu} \cdot \text{g}^{-1}$, and $184.7 \mu\text{g Zn} \cdot \text{g}^{-1}$) corresponded with sediments from F, the most upstream sampling location. Minimum metal concentrations were identified at the mid-transect locations. The lowest values of Cd, Cu, and Zn were found at C ($1.45 \mu\text{g} \cdot \text{g}^{-1}$, $100.2 \mu\text{g} \cdot \text{g}^{-1}$ and $105.2 \mu\text{g} \cdot \text{g}^{-1}$, respectively), while the lowest Hg level was detectable at D ($0.64 \mu\text{g} \cdot \text{g}^{-1}$). Accordingly, the spatial distribution of metals in Neck Creek surface sediments showed a decreasing trend from the downstream to mid-transect locations, followed by an increasing trend between the mid-transect and inland locations.

Small-scale evaluation of Neck Creek sediments identified variable degrees of enrichment throughout the areal extent of the marsh transect. Spatial assessment of metal-specific EFs established that irrespective of location within the system, all surface sediments demonstrated Cd, Hg, Cu, and Zn contamination. Regardless of location along the longitudinal gradient, all Neck Creek samples showed the greatest sediment enrichment with respect to Cd, and successively less by Cu, Hg, and Zn. Laterally, Cd, Hg, Cu, and Zn illustrated parallel enrichment patterns that collectively demonstrate a specific trend with respect to distance. However, the analogous spatial variations in terms of sediment enrichment resulted in relatively

equivalent inter-elemental ratios, particularly with respect to the level of Cd enrichment; Cd EFs were generally greater than Cu and Zn by a factor of 1.5 and 9, correspondingly.

Apart from the spatial variations demonstrated by the maximum upstream EFs (21.9, 8.6, 17.8, 2.3 times background, respectively) and the substantially lower mid-transect EFs for Cd, Hg, Cu, and Zn (greater than background by factors of 13.2, 3.6 respectively), Neck Creek sediments showed comparable levels of metal-specific enrichment. Therefore, although concentrations/EFs were greatest upstream, minor lateral variations of each metal throughout the areal extent of the Neck Creek transect limited fluctuation of surface metal loads.

Overall, an indeterminate relationship between contamination magnitude of metal contamination and distance from the Arthur Kill characterized Neck Creek surficial pollution. It is noteworthy that surficial metal concentrations are evidently higher east and west of transect site C, which is ~ .5 m upland of a roadway overpass that transverses Neck Creek. Accordingly, the relatively lower surficial metal contents observable at transect site C suggest that the concrete foundation that replaces the sediment substrate west of the site, results in quicker currents and slower deposition. In contrast, it is likely that low tidal energy promotes settling and deposition of metals with increasing distance from C and that these processes are intensified at the most upstream areas. Alternatively, in the westward direction this trend demonstrably decreases until mid-transect. However, an increasing enrichment trend is particularly defined between the mid-transect and inland locations, which suggests upland sediments act as a sink for metal pollutants (Rozan, et al., 1999). This finding may imply that chemical constituents enter the upland marsh environment and accumulate in the sediment bed, which functions as a reservoir that primarily concentrates, rather than supplies, metals to the system.

The small-scale pollution gradient observed in the inland/eastward reach of the Neck Creek transect suggests the least inundated sediments are accumulating metals from a localized terrestrial source. This may indicate that tidal inundation causes dilution of metal-enriched sediments within the water column. Possible terrestrial sources include stormwater impacts and street runoff. However, samples from transect location C, which is located in close proximity to a roadway overpass and stormwater conveyance infrastructure, generally showed the lowest concentrations of most metals. Alternatively, tidal transport from a major downstream source could concentrate metals within the upstream sediments. Likewise, the Arthur Kill may serve as a source of metals, via resuspension of legacy contamination or current pollutant loadings associated with multiple point and non-point sources.

Longitudinal distribution of metals in Lemon Creek surface sediments

Surficial Cd, Hg, Cu, and Zn concentrations throughout the Lemon Creek marsh system were substantially lower and generally less variable than observed within Main Creek and Neck Creek surface sediments. Furthermore, compared with the Arthur Kill marshes, the range of metal concentrations detected at Lemon Creek were considerably smaller ($1.99\text{--}1.37\ \mu\text{g Cd}\cdot\text{g}^{-1}$, $0.07\text{--}0.34\ \mu\text{g Hg}\cdot\text{g}^{-1}$, $151.20\text{--}111.19\ \mu\text{g Cu}\cdot\text{g}^{-1}$, and $191.07\text{--}160.88\ \mu\text{g Zn}\cdot\text{g}^{-1}$). Apart from a few subtle variations, most metals were, for the most part, uniformly distributed without any particular spatial pattern.

Cd, Cu and Zn concentrations exceeded background levels regardless of location along the Lemon Creek lateral transect. In contrast, only locations greater than ~900m north of the Raritan Bay showed Hg enrichment at levels indicative of anthropogenic pollution. In samples

from the two most proximal locations to the Raritan Bay, Hg measured less than half ($0.07 \mu\text{g} \cdot \text{g}^{-1}$) and equal to the regional background value ($0.18 \mu\text{g} \cdot \text{g}^{-1}$) at A and B, respectively.

The extent of enrichment exhibited by Lemon Creek sediments was metal-dependent. Throughout the span of the Lemon Creek transect, sediments demonstrated the greatest enrichment by Cd, and successively less by Cu, Zn. On average Cd EFs (18.1-12.5 times greater than background) were 1.6 and 6.7 higher than Cu and Zn EFs, respectively. In contrast with Main Creek and Neck Creek, all Lemon Creek sediments exhibited the least enrichment by Hg. Evaluation of EFs along the Lemon Creek longitudinal transect confirmed that Lemon Creek surface sediments are generally less contaminated than Main Creek and Neck Creek sediments and all locations serve as depositional areas for sediment bound metals. Spatially, all elements fluctuated. However metal-specific enrichment peaks were predominately minimal, unsystematic, and inconsistent. Of all the elements studied, the longitudinal variation of Zn EFs (2.4-2.0 times) demonstrated the most uniformity, which is consistent with Main Creek small-scale trends and temporal and broad-scale spatial patterns, as previously mentioned.

Apart from Hg, no substantial contamination trends were evident in upstream versus downstream sediments because relatively similar magnitudes of Cd, Cu, and Zn enrichment were observable throughout the Lemon Creek study area. Collectively, Cd, Cu, and Zn enrichment patterns were relatively steady and thereby, mainly analogous with respect to distance from the Raritan Bay. In contrast, the comparatively lower Hg EF identified in downstream sediments revealed Hg contamination increased in accordance with distance upstream. Consequently, this finding influenced the otherwise consistent surficial contamination, and resulted in a subtle

pollution gradient in which sediment samples exhibited successively greater total metal loads towards the northern extent assessed at Lemon Creek.

Comparison of Main Creek, Neck Creek and Lemon Creek transects

Assessments of the lateral distribution of metals along spatial gradients at Main Creek, Neck Creek and Lemon Creek established that all sites demonstrated small-scale variations, which define different metal trends and magnitudes of contamination. As expected from mean surface concentrations, relatively similar levels of Zn were detectable in all three transects. However, lower Cd, Hg and Cu values were observable in Lemon Creek surface sediments than exhibited by Main Creek and Neck Creek transects.

According to evaluations with regional background metal concentrations in local sediments, sediment quality in all systems indicated significant enrichment levels (Bowen, et al., 1980; Hirschberg, et al., 1994; Valiela, 1995; Bopp, et al., 2006). Small-scale assessments revealed that apart from Hg, all sites exhibited Cd, Cu, and Zn pollution throughout the areal extent of each site. Therefore, anthropogenic metal contributions affect marsh quality throughout the study area.

Between transect locations, sediment metal concentrations detected in Main Creek samples exhibited the greatest spatial variability, while sediments of the Lemon Creek transect demonstrated the least variations. Likewise, lateral contaminant trends were successively less erratic within Main Creek, Neck Creek and Lemon Creek. The episodic concentrations observed in Main Creek surface sediments characterized variable surficial contamination. Conversely, the relatively constant Cd, Hg, Cu, Zn concentrations identified along Neck Creek and Lemon Creek longitudinal transects suggested consistent surface sediment contamination (Aalto, et al., 2005).

Spatially, the minor longitudinal variations demonstrated by Neck Creek contrasted with the episodic pollutant patterns exhibited by Main Creek; however, both sites showed comparable ranges of magnitudes of Hg, Cu, and Zn enrichment/contamination and similar sediment composition. Conversely, the Lemon Creek transect exhibited the least variable metal contents and demonstrated the greatest heterogeneity in sediment composition and distance between locations. Although the Arthur Kill marshes demonstrated site-specific metal variations, the inconsistent small-scale trends did not affect the overall comparable degree of metal pollution associated with Main Creek and Neck Creek, but rather, substantiated the large-scale pollution gradient in temporal and surficial contamination.

Localized marsh dynamics: natural biogeochemical and physical processes

Metals are associated with marsh sediments in a variety of ways, which can influence the mobility and distribution of metals on both large and small spatial scales (Ahumada, et al., 1999). Given that the spatial distribution of naturally-occurring radionuclides may be considered to be uniform, ^7Be activities were previously studied in Main Creek, Neck Creek and Lemon Creek sediments to discern the broad-scale variability of metal distributions (Borole, et al., 1982; Toole, et al., 1987; Ray, et al., 1995; Feng, et al., 1996; Feng, et al., 2002). In addition, analysis of samples containing detectable ^7Be activities indicated that (at least) the contaminated surface sediments at Main Creek, Neck Creek and Lemon Creek contained metals that were scavenged from the water column and deposited, within a year of collection (Bacon et al., 1976; Bopp et al., 1993; Feng et al., 1996; Chai et al., 2004).

Altogether, the conflicting ^7Be activity (see Chapter 2) distributions suggested various physical, chemical, and/or biological factors influenced the transport, deposition and redistribution of sediment bound constituents (i.e. radionuclides and metals) (Feng, et al., 2002;

Bopp, et al., 2006). Accordingly, localized environmental settings and sediment dynamics characterized by the study marshes were major factors governing transport and fate of contaminants within each system (Fox, et al., 1999; Sarin, et al., 1994; Boisson, et al., 2001). The unique depositional contexts that projected the geographic variability/broad-scale differences with respect to temporal metal distributions, may also relate to and explain the inconsistent small-scale spatial patterns (Weis, et al., 2005; Aalto, et al., 2005). However, the degree of metal enrichment and the contaminant trends identifiable with Main Creek, Neck Creek and Lemon Creek largely relied on observed results from analysis of multiple cores collected within a particular area of each marsh (see Chapter 2). Nevertheless, site-specific physical/biogeochemical processes likely played a role in the lateral metal distributions and dissimilar intra-spatial enrichment trends characterized by the three marshes (Aalto, et al., 2005; Weis, et al., 2005).

Biogeochemical factors

Small-scale differences in metal concentrations may reflect variations in the natural environment at Main Creek, Neck Creek and Lemon Creek which may result from many physical, chemical and biological processes (Förstner, 1976). Likewise, site-specific geomorphological and hydrographical conditions may have influenced the longitudinal variations demonstrated by each marsh transect (Perttilä, et al., 1991; Neumann, et al., 1997). In contrast to the consistent mudflats which characterized the Main Creek and Neck Creek transects, spatial variability of the sediment substrate was visually evident between the downstream sampling location and the mid-transect locations within the Lemon Creek study area.

Metal contents are expected to be correlated with grain size distribution; the inverse relationship between sediment concentration and particle size implies greater metal values in sediments having greater mud content (i.e. silt and clay) (Balcolm, et al., 2008). Therefore, the fine-grained fraction of all sediment samples were analyzed in order to disregard the influence that variable sediment grain size has on metal distributions (Forster, et al., 1981; Prasad, et al., 2006). Accordingly, biases based on particle size were limited, and may not account for slight small-scale variations observed within Lemon Creek or the large-scale spatial variability throughout the study area.

Biological characteristics of tidal marshes, including the occurrence of emergent vegetation, and bioturbation, can also facilitate both small-scale and large-scale spatial variability of metals within surface sediments (Du Laing, et al., 2008). To circumvent the complication of bioturbation, transect sampling locations that did not show physical evidence of biological disturbance were selected. However, various biogeochemical factors may have affected the surficial distribution trends characterized by Main Creek, Neck Creek and Lemon Creek. Accordingly, the broad-scale contamination gradient may, in part, be a collective result of variable environmental conditions among transect locations and marshes (Muller, 1999).

Although the determination of different chemical species, bonding forms or phases present in sediment was beyond the scope of this study, chemical speciation can also exert important controls on trace metal cycling in sediment and overlying water column in estuarine environments (Loska and Wiechula, 2002). For example, Mn-Fe oxides, can act as efficient scavengers for many metals, including Cu and Zn, which can also be associated with Fe-Al oxides in sediment (Singh and Subramaniam, 1984; Kabata-Pendias and Pendias, 1991).

Accordingly, these metals effectively adsorb to colloids and can form both soluble and insoluble complexes with many kinds of organic substances (Jenne, 1968).

Given that many sediment properties and chemical factors (i.e. organic matter, pH and ionic strength) influence metal retention (i.e. adsorption/desorption), variations regarding physical, chemical and/or textural characteristics, which are expected in marsh-creek sediment substrates, likely affected the lateral Cd, Hg, Cu, and Zn distributions depicted by Main Creek, Neck Creek and Lemon Creek transects (Lee, et al., 1990; Peijnenburg, et al., 1997). For example, Zn adsorption is largely influenced by available cation exchange sites (the negative sites that can absorb cations), which, in turn, are highly dependent upon soil texture and organic matter content (Coleman and Thomas, 1967). Accordingly, the spatial distribution of certain metals may be associated with organic matter. Thereby, increased concentrations observed between transect locations and marsh sites may be attributable to individual elemental associative properties with organic matter. Although the relationship/proportion of metals bound to organic matter was beyond the scope of this study, detrital bonds were likely important for Cu and Zn (Muller, 1999.) Therefore, in contrast to the non-biogenic elements analyzed (i.e. Cd and Hg), the lateral transport processes that are important for the distribution pattern of organic matter may also strongly influence the spatial variability of the biogenic metals studied (i.e. Cu and Zn) (Muller, 1999.)

Greater sediment concentrations of certain metals may also be related to the complex interaction of pH and dissolved oxygen of water and pH of sediment, which control the solubility of different elements (Ahrland, 1975). For instance, Cd solubility is strongly related to pH and may be largely controlled by organic matter when present in acidic sediments (Tiller, et al., 1979; Soon, 1981). Cd is not easily mobile in sediments with high pH, and Zn becomes

insoluble when values are higher than 6 (Kabata-Pendias and Pendias, 1991). Furthermore, depending on water column pH, minerals within sediment can react to adsorb specific metals (i.e. Cu) (Thompson and Troeh, 1978).

Similar regional and global studies have demonstrated that physical, as opposed to chemical, processes predominately affect spatial distribution trends (Bonnevie, et al. 1997, Neumann et al., 1996; Emeis, et al., 1998). However, the occurrence of different binding types may be important, particularly at different depths of the sediment column, and chemical partitioning can be integral in contamination assessments (Neumann, et al., 1996; Muller, 1999; Emeis, et al., 1998). Spatial assessments at Main Creek, Neck Creek and Lemon Creek focused on spatial variations of total metals to characterize surficial pollution, rather than analysis of chemical partitioning/binding forms of metals present in the sediments. Therefore, many biogeochemical factors were not specifically examined, but are discussed here to consider that (to an indeterminate extent) longitudinal variations may reflect changing environmental conditions, which cause differences in a variety of systemic dynamics including the transport and sedimentation patterns of particulates, the occurrence of migration processes and bond types (Muller, 1999).

Physical processes

Fluctuating/irregular physical factors, including differential tidal currents, flows, freshwater inputs, water table levels and bottom shear stress (which is associated with water depth, creek morphology, and hydrodynamics), likely affected deposition and redistribution of particulates (i.e. sediments and metals) within each marsh (Ullman, et al., 1998; Du Laing, et al., 2008). Therefore, variable physical processes and localized dynamics resulted in site-specific longitudinal variations/small-scale distribution trends, which collectively attributed to the large-

scale variability of inter-spatial contamination. This finding is consistent with prior observations, which demonstrated that sediment dynamics (i.e. deposition/erosion), transport, and fate were marsh-dependent, regardless of geographic proximity or location within the study area (i.e. western shore vs. eastern shore; connectivity with the AK vs. RB). However, it may be plausible that site-specific variables may have affected the systemic processes that govern metal deposition and contributed to relatively greater concentrations/enrichment/pollution identified in Main Creek and Neck Creek surface sediments (Feng, et al., 2002; Wan, et al., 2005; Aalto, et al., 2005).

In shallow marsh environments, relatively weaker bottom currents and shear stress can inhibit resuspension and redistribution of all deposited sediment bound metals; thereby, fine-grained deposits tend to accumulate in these areas, as confirmed by the observed composition of inland sediments from all sites (Ullman, et al., 1998; Weis, et al., 2005). Conversely, where tidal flows effectively resuspend and transport sediments (presumably in downstream areas near confluence with the AK/RB), net particle and associated contaminant accumulation was expectedly more limited. This dynamic may explain the slightly increasing trend in the inland direction at Lemon Creek, but rather was more likely to have occurred in the mid-transect area at Neck Creek and not obvious at any Main Creek site. In contrast, the inconsistencies observed in the metal trends at Main Creek suggested that at no particular location was metal accretion limited for all elements, which may be attributable to the greater inland distance of the downstream sites, compared with Neck Creek and Lemon Creek.

Downstream Lemon Creek sediments, particularly those proximal to the Raritan Bay, were mainly mud veneered with rubble, shell hash, and gravel. Thereby, this field description indicated that the bottom sediment in this area is subject to highly energetic tidal currents and

flow (Ullman, et al., 1998). Given that all samples were normalized by grain size prior to metal analysis, heterogeneous sediment composition identified at Lemon Creek is not correlated to the overall lower pollution, compared with the Arthur Kill sites. Furthermore, the relatively coarser sediments and higher sand content characterized at Lemon Creek transect locations A and B may not explain the lower metal contents in downstream sediments.

Sediment dynamics

Collectively, Main Creek, Neck Creek and Lemon Creek transects illustrate differential spatial variability and small-scale metal enrichment trends, which may be attributable to variable sediment dynamics within each system. Prior analysis of samples containing detectable ^7Be activities indicated that (at least) the contaminated surface sediments at Main Creek, Neck Creek and Lemon Creek, contained metals that were scavenged from the water column and deposited, within a year of collection (Feng, et al., 1999; Bopp, et al., 2006). ^7Be analysis found Neck Creek sediment dynamics contrasted with the similar deposition rates characterized in Main Creek and Lemon Creek surface sediments. The considerably higher inventories of detectable ^7Be identifiable with Main Creek and Lemon Creek implied sediment accumulation rates were comparatively lower at Neck Creek (see Chapter 1).

Episodic sediment accumulation along the Main Creek longitudinal transect may have contributed to the inconsistent small-scale metal distribution trends identifiable within this site. Conversely, more consistent sediment accumulation may have influenced the considerably greater spatial uniformity characterized within Neck Creek and Lemon Creek (Aalto, et al., 2005; Weis, et al., 2005). This research component confirmed that throughout the extent studied at Main Creek, Neck Creek and Lemon Creek, all areas acted as depositional environments for particle-associated metals. Therefore, areas of increased deposition may affect site-specific

surficial trends; however fewer depositional areas and lower accumulation rates do not solely explain the lower metal concentrations/enrichment at Lemon Creek.

Spatial variation of sediment properties, and consequently metal contents, are generally expected within the study marshes, however they may be exacerbated by anthropogenic activities (Prasad, et al., 2006). Therefore, although further studies are required for a better understanding of the effect of natural processes (i.e. role of oxidation, subsequent acidification and weathering) on the mobilization, redistribution and dispersion of metals in Main Creek, Neck Creek and Lemon Creek, the calculated EFs suggests/confirms that metals in the Main Creek, Neck Creek and Lemon Creek sediments are influenced by anthropogenic contributions (Tam, et al., 2000). The high metal values found in all three systems studied indicate that a combination of discrete and widespread sources related to anthropogenic activities impact the environmental integrity of the entire region. Localized inputs linked to anthropogenic activities also played a role in the greater contamination at the Arthur Kill sites.

Anthropogenic factors suspected to influence metal enrichment in Main Creek, Neck Creek and Lemon Creek sediments

The results obtained from metal analysis were used to determine large-scale and small-scale spatial distribution of metals but also potential regional/pervasive and localized sources of these metals to Staten Island marsh environments. The EF values calculated throughout the span of Main Creek, Neck Creek and Lemon Creek transects often substantially exceeded 1, which indicates all study metals can be considered to be largely anthropogenic, rather than terrigenous, in origin. However, reported EFs show the concentration and distribution of certain metals are greatly influenced both by natural and anthropogenic sources. Cu and Zn exhibited the highest metal concentrations in sediments throughout the study area, however, Cd and Cu primarily

dominated surficial enrichment. This demonstrated the chemical composition of the parent rock/bedrock is a major contributor to the high Zn concentrations found throughout the study area. Accordingly, respective contents and variability of metals observed in Main Creek, Neck Creek and Lemon Creek sediments are not solely associated with natural environmental factors (i.e. geology and weathering), but rather are further affected by anthropogenic inputs, which augment the natural components (Prasad, et al., 2006).

Suspected regional sources

Urban runoff, wastewater, CSOs and treatment plant effluents, petroleum refineries and fossil fuel burning have been shown to be regional sources of all study metals (Cd, Hg, Cu, and Zn) (Whipple, et al., 1976; Ellis, et al., 1980; Zoller, et al., 1983; Mytelka, et al., 1993). Clean Water Act legislation has reduced metal contaminated effluents from industrial and commercial point sources. However, few preventative measures control metal contributions from non-point sources (Bakan and Ozkoc, 2007). Accordingly, metal inputs to waterways have decreased. However non-point sources continue to contribute metals to receiving waters and marsh habitats (Rose, et al., 2007). Therefore, anthropogenic activities and changing land uses heavily influences the environmental quality of the entire study area (Suskowski, et al., 2006).

In addition to various environmental stresses related to increased development pressures, the high metal content in Main Creek, Neck Creek and Lemon Creek surface sediments indicated a combination of discrete and widespread sources affect each site. Given that stormwater runoff drains into marshes, the degree to which runoff becomes polluted is related to land-uses in surrounding watersheds (BMP). Non-point source metal loadings enter Main Creek, Neck

Creek and Lemon Creek via dry weather and stormwater runoff derived from industrial, urban and residential land-use activities. Industrial and manufacturing facilities, motor vehicles and transportation infrastructure, municipal, commercial, and residential construction sites, and maintenance operations (i.e. phosphate fertilizers, insecticide application, atmospheric deposition, (Cu one) may serve as regional non-point sources of anthropogenic metals to Main Creek, Neck Creek and Lemon Creek. Collectively, even small metal inputs from a multitude of potential sources can compromise the environmental quality of all the study marshes. Therefore, it is likely that regional non-point source contributions may explain the widespread Cd, Hg, Cu, and Zn contamination that is apparent over the extent of the study area.

Metal-specific contamination sources

Of all the elements studied, Zn concentrations were the most consistent on both large and small spatial scales, whereas the Cd, Hg, and Cu distributions were less consistent. A possible Zn source may be associated with port activities (i.e. loading and offloading, ballasting and antifouling applications). However, it is apparent that Zn is extensively available throughout the extent of the study area. The major contributors of anthropogenic Zn may be attributable to atmospheric deposition, stormwater runoff and motor vehicle transportation. Zn is prevalent in air and, in relation to the other study metals, atmospheric values of Zn are comparatively higher. Traffic is another noteworthy source of Zn deposition (Franco, 2005). The combined impact of these sources likely explained the consistent levels and large-scale Zn contamination (Otabbong, et al., 2002). Additional localized sources of Zn loads in Main Creek, Neck Creek and Lemon Creek sediments may be related to burning (i.e. wood, petrochemical), and dumping of different kinds of waste (i.e. electronic waste, anticorrosive, plastic, batteries), and particles washed

from rooftops (i.e. via wearing of roofing materials) (Van Metre, et al., 2003; Chang, et al., 2004)

Anthropogenic inputs of Cd that may explain widespread enrichment throughout the study area include a Cu smelting facility. Cd is produced as a byproduct from smelting and refining sulfide ores of zinc and Cu. Additional sources of atmospheric deposition of Cd-contaminated dust may be recycling activities of iron and steel scrap. Cu enrichment in sediments results from anthropogenic applications of Cu material such as fertilizers, sprays and agricultural or municipal wastes, as well as from industrial emissions. Cu contents could be associated with water pipelines, which discharge Cu into soils. Other examples are mining, metal production, wood production and phosphate fertilizer production.

Sources of Hg pollution in regional estuarine environments likely include industrial and municipal point and non-point sources (i.e., sewage sludge, landfill leachates, waste incineration, industrial discharges and urban runoff) and atmospheric deposition from industrial sources in the Midwest and the Delaware Valley (Bonnevie, et al., ANSP 1994). It is noteworthy that metal loading surveys in the NY/ NJ Harbor Estuary indicate that municipal discharges may contribute as much as 40 % of the Hg input to the Estuary (HydroQual 1991).

Localized sources

The metal contents in contaminated sediments varied from site to site, which is likely a result of the different types and duration of anthropogenic activities that have been associated with the watersheds surrounding Main Creek, Neck Creek and Lemon Creek. A major factor governing the spatial distribution of metals in this study is variability and proximity to pollutant sources (Feng, et al., 1998; El-Moselhy, et al., 2004; Bopp, et al., 2006; Long, et al., 2006).

Accordingly, the highest values of metals in sediment occur in areas influenced by various pollution sources such as industrial discharges, wastewater effluents, tidal exchange, legacy contamination, stormwater outfalls and combined sewer overflows, atmospheric input and urban runoff (El-Moselhy, et al., 2004). Therefore, depending on location within the study area, traffic intensity, history and land use activities likely affect the metal content in Main Creek, Neck Creek and Lemon Creek surface sediments and may explain the relatively higher magnitude of surface enrichment observed for most metals in Arthur Kill marshes.

Local sources, including smelting operations, metal based industries, paint and dye formulators and chemical manufacturing plants may release and accumulate Cd, Hg, Cu, and Zn in marsh sediments throughout the study area, but are particularly suspected to impact Main Creek and Neck Creek (Bonnevie, et al., 1994; Al-Masri, et al., 2002). In addition, Arthur Kill sites may be susceptible to numerous long-standing threats and legacy contamination associated with discharges from historical industrial and commercial facilities, such as tanneries, scrap-metal yards and several paint manufacturers (PVSC, 1970). These additional impacts, along with site-specific sources and mechanisms that transport/distribute metals, may largely influence Main Creek and Neck Creek sediment quality and explain the broad-scale pollution gradient observed over the extent of the entire study area (Wallace and Luoma, 2003).

Upstream vs. downstream impacts

In addition to confirming the pervasive anthropogenic pollution of marshes throughout Staten Island, characterization of metal distribution trends helped assess variability and compare the relative contamination of upstream and downstream areas studied within Main Creek, Neck Creek and Lemon Creek surface sediments. Beyond the presence of regional sources and watershed impacts, additional metal loadings may result from the influx of contaminants from

adjoining bodies of water (i.e. Arthur Kill and Raritan Bay). Various natural and anthropogenic mechanisms can cause remobilization of contaminated estuarine sediments to adjacent marsh areas (Wolfe, et al., 1996; Seebaugh and Wallace, 2005; Dimou, et al., 2006).

The higher metal enrichment evident in sediments from the Arthur Kill study sites, suggests Main Creek and Neck Creek are susceptible to greater anthropogenic stressors due to the impact of shipping traffic, dredging, petrochemical industries and commercial development activities. The Arthur Kill serves as receiving waterway for a variety of industrial and commercial land use activities, which continue to impact environmental quality (See Chapter 2). Tidal exchange with the Arthur Kill could cause the advection of metals into the adjacent systems. Main Creek and Neck Creek could potentially act as a conduit for metals and the slower upstream currents would allow metals (suspended and dissolved) within the water column to settle out, deposit and become concentrated within surface sediments.

To some degree, it was projected that advective transport and/or tidal dynamics would cause higher metal contamination in upstream areas (greatest distance from AK and RB) compared to downstream areas. In contrast to the subtle increase in inland sediment load of total metals load at Lemon Creek, the more complex spatial distribution trends revealed in evaluation of Main Creek and Neck Creek surface sediments suggested the twofold affect of terrestrial and estuarine impacts. Characterization of site-specific sources is challenging in urban marsh environments for various reasons attributable to dynamic geochemical processes and multiplicity of proximal pollutant sources. The complexity and or indeterminate relationship between metal concentrations and distance upstream uniquely characterized by each of the Arthur Kill marsh systems (MA and NC) further complicated recognition of downstream/upstream impacts. In particular, the inconsistent sediment concentrations and incongruous metal-specific trends

identified at Main Creek suggested elevated enrichment levels are indicative of enhanced deposition from additional localized metal-specific sources.

The relative influence of localized and systemic inputs and contribution of terrestrial versus estuarine sources needs further examination in order to determine if tidal exchange/connectivity with the Arthur Kill is a factor in the greater metal contamination in adjacent marshes (MA and NC) and would explain the broad spatial variability characterized throughout the study area. Although the influence of the Arthur Kill remains inconclusive, it is important to recognize that the upland environment dually acts as a repository of metal pollutants and a habitat for many species (Olsen, et al., 1978; Olsen, et al., 1981; Hirschberg, et al., 1996). Accordingly, there is a need to identify ongoing sources of pollutants in the Arthur Kill given that observed pollution in sediment and ambient waters may be indicative of either current point sources, historical contamination, leaching from contaminated soils, transport from other contaminated waterways or any combination of these possible sources (Valiela, 1995).

CONCLUSION

Comparative evaluations of the spatial distribution and magnitude of surficial metal concentrations within Main Creek, Neck Creek and Lemon Creek determined the levels of contamination currently found in these marsh systems. Recent assessments of the lateral distribution of metals along spatial gradients at Main Creek, Neck Creek and Lemon Creek achieved a better understanding of sediment/habitat quality in these marsh systems. In addition, small-scale spatial variability evidenced in Main Creek, Neck Creek and Lemon Creek transects established surficial metal trends and magnitudes of contamination. Fluctuating sediment concentrations characterized episodic levels of metal contamination at Main Creek. Conversely,

the greater consistency regarding Cd, Hg, Cu, Zn concentrations at Lemon Creek were indicative of steady surface sediment contamination (Aalto, et al., 2005).

Collectively, lateral metal variations within each marsh confirmed the site-specific contamination previously depicted at Main Creek, Neck Creek and Lemon Creek. Small-scale assessments revealed Cd, Cu, and Zn enrichment throughout the areal extent of each site. Therefore, anthropogenic metal contributions affect quality of various Staten Island marshes (Bowen, et al., 1979; Valiela, 1995; Hirschberg, et al., 1996; Bopp, et al., 2006). With the exception of Zn, an increasing order of anthropogenic pollution was observed (LC<NC<MA) for all metals studied in Staten Island marsh sediments. Furthermore, comparable levels of most metals in marsh sediments from the western margin of the study area (NC and MA) demonstrated significantly greater anthropogenic metal contamination than sediments analyzed from the southern shore (LC). Accordingly, the present study established that a broad-scale pollution gradient describes metal contamination (surficial and temporal) over the extent of the study area.

The multiplicity of potential local and endemic/regional pollution sources (i.e. stormwater, land runoff, motor vehicle transportation), combined with site-specific natural factors (i.e. geographic features, hydrodynamics, biogeochemical processes), complicated identification of individual sources, specification of the origin (i.e. terrestrial/estuarine) and contribution of upstream vs. downstream impacts. The generally comparable magnitudes of surficial and temporal contamination and relatively greater variance exemplified by small-scale distributions of Cd, Hg, Cu, and Zn in Main Creek and Neck Creek sediments suggests the persistent metal pollution observed at these sites may be attributable to advective transport of metals from the Arthur Kill, in conjunction with terrestrial sources. Additional research is

necessary to determine the principal factors and dynamics affecting metal transport, distribution and fate within Main Creek, Neck Creek and Lemon Creek and thereby, predominantly influencing small and large-scale pollution gradients (Rozan, et al., 2001). Accordingly, the role that tidal exchange and connectivity with the Arthur Kill plays in the higher contamination identified in sites along the western of shore Staten Island requires further examination.

Table 3-1. Latitude and longitude surface sediment sampling locations along Main Creek, Neck Creek, and Lemon Creek transects.

Site	Latitude D°M'S"	A	B	C	D	E	F
	Longitude D°M'S"						
Main Creek	40°35'51.7"N	40°35'54.0"N	40°35'58.2"N	40°36'1.1"N	40°36'5.4"N	40°36'8.0"N	
	74°10'33.3"W	74°10'32.6"W	74°10'27.6"W	74°10'22.2"W	74°10'20.1"W	74°10'18.4"W	
Neck Creek	40°35'47.7"N	40°35'47.2"N	40°35'47.3"N	40°35'50.0"N	40°35'52.3"N	40°35'53.4"N	
	74°11'32.1"W	74°11'27.8"W	74°11'23.8"W	74°11'21.8"W	74°11'18.8"W	74°11'17.1"W	
Lemon Creek	40°30'49.0"N	40°30'59.7"N	40°31'4.2"N	40°31'5.6"N	40°31'13.0"N	40°31'17.1"N	
	74°11'55.4"W	74°12'3.0"W	74°12'4.2"W	74°12'9.8"W	74°12'10.6"W	74°12'17.7"W	

Geographic coordinates (reported in degrees, minutes, seconds ((D°M'S")) of intra-marsh surface sediment sampling locations (n=6) along lateral transects spanning the tidal reach of Main Creek, Neck Creek, and Lemon Creek from 2009 surveys.

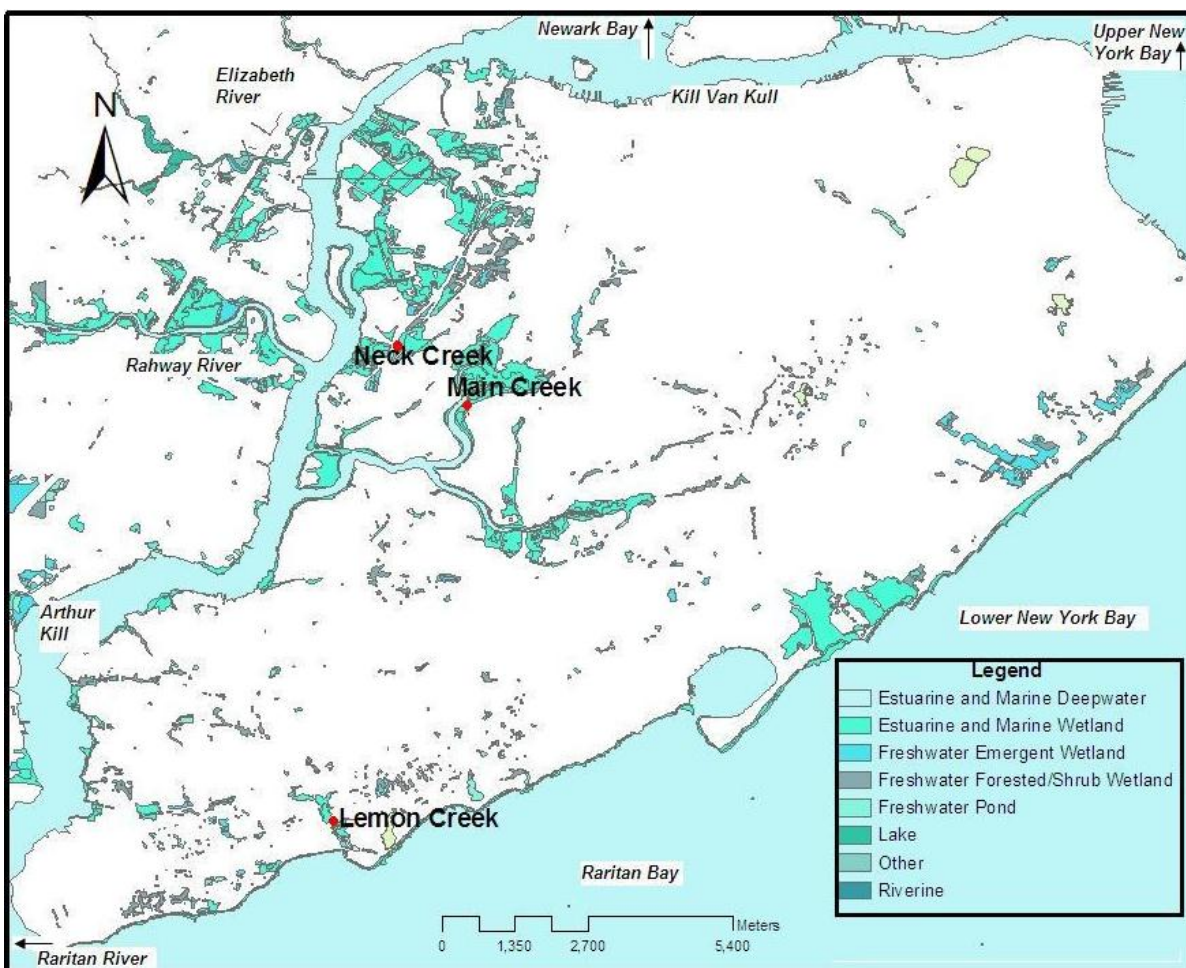


Figure 3-1. General study area and location of Main Creek (MA), Neck Creek (NC), and Lemon Creek (LC) study sites. Situated along the western (MA and NC) and southern (LC) shores of Staten Island, all three marsh-creek systems are classified as estuarine wetlands and exchange water with open waters of the New York/New Jersey Harbor Estuary (NY/NJ HE). MA and NC are tidally influenced by the Arthur Kill, located in the mid-western portion of the NY/NJ HE system, and LC drains into the Eastern Raritan Bay watershed.

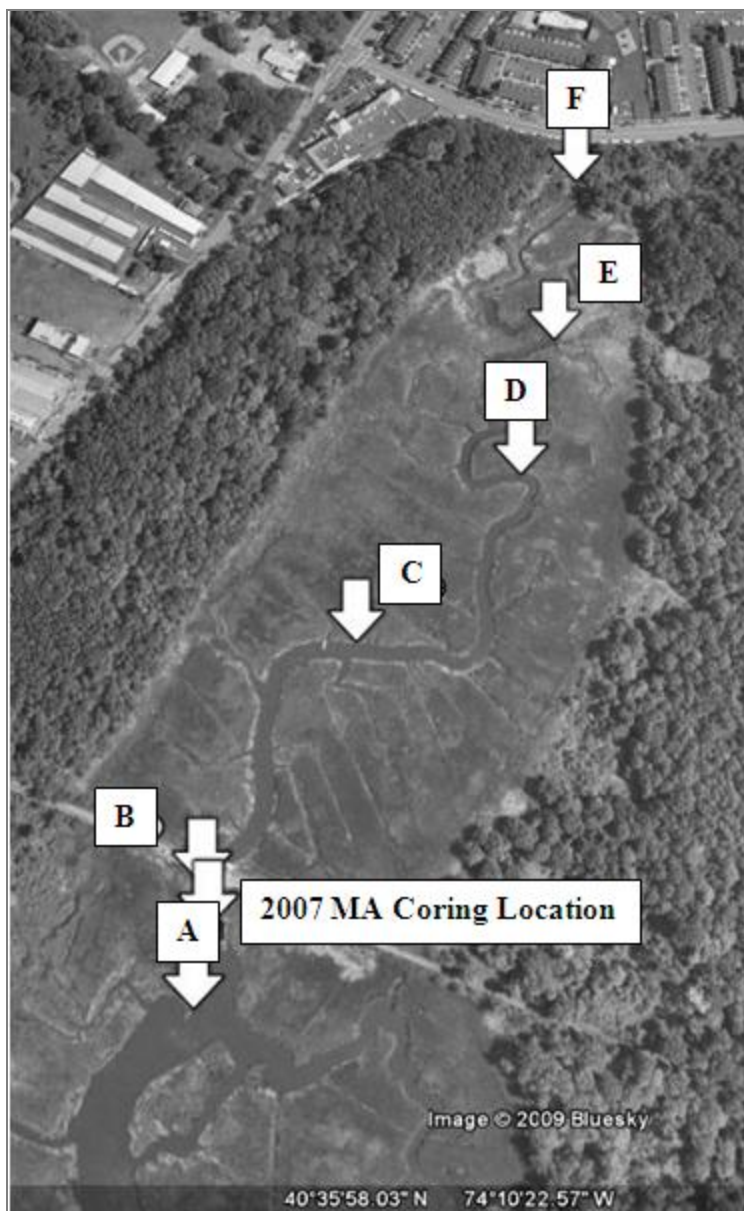


Figure 3-2. Main Creek surface sediment transect. Sampling location A is approximately 4.7 km east of the Arthur Kill. Location B is an additional 100m upstream (4800m) and adjacent to the roadway culvert that bisects Main Creek. Locations C-F are 200m, 400m, 600m, and 800m, respectively, upstream of this cross-section, where Travis Avenue bisects Main Creek.

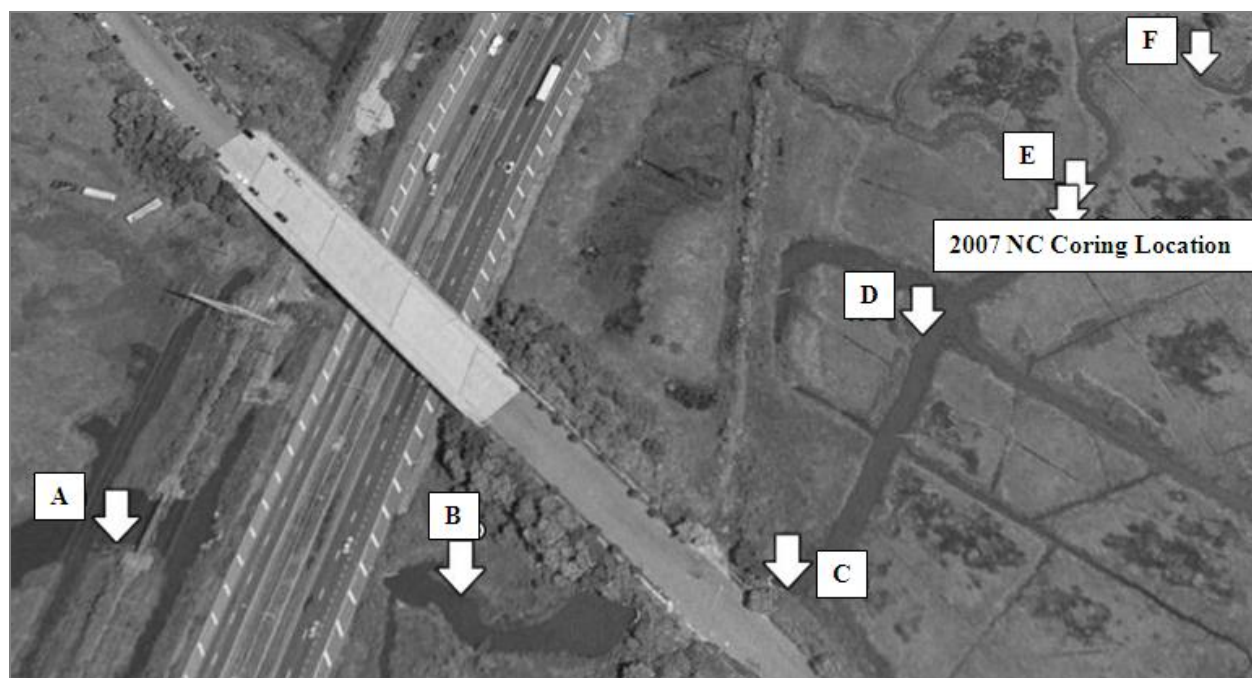


Figure 3-3. Neck Creek surface sediment transect. Sampling location A is ~800m upstream of the Arthur Kill. Successive transect sampling locations B-F are 100m apart; location F reaches 1300m upstream of the Arthur Kill.



Figure 3-4. Lemon Creek surface sediment transect. Sample location A is ~300m upstream of Raritan Bay. With increasing distance from the Raritan Bay, sampling locations B, C, D, E are 750m, 900m, 1050m, 1300m upstream, consecutively. F is the furthest upstream location (~1750m from the Raritan Bay).

Table 3-2. Trace metal concentrations in surface sediments along MA, NC, and LC marsh transects.**Table 3-2a. Lateral metal concentrations in marsh surface sediments collected from Main Creek (2009).**

Site		Cd ($\mu\text{g}\cdot\text{g}^{-1}$)				Hg ($\mu\text{g}\cdot\text{g}^{-1}$)				Cu ($\mu\text{g}\cdot\text{g}^{-1}$)				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
MA	n	Range	Mean	SE		Range	Mean	SE		Range	Mean	SE		Range	Mean	SE
A	4	4.66-5.23	4.93±0.29	0.17		2.40-2.50	2.44±0.05	0.03		79.6- 92.0	85.4±6.25	3.61		185-201	192±8.09	4.67
B	4	3.93-4.10	4.04±0.10	0.06		2.36-2.52	2.44±0.08	0.04		41.2- 48.4	44.8±4.99	3.53		117-122	119±4.06	2.87
C	4	4.71-5.24	5.04±0.29	0.16		2.33-2.39	2.37±0.03	0.02		151-153	152±1.03	0.73		322-322	322±0.08	0.06
D	4	3.84-3.86	3.85±0.02	0.01		0.26-0.25	0.25±0.0	0.00		328-371	353±22.1	12.8		275-299	289±12.7	7.31
E	4	1.28-1.32	1.30±0.03	0.02		0.03-0.03	0.03±0.0	0.00		307-360	331±27.0	15.6		245-254	250±4.55	2.62
F	4	1.54-1.66	1.62±0.07	0.04		0.04-0.04	0.04±0.0	0.00		298-328	317±16.6	9.56		253-279	267±13.6	7.88

Table 3-2b. Lateral metal concentrations in marsh surface sediments collected from Neck Creek (2009).

Site		Cd ($\mu\text{g}\cdot\text{g}^{-1}$)				Hg ($\mu\text{g}\cdot\text{g}^{-1}$)				Cu ($\mu\text{g}\cdot\text{g}^{-1}$)				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
NC	n	Range	Mean	SE		Range	Mean	SE		Range	Mean	SE		Range	Mean	SE
A	4	2.03-2.11	2.07±0.05	0.04		1.19-1.22	1.20±0.01	0.01		177-179	178±1.46	1.04		168-181	174±9.09	6.43
B	4	1.76-1.88	1.83±0.07	0.04		1.22-1.24	1.23±0.01	0.01		162-169	166±3.57	2.06		152-156	154±2.29	1.32
C	4	0.82-2.08	1.45±0.89	0.63		1.06-1.10	1.07±0.02	0.01		60.9-163	100±54.6	31.51		70.9-156	105±45.2	26.1
D	4	1.71-1.95	1.84±0.12	0.07		0.63-0.65	0.64±0.01	0.01		146-163	156±9.01	5.20		147-163	157±8.63	4.98
E	4	1.78-1.89	1.82±0.06	0.04		1.12-1.19	1.15±0.04	0.02		199-206	201±4.41	2.55		162-169	165±3.52	2.03
F	4	2.18-2.76	2.41±0.41	0.41		1.50-1.59	1.55±0.04	0.03		249-249	249±0.00	0.00		185-185	185±0.00	0.00

Table 3-2c. Lateral metal concentrations in marsh surface sediments collected from Lemon Creek (2009).

Site		Cd ($\mu\text{g}\cdot\text{g}^{-1}$)				Hg ($\mu\text{g}\cdot\text{g}^{-1}$)				Cu ($\mu\text{g}\cdot\text{g}^{-1}$)				Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
LC	n	Range	Mean	SE		Range	Mean	SE		Range	Mean	SE		Range	Mean	SE
A	4	1.41-2.08	1.81±0.36	0.21		0.06-0.07	0.07±0.00	0.00		132-162	150±16.0	9.21		158-215	191±29.2	16.9
B	4	1.48-1.52	1.50±0.02	0.01		0.17-0.18	0.18±0.00	0.00		123-137	132±7.92	4.57		159-165	163±3.05	1.76
C	4	1.36-1.38	1.37±0.01	0.01		0.27-0.27	0.27±0.00	0.00		117-121	119±2.61	1.85		159-162	161±1.97	1.40
D	4	1.41-1.49	1.45±0.04	0.02		0.27-0.28	0.28±0.00	0.00		148-153	151±2.75	1.58		174-176	175±0.87	0.50
E	4	1.49-1.52	1.51±0.01	0.01		0.34-0.35	0.34±0.00	0.00		101-117	111±8.77	5.06		166-228	186±35.9	20.7
F	4	1.96-2.04	1.99±0.04	0.02		0.33-0.34	0.34±0.00	0.00		113-120	117±3.39	1.96		179-181	180±1.53	0.88

Table 3-3. Background Metal Concentration Comparison with Surface Sediment Mean.

Metal	Background Concentration¹ ($\mu\text{g}\cdot\text{g}^{-1}$)	Main Creek Transect Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	Neck Creek Transect Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	Lemon Creek Transect Mean ($\mu\text{g}\cdot\text{g}^{-1}$)
Cadmium	0.11	3.46	1.90	1.61
Mercury	0.18 ²	1.26	1.14	0.24
Copper	14.0	214	175	130
Zinc	81.0	240	157	176

Literature-based background concentrations (Cd, Hg, Cu, and Zn) derived from Hudson River sediment data (Hirschberg et al. 1996¹, Bowen et al. 1979²). Site-specific mean Cd, Hg, Cu, and Zn concentrations calculated from the average of all surficial samples (n=60), which included analysis of 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

Table 3-4. Regional Enrichment factors ($EF = C_{\text{observed}}/C_{\text{background}}$) per Transect Location at Main Creek, Neck Creek, and Lemon Creek.

Main Creek	Cd EF¹	Hg EF²	Cu EF	Zn EF		Neck Creek	Cd EF	Hg EF	Cu EF	Zn EF		Lemon Creek	Cd EF	Hg EF	Cu EF	Zn EF
A	44.8	13.6	6.10	2.37		A	18.8	6.68	12.7	2.15		A	16.5	0.37	10.7	2.36
B	36.7	13.6	3.20	1.47		B	16.6	6.85	11.8	1.90		B	13.6	0.98	9.41	2.01
C	45.8	13.2	10.9	3.98		C	13.2	5.97	7.16	1.30		C	12.5	1.50	8.51	1.99
D	35.0	1.41	25.2	3.57		D	16.8	3.55	11.1	1.93		D	13.2	1.53	10.8	2.16
E	11.8	0.19	23.1	3.09		E	16.6	6.38	14.4	2.03		E	13.7	1.91	7.94	2.30
F	14.7	0.22	23.5	3.30		F	21.9	8.63	17.8	2.28		F	18.1	1.87	8.33	2.23
Mean	31.5	7.02	15.3	2.96		Mean	17.3	6.34	12.5	1.93		Mean	14.6	1.36	9.28	2.17

¹Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996 and Bowen et al. 1979). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations (n=60). Mean metal contents for Main Creek, Neck Creek, and Lemon Creek transects were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

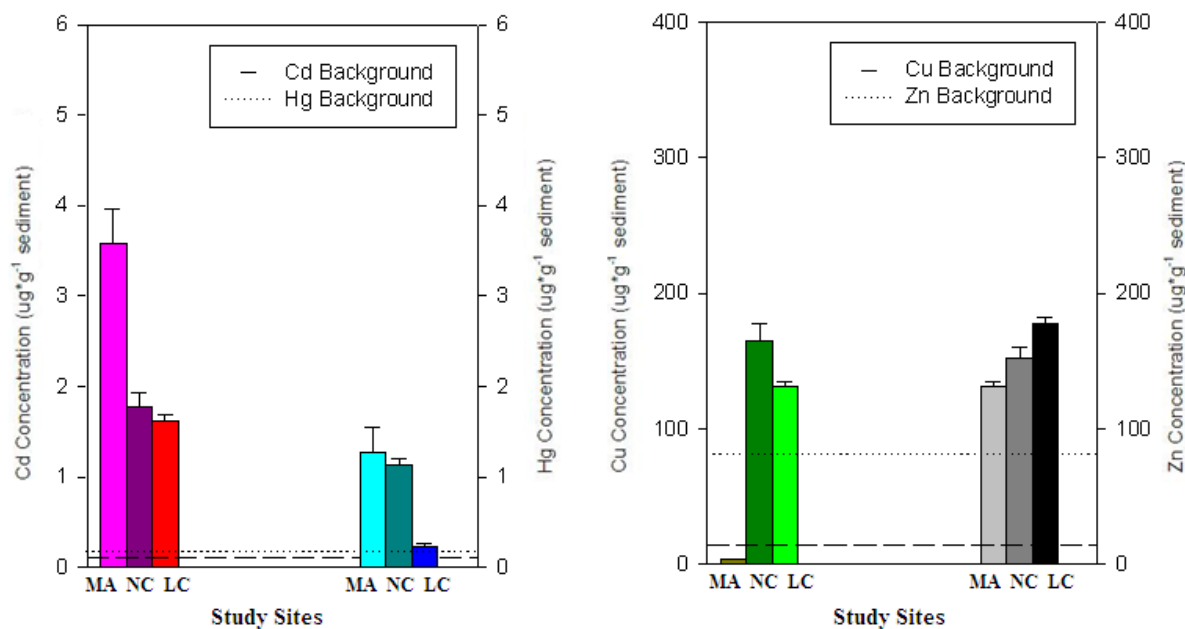


Figure 3-5. Average metal concentrations in MA, NC, and LC surface sediments.

Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations ($n=60$). Mean metal contents for Main Creek, Neck Creek, and Lemon Creek were calculated from acquired surficial datasets that included site-specific sediment samples ($n=3$) from each transect location ($n=6$), which were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure. Literature-based background concentrations (Cd, Hg, Cu, and Zn) derived from Hudson River sediment data (Hirschberg et al. 1996¹, Bowen et al. 1979).

Table 3-5. Metal Concentration Comparison with Regional Background Concentration.

MA	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		NC	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		LC	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)
A	4.93	2.44	85.4	192		A	2.07	1.20	178	174		A	1.81	0.07	150	191
B	4.04	2.44	44.8	119		B	1.83	1.23	166	154		B	1.50	0.18	132	163
C	5.04	2.37	152	322		C	1.45	1.07	100	105		C	1.37	0.27	119	161
D	3.85	0.25	353	289		D	1.84	0.64	156	157		D	1.45	0.28	151	175
E	1.30	0.03	323	250		E	1.82	1.15	201	165		E	1.51	0.34	111	186
F	1.62	0.04	329	267		F	2.41	1.55	249	185		F	1.99	0.34	117	180
Reg. Bkgd ¹	0.11	0.18	14.0	81.0		Reg. Bkgd ¹	0.11	0.18	14.0	81.0		Reg. Bkgd ¹	0.11	0.18	14.0	81.0

¹Background concentration data from Hudson River sediments for Cd, Cu, Zn (Hirschberg et al. 1996) and Hg (Bowen et al. 1979).

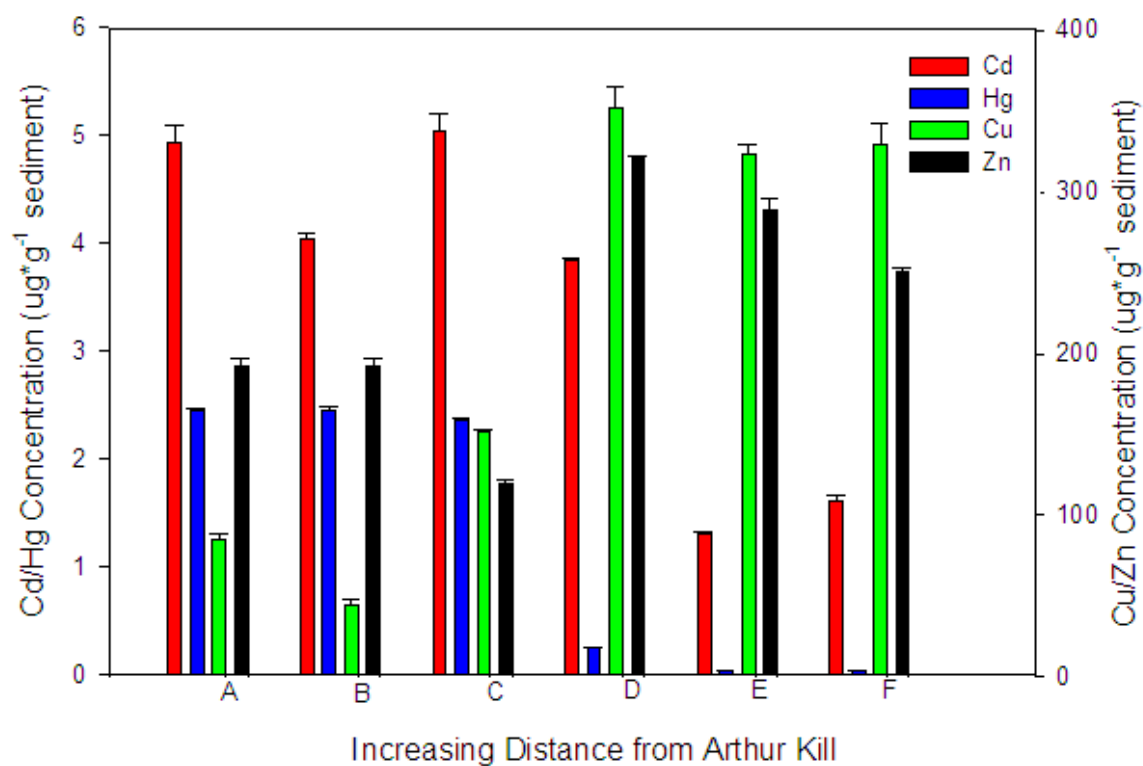


Figure 3-6. Main Creek lateral transect: surface sediment metal concentrations. Positive error bars reflect +1 standard error (S.E.) from mean metal-specific concentration (dry wt⁻¹ sediment) at each sampling transect location (n=6).

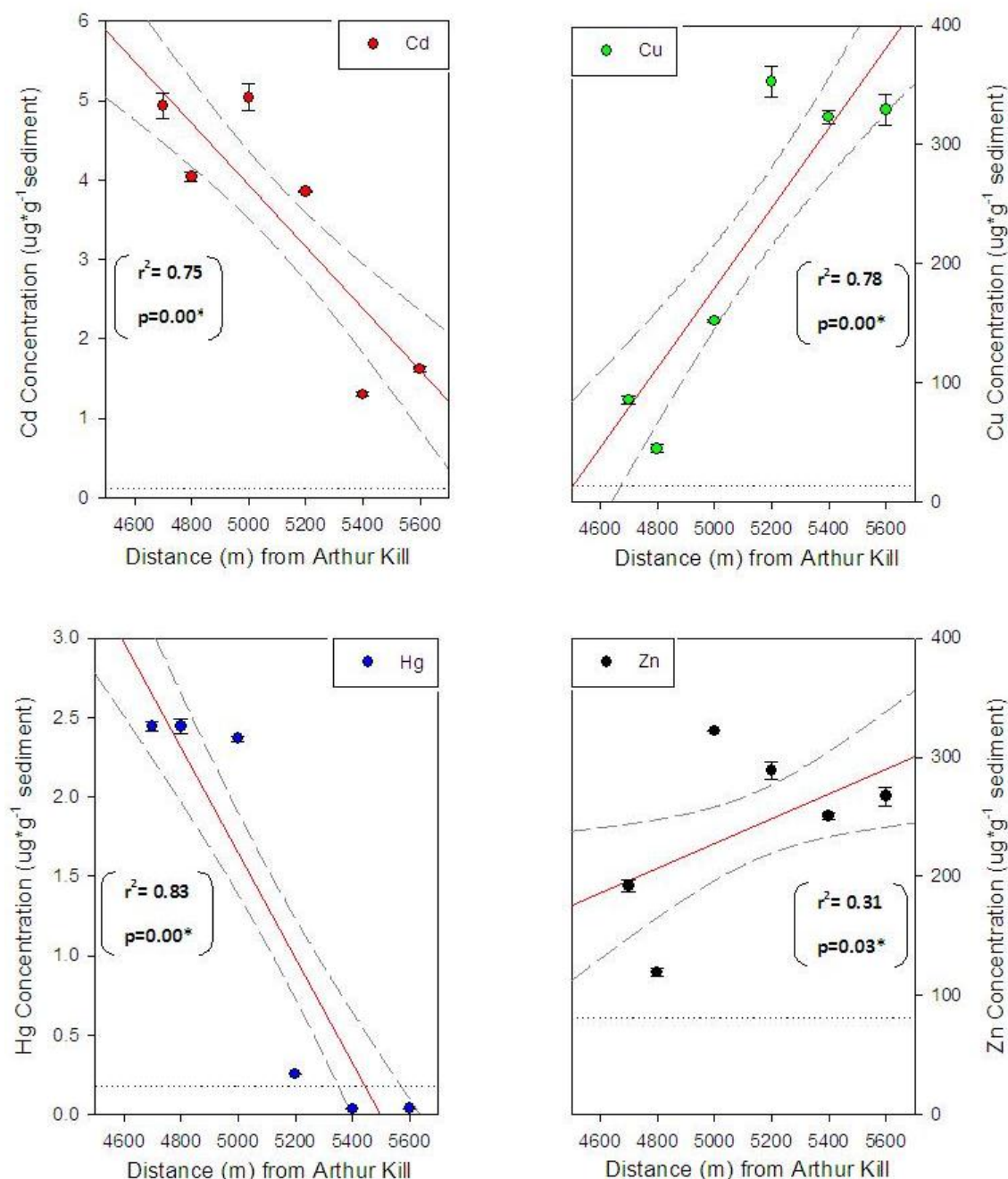


Fig. 3-7. Intra-marsh Variation of Metal Distributions in Main Creek Surface Sediments: Distance vs. Metal Concentration. Results from Cd, Hg, Cu, and Zn linear regression analyses were significant for Main Creek (MA) as denoted by the asterisk (*), which reflected significant values for r^2 ($p < 0.05$). Solid regression line demonstrates a significant correlation between metal concentration and distance from the Arthur Kill. Broken grey lines show the 95% Confidence Intervals (C.I.) for data points from each metal-specific dataset. Solid circles (●) and error bars reflect the mean of surface sediment concentrations ($n=3$) $\pm$ 1 standard error (S.E.) for respective intra-marsh transect locations ($n=6$). Dotted line represents regional elemental background level derived from Hirschberg et al. 1996 and Bowen et al. 1979.

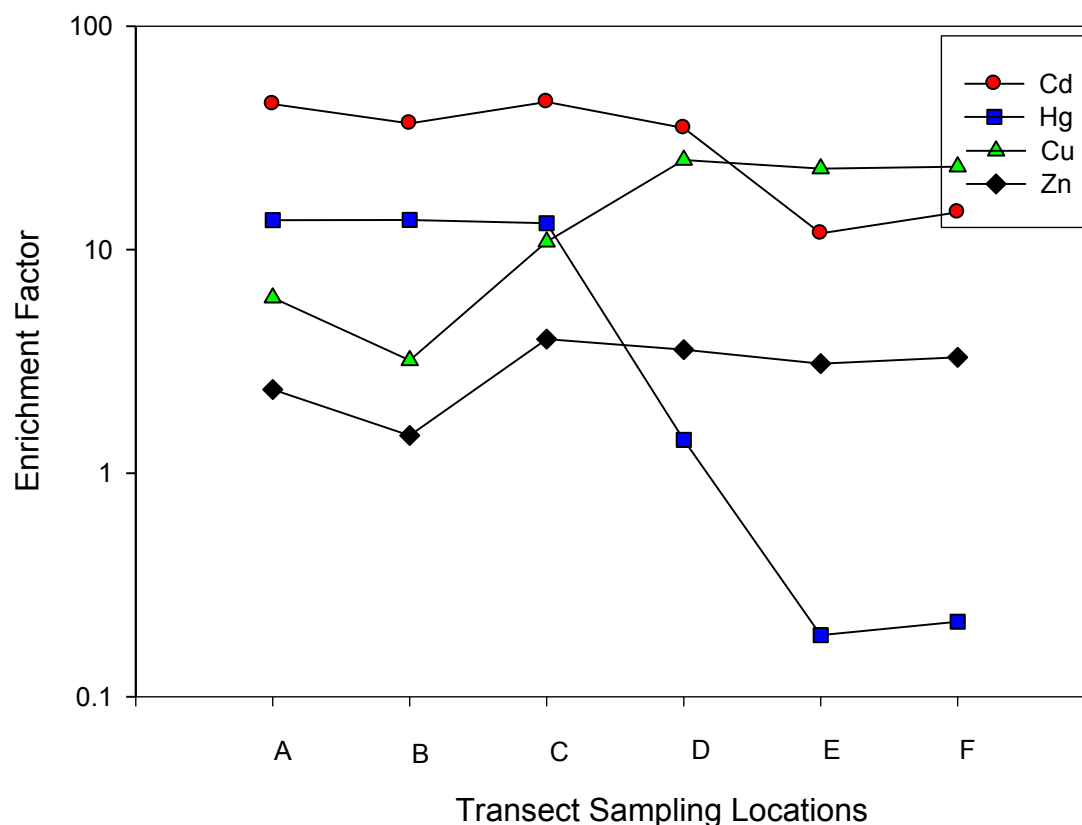


Figure 3-8. Regional Enrichment factors ($EF = C_{\text{observed}}/C_{\text{background}}$) per transect location at Main Creek. Figure reflects lateral surface sediment enrichment factors along respective transect locations extending the wadable extent of the tidal extent of Main Creek. Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996 and Bowen et al. 1979). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations ($n=60$). Mean metal contents for transect sampling locations were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location ($n=6$), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

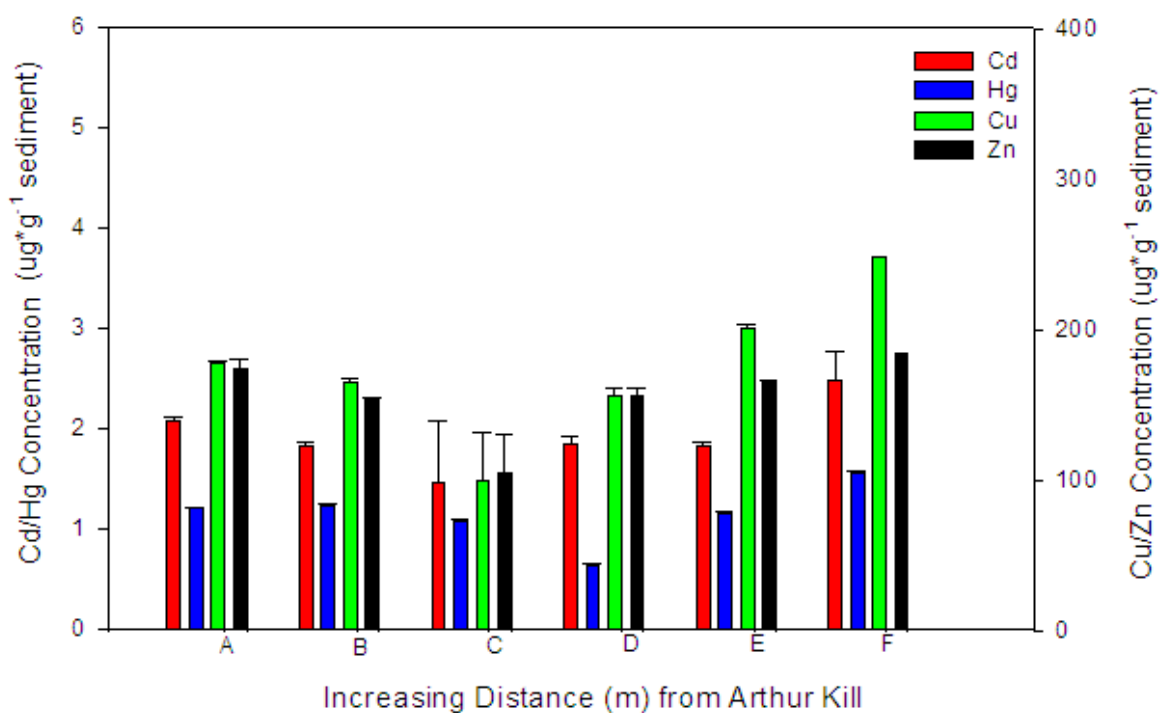


Figure 3-9. Neck Creek lateral transect: surface sediment metal concentrations. Positive error bars reflect +1 standard error (S.E.) from mean metal-specific concentration (dry wt^{-1} sediment) at each sampling transect location ($n=6$).

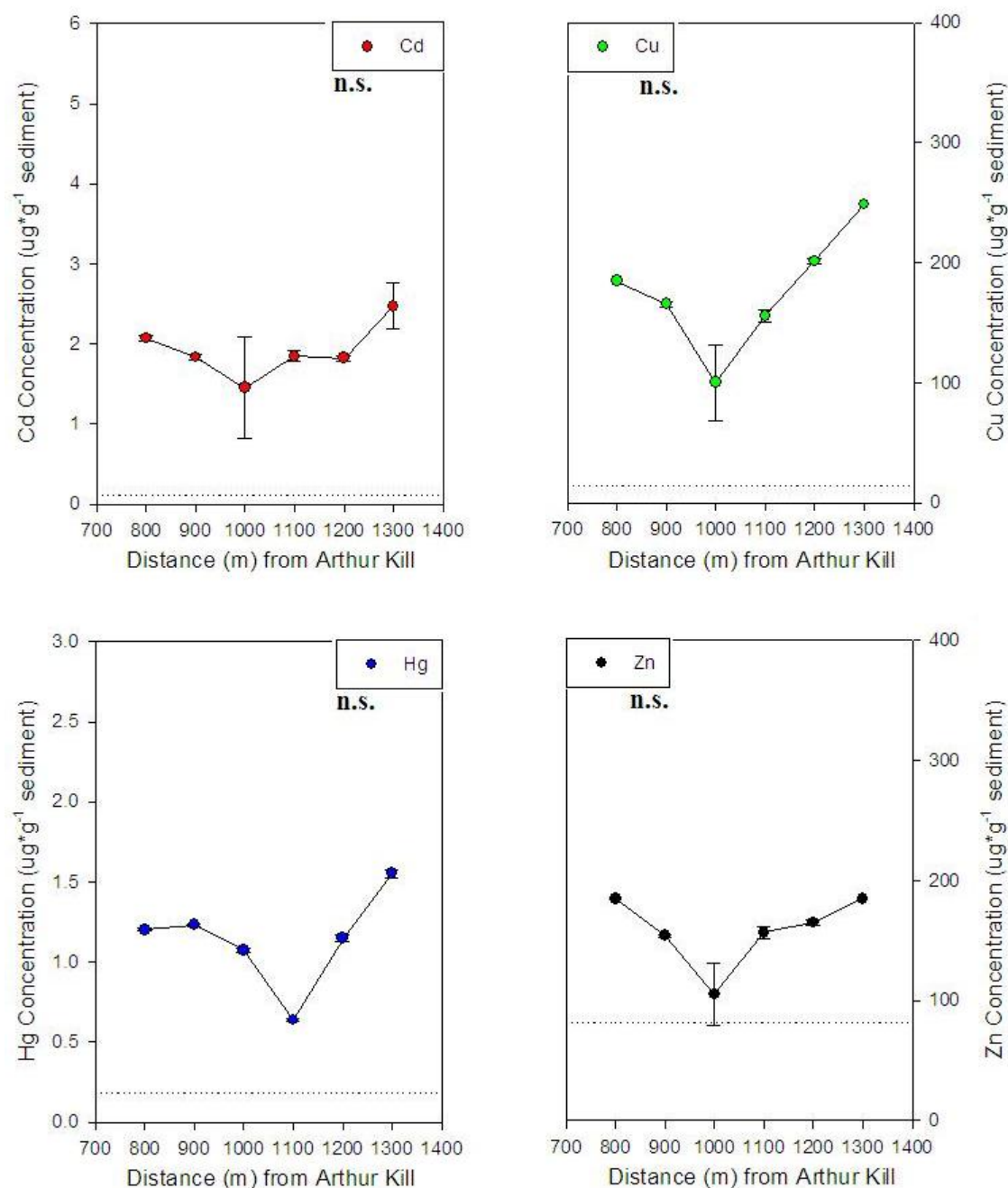


Fig. 3-10. Intra-marsh Variation of Metal Distributions in Neck Creek Surface Sediments: Distance vs. Metal Concentration. Linear regression analyses were not significant at Neck Creek; n.s. denotes non-significant values for r^2 ($p>0.05$) and demonstrates no significant correlation between metal concentration and distance from the Arthur Kill. Solid circles (●) and error bars reflect the mean of surface sediment concentrations ($n=3$) $\pm$ 1 standard error (S.E.) for respective intra-marsh transect locations ($n=6$). Dotted lines represent metal-specific regional elemental background level derived from Hirschberg et al. 1996 and Bowen et al. 1979.

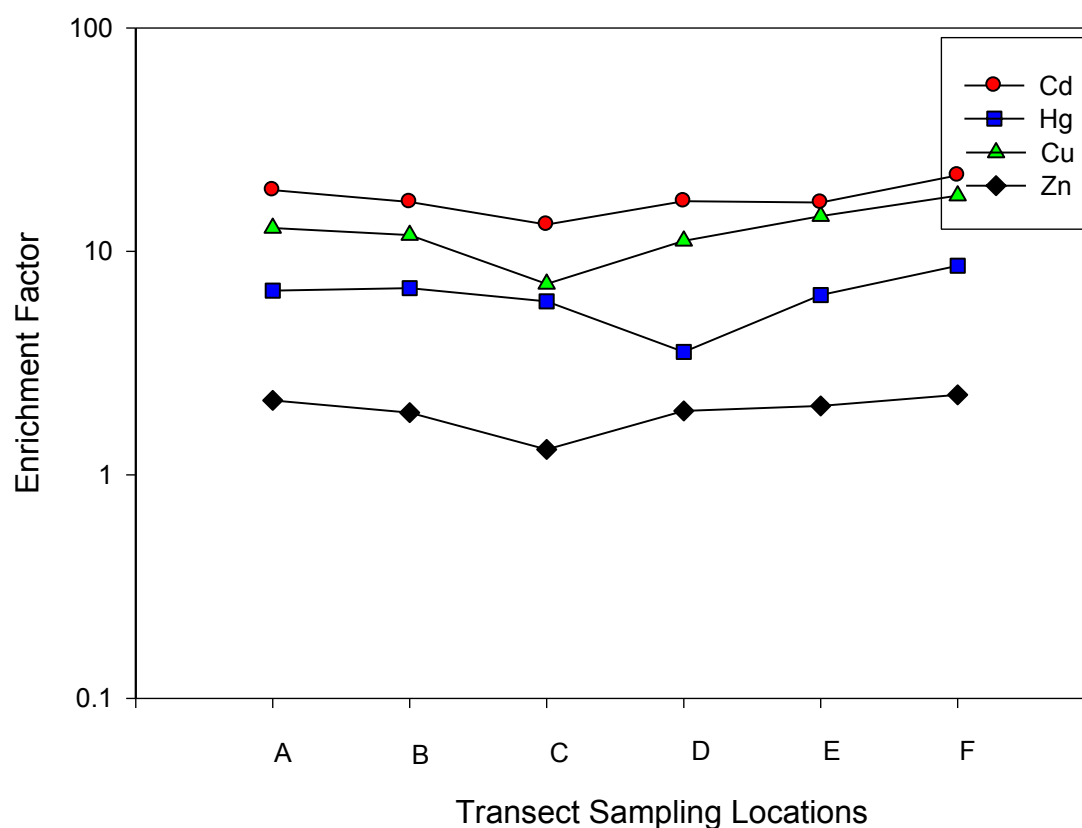


Figure 3-11. Regional Enrichment factors ($EF = C_{\text{observed}}/C_{\text{background}}$) per transect location at Neck Creek. Figure reflects lateral surface sediment enrichment factors along respective transect locations extending the wadable extent of the tidal extent of Neck Creek. Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996 and Bowen et al. 1979). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations ($n=60$). Mean metal contents for transect sampling locations were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location ($n=6$), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

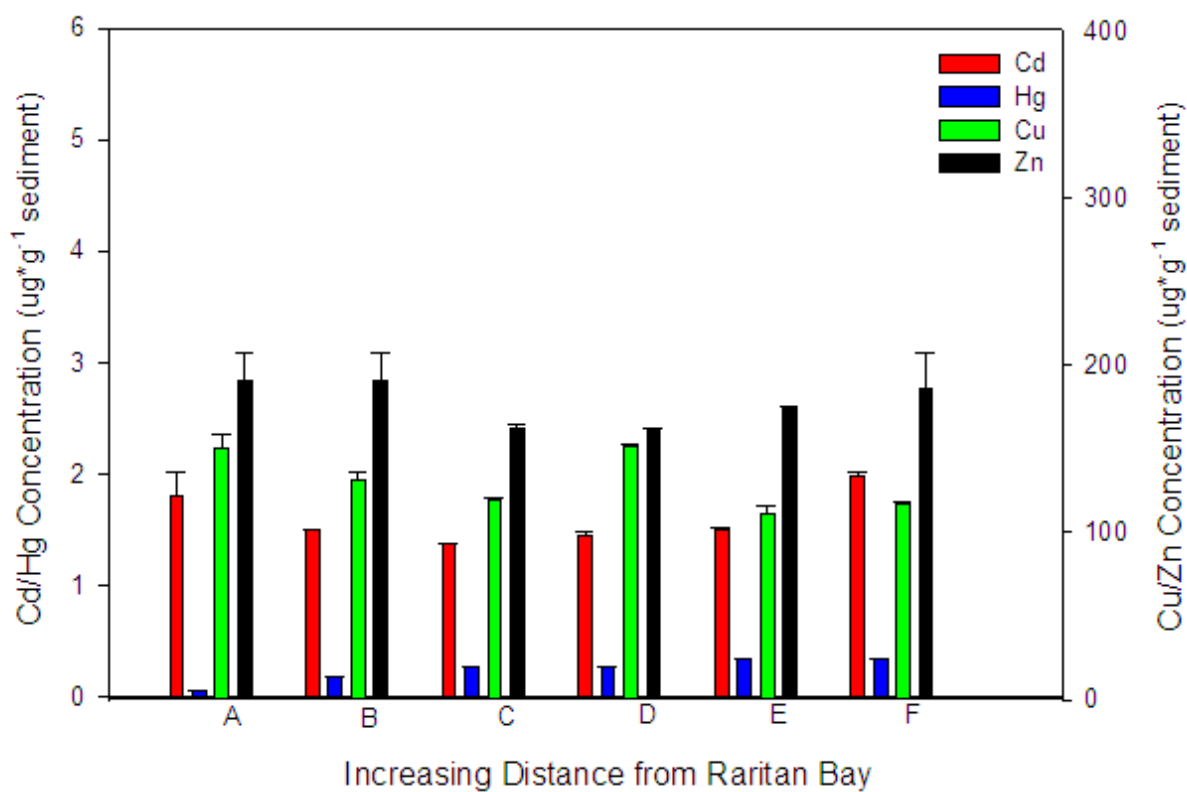


Figure 3-12. Lemon Creek lateral transect: surface sediment metal concentrations. Positive error bars reflect +1 standard error (S.E.) from mean metal-specific concentration (dry wt⁻¹ sediment) at each sampling transect location (n=6).

Lemon Creek Lateral Transect: Surface Sediment Metal Concentrations

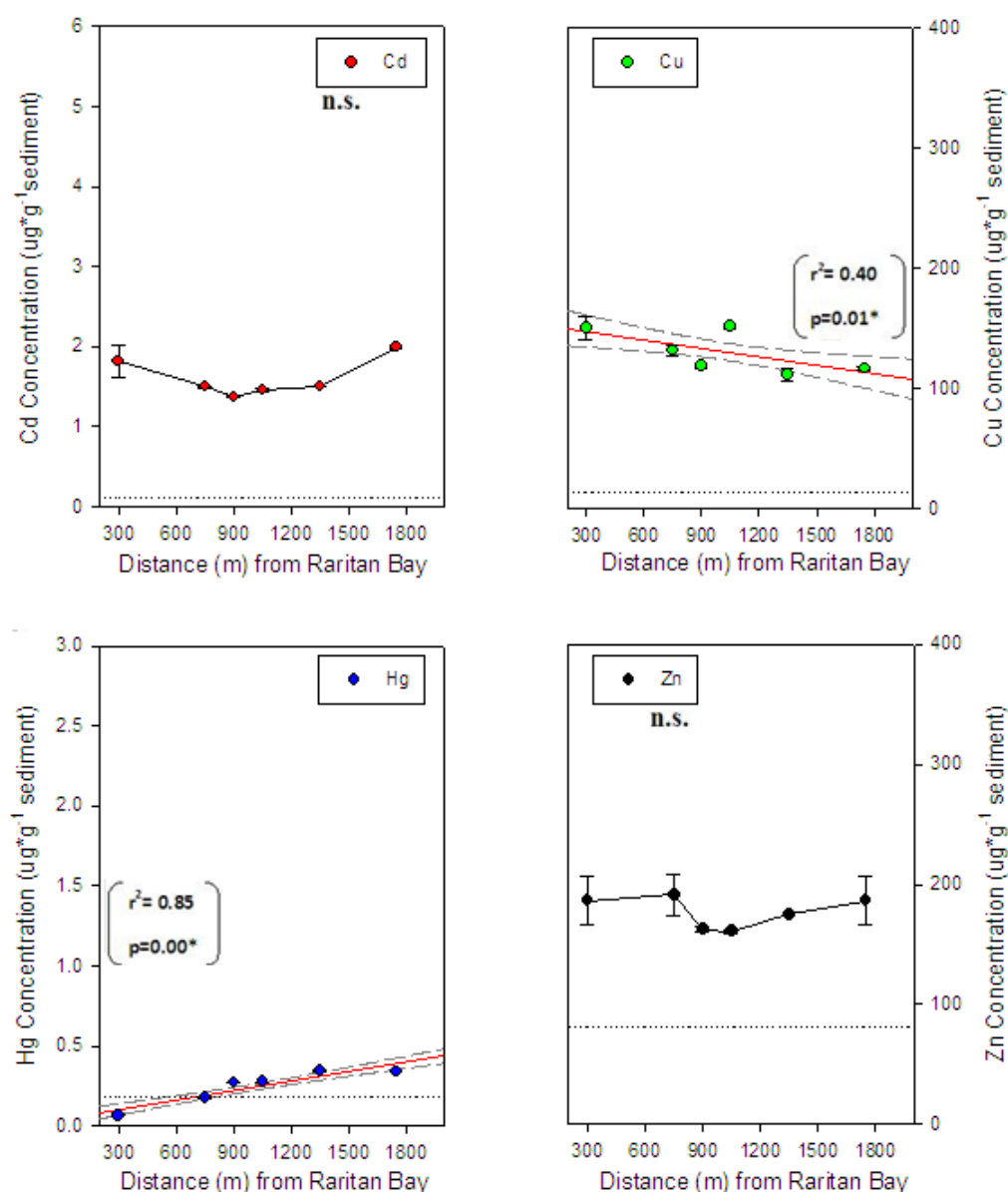


Fig. 3-13. Intra-marsh Variation of Metal Distributions in Lemon Creek Surface Sediments: Distance vs. Metal Concentration. Linear regression results from analysis of Hg and Cu datasets were significant as denoted by the asterisk (*), which indicates a significant value for r^2 ($p < 0.05$). Solid regression line demonstrates significant correlation between metal concentration and distance from the Raritan Bay; **n.s.** denotes non-significant values for r^2 ($p > 0.05$) and demonstrates no significant correlation between Cd and Zn concentration and distance from the Raritan Bay. Broken grey lines show the 95% Confidence Intervals (C.I.) for data points from each metal-specific dataset that showed significant p values (Hg and Cu). Solid circles (●) and error bars reflect the mean of surface sediment concentrations ($n=3$) $\pm$ 1 standard error (S.E.) for respective intra-marsh transect locations ($n=6$). Dotted lines represent metal-specific regional elemental background level derived from Hirschberg et al. 1996 and Bowen et al. 1979.

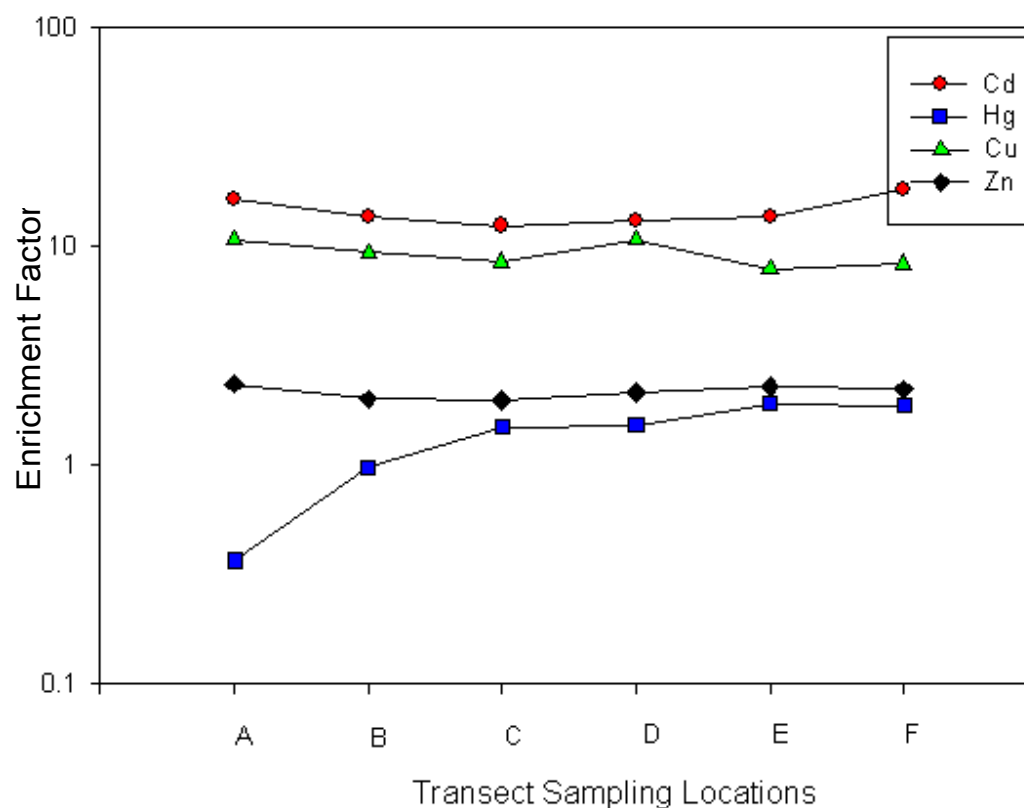


Figure 3-14. Regional Enrichment factors ($EF = C_{\text{observed}}/C_{\text{background}}$) per transect location at Lemon Creek. Figure reflects lateral surface sediment enrichment factors along respective transect locations extending the wadable extent of the tidal extent of Lemon Creek. Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996 and Bowen et al. 1979). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations ($n=60$). Mean metal contents for transect sampling locations were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location ($n=6$), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

LARGE AND SMALL-SCALE VARIABILITY OF METALS DISTRIBUTIONS AND
ANTHROPOGENIC ENRICHMENT LEVELS WITHIN STATEN ISLAND MARSH-CREEK
SYSTEMS. DOES PROXIMITY TO THE ARTHUR KILL INFLUENCE SPATIAL AND
TEMPORAL CONTAMINATION AND POTENTIAL FOR SEDIMENT TOXICITY IN NY/NJ HE
MARSH HABITATS?

by

Caitlyn P. Nichols

Volume II

A dissertation submitted to the Graduate Faculty in Earth and Environmental Sciences in partial
fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of
New York

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Chapter 4

Characterization of Suspended Particulate Metals and the Role of Tidal Advection in Main Creek, Neck Creek and Lemon Creek

CHAPTER SUMMARY

Current velocity, cross-sectional area, suspended particulate matter (SPM) and metal concentrations were measured in three wetland creeks in western and southern Staten Island, in order to determine magnitude and direction of suspended material transport across the marsh surface. Distributions of SPM and Cd, Cu, Zn, and Hg, suspended within the water column, were studied at each site to examine variability over the extent of a complete tidal cycle. To characterize a range of flow conditions (i.e. springs and neaps) that represented maximum and minimum tidal ranges, two complete tidal surveys were conducted during spring and neap tides at the Arthur Kill study sites (Main Creek and Neck Creek). The product of instantaneous water flows, SPM and metals were comparatively assessed in terms of tidal current (flood vs. ebb), to evaluate the scalar transport and lateral movement of suspended constituents entering and leaving the upland marsh habitats at Main Creek, Neck Creek, and Lemon Creek. Calculation of a net import or export term (+/-), via the difference in contaminant fluxes transported on incoming and outgoing tides, represented the net tidal exchange of metal-specific fluxes. This research component identified large-scale variability with respect to the degree of anthropogenic metals within suspension, in the particulate fraction. Furthermore, it provided the background information necessary for future research into the surficial processes controlling net deposition, cycling/availability, and exchange of metals in various environmental compartments,

which control the distribution, transport and fate of metals among biotic and abiotic system components within the study area.

INTRODUCTION

Particle-reactive properties cause metals to adsorb to sediments and accordingly, the majority of metals introduced into receiving waterways become associated, and subsequently transported, with sediments. The ability of sediments to incorporate and accumulate particle-reactive contaminants from the water column is problematic considering that the most distinguishing feature of metals from other toxic pollutants is their inability to biodegrade, which can cause deleterious ecosystem effects (Sanudo-Wilhelmy et al., 1999). Resident biota may feed directly upon these suspended particles, or indirectly once they become part of the bed load. Associated contaminants would then be available for possible bioaccumulation and trophic transfer (Luoma et al., 1989).

Although contaminated sediments can settle and become buried, sediment bound metals can become resuspended in the water column via scouring, dredging activities, bioturbation, increased water velocities, wave action and/or currents. Subsequently, they re-enter the system. This redistribution is an important factor in determining the mobility and the toxicity of trace metals within estuaries (Audry et al. 2006). Once sediment is remobilized, complexation processes and particle chemistry partition and cycle metals between dissolved and particulate phases and thus influence metal fate and bioavailability (Censi et al. 2006). Therefore, favorable physic-chemical conditions can release [metals can repartition between the particulate and dissolved phases] and supply sediment-bound metals to surrounding ecosystems (Rozan et al., 2001; Harikumar et al., 2009; Sanudo-Wilhelmy et al., 1999).

A composite of complex sedimentological and geochemical processes are integral in the spatial distribution and burden of metal pollutants in estuarine systems (Monbet, et al., 2004). Various dynamics associated with coastal environments and physicochemical reactions that occur at the water/sediment interface (i.e. precipitation, adsorption/desorption, flocculation/aggregation, and settling/sedimentation) control the mobility, transport and fate of contaminants in marsh ecosystems (Benoit, et al., 1994; Williamson, et al., 1996; Herut, et al., 1997; Censi, et al., 2006). In contrast to overlying waters, surface sediments retain the majority of the metals available for exchange in aquatic environments (Rozan, et al., 1999). While sediments can adsorb and accumulate contaminants within the water column, they can also remobilize, release and supply them to surrounding ecosystems (Rozan, et al., 1999; Harikumar, et al., 2009). Granular composition largely affects metal enrichment of sediments (de Groot, 1995). Metals are often associated with the surfaces of fine-grained particles which, when suspended, can serve as carriers, transporting, and dispersing metal contaminants throughout the environment (Herut, et al. 1997). Thereby, the ability of marsh sediments to bind and release metals determines their capacity as metal sinks and sources, which, together with the impact of source contributions, influences the extent of spatial contamination (Du Laing, et al., 2008).

Investigations of the environmental conditions of the New York/New Jersey Harbor Estuary have found that the overall health of this estuary has vastly improved over the last thirty years but that, certain areas are still impaired by historic as well as contemporary contaminant loadings (Sanudo-Wilhelmy, et al., 1999; Steinberg, et al., 2004). Previous research has established that the Arthur Kill is a polluted urban waterway that functions as a sink for toxic pollutants (Thomann, 1989; Gillis, et al., 1995; Huntley, et al., 1995; Sanudo-Wilhelmy, 1999; Steinberg, et al., 2004). Although pollutant loadings have declined in recent years, the waterway

is still impaired by historic as well as contemporary contaminant loadings, and it has been found that, that in terms of toxic contaminants, Arthur Kill waters “remain primary geographic areas of concern” (Gillis, et al., 1995; Sanudo-Wilhelmy, et al., 1999; Steinberg, et al., 2004).

Sediments within the main channel of the Arthur Kill can become remobilized via tidal action, shipping, and dredging activities, and serve as metal carriers to marsh habitats. Subsequently, contaminant-laden suspended sediments may be redistributed to marsh habitats, and resident biota may feed on particulates suspended within the water column, and/or on fine-grained fractions that settle and deposit on marsh flats. These particles may have toxic metals bound to them, that bioaccumulate through potential trophic transfer (Luoma, 1989; Hornberger, et al., 1999; Audry, et al., 2006).

Understanding the exchange of metals between the Arthur Kill and associated tidal wetlands is a critical step in gaining an overall understanding of metal transport processes and redistribution dynamics within a sensitive system of both ecological and economic importance. Insight regarding regional and local natural factors and anthropogenic stressors are key to measuring future effects and may be applicable and useful in studies aimed at determining the impact of metals in heavily impacted estuaries, such as the NY/NJ Harbor Estuary (Luoma, 1989; Hornberger, et al., 1999; Audry, et al., 2006).

Prior trace metal studies have determined that marshes buffering the Staten Island shoreline demonstrate temporal and geographic variability with respect to distribution and extent of pollutants (Ward, 2001; Nichols, 2004). Recent assessments of Staten Island marsh sediments (2007) have confirmed previous coring surveys (2001). Both studies found Arthur Kill marshes had similar magnitudes of metal contaminants, which were demonstrably greater

concentrations than exhibited by an external site. The comparable extent of temporal contamination detected indicated that, in addition to any site-specific sources, a continuous, unknown influence maintained the constantly high magnitudes of enrichment identifiable with these sites. Baseline metal data within these marshes suggests that the observed pollution may be attributable to various contributions from historic and present-day anthropogenic activities. However, it is plausible that tidal exchange with the Arthur Kill may also serve as an active source of metal pollutants, which contributed to greater scales of metal contamination than observed in marsh environments outside the Arthur Kill complex.

Research into tidally mediated resuspension and redeposition of contaminated sediments in a polluted estuarine system, such as the Arthur Kill, is essential from a habitat restoration standpoint. Many areas bordering the Arthur Kill are slated for restoration, acquisition, and/or remediation projects and the successes of these efforts may be compromised by the environmental quality of the Arthur Kill. For example, if sites are remediated and subsequently become re-contaminated via localized impacts/stressors, like the remobilization of legacy contaminated Arthur Kill sediments; these efforts may be both inefficient and ineffective, resulting in the loss of time and resources

The significance of this project aligns closely with various current management goals that are being pursued within the region. For example, habitat acquisition and restoration of ecologically important areas that are threatened by pollution and development is a major focus of the NY/NJ Harbor Estuary Program and many sites along the Arthur Kill are slated for such efforts (USACE, 2010; HEP CCMP, 2006). Furthermore, information concerning sediment metal loadings within marsh habitats would be important data to supplement the NY/NJ HEP Contaminant Assessment Reduction Program and is critical step in gaining an overall

understanding of the transport and redistribution dynamics of contaminants within this ecologically important and sensitive system. Site assessment of contaminants and an understanding of the exchange of contaminants between the Arthur Kill and associated marsh habitats would be a useful management tool in prioritizing, as well as setting target criteria for restoration initiatives within the NY/NJ HE.

An assessment of current conditions (in terms of sediment metal concentrations and exchange with the Arthur Kill) will aid in tracking success of efforts to protect local waterways from metal contamination. This will help characterize the environmental state of the region, which is essential in providing insight regarding contributing factors propagating “hot spots” of sediment contamination within the NY/NJ HE, and inform and drive policy decisions. Particles derived from estuarine, riverine, and terrestrial sources may become associated with contaminants linked to past or present watershed activities. Thereby, both land-based and estuarine mixing and remobilization can contribute to site-specific metal distributions. Understanding the tidal exchange and lateral advective transport of metals among open waters of the NYNJ HE, particularly the heavily polluted Arthur Kill and inland wetland habitats, is critical to monitor ecosystem health, assess the vulnerability of ecologically-important species and design, implement, and assess the success of site remediation and ecological restoration.

METHODS

Subsequent to a series of sediment chemistry studies, this study was undertaken to determine the presence of particulate metals within the water column over the extent of a tidal cycle to complement previous research components and further address metal distribution,

transport and fate among the NY/NJ HE Complex and adjacent wetland habitats. Fundamental physics and chemistry specific to the study area were incorporated to examine tidal mediated metal fluxes (Cd, Cu, Zn, and Hg), among the Arthur Kill and Raritan Bay, and marsh-creek systems (Main Creek, Neck Creek and Lemon Creek). Two seasonal surveys were conducted in three marsh-creek systems in the NY/NJ HE in the fall (2008) and spring (2009).

This research component tested two hypotheses: a) marsh habitats adjacent to the Arthur Kill exhibit greater concentrations of metals relative to an external marsh site; and b) net differences in metal concentrations between tidal phases (ebb and flow) are indicative of a tidal transport of metals into marsh habitats and demonstrate that the Arthur Kill is a source of particle-bound metals to adjoining salt marshes/creeks.

The approach of this research component was to investigate the flux of particle-bound metals (Cd, Cu and Hg) between the Arthur Kill and the study sites over time. Sampling was conducted from bridges above creek conduits over two complete tidal cycles (once at neap tide and once at spring tide). The concentration of particle-bound metals will be determined in conjunction with a variety of other hydrodynamic (i.e., flow rates, depth and width of water column, etc.) and physicochemical parameters. Net flux of metals between the Arthur Kill and the inland marshes were estimated (Hazen and Kneip, 1980; Sokal, et al., 1996; Weis, et al., 2005; Bopp, et al., 2006).

An effort was made to characterize short-term variability metal (Cd, Cu, Zn, and Hg) concentrations that would indicate transport patterns and to determine if the Arthur Kill is a source for metals. Measurements of metals, and total suspended solids were made over a tidal cycle on two separate sampling events (spring and neap tide) at two considerably-highly

contaminated marshes that extend from the Arthur Kill and one moderately contaminated site, Lemon Creek, which is external to the Arthur Kill and drains into the Raritan Bay (Appendix A).

Experiential Design

Particle-bound metals were determined in water column samples at Main Creek and Neck Creek over two complete tidal cycles, once each during a neap (low tidal energy) and spring (high tidal energy) tide, in order to bracket the range of possible "fluxes" that could occur between the Arthur Kill and the study sites. Lemon Creek sampling was conducted over the extent of a tidal cycle that fell between a neap and spring tide, to represent an intermediate flow. Sampling was conducted from roadway bridges above the creek conduits. The concentration of suspended metals was determined in conjunction with a variety of other measurements (i.e., flow rates, depth and width of water column, etc.) in order to calculate the "net flux" of metals between the Arthur Kill and adjoining salt marshes/creeks was calculated.

Following field collection, samples were transported to the laboratory for analysis of particulate bound Cd, Cu, and Hg (ICPAES for Cd, Cu; flow injection mercury analyzer - FIMS for Hg). Concentrations of particulate metals were multiplied by suspended solids per filtered water volume in order to determine total gross fluxes of metals, which was calculated by the difference between influx and efflux data sets (Hazen, et al., 1980; Lion, et al., 1982; Sokol, et al., 1996; Mackie, et al., 2007). In addition, monitoring activities during the last event at each site included surface sediment samples that were collected on exposed flats at dead low tide.

Study Sites

Main Creek (MA) Neck Creek (NC) and Lemon Creek (LC) were targeted study sites based on evidence of site-specific levels of metal bioavailability and contamination derived from

baseline datasets from marshes reaching along the Western and Southern margins of Staten Island. They were also deemed appropriate due to general comparability of the systems in terms of type of wetland environment (i.e. estuarine wetland), and in terms of basic the geography and ecology of tidal creek and upland marsh habitats (NYS DEC 2009) (Fig.1). Main Creek (MA) and Neck Creek (NC) were targeted as representative Arthur Kill study sites based on geographic relativity to the Arthur Kill proper (Fig. 1). Both creeks (MA and NC) are perpendicular to the Arthur Kill main channel and the western shore of Staten Island and extend inland toward upland marsh habitats from their confluence with the main channel (Figs 1, 7a-c). Both have shown to exhibit considerable to very high contamination degrees (Appendix A).

Both sites are located within the Arthur Kill Complex and, to varying degrees, are subject to a combination of sources related to past and present metal pollution. In addition, Lemon Creek served as a regional ‘reference marsh’, in that it does not share a direct hydraulic connection with the Arthur Kill. Thereby, the value of Lemon Creek as a regional reference site is that it may help to assess if connectivity to the Arthur Kill or site-specific inputs are major sources of metal contaminants to study sites. Furthermore, this facilitated comparisons between study sites regarding metal-specific distributions, the role of localized vs. regional inputs and the influence of natural vs. anthropogenic disturbances and/or stressors in metal-specific distributions.

Within each marsh-creek system (Main Creek, Neck Creek and Lemon Creek), study locations were selected based upon logistical feasibility (i.e. sampling practicability and site accessibility) (Table 1). It was deemed important to select sampling locations where water inputs to marsh areas were controlled and limited (Fig. 4a-c). In recognition of the time-intensive scope of this research component, and that it involved conducting fieldwork over a

complete tidal cycle, a concerted effort sought to obtain official access and documented permission to sample the elected site-specific cross-sectional areas. However, with respect to Main Creek, access to certain locations that were preferable because they were in closer proximity to the Arthur Kill, was denied and therefore, sampling took place further inland by default. In addition to accessibility restrictions and other logistical reasons, sampling took place accordingly on the west side of Travis Avenue, the east side of Meredith Avenue and north of Hylan Boulevard, to assess the water column in close proximity to prior coring locations (Tables 1-2, Figs 1a-b, 7a-c.).

Field Sampling

Sampling Design

The primary goal of this study was to determine the concentrations of heavy metals in the particulate phase of water fluxing into and out of tidally-influenced marshes adjoining the Arthur Kill. Metal concentrations in creek water columns were determined at each site, and took place during dry weather at a neap (low tidal energy) and a spring (high tidal energy) tide in order to bracket the range of "fluxes" that could occur at each site. In addition, monitoring activities during the Spring of 2009 event at each site included sediment samples that were collected on exposed flats at dead low tide.

Water Column Collection

Particulate matter for measuring trace metals was obtained by collecting a series of discrete water samples (n=9) over a complete ebb tide and flood tide, or 2 half ebbs and a complete flood tide (Appendix b 1-3), in order to determine tidal/temporal variation in particulate-bound metal concentrations.

Water samples were collected over complete tidal cycles in order to determine temporal variation in particulate metal concentrations. Sampling logistics commenced in accordance with slack water and captured maximum tidal heights. Glass sampling jars (2L) were lowered from the midpoint of the bridge/culvert above Main Creek, Neck Creek and Lemon Creek and filled by moving the jar through the water column until filled. After dunking/rinsing the sampling unit (heavyweight glass jar and extendable sampling stick or line attachment) with ambient water three times, duplicate samples were collected in high-density polyethylene (HDPE) carboys. Immediately after collection, samples were split and transferred into acid-washed (5L) high-density polyethylene (HDPE) carboys and stored on ice until filtration in the laboratory. Preliminary fieldwork and laboratory analyses have determined 1L samples were adequate to obtain reliable metals data (Fig. 3).

In addition to water column samples, tidal height/depth and velocity were concurrently, measured at each site. A Marsh McBirney FloMate Model 2000 open channel flowmeter was used to measure current velocity (m/s) of the ebbing/flooding tide. Over the temporal extent of each tidal survey, lateral flows were determined at each tidal stage according to the methods further detailed in sections below (Figs. 6a-b). At each sampling site, the width under the bridges served as a proxy for the width of creek channels. By dividing into equal segments, a depth profile was created prior to sampling. For each site, velocity measurements were taken *in situ* at the centerline of the cross-section at .2 x Depth; .6 x Depth; .8 x Depth (Fig. 6b). Additional environmental parameters, including pH (psu), temperature (°C), dissolved oxygen ($\text{mg}\cdot\text{L}^{-1}$), and salinity (ppt) were directly determined in the water column using a multi-parameter (YSI Model 85) handheld field instrument to describe environmental settings of collection sites.

Water Column Sample Processing

Acid-washed resistant-glass or HDPE plastic carboys were used for sampling and processing so that the suspended material did not adhere to container walls. Analysis began as soon as possible after samples were transported to the laboratory, as sample preservation was not applicable for analysis of metals in suspended particulates. Samples were kept on ice ($<4^{\circ}\text{C}$) up to the time of analysis to minimize microbiological decomposition of solids and were, and were not held more than 24-36 hours before filtration.

In order to control metal contamination during sample analysis, all field supplies and labware used for sample processing and analysis preparation were acid-washed prior to use according to in-house analyte-specific procedures (USEPA Method 1669; USEPA, 1995b). Samples were prepared separately for the determination of Hg than for other metals (Cd, Cu, and Zn). For metals other than Hg, all glassware and processing materials were acid-washed accordingly. Labware was pre-soaked overnight in detergent and thoroughly rinsed with DI and NanoPure® water before soaked for 24 hours in a covered, diluted nitric acid bath, and subsequently rinsed three times with NanoPure® water. Alternatively, labware specifically dedicated the preparation of samples for Hg analysis was acid-washed via a dilute (20%) hydrochloric acid soaking procedure and wrapped with Parafilm® prior to use.

All field and laboratory procedures incorporated appropriate vigilance to minimize the possible risk of contamination during sample collection, splitting, filtering, and digestion. In addition, only Ultra-pure trace metal grade reagents were used for sample preparation and analysis.

Filtration of water column samples

Given that the filtration process required for direct particulate metals measurements potentially presented another major source of bias, in addition to sample collection and filtering, preliminary datasets were used for selection of the most appropriate filtration apparatus and technique that achieved both minimal sample contamination and the capacity to filter adequate sample volumes within a practicable amount of time (Kamera, et al., 1997).

Samples were filtered through previously acid-washed filters, of which were previously acid washed, dried, and weighed until a constant weight was recorded. Replicate samples were filtered with previously weighed and dried 0.4 μm polycarbonate membranes (142 mm Nucleopore Whatman) and 0.45 μm nitrocellulose acetate membranes (147mm Millipore) in order to collect suspended particles for metals analysis by inductively coupled plasma-atomic emission spectrometry (ICP- AES) (Cd, Cu, and Zn) and flow injection mercury analyzer (FIMS for Hg), respectively. Prior studies have established that 0.45 and .40 μm filters are an appropriate size for separating suspended and dissolved metals and have been chosen in order to obtain representative samples that best represent particle-associated metals at the sites (PSWQA, 1997; USEPA, 2001; Bibby, et al., 2006).

Due to their low metal concentration and ability to acid-wash, polycarbonate membrane filters were selected for the determination of particulate/suspended metals. Polycarbonate membranes are generally recommended for the filtration of natural water samples and widely utilized in similar trace metal studies. Although their application is common, the use of polycarbonate filters for Hg analysis was deemed suspect and reconsidered subsequent to initial sampling at Main Creek and Neck Creek (in Fall 2008), due to the likely presence of detectable Hg, often associated with filter blanks. Although water samples collected from Main Creek and Neck Creek in the first survey (Fall 2008) were prepared for the determination of Hg, the

polycarbonate filters on which the particulate fractions were retained may have incidentally added a source of cross-contamination. Given that the initial processing steps involved in filtering may have compromised the integrity of these samples prior to digestion, these datasets were not included in this study. In an effort to minimize any contamination and rectify adsorption issues that challenge suitability of polycarbonate filters for Hg determination, cellulose acetate membrane filters were applied in the analysis of all reported Hg datasets (from Main Creek, Neck Creek and Lemon Creek in Spring 2009 surveys) due to practicability of low measurable concentrations in blank samples (Boevski, et al., 2007).

Filters were acid-washed prior drying and weighing in pre-washed petri dishes by soaking in 2M HCl (Ultra-Pure/Trace Metal Grade), rinsing with NanoPure® water and finally left to soak in NanoPure® water for a total of at least a week in NanoPure® water. Filters were left for approximately two days to dry and subsequently stored in a dessicator until a constant weight was achieved and recorded. The same procedure was applied for drying and weighing membranes after filtration of water samples for SPM (Pohl, 1997; Queremais and Cossa, 1997).

SPM/SS Analysis

SPM, also often categorized as suspended solids (SS) fraction, is defined as the particulate fraction and operationally defined as the material (i.e. fine sediments/colloids, bacteria, etc.) retained from solution by filters with 0.45 µm and 0.45µm pore sizes (Strumm and Morgan, 1981; Puget Sound Estuary Program, 1989; APHA Standard Methods, 1999). Acid-washed resistant-glass or PFTE plastic carboys were used for samples. Caution was taken to see that the material in suspension did not adhere to container walls. Analysis began as soon as possible because of the impracticality of preserving the sample. Samples were kept on ice

($\leq 4^{\circ}\text{C}$) up to the time of analysis to minimize microbiological decomposition of solids and were not held more than 24-36 hours before filtration. The accuracy of balance was checked with Class S weights and recorded before beginning analyses.

After rinsing the walls of the filtration apparatus with 2% nitric acid and NanoPure[®] water, an adequate, well-mixed aliquot of known sample volume was filtered through a glass filtration apparatus (Whatman) containing the pre-weighed polycarbonate or nitrocellulose membrane. Subsequently, the residue retained on the filters were dried to a constant weight according to the abovementioned drying and weighing procedure. The difference in weight of the filter and petri dish before and after filtration of the sample was used to represent suspended solids (SS)/SPM compartment (APHA Standard Methods, 20th Edition, 1999; Section 2540 A and D).

One liter of well-mixed sample was the aliquot volume targeted for filtration, because baseline research determined it sufficient to yield an adequate residue (between 2.5 and 200 mg) on the membranes. Samples were weighed to the nearest 0.00001g using an analytical laboratory balance (Mettler Toledo AX205). Sample repeatedly via a cycle of drying and weighing, until the membrane filter attained a constant weight, or until the weight change was less than 4% of the previous weight or 0.5 mg (whichever was less). Particular attention with respect to weight changes due to air exposure and/or sample degradation was accounted for when weighing dried samples. Only final recorded weights were included in the calculation of all analytical results presented in this study.

For all water samples collected during each tidal survey, suspended particulate matter (SPM) concentrations (also referred to as suspended solids) were determined via gravimetric

methods as outlined in Equation 1. The amount or mass of solids retained by the Nucleopore membrane (0.45 or 0.4 μm) after filtration was divided by the volume of the filtered sample, and was reported in $\text{mg}\cdot\text{L}^{-1}$.

$$\text{suspended solids } \text{mg}\cdot\text{L}^{-1} = [(A-B) \times 1000] / \text{Aliquot volume, mL} \quad \textbf{(Equation 1)}$$

where:

A=weight of residue + petri dish (final weight, mg)

B=weight of petri dish (initial weight, mg)

Metals in Suspended Particulate Matter: Processing and Analysis

Samples were vacuum filtered utilizing pre-weighed membrane filters (Whatman, Millipore) in order to collect suspended particles. Filters containing the suspended particulate matter (SPM) were left to dry as outlined above, re-weighed (to determine the mass of suspended sediment in the 1L volume of filtered water) and stored deep frozen in acid-washed Petri dishes until analysis (Pellenbarg, et al., 1979; Cobelo-Garcia, et al., 2005). Material retained on membrane filters, referred to as suspended solids (SS) or suspended particulate matter (SPM), was directly analyzed for metals (Cd, Cu, Zn, and Hg) using appropriate near total digestion methods for sample preparation prior to analysis via ICP (Cd, Cu, and Zn) and FIMS (Hg) (Cole, et al.; 2001) (Fig.3).

Cd, Cu, and Zn analysis via inductively coupled plasma-atomic emission spectrometry ICP- AES

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine the concentration of Cd, Cu, and Zn in suspended particulate matter (SPM) retained on polycarbonate membranes (0.4 μm) after the filtration of water samples. Particulate metal samples were digested prior to analysis via recommended sediment digestion method (USEPA

Method 3050b; USEPA, 1992b). Suspended elements were solubilized by near total acid digestion and brought into aqueous phase for subsequent ICP-AES analysis. For the determination of the suspended elements, the sample was filtered through a 0.45µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass filtering apparatus was used to avoid possible contamination. The portion of the sample used to rinse the filtration set-up was discarded after this portion and the volume of sample aliquot passed through the membrane filter was recorded.

Suspended material retained on filter membranes was weighed to accurately measure sample mass (0.0000g) for SPM determination. Metal samples were processed by gentle refluxing with hot nitric and hydrochloric acids. After cooling, the sample was made up to the designed volume, then mixed and allowed to settle overnight before filtration and analysis. SPM results were reported on a mass-mass weight basis using filter weight to make the conversion. Particulate metals were determined on a mass/volume basis using the suspended solids and SPM metal concentration results to make the conversion (Horowitz, et al., 1986; Puget Sound Estuary Program, 1990).

Flow Injection Mercury Systems (FIMS): Hg Analysis

Particulate total mercury (HgT) was determined directly by acid-leaching filters with a combination of (2:1) concentrated nitric (HNO_3) and sulfuric (H_2SO_4) acids. Filters were placed in sample digestion bottles with 100mL of reagent water (NANOpure[®]), and digested in diluted potassium permanganate (KMnO_4) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) solutions, oxidized and heated for 2 hours at 95°C in a covered water bath (USEPA, 1991; Cole, et al., 2001; McIntosh, et al., 2004). After cooling to room temperature, sodium chloride-hydroxylamine chloride

([NaCl(NH₂OH)HCl]) was added to reduce excess KMnO₄. Mercury in the sample digests was reduced with stannous chloride (SnCl₂·2H₂O) to elemental mercury and measured by the cold-vapor atomic absorption spectrophotometric method of Hatch and Ott (1968) using a PerkinElmer flow injection mercury analyzer (FIMS-100).

Quality Control

Standard stock metals solutions of 1000 mg L⁻¹ were obtained from Fisher Scientific, as well as nitric and hydrochloric acids (ultra-trace metals grade) used for comprising in-house calibration standards and QC samples for ICP-AES and FIMS analysis. In addition, instrument calibration standards (which needed to be from a separate vendor) were procured from SPEX Industries and Environmental Resource Associates (ERA) for the ICPAES and FIMS, respectively. Additional certified standard reference materials (SRMs) were obtained for applicable matrices and certified by either National Institute of Science and Technology (NIST) or ERA (NIST estuarine sediment 1646, ERA metals in soil and ERA metals in water).

The precision and accuracy of the abovementioned analytical procedures were determined by digestion of SRMs using appropriate modifications and/or agency revisions of EPA-approved methodologies. For example, the aqua regia digestion technique used for near-total recovery of elements, other than Hg, “suspended in water”, primarily based on EPA 200.7-v4, was also comparable to a common modification outlined for direct analysis of particulates, which has been derived from the digestion technique for near-total sediment/solids analysis. Elemental spike recoveries in digestates were determined for Cd, Cu, and Zn using ICPAES, and measured via FIMS for Hg,

The ICP-AES was standardized according to normal operating procedures, which included correction for peak interferences via quality control samples. Over 99% recovery was achieved from the analysis of the Fisher Scientific certified 1ppm Reference Standard for the screen of metals and therefore no subtraction was necessary for the procedural blanks. In order to ensure the proper use of each instrument, established standard operating procedures were derived from certified methods (USEPA 200.7, USEPA 3050b, and USEPA 1669, 245.1-7, respectively) and from the manufacturer's (Perkin-Elmer) detailed, instrument-specific instructions. Accordingly, this included steps required for analytical preparation and equipment maintenance. The in-house calibration standards and standard reference materials referenced above (Fisher Scientific, Spex, ERA, NIST) were applied at routine intervals (~every 10-12 samples), during ICP and FIMS analysis to check consistency and performance of the instruments. For additional quality assurance, filter and procedural blanks were concurrently analyzed, and monitored during, and verified subsequent to, sample analysis.

Polycarbonate membranes are generally recommended for the filtration of natural water samples, and widely utilized in similar trace metal studies (Kneflkamp, et al., 2007). Thereby, due to their low metal concentration and ability to acid-wash, Nuclepore polycarbonate membrane filters were selected for the determination of particulate/suspended metals. Although their application is common, use of polycarbonate filters for Hg analysis was deemed suspect and reconsidered subsequent to initial sampling at Main Creek and Neck Creek (in Fall 2008), due to the likely presence of detectable Hg, often associated with filter blanks (Boevski et al., 2007). Although water samples collected from Main Creek and Neck Creek in the first survey (Fall 2008) were prepared for the determination of Hg, the polycarbonate filters, on which, the particulate fractions were retained may have, incidentally, added source of cross-contamination.

Given the initial processing steps involved in filtering may have compromised the integrity of these samples prior to digestion, these datasets were not included in this study. In an effort to minimize any contamination and rectify adsorption issues that challenge suitability of polycarbonate filters for Hg determination, cellulose acetate membrane filters were applied in the analysis of all reported Hg datasets (from Main Creek, Neck Creek and Lemon Creek in Spring 2009 surveys) due to practicability of low measurable concentrations in blank samples (Boevski, et al., 2007).

Field instrument calibration was performed at least once, prior to the start of sampling, and during each tidal survey. For all field instruments, measurement range was defined as the range of reliable readings of the meter or measuring device, as specified by the manufacturer. Details on the operation, calibration and accuracy of the Flo-Mate Model 2000 portable flowmeter are further detailed online at http://www.hachflow.com/pdf/Model_2000_Manual.pdf. Further information regarding the measurement ranges for temperature, dissolved oxygen, and salinity are outlined within the instrumentation specifications section of the YSI 85 multi-parameter probe user manual (available at <http://www.YSI.com>). Field reconnaissance at each of the study sites was performed prior to sampling to verify that the range for velocity measurements, specified in the manual for the Marsh-McBirney Flo-Mate Model 2000, were suitable.

Data Analysis and Calculations

Flow Measurement

Current velocity measurements were collected using a Marsh-McBirney Flo-Mate Model 2000 portable flowmeter. The Flo-Mate Model 2000 portable flowmeter measures water velocity readings in feet per second (ft/s) and meters per second (m/s). Technical procedures and specifications for measurement of stream discharge followed are outlined in the Flo-Mate Model 2000 manual. The technique applied for measuring current velocity is in conformance with the velocity area method developed by the U.S Geological Survey (USGS) as a standard procedure to determine velocity discharge (available on-line for review at:

www.rcamnl.wr.usgs.gov/sws/fieldmethods)

Flow calculations were determined by dividing the total channel width of Main Creek, Neck Creek and Lemon Creek into segments of equal length (d), which ranged from 15-11m, 2.5m, and 16-22m (at MA, NC, and LC, respectively). Prior to sampling, depth channel profiles were constructed by summing the areas of each segment (trapezoids at MA and LC) in order to determine the area (m²) of each cross-section (Fig. 6).

Temporal flow measurements were taken throughout each tidal cycle from the mid-point of creek channels. Velocity readings were recorded *in situ* at the .2, .6, .8 velocity positions on the segment centerline (.5 of conduit width) as described in Figure 6b. Subsequent to measuring the velocity at the .2, .6, and .8 positions, the .2 and .8 velocity values were averaged; the resulting value was averaged with the .6 velocity value. Accordingly, this permitted the calculation of flow via cross-sectional area and velocity measurements, taken over the course of the tidal cycle. Mean velocity measurements were multiplied by the cross-sectional area to determine the total water fluxes (m³·s⁻¹).

Suspended and Particulate Metal Concentrations

Concentrations of particulate metals and metals in marsh sediments were calculated from instrumentation measurements. The metal concentration of the material left on the membrane, measured as dry weight ($\mu\text{g}\cdot\text{g}^{-1}$), was termed the SPM metal concentration. The concentration of metals in the suspended sediment was calculated via the following equation:

$$\text{Mass}\cdot\text{Mass Calculation (x) } \text{mg}\cdot\text{kg}^{-1} = c \cdot v \cdot d / w \quad \text{Equation 3.}$$

x = SPM metals concentration ($\text{mg}\cdot\text{kg}^{-1}$)

c = Concentration in extract ($\text{mg}\cdot\text{L}^{-1}$)

v = Volume of extract (L, 100 mL = 0.1L)

d = Dilution factor (undiluted = 1)

w = Weight of sample aliquot extracted ($\text{g} \times 0.001 = \text{kg}$)

Suspended-phase metals were those metals in the unacidified sample that are retained by a .4 or .45 μm membrane filter. The concentration of these metals (left on the membrane) in the water sample, measured on a mass per volume basis, was called the particulate metal concentration ($\mu\text{g}\cdot\text{L}^{-1}$). It was obtained from the product of the SPM metal concentration and the suspended sediment concentration (Horowitz et al. 1986).

$$\text{Mass}\cdot\text{Volume Calculation (p) } \mu\text{g}\cdot\text{L}^{-1} = (\text{x}) \mu\text{g}\cdot\text{g}^{-1} \cdot (\text{m}) \text{g}\cdot\text{L}^{-1} \quad \text{Equation 4.}$$

p = Particulate concentration ($\mu\text{g}\cdot\text{L}^{-1}$)

x = SPM metal concentration ($\mu\text{g}\cdot\text{g}^{-1}$)

m = SPM ($\text{g}\cdot\text{L}^{-1}$)

Flux Calculations

To determine if any of the study sites demonstrated a net import (landward) and/or export (seaward)] transport of particulate metals, estimations of particle-associated Cd, Hg, Cu, and Zn fluxes were calculated via previously described methods (Hazen, et al., 1980; Lion, et al., 1982; Sokol, et al., 1996; Mackie, et al., 2007). The dimensions of the opening beneath the bridges

where time-based water column samples were collected at each sampling site, served as proxies for the area of water movement between the Arthur Kill and respective marsh sites. The width (in meters) under the bridges served as the width (in meters) of creek channels. Water column height measurements (in meters) taken at each sample collection interval served as the length parameter. Cross-sectional area (A), calculated in square meters, at the time of each sample was collected was calculated using site-specific depth profiles for each creek cross-section and determined as the product of bridge width (W) and water column height (H) (Equation 5).

$$\text{Cross-sectional area (A)} = W \cdot H \quad \textbf{Equation 5.}$$

Where,

A=cross-sectional area (meters)

W= width

H= height

The net direction (+/-) of lateral advective tidal transport/horizontal tidal exchange was determined by estimation of particle-associated metal fluxes between the study sites and the NY/NJ HE waterway into which they open/drain (Hazen, et al., 1980; Lion, et al., 1982; Sokol, et al., 1996; Mackie, et al., 2007). Calculated metal fluxes were calculated by multiplying the metal (Cd, Hg, Cu, and Zn) concentration data at sampling time and the volume of water entering or leaving the marsh. Water velocity ($\text{m}\cdot\text{s}^{-1}$) and cross-sectional area (m^2) data was used to estimate the respective volume (m^3) of water exchanged during which consecutive temporal samples were collected over the tidal cycle. In order to calculate the flux (F), the product of the cross-sectional area (A), velocity (V) at the time of sample collection, and the concentration of each element (C) were calculated as follows (Mackie et al. 2007):

$$F = A \cdot V_{t=1} \cdot C_{Cd,Hg,Cu,Zn} \quad \text{Equation 6.}$$

The import/export term for each metal was determined for each sampling event by summing fluxes for the flood and ebb portions of the sampling event. The trapezoidal rule was applied to integrate and compare the area under the respective curves for instantaneous fluxes measured on flood and ebb tides according to the following algorithm (SigmaPlot 7):

$$\begin{aligned} &\text{sigma } i \text{ from } 0 \text{ to } n-1 \\ &\text{or} \\ &\{y_i(x_{i+1} - x_i) + (1/2)(y_{i+1} - y_i)(x_{i+1} - x_i)\} \end{aligned} \quad \text{Equation 7.}$$

Accordingly, the total metal exchange was calculated using the difference between the influx (flood tide) and efflux (ebb tide) concentrations of each metal over the sampling period at Main Creek, Neck Creek, and Lemon Creek (Tables 17, 18, and 19) (Hazen, et al., 1980; Lion, et al., 1982; Sokol, et al., 1996; Mackie, et al., 2007). For the Arthur Kill sites, the time series datasets from neap and spring tide surveys, were then averaged to bracket metal exchange during low and high tidal energy conditions, and thereby, estimate a budget of metal exchange over tidal cycle (Sokol et al. 1996, Hazen et al. 1980).

Statistical analysis

To test for temporal and spatial differences, individual samples collected in each survey (n=9) were analyzed for metals as independent replicates in triplicate for all surveys (n=27). In addition, neap surveys also included collection and analysis of duplicate grab samples for SPM (n=36). Statistical analysis of results were incorporated where deemed appropriate to determine the significance of differences in marsh-specific metal concentrations (SPM, particulate and surface sediment fractions) and literature based local background concentrations (Bowen, 1979;

Hirschberg, et al., 1996). Further statistical analyses were applied to detect differences in concentrations of metals during ebb vs. flood tidal phases.

Statistical analysis of datasets included Student's *t*-tests (or *t'*-test when variances were not homogeneous) and the Mann-Whitney-Wilcoxon test, using Statistica version 7 (2005). To detect differences between metal concentrations in the water column during incoming vs. outgoing tides, the Mann-Whitney-Wilcoxon test (MWW) was applied to test the significance of particular metal fluxes were greater on either the flooding or ebbing tidal stages (Mackie et al. 2007).

RESULTS

***In situ* Environmental Monitoring**

Water quality parameters monitored at each of the three study sites over the course of each tidal event included: temperature (degrees °C); pH (standard units); dissolved oxygen ($\text{mg}\cdot\text{L}^{-1}$); salinity (ppt.). These *in situ* data field parameters were averaged for each survey and summarized in table 8. A detailed account of *in situ* data collected during each of the spring and neap surveys at MA and NC are provided in Appendix C-1-2 and Appendix C-3-4, respectively. An outline of Lemon Creek tidal survey *in situ* data is included in Appendix C-5.

Over the course of two half-ebb and a complete flooding tidal cycle (MA and NC) water column samples were collected for metal determination along with additional environmental parameters, including pH, temperature and dissolved oxygen. Temperatures ranged from 2.4-5.6 degrees Celsius; pH ranged between 7.42-7.78; and dissolved oxygen levels fell between 7.82-8.85 $\text{mg}\cdot\text{L}^{-1}$.

The times in which water samples and corresponding hydraulic measurements were taken over the tidal cycle monitored at Main Creek, Neck Creek and Lemon Creek are displayed in Appendix B. Monitoring over each tidal cycle involved the collection of samples and concurrent velocity measurements during flood, slack, and neap tidal stages (Appendix C).

At each site, the greatest velocity readings aligned with the last sample collected before high tide (maximum flood current preceded high tide); or where there was the greatest change in depth between sampling intervals. During each sampling event, “slack water” conditions was identified at instances where the direction of tidal current was indecipherable or observed to be setting in the opposite direction. In some instances this coincided concurrently with sampling at Main Creek, Neck Creek and Lemon Creek, and either was characterized as “—” or represented the minimum current speed of the preceding tidal phase. The relative magnitude and strength of respective flood and ebb currents characterized the horizontal movement of water (in and out) flowing in opposite directions, not in terms of vertical rising/falling of tidal stages. Accordingly, Figures 12 and 13 described current velocities, tidal flow, and flux as either progressing in/towards upland marsh (+) or out/towards Arthur Kill (-) at Main Creek and Neck Creek, respectively. Additional site-specific hydrodynamic data and information observed during each tidal survey is detailed and quantified within Appendix C.

Suspended Solids/Suspended Particulate Matter (SPM)

For each respective sampling interval over the course of the November tidal cycle surveys (during neap tide) performed at Main Creek and Neck Creek, duplicate samples were collected and analyzed (Appendix B-1-2). Individual samples (n= 18) were subsampled for SPM determination (n=2) and analyzed in triplicate for Cd, Cu, and Zn (n=3). Mean temporal values

were determined from SPM (n=4) and metal (n=3) concentrations yielded from duplicate analysis for each sampling interval at Main Creek and Neck Creek (Tables 12,14, Figs. 9-10). For each respective sampling interval (n=9) over the course of the tidal cycle survey conducted at Lemon Creek and during the second set of tidal surveys at the Arthur Kill sites (during spring tide), individual grab samples were collected, and subsampled for suspended sediment and metal analyses.

Average suspended particulate matter (SPM $\text{mg}\cdot\text{L}^{-1}$) concentrations from all water samples were determined via gravimetric methods and are reported in Tables 5, 9, 10 and 11. (mass of solids retained by the Nucleopore membrane (0.45 or 0.4 μm) divided by the volume of the filtered sample). SPM concentrations were greatest at LC. Mean SPM ($216 \text{ mg}\cdot\text{L}^{-1}$) calculated over the extent of the tidal cycle was 4.6-fold and 3.2-fold the values calculated for NC and MA, respectively (Table 5).

SPM Metal Concentrations

Individual samples (n= 9) were split for SPM determination (n=2); and digested filtrates were analyzed in triplicate for Cd, Cu, Zn and Hg (n=3) (Fig. 3). Separate metal processing techniques and analytical procedures were followed for the determination of Hg and non-Hg metals, which included application of element-specific instrumentation (FIMS and ICP-AES, respectively).

The metal concentration of the material left on the membrane, measured as dry weight ($\text{ug}\cdot\text{g}^{-1}$), was called the SPM metal concentration. The range and average concentration of trace metals in suspended particulate matter of the three systems are given in Table 5. Laboratory reagent blank (LRB) values did not exceed respective analytical minimum detection limits

(MDL), however, analysis of filter blanks confirmed polycarbonate filters contained inherently low levels of certain metals, including Hg and Zn (as expected), and to a lesser extent Cu. Thereby, this suggested the natural composition of polycarbonate filters, rather than field, laboratory, or reagent contamination, may have been an additional source of trace elements, and inadvertently skewed (elevated) metal-specific SPM and particulate concentrations (i.e. notably Zn and Cu).

Although SPM concentrations derived from Lemon Creek were significantly ($p < 0.05$) lower than Main Creek and Neck Creek, mean SPM concentrations of all metals were greater than background proxies (Table 5) (Persaud et al; 1993, Horowitz et al.; 1991). Regardless, the site-specific patterns reflected by the co-occurrence of metals suspended in the water column were generally consistent with those characterized among metals observed surface sediments at Main Creek, Neck Creek and Lemon Creek. Consistent with findings from analysis of cores and surface sediments, Cu and Zn demonstrated the greatest concentrations at all sites. Enriched levels of all metals were identified in both the water column (particulate and SPM) and marsh bed sediments. Mean concentrations of metals in bed sediments, SPM, at all sites were significantly greater than background indices (i.e. shale or worldwide river sediment (Table 4, Figs.8a-c). The Cd, Hg, Cu, and Zn contents of Main Creek, Neck Creek and Lemon Creek sediment samples were twice as high as the average abundances in shale (Table 5b).

Particulate Metal Distributions

Collectively, suspended sediment (SPM) values ($\text{mg}\cdot\text{L}^{-1}$) and respective metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) yielded for each sampling interval were used to determine temporal suspended sediment-associated elemental concentrations in mass volume⁻¹ units ($\text{mg}\cdot\text{L}^{-1}$) over each tidal cycle performed at Main Creek, Neck Creek and Lemon Creek (Tables 12-16, Figs. 9-

11). Thereby, the particulate metal concentration ($\mu\text{g}\cdot\text{L}^{-1}$), or the concentration of metals (left on the membrane) in the water sample, measured on a mass per volume basis, was determined from the product of the SPM metal concentration and the suspended sediment concentration.

The range and average concentration of metals in particulate matter of the three marsh-creek systems are given in Table 5. From the data in Table 5b, it is evident that the Arthur Kill sites contained the highest particulate metals, relative to the external site, Lemon Creek. The highest metal concentrations were detectable in the water column samples from Main Creek (Table 5b; Table 9a-c, Fig. 6). Mean temporal particulate metal concentration values, shown in Figures 9-11, were determined for the extent of the tidal cycle at Main Creek, Neck Creek, and Lemon Creek from SPM ($n=4$) and metal ($n=3$) concentrations, yielded from replicate analysis for each sampling interval (Figs. 9-11, Tables 13, 15, 16).

Background Comparisons

Elevated levels of metals were present in both water and sediment compartments at all sites (Table 3, 4, Figure 6). In order to put the environmental significance of mean site-specific metal concentrations into context, SPM and particulate metals datasets were collated with respective surface sediment results collected during low tide in the Spring of 2009, and compared with global background values (Figs 8a-c). Two common literature-based global background indices, mean world shale and average worldwide river concentrations were used to put mean particulate and SPM metal concentrations into perspective ((Wedpohl et al.; 1968, Martin and Windom 1991) (Figs. 8a-c). Figure 8 compares mean particulate metals and surface sediments from Main Creek, Neck Creek, and Lemon Creek to mean world-wide shale concentrations. Logscale metal concentration units were measured as a mass·volume ($\mu\text{g}\cdot\text{L}^{-1}$)

and mass·mass dry weight ($\mu\text{g}\cdot\text{g}^{-1}$) for particulate and surface sediments, respectively. Y-axis values reflect site-specific mean Cd (n=54), Hg (n=18), Cu (n=54), and Zn (n=54) concentrations determined from average temporal particulate metal concentrations determined over complete tidal cycles during neap (2008) and spring (2009) tidal surveys at Main Creek and Neck Creek, in 2008 and 2009, respectively. For Lemon Creek mean particulate concentrations were determined over a median tidal cycle survey (intermediate flow conditions between neap and spring tide) at Lemon Creek (n=18) (2009). Mean surface sediment values for each site (n=54) show 2009 average of lateral transect samples from Main Creek, Neck Creek, and Lemon Creek. Literature-based background concentrations, derived from worldwide average shale values for elemental Cd, Hg, Cu, and Zn contents, were used as global proxies for natural background concentrations (Wedpohl et al. 1968). Site-specific regression lines are reflected for particulate metals suspended in the water column at Main Creek, Neck Creek, and Lemon Creek, respectively (Fig. 8a). As a means of comparison, the 1:1 correlation between particulate Cd, Hg, Cu, and Zn concentration vs. background reference values is also shown. As a secondary background reference, natural elemental concentrations were also derived from world average concentrations in river sediments (Martin and Windom 1991). Figure 8c compares site-specific mean particulate metals to mean world-wide river concentrations.

Regional background sediment concentrations were also applied as a means of reference to comparatively assess site-specific particulate metal concentrations (Figs. 9-11). It is important to note that background values are measured as a concentration per gram dry sediment, whereas particulate metals are measured as a concentration per liter. However, this approach was used to remain consistent with previous research components, and also highlight demonstrable differences among sites. In contrast to the Arthur Kill sites, Lemon Creek values did not exceed

Hudson River background concentrations, which were used as proxies for natural elemental background levels in regional sediments (pre-industrial levels) (Hirschberg et al; 1996, Bowen et al., 1979). Main Creek was the only site to show particulate Hg concentrations that were greater than background values. Furthermore, the contrast between neap tide and spring tide surveys was particularly apparent when site-specific tidal samples were comparatively assessed with respect to background concentrations. For example, relative to neap tide survey results, Main Creek reflected higher particulate Cu and Zn concentrations over the spring survey, but lower Cd concentrations. Conversely, Neck Creek showed higher Cd and Zn during the neap survey. However, both Arthur Kill sites demonstrated greater Cu levels over tidal cycle surveys conducted under spring tide conditions.

Another approach used to evaluate relative impacts throughout the study area was to, comparatively assess Main Creek, Neck Creek and Lemon Creek values detected in suspension with emission rates of atmospheric metals released from natural and anthropogenic sources (Table 3; Millward, et al., 2001).

Tidal Currents, Hydraulic and Flow Results

All sites demonstrate a semi-diurnal range (the difference in height between high and low waters over about half a day) varies in a two-week cycle. In this study flood and ebb velocities were given positive (+) and negative (-) signs, respectively. Tidal flow information, presented as a table of flow speeds and directional bearings at hourly intervals, with separate tables for spring and neap tides are presented in Appendix C. Prior to sampling, initial site reconnaissance at study sites, in combination with available tide flow data was accessed online from proximal gauging locations with similar patterns of tidal behavior (<http://saltwatertides.com>). New Jersey Arthur Kill tributary locations (Woodbridge and Rahway River) were utilized to estimate relative

time to high water for Main Creek and Neck Creek surveys, and Great Kills Harbor was used as a proxy for Lemon Creek.

Flux Calculations

For each survey, a tidal prism, (i.e. the net difference in the volume of water entering and leaving at flood and ebb tides) was calculated as the volume of water exchanged over each complete tidal cycle sampled at Main Creek (n=2), Neck Creek (n=2) and Lemon Creek (n=1) (Luketina 1998, Davis and Fitzgerald 2004). The volumes of water exchanged during the neap and spring tidal surveys at Main Creek varied from 1.88 m³ to 10.6 m³, respectively. In contrast, the volumes of water exchanged during the neap (1.68 m³) and spring (0.94 m³) tidal surveys at Neck Creek were consistent. In the Spring of 2009, the greatest tidal prism was calculated for the Main Creek spring tide survey (10.6 m³), which was very similar to that measured for the intermediate (mid neap-spring) tidal survey conducted at Lemon Creek (10.3 m³).

The errors associated with discharge measurements (*Q*) typically are, based on manufacturer specifications (Marsh McBirney Flomate 2000), 3–5% (Sauer and Meyer, 1992). Actual suspended sediment concentration measurements, based on replicate samples, as well as measurements of filter and procedural blanks and interlaboratory standards, were less than 10%. The vast majority of suspended sediment concentrations used in the calculations had varying degrees of error associated with them depending on the site as well as the discharge (Horowitz et al., 2001).

For each sampling interval (n=9), metal fluxes were calculated via multiplication of water column measurement for instantaneous flow (average velocity (m·s⁻¹) · cross-sectional area (m²)) and mean particulate metal concentration (µg·g⁻¹). The total metal exchange was calculated using the difference between the influx (flood tide) and efflux (ebb tide) concentrations of each

metal over the sampling period at Main Creek, Neck Creek, and Lemon Creek (Tables 17a-c, 18a-c, and 19a-b) (Hazen, et al., 1980; Lion, et al., 1982; Sokol, et al., 1996; Mackie, et al., 2007). For the Arthur Kill sites, the time series datasets from neap and spring tide surveys, were then averaged to bracket metal exchange during low and high tidal energy conditions, and thereby, estimated a budget of metal exchange over tidal cycle (Table 17d, 18d) (Sokol et al. 1996, Hazen et al. 1980).

The significance of tidal stage and influence of current direction on water volumes, and fluxes of SPM and associated metals moving in (+) and out (-) of Main Creek (Tables 17 a-b), Neck Creek (Tables (18 a-b), and Lemon Creek (Table 19 a-b) was tested by comparison of median flood (F) and ebb (E) tide values (non-negative) via Mann-Whitney U analysis of site-specific datasets.

Figure 12a depicts incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete neap tidal cycle at Main Creek (November 2008); all parameters tested had p values >0.05, which indicated no significant difference of fluxes with respect to current direction Cd, Cu, Zn, and SPM fluxes (Table 17a; Appendix H-1). However, the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-) showed a demonstrable contrast in metal-specific datasets between incoming and outgoing tides (Table 17a). Figure 12b. shows incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg were determined from water column samples collected over the extent of a complete spring tidal cycle at Main Creek (March 2009). In contrast to the Main Creek neap tide survey, all particulate metals and SPM showed significant differences among non-negative medians in the spring tide survey; the difference among incoming and outgoing water volume flows was

considered insignificant ($p>0.05$) (Appendix H-2). Furthermore, the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-)) showed a net import (+) for all parameters, towards the upland Main Creek marsh-creek habitat (Fig 12b, Table 17b).

Statistical analysis showed that neither neap, nor spring tidal cycle surveys conducted at Neck Creek showed significant differences ($p>0.05$) between flood and ebb tide flux values (non-negative medians) (Tables 18a-b). In general, Neck Creek surveys contrasted in terms of the net direction of tidal transport of Cd, Cu, Zn, and Hg on particles suspended within the water column during neap and spring tidal flow conditions. Positive values were determined for all parameters during the Neck Creek neap tide survey (i.e. SPM, Cd, Cu, and Zn) but, the difference between directional datasets (incoming vs. outgoing tides) showed only a net import of SPM during the spring tide survey (Appendix G-2). Therefore, under the higher tidal energy conditions at Neck Creek, the net difference between ebb and flood area curves reflected negative values for all metals (Cd, Cu, Zn and Hg) (Fig. 13b, Table. 18b-c)

Instantaneous incoming ($n=4$) and outgoing ($n=4$) fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete tidal cycle (intermediate flow conditions) at Lemon Creek are listed in Table 19a and depicted in Figure. 14. Hg and SPM fluxes did not show significantly different fluxes with respect to current direction (+/-). This observation was further highlighted in the by the summation of metal-specific fluxes at Lemon Creek with respect to current direction (flood (+) and ebb (-)), which showed a demonstrable contrast with respect to metal-specific datasets between incoming and outgoing tides (Fig. 14).

DISCUSSION

Relative to other systems, the NY/NJ HE is a relatively complicated estuary, particularly the western portion of this system, stretching along the Arthur Kill (Young et al., 1984). The greater study area, extending from Newark to Raritan Bays, receives multiple freshwater sources (directly and indirectly) from regional rivers (i.e. Rahway, Elizabeth, Passaic, Raritan, Hudson Rivers), is known to contain relatively high concentrations of metals, and is further challenged by high residence time of pollutants due to low flushing rates (USFWS 1997, Vitaliano et al., 2009). This research component examined the presence of metals associated with the suspended sediments within the water column of Main Creek, Neck Creek and Lemon Creek to further understanding of the site-specific distribution, transport and fate of metals within these three important marsh-creek habitats of the NY/NJ Harbor Estuary Complex.

The particulate phase is largely responsible for the transport of metals in surface water because trace metals adsorb strongly on particles and are preferentially associated with particulate matter (Masson 2006, Butler et al. 2008). From concentrations of suspended particulate matter and associated contaminants, calculations can be made to determine fluxes of metals and the net tidal transport of each component (Cole et al. 2001, Church et al. 1981). Fluxes of suspended sediments entering and leaving tidal marsh habitats are important for a variety of reasons, including habitat restoration efforts, and the possibility for pollutant accumulation (Ganju et al. 2005).

Metals associated with the particulate (opposed to dissolved) fractions of total solids suspended within the water column were directly determined to examine their presence and elemental distributions. The particulate phase is largely responsible for the transport of metals in

surface water because trace metals adsorb strongly on particles and are preferentially associated with particulate matter (Masson, 2006; Butler, et al., 2008). Fundamentally, the unfilterable material retained on filter membranes ($>40\text{ }\mu\text{m}$) was used to represent the suspended matter particulate matter within Main Creek, Neck Creek and Lemon Creek water column samples. This fraction is also considered that which is available to filter feeding organisms (Weis et al. 2006).

In this research component, particulate metal concentrations (Cd, Hg, Cu, and Zn) were determined in the water column of three tidal creek conduits (Table 1, Figs. 1, Figs. 7a-c) in three Staten Island estuarine wetland systems. Temporal grab samples were collected nine times over each complete tidal cycle to determine the concentrations and distribution of study metals suspended in the particulate phase within the water column of Main Creek, Neck Creek, and Lemon Creek. Four samples collected during respective flood and ebb tidal stages were comparatively assessed in order to calculate the fluxes (influx vs. efflux) of metals between the upland marsh habitats and the adjacent open waters of the NY-NJ HE, by incorporating concurrent water flow measurements from incoming and outgoing tidal currents.

Based on tidal connectivity, in addition to geographic relativity to the Arthur Kill Proper, Main Creek (MA) and Neck Creek (NC) were targeted Arthur Kill study sites, whereas Lemon Creek served as the external study site, representative of the RB watershed (Fig. 1, Table 1). Comparability of the systems was accounted for in terms of the specific type of wetland environment (i.e. all categorized by NYS DEC as estuarine wetlands), along with basic geomorphology and ecological characteristics of the tidal creek and upland marsh habitats (Figs. 1a-c, Figs. 7a-c).

Particulate metal fluxes were calculated through well-defined cross-sections of each tidal creek using velocity/current meter, depth, suspended matter and metal concentration data to gain insight into contributory factors, including particle dynamics, tidal exchange and advective transport processes that may be propagating and sustaining the large-scale temporal and spatial metal contamination gradients demonstrated throughout the study area. The primary objective was to substantiate the pattern of higher contamination in Staten Island marsh systems within the Arthur Kill watershed (along the western shore), relative to an external marsh within the Raritan Bay watershed (along the southern shore). The impetus of this study was to examine the role of estuarine tidal exchange and lateral transport of particulate metals between upland marsh habitats and the Arthur Kill Proper as a contributory factor. In this effort, this study compared SPM and metal fluxes on incoming and outgoing tides to determine the net direction of tidal transport (import vs. export) and identify net differences in metal-specific magnitudes between tidal stages and phases (i.e. flooding and ebbing tides).

Within Main Creek, Neck Creek and Lemon Creek tides flow from open waters of the NY/ NJ Estuary (i.e. Arthur Kill and Raritan Bay). Initial assertions of this study were that any potential tidal exchange with adjoining creeks occurred via the horizontal movement of water among ebb and flood phases, which was primarily responsible for the transport of fine particles, upon which particle reactive metals tend to adsorb and act conservatively (Horowitz et al.; 1996). Accordingly, from concentrations of suspended particulate matter and associated contaminants, calculations were made to determine fluxes of metals and the net tidal transport of each constituent (Church, et al., 1981; Cole, et al. 2001).

It has been determined that concentrations of metals in sediments from the study sites around Staten Island have decreased (in general) over the past 10 years. However, evidence of

such decline appeared to be site-specific, and not necessarily indicative of attenuation. For instance, in terms of specific metals and temporal datasets, Main Creek, a site in close proximity to the Fresh Kills complex, exhibits lower surface sediment metal concentrations than does a site external to Fresh Kills complex, Neck Creek (yet still connected to the Arthur Kill) (Table 5). However, both sites exhibit concentrations indicative of continuous impact (most likely associated to their connectivity to the Arthur Kill) (see chapters 2 and 3; Appendix 4-A).

On November 19th, 2008 and March 24, 2009 sampling events were conducted at Main Creek and Neck Creek to characterize the lateral/longitudinal advective transport of metals suspended within the water column over spring and neap tidal cycles, respectively, and thereby provide an estimate to bracket the flux of metals between the Arthur Kill and upland/inland marsh-creek habitats/areas. At each site, particulate metal flux was calculated through well-defined cross-sections of the tidal creeks using velocity/current meter, depth, suspended matter and metal concentration. Flux calculations were determined from the collection of grab water samples (~ .5m below surface) and concurrent velocity and depth measurements observed over the extent of two tidal cycles at Main Creek and Neck Creek, and one at Lemon Creek.

A series of current-meter velocity measurements were made while concurrently collecting water column samples over the extent of a tidal cycle at each site. For Main Creek and Neck Creek, two sampling surveys were conducted to include both spring and neap tidal stages which bracketed the site-specific conditions characterized during variable flows and tidal ranges.

Supplemental velocity measurements were made at all sites in order to provide additional data, though temporal differences were comparable relative to those observed within a tidal

cycle. Given that Main Creek, Neck Creek and Lemon Creek are characterized as stable channels with respect to scour and fill (as opposed to unstable alluvial channels) area measurements were deemed sufficient (Rantz, et al., 1982). However, given the variability of SPM, specifically with respect to water column depth (greatest at low tide), a supplemental series SPM determinations, will be considered in the future, in conjunction with any additional discharge measurements.

In order to determine if any of the study sites (Main Creek, Neck Creek or Lemon Creek) demonstrated a flux (either net import [landward] and/or export [seaward] transport) of particulate Cd, Hg, and Cu, a mass balance approach was used. Fundamental to this goal was the calculation of representative ranges of fluxes for ebb and flood tidal stages at each site that also accounted for flow differences due to tidal state (neap and spring).

A mass balance approach aimed to characterize the tidal exchange of metals suspended within the water column among the Staten Island wetland sites and the respective open waters of the NY/NJ HE area into which they empty. Over the extent of a complete tidal cycle, the net import/export of metals, namely Cd, and Hg, was examined in order to establish if these sites serve as pollutant conduits to inland habitats (marsh-creek systems within the Arthur Kill and Eastern Raritan Bay watersheds).

Collectively, suspended sediment values ($\text{mg}\cdot\text{L}^{-1}$) and respective particulate metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) yielded for each sampling interval were used to determine temporal suspended sediment-associated elemental concentrations in mass volume⁻¹ units ($\text{mg}\cdot\text{L}^{-1}$) over each tidal cycle performed at Main Creek, Neck Creek and Lemon Creek. Suspended sediment-

associated elemental concentrations (Cd, Cu, Zn, and Hg) were reported in mass volume⁻¹ units) in order to estimate metal fluxes (Eq. 3).

An ancillary goal of this study was comparatively assess relative magnitudes of site-specific metal concentrations and enrichment levels exhibited by sediments in suspension (in the water column) with reference to ‘biologically active’ surface deposits (Appendix A). This approach effectually tested the applicability of the assertion that sampling marsh bed sediments, and particularly environmentally relevant surface layers, can be considered representative of fine-grained suspended matter transported with the overlying flow of creek conduits within marshes, and alternatively, the predicative ability of water column samples analyzed on dry weight basis (mass·mass). This is critical given that sampling marsh bed sediments, and particularly ‘biologically active’ surface layers, can be considered representative of fine-grained suspended matter. Laboratory reagent blank (LRB) values did not exceed respective analytical minimum detection limits (MDL), however, analysis of filter blanks confirmed polycarbonate filters contained inherently low levels of certain metals, including Hg and Zn (as expected), and to a lesser extent Cu. Thereby, this suggested the natural composition of polycarbonate filters, rather than field, laboratory or reagent contamination, may have been an additional source of trace elements and inadvertently skewed (elevated) metal-specific SPM concentrations (i.e. notably Zn and Cu). Accordingly, metal-specific SPM concentrations were found to be greater than surface metal contents by over a magnitude with respect to Zn and Cu, and thereby challenging the comparability between these environmental compartments. Relative to surface sediment samples, the extent of anthropogenic contamination, reflected by Contamination Factors (CF), determined for sediment samples suspended within the water column, were lower by an order of an magnitude for the Arthur Kill sites (very high vs. considerable contamination

respectively) (Appendix A, Tables 7a-c). In contrast, Lemon Creek surface sediments showed greater anthropogenic contamination; sediment samples collected from the surface at low tide showed CF values in the moderate range, whereas, sediments suspended within the water column at Lemon Creek were in the low range. Regardless, the site-specific patterns reflected by the co-occurrence of metals suspended in the water column were generally consistent with those characterized among metals observed surface sediments at Main Creek, Neck Creek and Lemon Creek.

Presence of SPM and Associated Contaminants in the Water Column and Temporal and Spatial Variations

Particulates carry and account for a major portion of metals present in a waterbody and therefore, measurements of suspended particles are useful in metal flux/transport studies (Yigiterhan, et al., 2007; Butler et al., 2008; Balcom, et al., 2008). When summed together, with the dissolved solids fraction, the particulate component (SPM) is termed total suspended solids (TSS). In contrast to other conventional water quality parameters (i.e. pH, temperature, dissolved oxygen, biochemical oxygen demand (BOD) and nutrients), SPM includes inorganic and organic particles from various sources (point and nonpoint), along with plankton and bacteria.

Suspended solids (SS) consist of an organic (carbon) fraction and inorganic fraction that act as “traps” for hydrophobic and trace metal contaminants. However, sorption is not an irreversible phenomenon. The toxicity of SS is dependent on what contaminants partition onto them and to what extent the physical transport of SS takes into account longitudinal advective and dispersive transport as well as vertical transport (the latter allows for an estimation of net

deposition and bed burial rates). Depending on the contaminant's structure and physical-chemical characteristics, it will sorb/interact with either fraction.

Inter-marsh Variations: SPM and Metal Concentrations within the Water Column

The distributions of particulate trace metals associated with SPM concentrations suspended within the water column of Main Creek, Neck Creek, and Lemon Creek, are discussed in order to gain insight into the factors controlling variability among and between these estuarine wetland ecosystems. It was obvious that water column samples from Arthur Kill marshes contained higher SPM metals compared to the Lemon Creek/Raritan Bay watershed region. Although SPM metal concentrations derived from Lemon Creek were significantly lower than Main Creek and Neck Creek, where concentrations of all SPM metals were greater than background proxies (Fig. 8b) (Martin and Windom 1991). Cu and Zn demonstrated the greatest concentrations at all sites, and in particulate phase as well (Figs. 4-8b-c, Table 5).

The range and average concentration of metals in particulate matter of the three marsh-creek systems demonstrates that the Arthur Kill sites contained the highest particulate metals, relative to the external site, Lemon Creek. However, mean SPM concentrations measured at Main Creek ($67.5 \text{ mg}\cdot\text{L}^{-1}$) and Neck Creek ($47.1 \text{ mg}\cdot\text{L}^{-1}$) were comparatively lower than the high concentration of SPM at Lemon Creek ($216 \text{ mg}\cdot\text{L}^{-1}$).

SPM concentrations measured at the Arthur Kill sites (ranging from $36.2\text{-}98.7 \text{ mg}\cdot\text{L}^{-1}$ at Main Creek and $23.7\text{-}70.6 \text{ mg}\cdot\text{L}^{-1}$ at Neck Creek), bracketed results from surveys conducted during low and high energy tidal conditions (neaps and springs), were comparatively lower than respective minima and maxima values determined at Lemon Creek ($72.1\text{-}326 \text{ mg}\cdot\text{L}^{-1}$) (Table 6b). Thereby, relative to both Arthur Kill sites, SPM concentrations were substantially greater at Lemon Creek. Although Lemon Creek was sampled once during an intermediate tide (i.e.

between spring and neap tidal phases), even the minimum SPM measured ($72.1 \text{ mg}\cdot\text{L}^{-1}$) was greater than the entire range of values determined in either of the neap or spring tidal surveys conducted at Neck Creek ($23.7\text{-}70.6 \text{ mg}\cdot\text{L}^{-1}$) (Tables 5, 10, 11). The minimum Lemon Creek SPM concentration ($72.1 \text{ mg}\cdot\text{L}^{-1}$) was also slightly greater than that of the average SPM content characterized at Main Creek ($67.5 \text{ mg}\cdot\text{L}^{-1}$) (Table 5).

Overall, the order in which sites ranked, $\text{MA} > \text{NC} > \text{LC}$, in terms of highest to lowest average metals suspended within the water column, corresponded to the overall patterns demonstrated by analysis of surface sediments (Fig. 8a, Table 4). The analogous concentrations of SPM and metals (both SPM and particulate) reflected inter-marsh variability that aligned with the large-scale spatial and temporal distribution and enrichment gradients exhibited by comparative assessments of Main Creek, Neck Creek and Lemon Creek Arthur Kill and Raritan Bay watershed sediments.

The lower concentrations of particulate metals found within the water column of Lemon Creek, compared to the Arthur Kill sites may be due to the greater tidal flushing and fresh groundwater inputs (NYS DEC 2009). High concentrations of particulate trace metals (i.e. Cu, Zn) in estuarine environments may be due to the remineralization from sediments and organic matter when in lower salinity conditions prevail. However, this was not observed in this study. Further research into chemical speciation and partitioning of metals among dissolved and particulate phases are required for additional insight into the influence of localized geochemical processes and site-specific environmental dynamics on metal-SPM interactions. The degree to which important physicochemical factors, including the impact of freshwater mixing, nutrient and particle removal dynamics, affect site-specific factors (i.e. flocculation and particle scavenging) ultimately impacts metal (re)distribution, cycling and fate within each system.

Intra-site Variability of SPM and Metals within the Water Column Between Tidal Surveys

Overall, there was evident temporal variability in the SPM and metal distribution patterns within the water column of each study site, as well as between Main Creek, Neck Creek, and Lemon Creek. However, there were a few consistent differences in the distribution patterns between the neap and spring tide surveys [in the Arthur Kill sites].

Although, Neck Creek consistently demonstrated respectively lower mean SPM concentrations than Main Creek, however, both Arthur Kill sites demonstrated relatively similar average SPM concentrations with respect to neap ($36.3 \text{ mg}\cdot\text{L}^{-1}$ and $23.7 \text{ mg}\cdot\text{L}^{-1}$) and spring ($98.6 \text{ mg}\cdot\text{L}^{-1}$ and $70.6 \text{ mg}\cdot\text{L}^{-1}$) tidal surveys (Tables 9, 10). In addition to SPM, particulate Cu was the only other constituent that consistently showed greater mean concentrations for the spring tide surveys at the Arthur Kill sites. Accordingly, there was no consistent trend with respect to the variability of mean Cd and Zn (suspended sediment and particulate) in response to changing tidal conditions (i.e. neap/spring tides); Main Creek neap tide Cd values exceeded spring tide concentrations by approximately three-fold ($0.67\mu\text{g}\cdot\text{L}^{-1}$ - $0.22 \mu\text{g}\cdot\text{L}^{-1}$) half, whereas, mean Neck Creek particulate Cd values from the spring tide survey were about twice as high as those measured for the neap tide survey ($1.15\mu\text{g}\cdot\text{L}^{-1}$ and $0.55\mu\text{g}\cdot\text{L}^{-1}$, respectively) (Tables 9, 10).

Therefore, In addition to the evident intra-marsh spatial variation reflected by regression analysis of Main Creek surface sediments (collected in 2009), which reflected significant differences in surficial Cd, Cu, Hg, and Zn concentration and anthropogenic enrichment level, with respect to distance from the Arthur Kill, demonstrable temporal variability was also observed, in terms of the presence of metals suspended within the water column; particularly in terms of Cu and Zn, with several tidal cycle samples showing relative standard deviations exceeding 50% of the mean. This finding was also reflected by Neck Creek samples.

Nonetheless, metals generally appeared to co-occur, with analogous patterns reflected over the tidal cycle at each site. The most evident trend was shown at Lemon Creek, where Cd, Cu, and Zn reached maximum levels during the beginning of ebb tide, immediately following slack tide.

Initial analysis of particulate metal results did show some consistent differences/trends that may be indicative of potential sources and/or suspended sediment and contaminant transport. The increased particulate Cu concentrations with respect to increased suspended particulate matter during greater tidal energy (spring tide conditions), may be indicative of either remobilization and transport of seaward contaminants or non-point source loadings (i.e. erosion, runoff within the catchment area) (NJTRWP 2001).

Factors affecting supply and deposition of particles

Both localized factors attributable to anthropogenic (present and past land-use activities) and natural dynamics (site-specific creek morphology and hydraulic dynamics) influence the depositional context, and thereby, the transport, distribution and fate of metals and other particle-reactive constituents. It was anticipated that the regional supply (and deposition) of solids exchange among the NY/NJ HE system and inland marsh systems were more contaminated than local particles derived directly from surrounding terrestrial sources within local catchment areas (i.e. roadways, Freshkills Landfill, CSOs). Accordingly, a combination of physiochemical processes (i.e. adsorption/flocculation, etc.) and contributory estuarine dynamics, including remobilization, lateral transport and tidal exchange of legacy contaminants within the Arthur Kill, may support this plausible explanation for the evidently greater temporal and spatial metal enrichment identified in marsh sediments within the Arthur Kill watershed.

Although previous research established greater anthropogenic metal enrichment in study sites that are adjacent to the Arthur Kill, known as a regional hotspot of sediment contamination,

both the States of New York and New Jersey have classified the Raritan Bay, in addition to the Arthur Kill, as an impaired waterway on account of reported levels for various conventional water quality parameters that do not meet current (i.e. pathogens and floatables) (NJ DEP 2012, NYS DEC 2010). However, dependent on State and assessment year, the Arthur Kill and tributaries have also been listed as impaired in terms of metal contaminated sediments (i.e. Cd and Hg) (NJ DEP 2012, NYS DEC 2010). Thereby, characterization of tidal variations of particulate metals was fundamental to examination of the exchange and lateral advective transport of metals among inland marshes and the open waterbodies into which they drain (the Arthur Kill and Raritan Bay). Ultimately, both local and regional disturbances in NY/NJ HE marsh solids and contaminants concentrations are retained in site-specific sedimentary records. As expected, study sites within Arthur Kill (MA and NC) and Raritan Bay (LC) watersheds demonstrated differences in the supply and deposition of contaminated particle loads due to current and historical inputs and type, and variety of land-use (Figs. 4a-b)

Anthropogenic sources of particles

The atmospheric inputs are relatively small in the NY/NJ HE compared to river inputs of particles (Young et al., 1984). For example, SS loadings into the NY/NJ Harbor amount to a total of 2396 mt day⁻¹ in the following percentages tributary inputs, 79.5% (dominant); municipal discharges, 11.1%; CSOs, 5.4%; atmospheric deposition, 1.0%; storm water, 2.7%; landfill leachate, 0%; industrial discharges, 0.3% (HydroQual, 1991). But, given the proximity to the Fresh Kills and Brookfield Landfills, and that the study area is downwind of one of the world's largest petrochemical industries, localized stressors may impact the study area, reflected by relatively higher fraction of percentages. Other mechanisms included the input of contaminants

due to the cleaning and maintenance of power plants and other industrial contributions (Olsen, et al., 1978, Young et al., 1984).

The sedimentary particles, generally characterized by the clay and silt-sized fractions, suspended within the water column of Main Creek, Neck Creek and Lemon Creek were likely, initially derived from regional tributaries and/or localized watersheds, vehiculated via estuarine transport/tidal advection and/or land-based runoff, and/or resuspended sedimentary particles.

Tidal cycle

In addition to sediment export, phenomena (other than loss) are generally known to cause spatial and temporal variations among solids concentrations in the NY/NJ Harbor Estuary, and thereby, attributable to SS concentrations that vary over a tidal cycle and seasonally, by a factor of four and six, respectively (NYCDEP, 1993). Suspended solids concentrations and the particulate concentration of the contaminants that they carry, usually vary over the tidal cycle due to scouring. In general, they are well mixed vertically, with highest concentrations occurring at low tides. This has implications on contaminant loadings. In this study it was obvious by visual observation that the greatest SPM were concurrent with low tides, at all sites, except perhaps, Lemon Creek which did not drop to depths at the sampling location where scouring was evident.

Resuspension and deposition

The continuous resuspension (and deposition) of sediments in estuaries is the main cause of increases in suspended solids concentration compared to levels found in tributaries (the effects of stratification/resuspension are detected by analysis of samples over the depth of the water

column). For example, in the Hudson River, elevated solids occur along the estuary in the vicinity of the Harlem-Hudson junction (HydroQual, 1995).

In contrast to certain substances (i.e. nutrients, carbon) suspended within the water column, it has been suggested that particle-reactive constituents (i.e. trace metals or radionuclides) tend not to change in concentration during their passage through tidal channels (Gomez, et al., 2000a, b; Gomez, et al., 2004). This presumption served as the basis for the initial experiential design of this research component. It was reasonably expected that the metals studied (Cd, Cu, Zn, and Hg) characterized homogeneity, in terms of spatial and temporal distributions and changes of concentration while in transit (lateral advective transport) through Main Creek, Neck Creek and Lemon Creek (Gomez, et al., 2000b; Santana-Casiano, et al., 2002). Therefore, an estimation of metal inputs (imports (+) and exports (-)) can be determined from the product of water fluxes and the elemental concentration (i.e. Cd, Cu, Zn, and Hg) in the water mass (e.g., Elbaz-Poulichet, et al., 2001a,b).

However, it was acknowledged and taken into great consideration that the validity/success of such an approximation was ultimately based on several important precursors regarding a few key parameters. The assumedly homogenous and relatively constant concentrations were derived from the collection of representative temporal samples. Although the collection of grabs was to obtain characteristic water samples over a complete tidal cycle demonstrative of each water mass, individual samples collected at a singular point in time makes this challenging in any natural/real-world environmental setting.

Appropriate modifications were applied to improve the demonstrative ability (of grab samples) to represent the entire flowing water column, and ensure the relative precision/accuracy

to depict respective water chemistry (elemental concentrations, SPM/SS), concurrently with *in situ* measurements (i.e. velocity, depth measurements,).

The unique and dynamic environment of each marsh-creek system, characterized by the site-specific spatiotemporal variability of particle-reactive constituents collectively, reflected the heterogeneous context of the study area. Thereby, the relative role of temporal and spatial variability previously demonstrated over time and space, at depth and in surface sediments, within Main Creek, Neck Creek and Lemon Creek was taken into account when calculating/estimating particulate/SS metal over a tidal cycle (Gomez, et al. 2000a,b; 2001; Gomez, et al. 2004). For example, radionuclide and metal distributions in Neck Creek and Main Creek, respectively demonstrated greatest variability demonstrated by the radionuclides studies and metal distributions, and therefore, likely that metals suspended within the water column may also reflect this heterogeneous depositional environment of Neck Creek and Main Creek (Chapters 2 and 3).

Mechanistic studies regarding flow and sediment transport conditions have proposed that in areas with slow currents (i.e. salt marshes), the processes controlling sedimentation and resuspension do not vary among tidal conditions; thereby, suggests these dynamic processes are not affected by tidal amplitude, and therefore, not driven by tidal currents (Jordan, et al., 1982; Christiansen, et al., 2000).

In such environments characterized by relatively low velocities, as demonstrable by the marsh-creek systems in the present study, rather than driven by tidal currents, sediment deposition occurs within a range of rising tidal amplitudes (minimally flooding to high spring

tides) largely because fine suspended sediments formed flocs within the water column (Christiansen, et al., 2000).

Marsh sedimentation occurs largely via the settling of flocs, and it has been found that during neap tides, sediment in the tidal creeks is primarily in the form of flocs with a settling velocity ranging between 0.02 and 0.20 mm/s and a mean particle size of 25–75 μm . Spring tides yielded sediment in larger flocs, with larger sizes of individual grain particles (Voulgaris, 2004). However, comparable settling velocities have been observed during both neap and spring tides (0.24 mm/s), indicating that these tidal cycles control marsh sedimentation through sediment availability for deposition and inundation time (Voulgaris, 2004).

Environmental dynamics affecting tidal transport and variability of particulate metals

This study provided insight regarding small-scale fluctuations (over tidal cycle) and larger-scale temporal variations (i.e. fall/spring and neap/spring tides) with respect to physiochemical parameters that can be integral in the partitioning of metals among dissolved and suspended solids. Comparatively, mean temperature, dissolved oxygen (D.O.), pH, and salinity values characteristic of Main Creek, Neck Creek and Lemon Creek which accounted for intra-site temporal and spatial (small and large scale) variability, were comparable to site-specific averages illustrated in earlier biological studies (2004). It was apparent that both studies aligned in terms of the inter-marsh variability reflected by the above-mentioned environmental parameters (temp., D.O., pH, salinity) that resonated large-scale geographic patterns shown by radionuclides (Chapter 2), rather than metals; Main Creek and Lemon Creek were more similar with respect to these physicochemical variables than Neck Creek.

Comparatively, mean values for site-specific average temperature, dissolved oxygen (D.O.), pH, and salinity characteristic of Main Creek, Neck Creek and Lemon Creek which accounted for intra-site temporal and spatial (small and large scale) variability, were comparable to demonstrated mean inter-marsh variations with respect to DO aligned to biological studies (Goto, 2010) conducted within the same study areas (summer 2004) and provided complementary physiochemical data with respect to conventional environmental parameter measured in this study. It was likely that storm events likely had a greater effect on the intervariability of SPM concentrations due to runoff than differences in tidal states. Higher values of flux during runoff were likely due to increased water flows rather than increased SPM concentrations (Young, et al. 1984).

Differences in results may also be attributable to physiochemical/biogeochemical dynamic properties and factors which would prompt cyclic metal desorption from particles, thereby possibly contributing to phase changes within environmental compartments and disparities among and within sites (i.e. influencing temporal variations in greater dissolved metal enrichment in the water column (i.e. during the estuarine transit of Cu).

Environmental factors such as salinity, dissolved oxygen and pH in water showed little influence on the variations of particulate heavy metals over the course of the tidal cycle at Main Creek, Neck Creek and Lemon Creek. The high adsorptive capacity of fine-grained sediments/particles provide prime surfaces and ample contact for metals to adsorb to continuously cycle throughout urban ecosystems via particulate settling and deposition, and resuspension/remobilization. (Meade, 1954; Garside, 1976; Young, et al., 1984). Estuaries are recognized as traps of fine particles and reservoirs of pollutants which repeatedly cycle and resuspend throughout the NY/NY HE.

In situ field measurements and water samples were taken from cross-sections that transversed each study site. These sites were generally located at the end of the tidal reach of each creek, proximal to the upland marsh habitat, rather than towards the confluence with the open water NY/NJ HE waterway (i.e. Arthur Kill or Raritan Bay). As hydroperiod is an important variable affecting sediment quality, it is noteworthy that the cross-section sampled at Neck Creek was not completely inundated for a short duration (at low tide). The sampling locations at Main Creek and Lemon Creek remained inundated throughout the extent of each survey, which may have influenced dilution of pollutants.

One of the basic assumptions of the study approach was that the water in the tidal reach is substantially of homogeneous density, thereby eliminating the possibility of density currents. Therefore, consideration was limited to those portions of tidal reaches that are affected by the propagation of long, low-amplitude, translator waves, but in which salinity intrusion does not cause a saline wedge to form or cause distinct stratification of flow.

Temporal and spatial concentration and current velocity observations were combined to estimate average SPM fluxes, which were used to examine the distribution of particulate metals imported/exported into the marsh-creek systems from the Arthur Kill and Raritan Bay. In addition, physiochemical data (i.e. salinity) was collected to account for conservative and non-conservative behavior and variability among sites, along with conventional water quality indicators (i.e. dissolved oxygen, pH, temperature) to evaluate intra-site variations and determine additional stressors. In contrast to the deeper open waters of the NY/NJ HE and, perhaps likely in the adjoining waterways (Arthur Kill and Raritan Bay), vertical stratification was not anticipated to be noteworthy factor in the relatively shallow ambient waters of the study sites. As expected, *in situ* field observations confirmed the insignificant role of vertical stratification at

Main Creek, Neck Creek and Lemon Creek, particularly with no definable temperature and/or salinity gradients, which were demonstrably lacking in all of the tidal surveys (Howland, et al, 1999).

Tidal Currents, Hydraulics, and Flows

All sites demonstrate a semi-diurnal range (the difference in height between high and low waters over about half a day) varies in a two-week cycle. In this study flood and ebb velocities were given positive and negative signs, respectively. Water column samples were collected at neap and spring tidal states, during which physiochemical measurements were recorded for current speed and direction, salinity, temperature, the concentration of suspended particulate material (SPM), pH, dissolved oxygen, and particulate trace metals (in sediments and SPM) (Millward, et al., 1999). The neap tide corresponds with the first or third quarter of the lunar cycle, when the sun and Moon are separated by 90° when viewed from the Earth, and the solar tidal force partially cancels the Moon's. It is at this point in time when the tidal range is at its minimum. Conversely, spring tides result in the greatest range of flows. This occurs around new and full moon, when the sun, moon and Earth align (i.e. syzygy) and the tidal force attributed to the sun reinforces that due to the Moon. Relative to average tidal conditions, during spring tide high waters are often higher, low waters are lower, slack water time is shorter, and tidal currents are stronger. Neaps result in less extreme tidal conditions. Overall, this was observed at Main Creek and Neck Creek during neap and spring surveys conducted in November 2008, and late March 2009.

The tides' influence on current flow can be more difficult to analyze and data is more difficult to collect than simple tidal height measurements. A tidal height is a simple number

which applies to a wide region simultaneously. A flow has both a magnitude and a direction, both of which can vary substantially with depth and over short distances due to local bathymetry. A flow proceeding up a curved channel is the same flow, even though its direction varies continuously along the channel. Flow direction is determined by the upstream channel's shape, as opposed to the downstream channel's shape.

However, current analysis is similar to tidal analysis; examination of lateral movement of water through tidal conduits (i.e. current flows) parallels vertical analysis of tidal heights (vertical movement between high and low water). Accordingly, at a particular place in space and As with tide height predictions, the timing of tidal flows and current predictions are derived from astronomical factors, and do not account for meteorological dynamics. However, localized weather conditions (both present and preceding sampling) was recognized as a potential factor that may have impacted flow observations in the field that should be further studied; particularly in the case of the March and April events at Main Creek and Lemon Creek, respectively, as these sites were observed to receive discharges from stormwater outfalls during wet-weather (Appendix C-2 and C-5).

The times in which water samples and corresponding velocity measurements were taken over the tidal cycle monitored at Main Creek, Neck Creek, and Lemon Creek are displayed in Appendix C-1-2, C3-4, and C5 respectively. In general, wider ranges and higher mean velocity readings occurred during the spring tide surveys at Main Creek and Neck Creek (Table 4). Mean velocity measured in the spring tide survey was two times greater than the neap tide survey at Main Creek ($0.07 \text{ m}\cdot\text{s}^{-1}$ and $0.14 \text{ m}\cdot\text{s}^{-1}$, respectively), and greater than 2.6 times at Neck Creek ($0.3 \text{ m}\cdot\text{s}^{-1}$ and $0.8 \text{ m}\cdot\text{s}^{-1}$, respectively).

Relative to high or low tide, no consistent temporal trends among sites and surveys was apparent, with respect to the maximum flood current in terms of recorded velocity readings (Appendix C). However, for all study sites, the greatest velocity readings were often observed where there was also the greatest change in depth between sampling intervals. During each sampling event, “slack water” conditions was identified at instances where the direction of tidal current was indecipherable or observed to be setting in the opposite direction. In some instances, this coincided concurrently with sampling at MA and NC and LC, and either was not characterized (-) or represented the minimum current speed of the preceding tidal phase.

The relative magnitude and strength of respective flood and ebb currents characterized the horizontal movement of water (in and out) flowing in opposite directions, not in terms of vertical rising/falling of tidal stages. Accordingly, current velocities, tidal flow, and flux are described as either progressing towards upland marsh (+) or out/towards the open waters of the Arthur Kill/Raritan Bay (-) in Appendix B-1-3, and quantified in Table 17-19 and Figs. 12-14.

Material Transport and Tidal Exchange

Tidal Prism and Water Volume Exchange

In certain instances, calculations of tidal prism are useful in determining the residence times of water and contaminants in estuarine systems; by determining how much water is exported compared to how much of the estuarine water remains, it can be determined how long pollutants reside in that estuary. For instance, if the tidal prism forms a large proportion of the water in an estuary at high tide, subsequently, on an ebbing tide, it is likely that when the tide ebbs, the majority of the water will move with it, along with suspended sediments and particle-reactive pollutants. This means that the estuary has a good flushing time, or that the residence

time of water in that estuary is low (shallow estuaries). In contrast, in areas with relatively greater depths, the amount of water affected by the tidal influence is a relatively smaller proportion of the total water. The mean difference between high and low tide is comparatively lower than would be expected in shallow estuaries, which results in a smaller tidal prism and a longer residence time.

Since tidal prism is largely a function of area of open water and tidal range, it can be changed by alterations of the basin area of estuaries and inlets as in dredging; however, if the estuary or inlet is dredged, or the size changed, the channel will fill in with sediment until it has returned to tidal prism equilibrium. Tidal prism has also been correlated to the amount (mass) of sediment transport (i.e. imported (and deposited) or exported). A strong relationship between the magnitude of the tidal prism and the volume of sand in ebb dominated deltas has been widely established where the larger the tidal prism, the larger the amount of sand that is deposited in deltas in ebb-dominated estuaries (Walton and Adams 1976). Conduits with small tidal prisms have too little power to remove sand deposited from adjacent shores. Conversely, those with large tidal prisms can erode sand and deposit it in ebb-tidal deltas in deeper waters (National Research Council 2001). In general, the size of an estuary's tidal prism is dependent on the basin area, the tidal range and other frictional forces. For each survey, a tidal prism, (i.e. the net difference in the volume of water entering and leaving at flood and ebb tides) was calculated as the volume of water exchanged over each complete tidal cycle sampled at Main Creek (n=2), Neck Creek (n=2) and Lemon Creek (n=1) (Luketina 1998; Davis and Fitzgerald 2004). The contrast among flood and ebb tidal flows at all sites, which generally demonstrated greater import (influx) relative to export (efflux) of water, was reflected by calculation of MA, NC, and LC tidal prisms (Appendix G-1-3).

This simplistic tidal prism model was used to examine the relationship of metal pollutant discharges with respect to incoming and outgoing (inflows vs. outflows) to identify the magnitude of scalars and net direction (import vs. export) of tidal transport at each site, and thereby, determine if Main Creek and Neck Creek act as conduits for contaminants within the water column via tidal exchange with the Arthur Kill. As expected, site-specific cross sectional areas were also directly related to tidal prism. Relative to Main Creek and Lemon Creek, cross-sectional and water volume measurements calculated for Neck Creek were lower due to the comparatively narrower channel width of the site (by ~ 5 and 6 times at Main Creek and Lemon Creek, respectively). In contrast to the mean volume of water exchanged over two tidal cycles at Neck Creek, 1.31 m^3 , the greater mean tidal prisms shown at Main Creek (6.24 m^3) and Lemon Creek (10.3 m^3), reflected the increased in cross-sectional area at these sites. The evident range and variation in respective water volume exchange shown between Main Creek surveys conducted during neap and spring tides (1.88 m^3 to 10.6 m^3) clearly demonstrated the affect of varying tidal flow conditions. Compared to the Arthur Kill sites, Lemon Creek clearly showed a higher tidal prism value. Although, only one survey was used to characterize a tidal prism at Lemon Creek, it is likely that the site showed the maximum value of water volume exchanged on account of localized creek morphology, including the greater surface area ratio of the Raritan Bay, in conjunction with site-specific hydraulic factors that influenced greater tidal forcing and increased velocity measurements over the tidal cycle survey.

In general, anthropogenic modifications to channel morphology, characteristic of all marshes, likely affected localized velocity gradients and generated current asymmetries due to respective dynamics such as, shear flow dispersion and tidal trapping (Davis and Fitzgerald 2004). The evident contrast among flood and ebb tidal flows at all sites, which demonstrated greater import

(influx) relative to export (efflux) of water, was reflected by calculation of MA, NC, and LC tidal prisms. Upstream of MA, NC, and LC cross-sectional sampling locations, ancillary channels (i.e. mosquito channels) and diking of upland wetlands likely impacted net flux and movement of water parcels entering and draining the sites (on flood and ebb tides). The asymmetrical tidal prisms measured at all sites and surveys indicated the relative importance of marsh geometry. Thereby, localized marsh geometry likely affected hydrodynamics, and ultimately, scalar transport of metals within all systems.

Import and Export of Metal Fluxes and Net Tidal Exchange of Metals

For each sampling interval ($n=9$), metal fluxes were calculated via multiplication of water column measurement for instantaneous flow (average velocity ($\text{m}\cdot\text{s}^{-1}$) $\cdot$ cross-sectional area (m^2)) and mean particulate metal concentration ($\mu\text{g}\cdot\text{L}^{-1}$). Average contaminant fluxes entering (+) or leaving (-) the upland marsh habitat area, via tidal creeks (i.e. Main Creek and Neck Creek), on respective flood and ebb tidal phases, showed little variability, particularly in neap surveys from both Arthur Kill sites (Tables 17a-b, 18a-b). The similarity between median and mean values with respect to tidal stage (i.e. flood vs. ebb) reflected the comparatively more consistent particulate metal concentrations measured over these tidal cycles (Figs. 10, 11, Tables 17a, 18a).

In general, Neck Creek surveys contrasted in terms of the net direction of tidal transport of Cd, Cu, Zn, and Hg on particles suspended within the water column during neap and spring tidal flow conditions. Conversely, both Main Creek surveys demonstrated a net positive term (influx) for all constituents studied. The positive value determined for both Main Creek surveys indicated a net import of Cd, Cu, Zn, and Hg on particles suspended within the water column during both minimum (neap) and maximum (spring) tidal ranges and low and high flow conditions characteristic of neaps and springs. In general, Lemon Creek showed a net import for

all parameters except for Hg (i.e. Cd, Cu, Zn, and SPM). Although the net difference between ebb and flood area curves reflected a negative value for particulate Hg, the net export term was negligible.

The significance of tidal stage was tested via Mann-Whitney U analysis, which measured the central tendencies (medians) of respective non-negative fluxes from flood and ebb datasets. The distributions of fluxes from the 2 directional datasets (samples were grouped based on lateral movement of the tide +/-) were compared to determine differences among incoming and outgoing material fluxes; a significant difference among the distributions of fluxes entering (+) or leaving (-) the upland marsh habitat ($p \leq 0.05$). The difference between incoming (+) and outgoing (-) contaminant fluxes, calculated via the summation of the areas beneath the respective curves produced for each tidal stage (flood vs. ebb), determined the net direction of tidal transport for each parameter studied.

The neap tide survey conducted at Main Creek showed insignificant differences between flood and ebb tide instantaneous fluxes with respect to Cd, Cu, Zn, and SPM fluxes (Table 17, Appendix H). However, similar to Neck Creek and Lemon Creek, the summation of metal-specific flux curve areas with respect to current direction (flood (+) and ebb (-)) showed a demonstrable contrast in metal-specific datasets between incoming and outgoing tides.

Due to the known limitations to characterize significance with small sample sizes, few significant p values (< 0.05) were expected. However, in terms evaluating among-site differences between surveys, this approach provided a good metric to demonstrate the importance of water volume flows, or tidal prism, which varied demonstrably at Main Creek between neap and spring tidal surveys. Accordingly, the significant difference in the directional SPM and metal influx shown in the spring tide survey, and the lack of significance which showed a demonstrable mass

import/influx of these constituents during the spring tide survey of SPM and metals with respect to current direction (+/-) demonstrated by the Main Creek spring tide survey tidal prism likely contributed to the significantly greater influxes (vs. effluxes) seen in the spring tide survey (Appendix G, H).

Median incoming and outgoing water volume flows did not show significant differences between median (non-negative) values ($p=0.39$), however, flooding and ebbing tidal currents did show significant difference between SPM and metal fluxes (Cd, Cu, Zn, and Hg during the Spring tide survey at Main Creek. Statistical analysis showed that neither neap or spring tidal cycle surveys conducted at Neck Creek showed a significant difference ($p>0.05$) between flood and ebb tide flux values (non-negative medians) (Tables 18a-b).

Study Delimitations

It was anticipated that both terrestrial and estuarine inputs contributed metal-specific contaminants and intra-site variations observable in longitudinal studies of surface sediment transects, particularly at Main Creek and Neck Creek. Large and small scale differences may also be attributable to substantial transfer of particulate metals from the water column to the benthic compartment. This transfer could then explain the net impoverishment of the particulate phase in the water column during the estuarine transit. Prior Be^7 results in surface sediment accumulation demonstrated that metals accumulate appreciably within each of the study sites (Chapter 2).

The sedimentary particles, generally characterized by the clay and silt-sized fractions, suspended within the water column of Main Creek, Neck Creek and Lemon Creek, were likely derived from both regional tributaries and/or localized watersheds, vehiculated via estuarine

transport/tidal advection and/or land-based runoff, and/or resuspended sedimentary particles. There are challenges in calculating particulate metal fluxes because particles from the water column can accumulate over several years in the high turbidity zone of the estuary, depending on hydrological conditions, and show no correlation with salinity (Chiffoleau, et al., 1999). This study considered neap and spring conditions from 2 surveys, which approximates, but by no means precisely accounts for yearly quantities of particulate materials in each of the marsh-creek systems. The three different tidal creeks represented the two watersheds of the NY/NJ HE, Arthur Kill and Raritan Bay. It allowed an estimation of the quantity of particulate materials imported/exported among the adjacent estuarine waterways towards the coastal area, wetland areas, and upland marsh habitats.

Although this study focused on metals sorbed to the particulate matter, and does not include examination of dissolved metals, it was recognized that contaminants may be compartmentalized in both forms (dissolved and particulate) within the water column. Thereby, further studies will seek to incorporate analysis of total metals within the water column. This will allow for comparison with applicable ambient water quality standards, of which are derived by both federal (EPA) and state (NY and NJ) entities; although, such criteria are currently only established for total and dissolved metals, and such targets do not pertain to wetlands under present interpretation of the Clean Water Act legislation.

In addition, further research may be necessary to calculate an appropriate baseline of annual metal fluxes in peripheral Arthur Kill marshes prior to the initiation of any future dredging and Superfund projects (i.e. Joint Dredging Plan for the Port of New York and New Jersey and CERCLA Arthur Kill/Newark Bay). Further study of mass balance equations are required for examination of fate in these systems, in order to account for the variety of

mechanisms of input and loss not only within the water column, but also within separate sediment layers (i.e. pore waters, surface sediments, deeper sediments). In itself this does not adequately describe estimation of the input, let alone the complexity of physical and chemical processes that affect transfer, loss, and decay mechanisms such as particulate settling, resuspension, burial, diffusive exchange among layers, volatilization, biodegradation and photolysis (Thomann, 1989; Sokol, et al. 1996).

CONCLUSION

In general, site-specific differences between and among sites (and surveys) may be due to a variety of natural and anthropogenic factors, including spatial and temporal dynamics on both large and small scales. Regardless of tidal phase (i.e. spring/neap) or stage (i.e. ebb, flood) tidal flows effectively served to (re)suspend and transport sediments laterally among open water and inland wetland systems. In relation to LC, both MA and NC showed significantly lower concentrations of SPM and higher levels of all particulate (and SPM) metals. The greater magnitudes of metals within the water column (AK sites > LC) aligned with findings from prior coring and transect studies. However, this contrast between parameters (SPM concentrations and metals) shown by the study sites within the Arthur Kill and Raritan Bay watersheds implicated localized hydrodynamics and land-use are largely attributable to the evident geographic variability of water column constituents.

Fundamentally, the externality of LC, with respect the Arthur Kill, may have played a major role in limiting the supply of metals available to the catchment area (land-use, relatively lower magnitude of point sources and percentage of metal concentration loads in CSO, WWTP, Rivers). The distribution of metals through estuaries is controlled by dynamic sedimentological

and geochemical processes that occur at river-estuary and salt marsh sediment interfaces, including precipitation, adsorption/desorption reactions, flocculation/aggregation, and settling/sedimentation (Williamson et al. 1996, Censi et al. 2006, Benoit et al. 1994, Herut et al. 1997). Along with estuarine circulation, particle deposition and resuspension, these complex physicochemical and hydrological processes control residence times and predictions of fate and transport of particulate bound metals (Butler et al. 2008, Williamson et al. 1996, Feng et al. 2002).

Furthermore, the greater velocity and flow at LC may have been factor limiting net particle and associated contaminant accumulation (Weis et al. 2005). Freshwater flows, including groundwater and stormwater inputs, may have furthered dilution of any pollutants at LC. Dilution may have affected (re)distribution, transport, and fate of contaminated estuarine sediment, as the amount/availability for removal and release by particulates, redistribution, transport subjects the site to less contaminants than other sites. Ultimately, localized dynamics, including both natural processes and anthropogenic factors, are integral to explaining the inter-site differences that occurred between creeks and within sites (i.e. different surveys) and surveys.

It remains undetermined if tidal exchange with the Arthur Kill solely results in greater scales of metal contamination than observed in marsh environments external to this complex. However, site-specific factors, continue to compromise the environmental integrity of upstream marsh habitats along the western margin of Staten Island. Thereby, the potential role that tidal transport and material exchange with the Arthur Kill plays in the higher contamination observed within sites along the western of shore Staten Island requires further study. However, initial research shows that tidal connectivity with the Arthur Kill results in greater scales of metal contamination than observed in marsh environments external to this complex. The consistent

flux of Cd and Hg particulate loads and prior identification of maximum Cd and Hg surface enrichment at stations closest to the confluence (with the Arthur Kill) were indicative of a consistent, dominant downstream source that implicated metal-specific contaminants were derived from the Arthur Kill. Therefore, it remains feasible that tidal creeks serve as metal-specific contaminant conduits, redistribution and transport of metal-specific contaminants derived from the Arthur Kill. It is plausible lateral advection of metals occurs via tidal exchange with the Arthur Kill, and thereby, creek serves as a contaminant conduit, which would implicate the Arthur Kill as an active, ongoing source that serves as a possible explanation for the comparable magnitudes of some metals and steady enrichment demonstrated marsh sediments.

This research component provided the background information necessary for future research into the surficial processes controlling net deposition, cycling/availability, and exchange of metals in various environmental compartments, which control the distribution, transport and fate of metals among biotic and abiotic system components within the study area. Current velocity, cross-sectional area, suspended particulate matter (SPM) and metal concentrations were measured in three wetland creeks in western and southern Staten Island, in order to determine magnitude and direction of suspended material transport across the marsh surface. Distributions of SPM and Cd, Cu, Zn, and Hg, suspended within the water column, were studied at each site to examine variability over the extent of a complete tidal cycle. To characterize a range of flow conditions (i.e. springs and neaps) that represented maximum and minimum tidal ranges, two complete tidal surveys were conducted during spring and neap tides at the Arthur Kill study sites (Main Creek and Neck Creek). With respect to inter-site variations, the presence of mean SPM and metal concentrations in the water column presence were related to surficial metal contents, which identified temporal and spatial differences by depicting intra-site differences, among and

between, tidal cycle surveys. The product of instantaneous water flows, SPM and metals were comparatively assessed in terms of tidal current (flood vs. ebb), to evaluate the scalar transport and lateral movement of suspended constituents entering and leaving the upland marsh habitats at Main Creek, Neck Creek, and Lemon Creek. The net import or export term (+/-), representing the net tidal exchange, of metal-specific fluxes was calculated from the net difference in contaminant fluxes transported on incoming and outgoing tides. This research component identified large-scale variability with respect to the degree of anthropogenic metals within suspension, in the particulate fraction. This additional line of evidence aligned with the large-scale geographic contamination gradient described in Chapters 2 and 3; thereby, this further supported findings, which showed that, despite of any intra-marsh spatial and temporal differences (demonstrated among and between surveys), marsh sediments (suspended particulate fraction and surface bed deposits) from sites within the Arthur Kill watershed demonstrated greater levels of metal enrichment relative to Lemon Creek, which is located external to the Arthur Kill Proper, within the Eastern Raritan Bay watershed.

This study addressed the lack of understanding about suspended particulate metal concentrations and lateral flux of metals in tidal marsh-creek systems. Tidal creeks that hydraulically connect upland marsh habitats to the Arthur Kill may serve as contaminant conduits. Building on the weight of evidence approach outlined in this dissertation, the multiple lines of evidence provided by this research component established an assessment framework in which to evaluate the distribution of metals and relative magnitude of contaminants in multiple environmental compartments for a better understanding of the exchange of contaminants between the Arthur Kill and associated marsh habitats. From a management perspective, such

information is useful tool in prioritizing, as well as setting target criteria for restoration initiatives within the NY/NJ HE.

Insight concerning the processes that govern the exchange of metals within heavily polluted urban estuaries, as set forth in this research, provides useful information to programs that monitor ecosystem health, assess the vulnerability of ecologically-important species, and design, implement, and assess the success of site remediation and ecological restoration. Furthermore, information concerning sediment metal loadings within marsh habitats would be important data to supplement the CARP strategies and is a critical step in gaining an overall understanding of the transport and redistribution dynamics of contaminants within this ecologically important and sensitive system. An assessment of current conditions (in terms of metal concentrations in these wetland catchment areas) will aid in tracking success of efforts to protect local waterways from metal contamination. This will help characterize the environmental state of the region, which is essential to inform and drive policy decisions such as the possible future development of the Fresh Kills landfill into a park with a water contact recreation component.

The vectors of SPM and metals exchanges between the salt marshes and adjacent waterbody (AK, RB) have not been previously studied. Understanding the exchange of metals between the heavily polluted Arthur Kill and neighboring habitats, as set forth in this research, provide useful information to programs that monitor ecosystem health, assess the vulnerability of ecologically-important species, and design, implement, and assess the success of site remediation and ecological restoration.

In conclusion, intra-marsh differences in metal concentrations were observable both among, and between, environmental components studied. Results of this study suggested that

metal exchange may be an important factor in Arthur Kill marshes Main Creek, Neck Creek and Lemon Creek. For each system, water column samples collected over the tidal cycle showed site-specific temporal variations that paralleled the small-scale spatial differences in Main Creek, Neck Creek and Lemon Creek surface sediments exhibited by lateral/longitudinal transects (MA > NC > LC). The samples reflected magnitudes of particulate metals that collectively, reflected spatial and temporal enrichment gradients defined by marsh bed surface sediments and thereby, were consistent with the large-scale pattern depicted by sediment. Collections from the marsh bed surface and overlying water column also confirmed this observation.

It is recognized that contaminated sediments within the Arthur Kill are remobilized by tidal action and dredging activities, however the redistribution of such legacy contamination requires further study, particularly concerning the potential scalar flux and advective transport to adjacent wetland areas. Results of this study suggested that metal exchange may be an important factor in Arthur Kill marshes.

It should be noted that the mass-balance approach used to characterize the net import/export of metals may have oversimplified the complex processes involved in the tidal exchange of metals among the open waterways (i.e. Arthur Kill and Raritan Bay) and inland marsh ecosystems. Nonetheless, this study provided site-specific context regarding the variability of metals bound to suspended particulate matter and the effect of variable tidal conditions (i.e. flow, state/stage), and role of SPM on particulate concentrations. Furthermore, it provided insight into the relative influence of natural physical and geochemical processes governing the redistribution of anthropogenic metals within the water column and marsh bed sediments of Main Creek, Neck Creek and Lemon Creek. This has provided basic data to comparatively assess the Arthur Kill and Raritan Bay watersheds in terms of the greater impact

of anthropogenic stressors in tidally influenced marshes, including the relatively different influence of natural dynamics in shaping the respective large-scale contamination gradients.

The significance of this project aligns closely with a variety of regional management goals that are currently in pursuit within the area. For example, habitat acquisition and restoration of ecologically important areas that are threatened by pollution and development is a major focus of the NY/NJ Harbor Estuary Program and many sites along the Arthur Kill are slated for such efforts (Sanudo-Wilhelmy and Gill, 1999; Seebaugh, et al., 2005). Habitat acquisition and restoration of ecologically important areas that are threatened by pollution and development is a major focus of the NY/NJ Harbor Estuary Program and variety of sites within the Arthur Kill (i.e. Neck Creek Marshes) are slated for such efforts (NY/NJ HEP, 2006; CCMP, 2006, 2010) (Figs. 1a-b).

Table 4-1. Location of tidal survey cross-sections sampled within the study area.

Study site	Roadway bridge transverse	NY/NJ HE open waterway	Latitude	Longitude
Main Creek	Travis Avenue	Arthur Kill	40°35'53.97"N	74°10'32.61"W
Neck Creek	Meredith Avenue	Arthur Kill	40°35'47.26"N	74°11'23.77"W
Lemon Creek	Hylan Boulevard	Raritan Bay	40°31'4.23"N	74°12'4.15"W

Geographic coordinates (reported in degrees, minutes, seconds ((D°M'S'')) for Main Creek, Neck Creek, and Lemon Creek water column sampling locations (n=3). Overhead roadway bridges bisect creek conduits via culvert structures at each site.

Table 4-2. Main Creek, Neck Creek, and Lemon Creek surface sediment transect locations.

Study Site/location	a	b	c	d	e	f
Main Creek	40°35'51.68"N	40°35'53.97"N	40°35'58.17"N	40°36'1.08"N	40°36'5.42"N	40°36'7.97"N
	74°10'33.29"W	74°10'32.61"W	74°10'27.56"W	74°10'22.15"W	74°10'19.60"W	74°10'18.38"W
Neck Creek	40°35'47.71"N	40°35'47.20"N	40°35'47.26"N	40°35'49.97"N	40°35'52.26"N	40°35'53.41"N
	74°11'32.09"W	74°11'27.76"W	74°11'23.77"W	74°11'21.77"W	74°11'18.76"W	74°11'17.12"W
Lemon Creek	40°30'48.97"N	40°30'59.73"N	40°31'4.23"N	40°31'5.62"N	40°31'12.92"N	40°31'17.12"N
	74°11'55.40"W	74°12'2.99"W	74°12'4.15"W	74°12'9.80"W	74°12'10.64"W	74°12'17.67"W

Geographic coordinates (reported in degrees, minutes, seconds ((D°M'S'')) of intra-marsh surface sediment sampling locations (n=6) along lateral transects spanning the tidal reach of Main Creek, Neck Creek, and Lemon Creek from 2009 surveys.

Table 4-3. Atmospheric fluxes of metals from natural and anthropogenic sources¹.

Metal	Crustal abundance ¹ (nmol·g ⁻¹)	Global Avg. Shale ²	Regional Bkgd. ³	Global Atmospheric emission rate (t·y ⁻¹)			Major uses of metal & compounds.	Regional Sources ⁷
				Natural	Anthropogenic	Interference Factor ⁵		
Cd	2	0.11	0.3	1.4	7.6	5.3	Nonferrous metal production; cement/fertilizer manufacture; combustion ⁶	Transportation, wastewater, industry, power and petrochemical plants.
Hg	0.4	0.18 ⁵	0.16 ⁴	2.5	3.6	1.5	Chlorine cells; gold mining operations; combustion	Abandoned industrial sites. Power plants, combustion, medical waste incinerators, materials used for industrial operations, manufacturing (i.e. cement, steel).
Cu	510	14	45	26	35	1.2	Nonferrous metal production; biocides; wood treatment processes, combustion	Automobiles (tire, brake pads), wood, paint and dye manufacturers, power and petrochemical plants.
Zn	2000	81	95	45	131	3.0	Nonferrous metal production; steel/iron manufacturing; cement production	Automobiles (tire, brake pads) wood, paint and dye manufacturers, power and petrochemical plants.

¹Table adapted from Millward et al., 2001; <http://epa.gov/mats/powerplants.html> Accessed August 15.

²Wedpohl, et al., 1971.

³Hirschberg, et al., 1996.

⁴Bowen, et al., 1979.

⁵The interference factor is the ratio of the anthropogenic flux to the natural flux (Millward et al., 2001).

⁶The general term “combustion” refers to wood, coal, and oil combustion, along with incineration of waste (Millward et al., 2001).

⁷Abandoned industrial and other facilities (i.e. paint, dye, wood manufacturing, legacy contamination, waste transfer sites, CSOs, stormwater (separate sewer discharges and runoff), urban runoff (pesticides and pressure-treated wood, construction, infrastructure development activities, petrochemical, and non-petro refining industrial facilities.

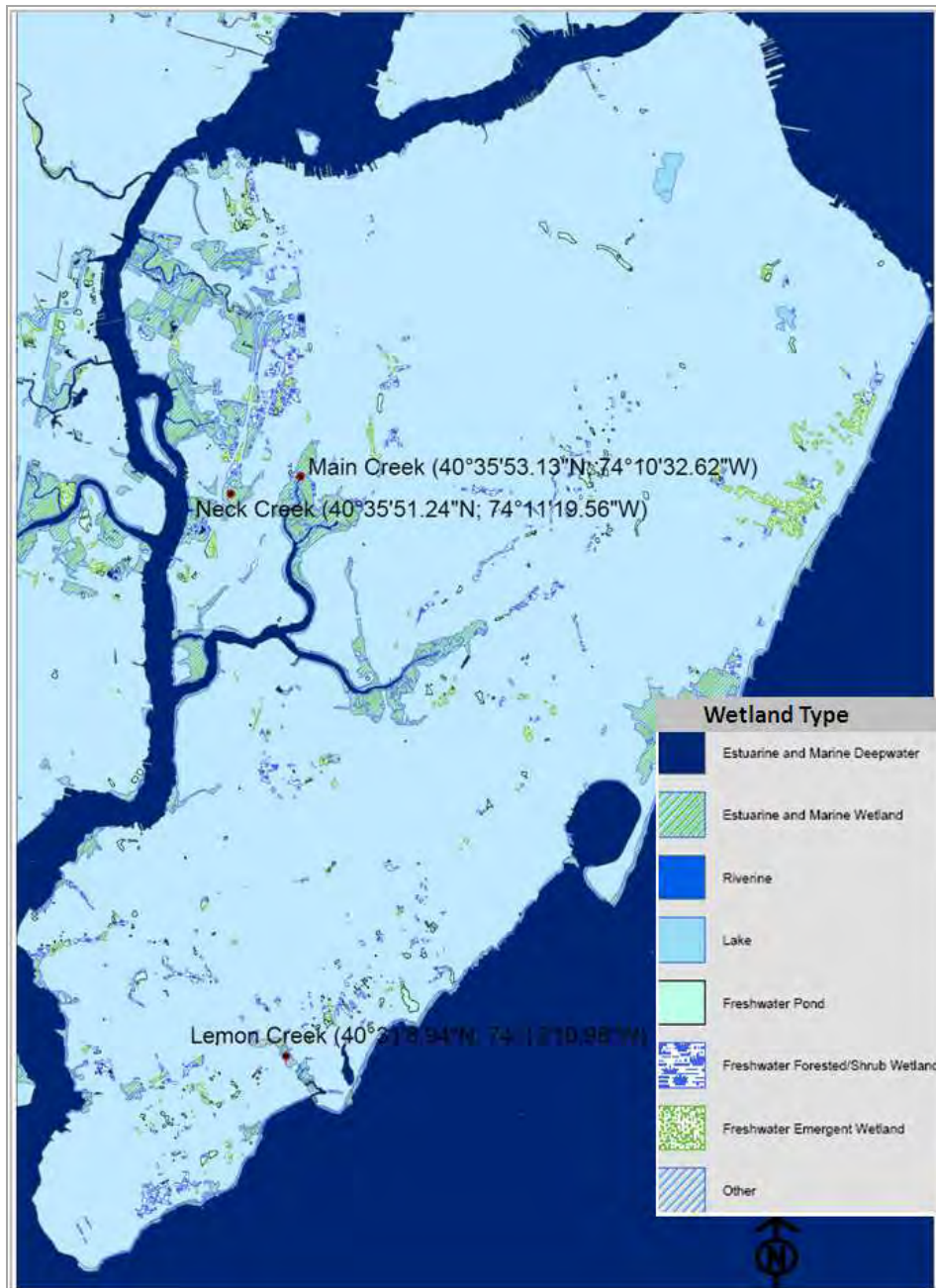


Figure 4-1. Wetland characterization of Staten Island study sites. Main Creek, Neck Creek, and Lemon Creek are all characterized as estuarine/marine wetlands as per New York State Department of Environmental Conservation (NYS DEC) wetland classifications (NYS GIS clearinghouse 2011).

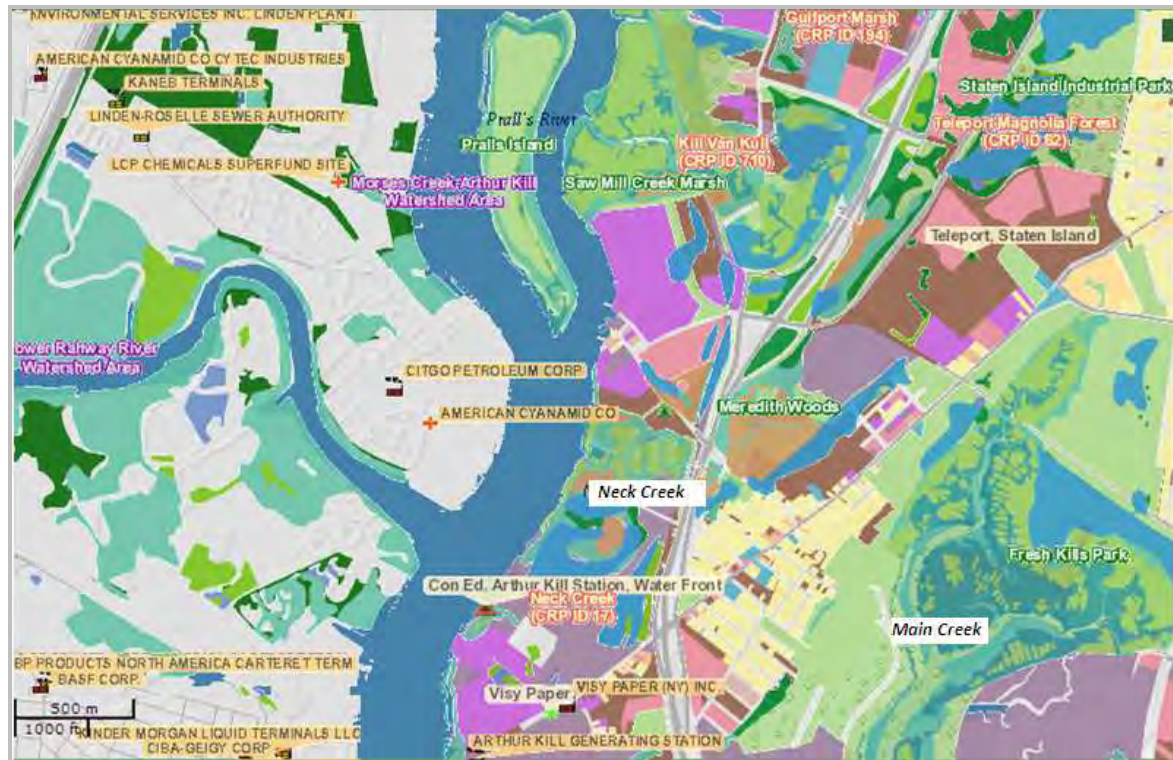


Figure 4-1a. Arthur Kill Watershed land-uses and wetland inventory (Oasis 2011).

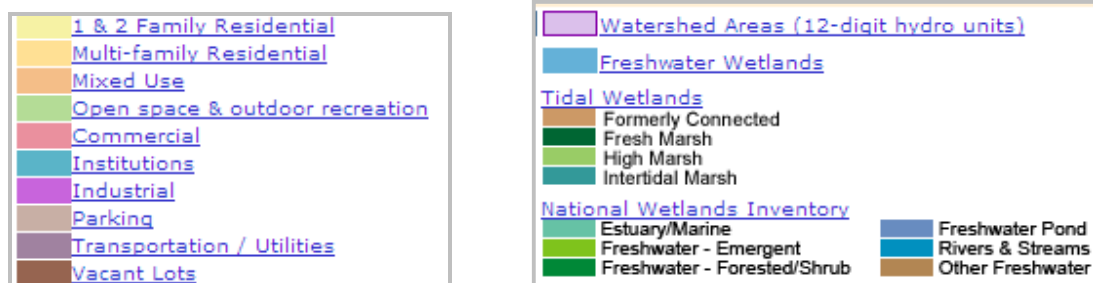
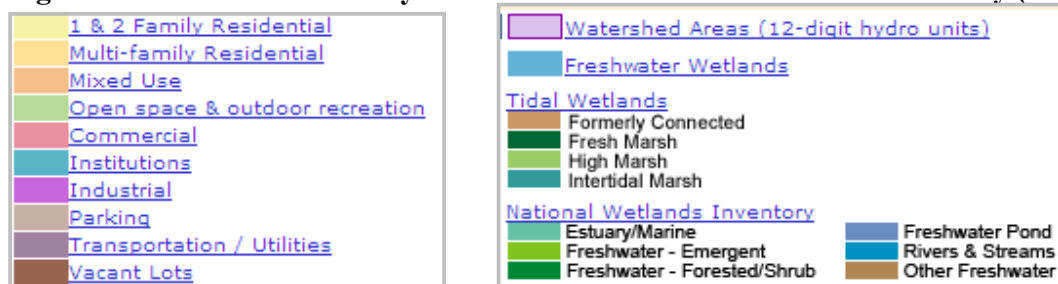




Figure 4-1b. East Raritan Bay Watershed land-uses and wetland inventory (Oasis 2011).



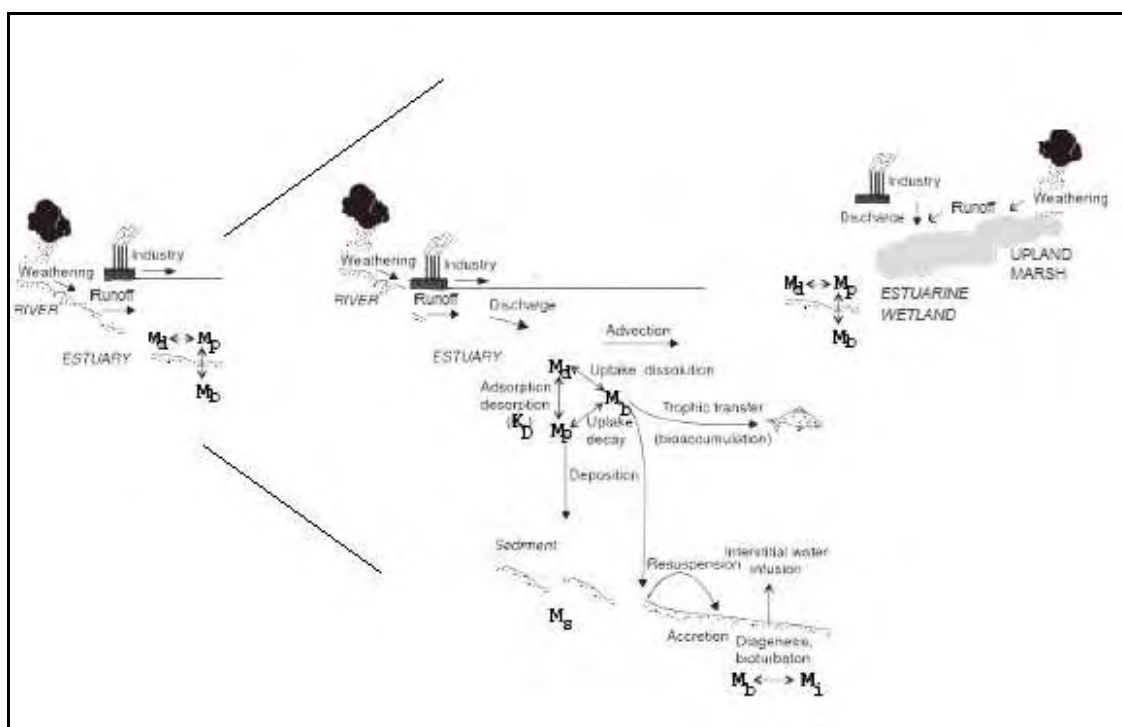


Figure 4-2. Processes affecting transport and biogeochemistry of metal pollutants in estuaries and wetlands. Metal compartments are designated as: M_d (dissolved); M_{sp} (suspended particulate); M_s (sediment); M_i (interstitial); M_w (water); M_b (biogenic). (Adapted from Millward et al., 2001 in Ed. Steele, 2009).

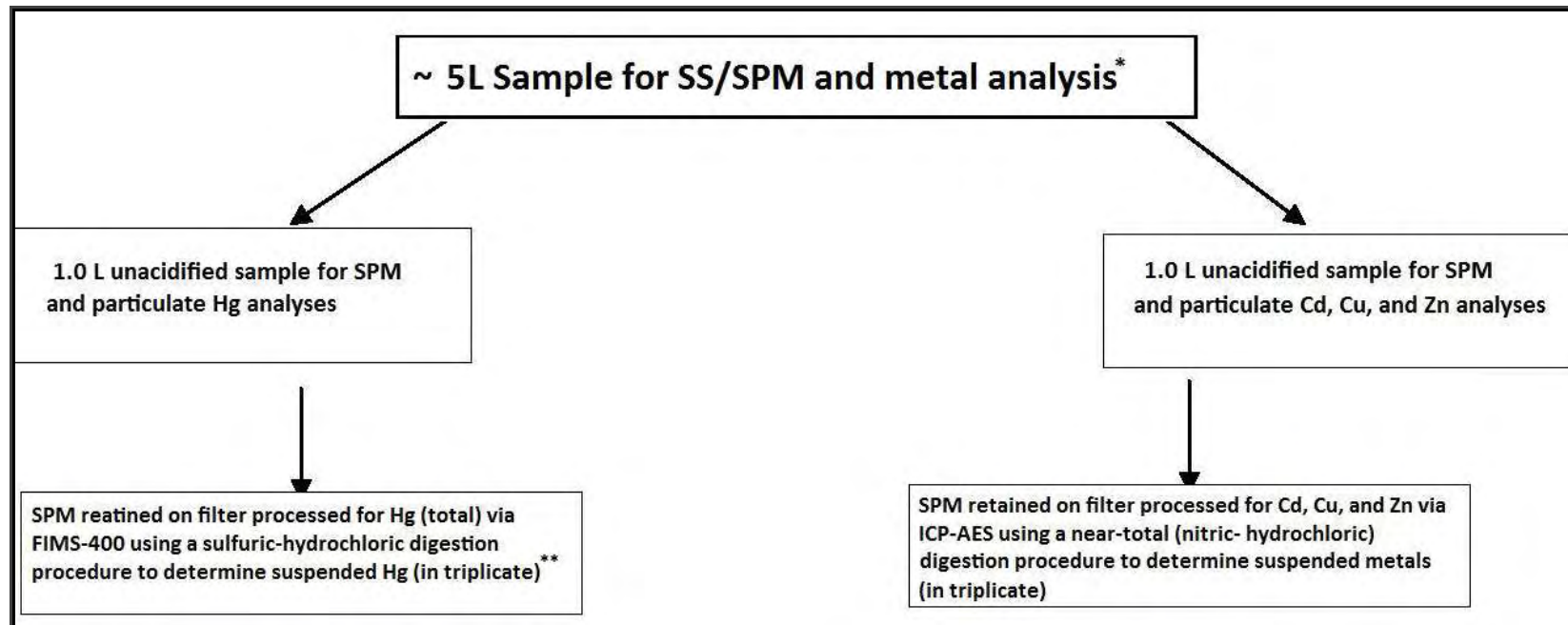


Figure 4-3. Schematic of metal sample processing and analysis.

*Duplicate grab samples were collected during the first tidal surveys (November 2008), resulting in 2 SPM samples (from particulate Cd, Cu, and Zn processing and analysis) and 2 SPM samples (from Hg processing); (SPM n=4).

** Samples collected during Main Creek and Neck Creek neap tidal surveys (November 2008) were processed for Hg analysis, but were not further analyzed due to unpredictable levels of this constituent found in the polycarbonate membranes that were used for sample filtration, which may have led to cross-contamination and skewed results. In latter surveys, conducted in the Spring of 2009, at all sites (MA, NC, and LC), nitrocellulose filter membranes were used specifically for Hg analysis, in order to minimize possible contamination.

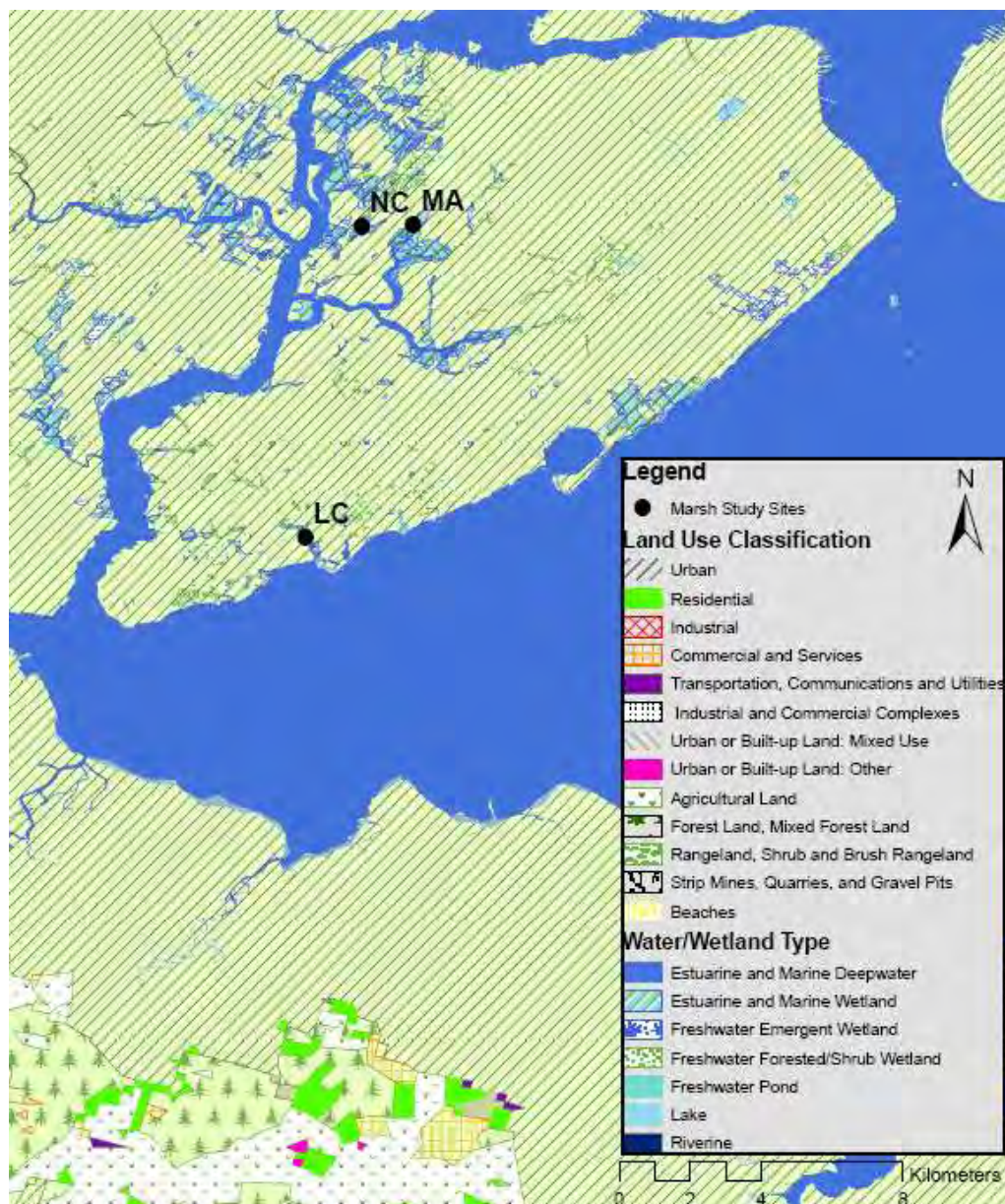


Figure 4-4a. Staten Island urban land-use classification.

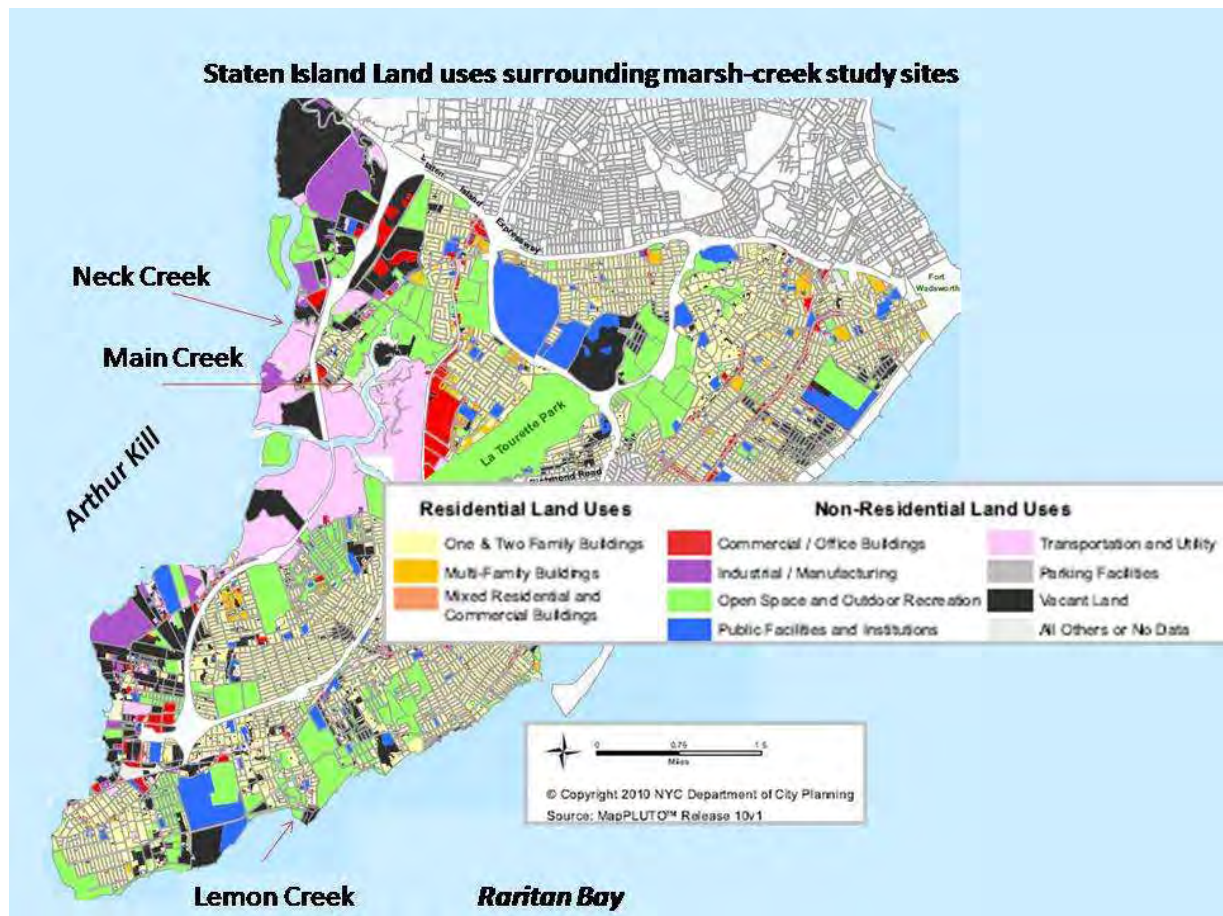


Figure 4-4b. Residential and non-residential land-uses surrounding Staten Island.

Arthur Kill study sites (Main Creek and Neck Creek) are characterized by more diverse non-residential land-uses including transportation and utility, commercial/office buildings, industrial/manufacturing, vacant land and open space. In contrast, the area surrounding Lemon Creek is characterized by both residential (one & two family buildings) and non-residential (open space and/or vacant land) land-uses.

Figure 4-5a. NY/NJ Harbor Estuary wastewater pollution control plant and combined sewer overflow locations in the greater study area.



Figure 4-5b. Stormwater, CSO and WWTP overflow locations.



*NJ Locations are those sampled by the New Jersey Harbor Dischargers Group Estuary Program Contaminant Assessment and Reduction Program [DeGraeve 2008].

**Figure adopted from NYC DEP 2009 WTP and Flow Map (NYC DEP 2009), Program [DeGraeve 2008].

(adapted from Riverkeeper's Swimmable NYC).

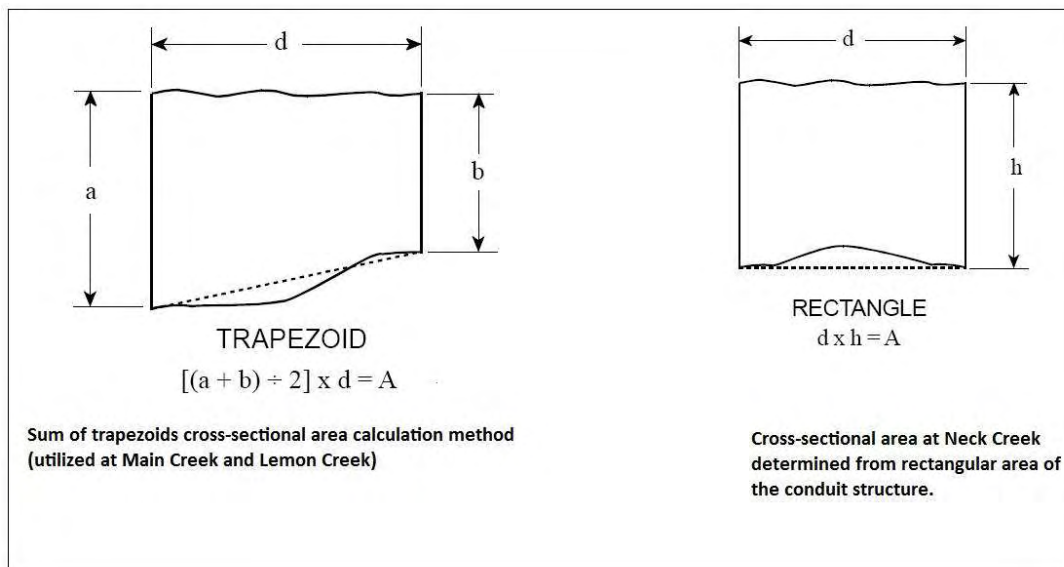


Figure 4-6. Cross-sectional area calculations.

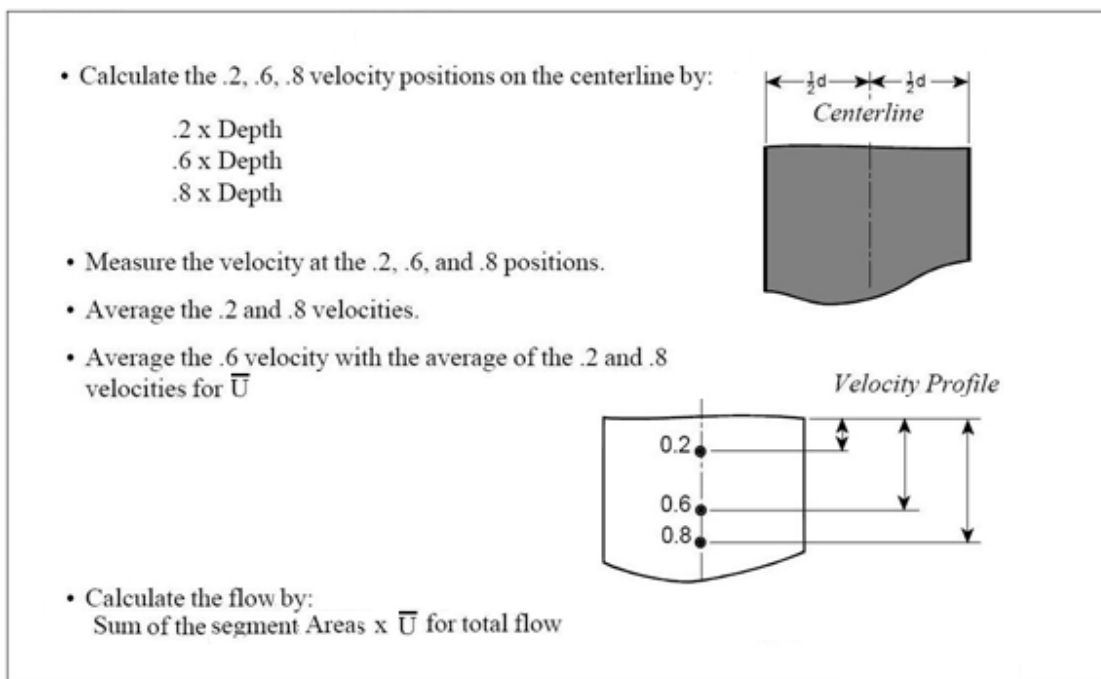


Figure 4-6a. Velocity depth profile and cross-sectional flow calculations.

Table 4-4. Comparison of MA, NC, and LC mean surficial and suspended Cd, Hg, Cu, Zn with literature-based reference values.

	Cd (ug·g ⁻¹)	Hg (ug·g ⁻¹)	Cu (ug·g ⁻¹)	Zn (ug·g ⁻¹)
Regional Hudson River Background¹	0.11	0.182	14	81
Mean World Shale²	0.3	0.16	45	95
Suspended Sediments background³	1.1	0.1	20	65
Suspended Sediments background⁴	<1.0	0.1	25	90
Avg. Crustal Abundance⁵	0.1	-	25	71
Avg. World Rivers⁶	1.2	-	100	250
Newark Bay⁷	1.76	<0.0197	141.9	237
Arthur Kill⁷	2.38	<0.0366	276.1	386
Hudson River⁷	0.9	<0.0025	91.8	205
Lower New York Bay⁷	1.17	<0.0258	122.5	195
East River⁷	1.18	<0.0651	185	188
MA mean of spring/neap tidal surveys (ug·g⁻¹)	36.0	2.03	1630	3055
NC mean of spring/neap tidal surveys (ug·g⁻¹)	37.6	0.37	706	37766
LC mean (mid-neap/spring tidal survey) (ug·g⁻¹)	0.77	0.42	48.8	141
MA mean of spring/neap tidal surveys (ug·g⁻¹)	36.0	2.03	1630	3055
MA Mean 2009 (ug·g⁻¹)	3.57	1.26	229	243
MA Mean 2007 (ug·g⁻¹)	5.62	1.42	255	291
MA Mean 2001 (ug·g⁻¹)	5.18	-	294	337
NC mean of spring/neap tidal surveys (ug·g⁻¹)	37.57	0.37	706	37766
NC Mean 2009 (ug·g⁻¹)	1.84	1.14	165	152
NC Mean 2007 (ug·g⁻¹)	4.52	1.79	345	245
NC Mean 2001 (ug·g⁻¹)	2.87	-	239	166
LC mean (mid- neap/spring tidal survey) (ug·g⁻¹)	0.77	0.42	48.8	141
LC Mean Surface 2009 (ug·g⁻¹)	1.62	0.24	131	177
LC Mean 2007 (ug·g⁻¹)	1.21	0.194	141	170
LC Mean 2001(ug·g⁻¹)	2.35	-	91.3	108
Tenth highest reported level⁸	2.5	1.7	180	380
Highest reported level⁸	11	4.3	320	570
Maximum concentration in contaminated estuaries⁹	862	1130	2540	16667

¹Hirschberg et al. 1996. Bowen et al. 1970

²Wedpohl et al. 1968.

³Persaud et al. 1993.

⁴Horowitz et al. 1991.

⁵Taylor et al. 1985.

⁶Martin and Windom (1991).

⁷Batelle Ocean Sciences

⁸NOAA 1998 (National Status and Trends Program). Sediments analyzed for chemical constituents from approximately 200 coastal and estuarine sites.

⁹Kennish 2002.

Table 4-5. Summary of mean SPM and particulate Cd, Hg, Cu, and Zn concentrations (incorporating all tidal surveys).

Site			SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
Suspended Sediments background¹				1.1	-	0.1	-	20	-	65	-
Suspended Sediments background²				<1.0	-	0.1	-	25	-	90	-
MA	Mean	67.5		36.0	0.45	2.03	0.10	1630	83.6	3055	190
	Range	36.2-98.7		30.5-41.5	0.22-0.67	2.03-2.03	0.10-0.10	1625-1636	35.6-132	2579-3531	53-327
NC	Mean	47.1		37.6	0.87	0.37	0.03	706	26.5	37766	306
	Range	23.7-70.6		17.0-58.1	0.55-1.18	0.37-0.37	0.03-0.03	605-806	11.5-41.5	2282-73250	9.18-604
LC	Mean	216		0.77	0.12	0.42	0.05	48.8	7.81	141	21.9
	Range	72.1-326		0.23-3.19	0.05-0.38	0.04-2.06	0.01-0.15	12.2-261	1.43-31.1	37.3-770	5.38-91.9

¹Persaud et al. (1993).²Horowitz et al. (1991).

Table 4-5a. Comparison of site-specific mass-mass Cd, Hg, Cu, and Zn mean concentrations (all tidal surveys)

Site/Survey	Cd ug·g ⁻¹	Hg ug·g ⁻¹	Cu ug·g ⁻¹	Zn ug·g ⁻¹
MA mean of spring/neap tidal surveys	36	2.03¹	1630¹	3055
NC mean of spring/neap tidal surveys	37.6¹	0.37	705	37766¹
LC mean (mid-neap/spring tidal survey)	0.77	0.42	48.8	141

¹Bold indicates greatest mean site-specific metal concentration (irrespective of number of event mean concentrations used for calculation (n= 18 for all MA and NC parameters, except Hg (n= 9); n=9 for all LC parameters).

Table 4-5b. Comparison of site-specific mass-volume Cd, Hg, Cu, and Zn mean concentrations (all tidal surveys)

Site/Survey	SPM mg·L ⁻¹	Cd ug·L ⁻¹	Hg ug·L ⁻¹	Cu ug·L ⁻¹	Zn ug·L ⁻¹
MA mean of spring/neap tidal surveys	67.5	0.45	0.10¹	83.6¹	190
NC mean of spring/neap tidal surveys	47.1	0.87¹	0.03	26.5	306¹
LC mean (mid-neap/spring tidal survey)	216	0.12	0.05	7.81	21.9

¹Bold indicates greatest mean metal concentration (irrespective of number of event mean concentrations used for calculation (n= 18 for all MA and NC parameters, except Hg (n= 9); n=9 for all LC parameters).

Figures 4-7a-c. Site-specific wetland acreage landward and seaward of tidal creek cross-sections.

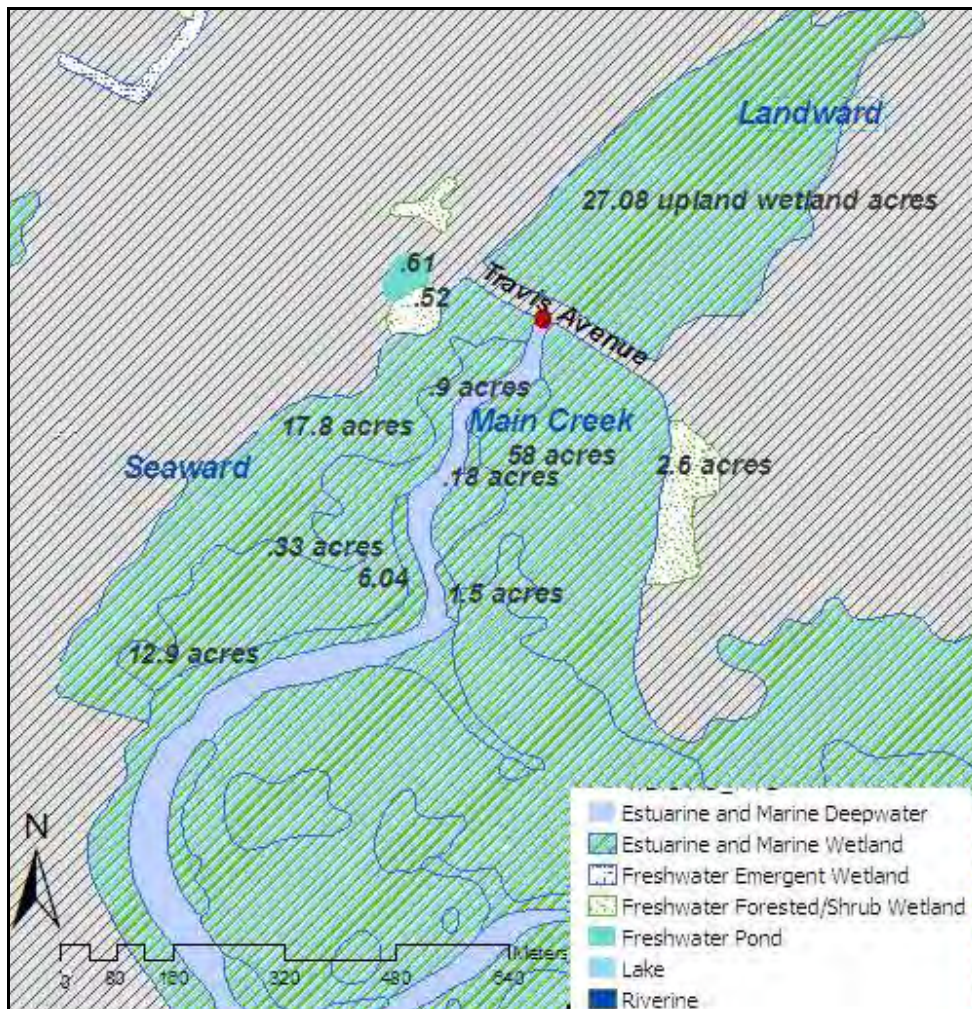


Figure 4-7a. Main Creek wetland acreage extending landward and seaward of Travis Avenue roadway culvert. The Main Creek study area encompassed approximately 27 acres of estuarine wetland habitat in the upland marsh area, upstream of the cross-sectional sampling point (●). GIS map compiled via New York State Department of Environmental Conservation (NYS DEC) wetland dataset (NYS GIS clearinghouse 2011).

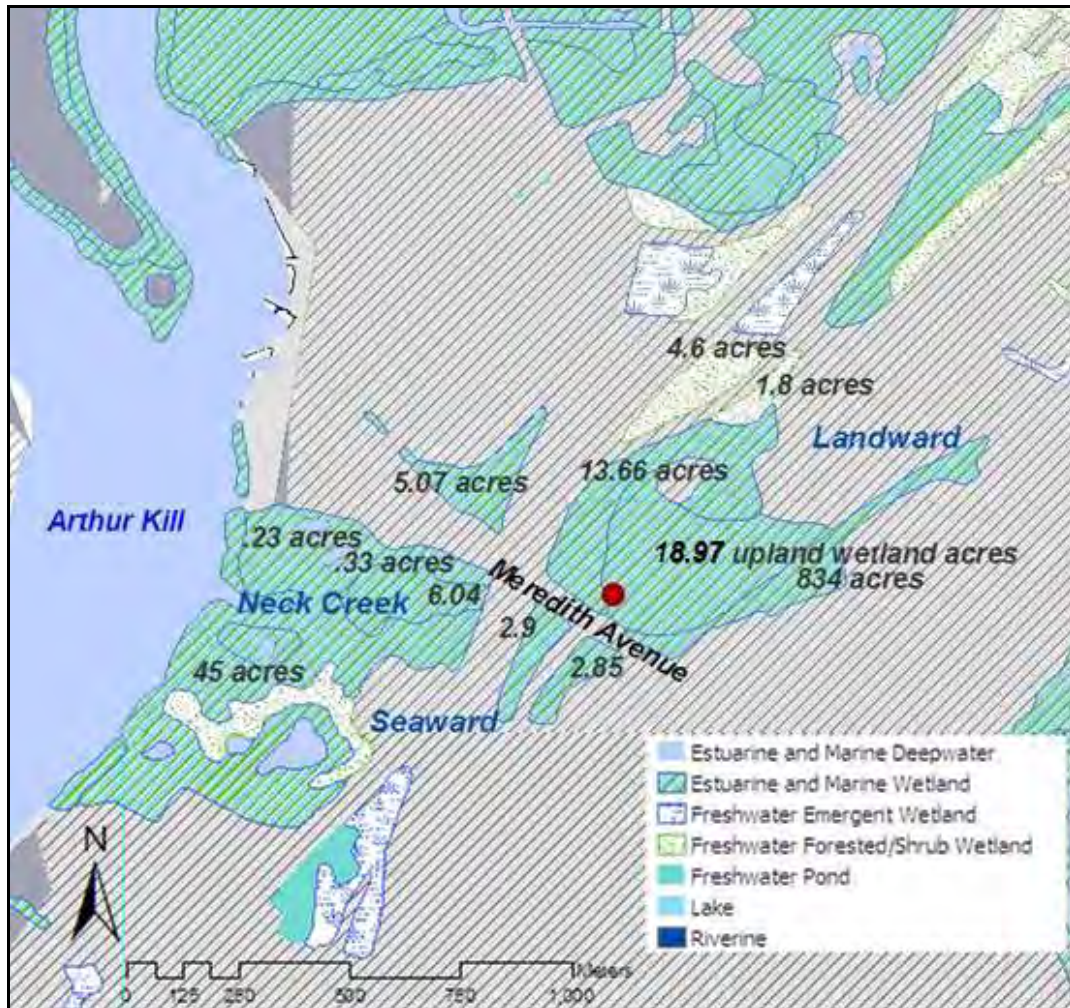


Figure 4-7b. Neck Creek wetland acreage extending landward and seaward of Meredith Avenue roadway culvert. The Neck Creek study area encompassed greater than ~40 acres of estuarine wetland habitat in the inland marsh area, upstream of the cross-sectional sampling point (●). GIS map compiled via New York State Department of Environmental Conservation (NYS DEC) wetland dataset (NYS GIS clearinghouse 2011).

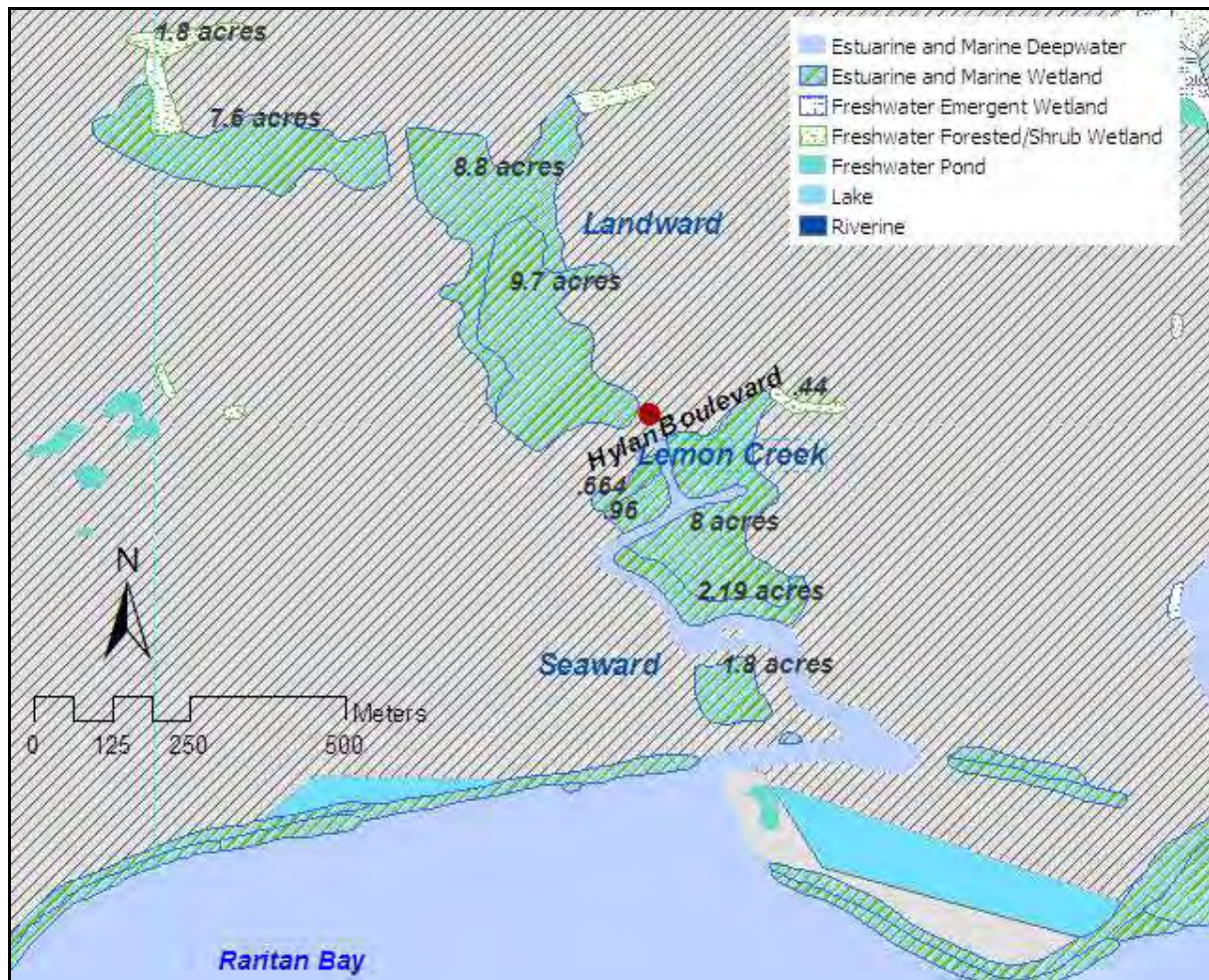


Figure 4-7c. Lemon Creek wetland acreage extending landward and seaward of Hylan Boulevard roadway culvert. The Lemon Creek study area encompassed greater than ~26 acres of estuarine wetland habitat in the inland marsh area, upstream of the cross-sectional sampling point (●). GIS map compiled via New York State Department of Environmental Conservation (NYS DEC) wetland dataset (NYS GIS clearinghouse 2011).

Figures 4-8a-c. Comparison of particulate, SPM and surface sediments to background indices.

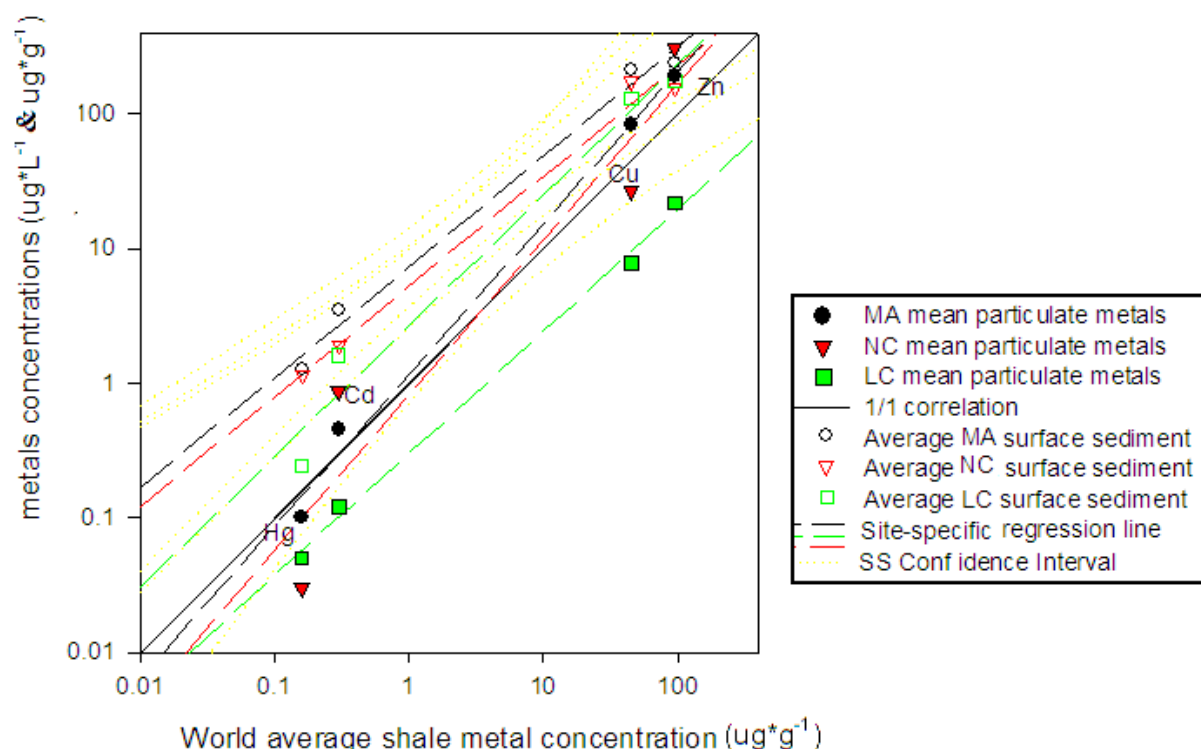


Figure 4-8a. Comparison of mean MA, NC, and LC particulate metals and surface sediments to mean world-wide shale concentrations. Logscale metal concentration units measured as a mass·volume ($\mu\text{g}\cdot\text{L}^{-1}$) and mass·mass dry weight ($\mu\text{g}\cdot\text{g}^{-1}$) for particulate and surface sediments, respectively. Y-axis values reflect site-specific mean Cd ($n=54$), Hg ($n=18$), Cu ($n=54$), and Zn ($n=54$) concentrations determined from average temporal particulate metal concentrations determined over complete tidal cycles during neap (2008) and spring (2009) tidal surveys at Main Creek ($\bullet$) and Neck Creek ($\blacktriangledown$) in 2008 and 2009, respectively. Downward solid triangular datapoints ($\blacksquare$) depict mean particulate concentrations determined over a median tidal cycle survey (intermediate flow conditions between neap and spring tide) at Lemon Creek ($n=18$) (2009). Mean surface sediment values for each site ($n=54$) show 2009 average of lateral transect samples from Main Creek ($\circ$), Neck Creek ($\blacktriangledown$), and Lemon Creek ($\square$). Literature-based background concentrations derived from worldwide average shale values for elemental Cd, Hg, Cu, and Zn contents were used as global proxies for natural background concentrations (Wedpohl et al. 1968). Broken black, green, and red lines show site-specific regression lines for particulate metals suspended in the water column at Main Creek, Neck Creek, and Lemon Creek, respectively. As a means of comparison, the blank solid line (—) reflects the 1:1 correlation between particulate Cd, Hg, Cu, and Zn concentration vs. background reference values. Broken yellow lines show the 95% Confidence Intervals (C.I.) for data points from particulate metals datasets from each study site.

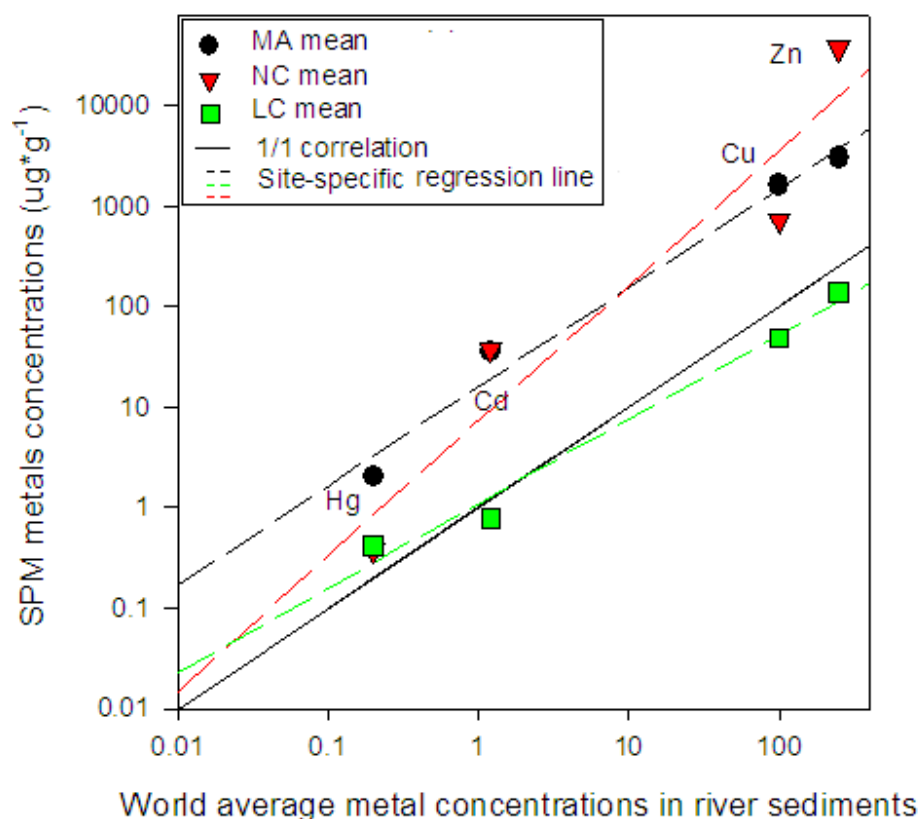


Figure 4-8b. Comparison of Mean MA, NC, and LC SPM metals to mean world-wide shale concentrations. Logscale metal concentration units measured on a mass-mass dry weight basis ($\mu\text{g}\cdot\text{g}^{-1}$). Y-axis values reflect site-specific average metal-specific concentrations determined from all acquired mean SPM concentrations determined from neap and spring tidal surveys at Main Creek and Neck Creek ($n=54$ for Cd, Cu, and Zn; $n=18$ for Hg) (conducted in 2008 and 2009, respectively) and a median tidal cycle survey (intermediate flow conditions between neap and spring tide) at Lemon Creek ($n=18$) (2009). Broken blank, green, and red lines show site-specific regression lines for particulate metals suspended in the water column at Main Creek, Neck Creek, and Lemon Creek, respectively. As a means of comparison, the blank solid line (—) reflects the 1:1 correlation between particulate Cd, Hg, Cu, and Zn concentration vs. background reference values. Natural elemental concentrations were derived from world average concentrations in river sediments (Martin and Windom 1991).

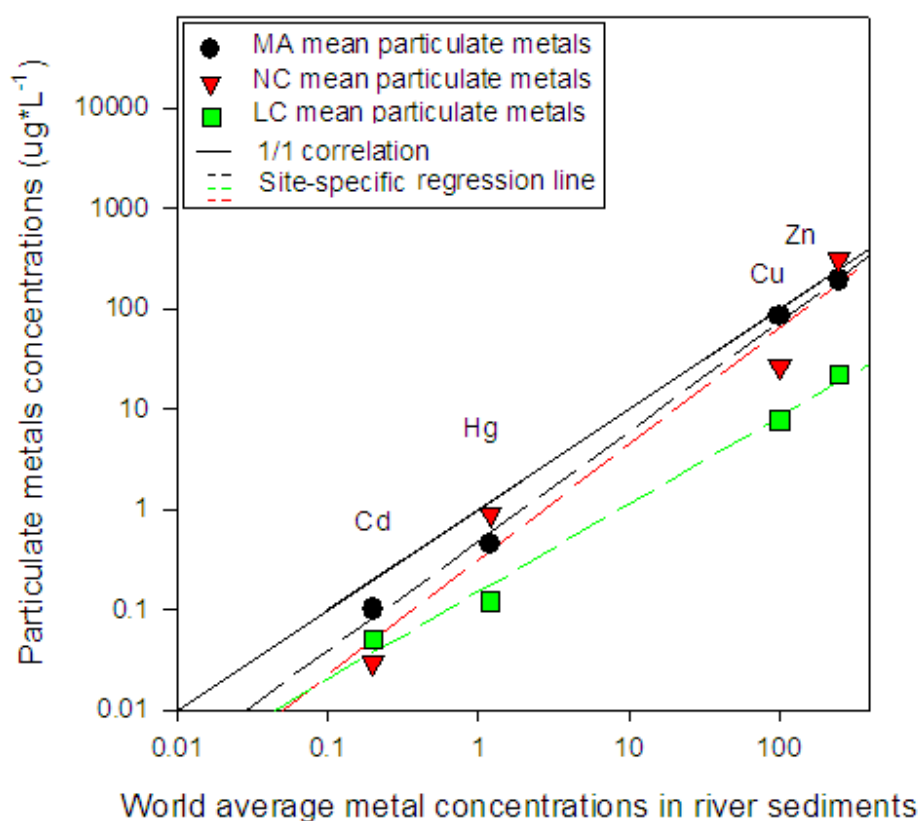


Figure. 4-8c. Comparison of Mean MA, NC, and LC particulate metals to mean world-wide river concentrations. Y-axis values reflect site-specific average metal-specific concentrations determined from all acquired mean sample concentrations determined from neap and spring tidal surveys at Main Creek and Neck Creek (n=54 for Cd, Cu, and Zn; n=18 for Hg) (conducted in 2008 and 2009, respectively) and the median tidal cycle survey (intermediate flow conditions between neap and spring tide) at Lemon Creek (n=18) (2009). Broken black, green, and red lines show site-specific regression lines for particulate metals suspended in the water column at Main Creek, Neck Creek, and Lemon Creek, respectively. As a means of comparison, the blank solid line (—) reflects the 1:1 correlation between particulate Cd, Hg, Cu, and Zn concentration vs. background reference values. Natural elemental concentrations were derived from world average concentrations in river sediments (Martin and Windom 1991).

Table 4-6a. Ranges of SPM Cd, Hg, Cu, and Zn concentrations (incorporating all tidal surveys).

Site/Survey	MA Range		NC Range		LC Range	
	Min	Max	Min	Max	Min	Max
Cd ug·g⁻¹	30.5	41.5	17.0	58.1	0.23	3.19
Hg ug·g⁻¹	2.03	2.03	0.37	0.37	0.04	2.06
Cu ug·g⁻¹	1625	1636	605	806	12.2	260
Zn ug·g⁻¹	2579	3531	2282	73250	37.3	770

Table 4-6b. Ranges of particulate Cd, Hg, Cu, and Zn concentrations (incorporating all tidal surveys).

Site/Survey	MA Range		NC Range		LC Range	
	Min	Max	Min	Max	Min	Max
SPM mg·L⁻¹	36.2	98.7	23.67	70.6	72.1	326
Cd ug·L⁻¹	0.22	0.67	0.55	1.18	0.05	0.38
Hg ug·L⁻¹	0.10	0.10	0.03	0.03	0.01	0.15
Cu ug·L⁻¹	35.6	132	11.45	41.5	1.43	31.1
Zn ug·L⁻¹	53.0	327	9.18	604	5.38	91.9

Table 4-7a. Contamination factor (CF), risk level of contaminants, contamination degree (CD) and pollution degree in MA, NC, and LC (2001, 2007, and 2009).

Contamination factor (CF)		Associated Risk Level of contaminants
CF Range	CF Level	Description
CF<1	Low	indicative of low metal-specific sediment contamination
1<CF<3	Moderate	indicative of moderate metal-specific sediment contamination
3< CF <6	Considerable	indicative of considerable metal-specific sediment contamination
CF ≥ 6	Very High	indicative of very high metal-specific sediment contamination
Contamination degree (CD)		Magnitude of Contamination
CD Range	CD Level	Description
CD<7	Low	unpolluted/minimal degree of anthropogenic contamination
7< CD <14	Moderate	moderate degree of contamination
14< CD < 28	Considerable	considerable degree of contamination
CD ≥ 28	Very High	very high degree of contamination indicating serious anthropogenic pollution

Table 4-7b. Relative differences in contamination factors and contamination degree between study sites.

Site/Survey	Cd ug·g⁻¹	CF	Hg ug·g⁻¹	CF	Cu ug·g⁻¹	CF	Zn ug·g⁻¹	CF	CD
MA mean of spring/neap tidal surveys	36	120	2.03	12.7	1630	36.2	3055	32.2	50.2
NC mean of spring/neap tidal surveys	37.6	125	0.37	2.31	706	15.7	37766	398	135
LC mean (mid- neap/spring tidal survey)	0.77	2.57	0.42	2.63	48.8	1.08	141	1.48	1.94

Table 4-7c. Metal-specific Contamination Factors and Contamination Degree.

Study Site	Year	Metal-Specific Contamination Factors								Contamination Degree (CD)	
		Cd		Hg		Cu		Zn			
Main Creek	2009 ¹	120	Very High	12.7	Very High	36.2	Very High	32.2	Very High	50.2	Very High
	2009	11.5	Very High	7.9	Very High	4.8	Considerable	2.5	Considerable	26.7	Considerable
Neck Creek	2009 ¹	125	Very High	2.31	Moderate	15.6	Very High	397	Very High	135	Very High
	2009	6.4	Very High	7.1	Very High	3.9	Considerable	1.7	Moderate	19.1	Considerable
Lemon Creek	2009 ²	2.57	Moderate	2.63	Moderate	1.08	Moderate	1.48	Moderate	1.94	Low
	2009	5.4	Considerable	1.5	Moderate	2.9	Moderate	1.85	Moderate	11.6	Moderate

¹Average MA and NC metal-specific SPM concentrations (n=81 for Cd, Cu, and Zn; n=27 for Hg) associated with suspended within the water column samples (n=27) included analysis of 27 grab samples (including duplicate samples in November 2008 survey) that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis (in triplicate). Hg data from November 2008 survey samples are not reported.

²Average LC SPM metal-specific concentrations (n=27) associated with suspended within the water column samples included analysis of 9 grab samples that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis (in triplicate).

Table 4-8. Averaged environmental parameters measured *in situ* over complete tidal cycles.
Results reflect data collected during sampling surveys at Main Creek, Neck Creek, and Lemon Creek in Fall 2008 and Spring 2009.

MA Neap Tide (November)	Range		Mean		MA Spring Tide (March)	Range		Mean
Velocity m/s	0.03	0.16	0.07		Velocity m/s	0.01	0.3	0.14
Velocity ft/s	0.1	0.54	0.24		Velocity ft/s	0.05	1	0.46
D.O	7.82	8.85	8.34		D.O	8.18	16	12.74
Temperature	2.4	5.6	4		Temperature	6.8	14	9.1
Salinity	14	7	9.4		Salinity	4.4	7.5	6.5
pH	7.42	7.78	7.63		pH	7.91	8.1	7.99
NC Neap Tide (November)	Range		Mean		NC Spring Tide (March)	Range		Mean
Velocity m/s	0.02	0.58	0.3		Velocity m/s	0.09	2	0.8
Velocity ft/s	0.06	1.9	0.99		Velocity ft/s	0.03	0.6	0.24
D.O	7.02	8.42	7.89		D.O	9.83	15	12.89
Temperature	1.2	9.7	5.4		Temperature	8.7	15	11.3
Salinity	6.3	15.8	11.64		Salinity	8.7	19	13.81
pH	7.47	7.79	7.57		pH	7.17	7.8	7.34
LC Intermediate Tide (April)	Range		Mean					
Velocity m/s	0.03	0.12	0.07					
Velocity ft/s	0.11	0.4	0.23					
D.O	8.56	13.73	10.1					
Temperature	10.5	10.7	10.6					
Salinity	1.7	11.8	5.5					
pH	7.38	7.67	7.52					

Table 4-9. Main Creek tidal surveys summary table.

Site/Survey	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
MA neap survey	36.2	30.5	0.67	-	-	1625	35.6	2579	53.0
MA spring survey	98.7	41.5	0.22	2.03	0.10	1635	132	3531	327
MA mean of neap/spring tidal surveys	67.5	36.0	0.45	2.03	0.10	1630	83.6	3055	190

Table 4-9a. Main Creek neap tidal survey summary table.

MA Neap Tidal Survey (November 2008)		SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
mean		36.2	30.5	0.67	1625	35.6	2579	53.0
range	minimum	7.66	6.30	0.10	516	8.49	635	10.4
	maximum	157	104	1.78	5176	94.4	8765	135

Table 4-9b. Main Creek spring tidal survey summary table.

MA Spring Tidal Survey (March 2009)		SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
mean		98.7	41.5	0.22	2.03	0.10	1635	132	3531	327
range	minimum	18.9	8.02	0.09	0.25	0.02	253	27.9	594	65.4
	maximum	227	111	0.45	10.1	0.31	3745	344	7126	1088

Table 4-10. Neck Creek tidal surveys summary table.

Site/Survey	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
NC neap survey	23.7	58.1	0.55	-	-	806	11.5	73250	604
NC spring survey	70.6	17.0	1.18	0.37	0.03	605	41.5	2282	9.18
NC mean of neap/spring tidal surveys	47.1	37.6	0.87	0.37	0.03	706	26.5	37766	306

Table 4-10a. Neck Creek neap tidal survey summary table.

NC Neap Tidal Survey (November 2008)		SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
mean		23.7	58.1	0.55	806	11.5	73250	604
range	minimum	5.80	7.70	0.14	256	2.13	5237	108
	maximum	91.3	263	1.52	3571	32.5	398151	2310

Table 4-10b. Neck Creek spring tidal survey summary table.

NC Spring Tidal Survey (March 2009)		SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
mean		70.6	17.0	1.18	0.37	0.03	605	41.5	2282	9.18
range	minimum	36.3	3.68	0.17	0.15	0.01	178	10.0	1051	2.41
	maximum	109	54.4	3.12	0.73	0.06	1775	102	5235	20.0

Table 4-11. Lemon Creek tidal surveys summary table.

Site/Survey		SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
LC mean (mid-neap/spring tidal survey)		216	0.77	0.12	0.42	0.05	48.8	7.81	141	21.9
LC range	minimum	72.1	0.23	0.05	0.04	0.01	12.2	1.43	37.3	5.38
	maximum	326	3.19	0.38	2.06	0.15	261	31.1	770	91.9

Table 4-12. Average concentrations surveyed at Main Creek from water column samples collected over a neap tidal cycle (November 2008).

Sample ID	SPM mg·L⁻¹	Cd ug·g⁻¹	Cd ug·L⁻¹	Cu ug·g⁻¹	Cu ug·L⁻¹	Zn ug·g⁻¹	Zn ug·L⁻¹
MA 1-1 mean¹	157	11.4	1.78	602	94.4	866	136
MA 2-2 mean	70.6	14.9	1.05	768	54.2	1064	75.1
MA 3-3 mean	22.3	14.4	0.32	815	18.1	1136	25.3
MA 4-4 mean	14.0	22.4	0.31	1131	15.8	1631	22.8
MA 5-5 mean	16.4	6.3	0.1	516	8.5	635	10.4
MA 6-6 mean	13.1	27.8	0.36	1972	25.8	2738	35.8
MA 7-7 mean	7.7	28.4	0.22	1627	12.5	4082	31.3
MA 8-8 mean	12.7	44.7	0.56	2013	25.5	2295	29.0
MA 9-9 mean	12.7	104.0	1.32	5176	65.9	8765	117

¹ Average calculated from SPM metal concentrations associated with suspended within the water column samples (n=27), which included analysis of 9 grab samples (n=18) that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis (in triplicate). Hg data from November 2008 survey samples were not reported.

Table 4-13. Average concentrations surveyed at Main Creek from water column samples collected over a spring tidal cycle (March 2009).

Sample ID	SPM mg·L⁻¹	Cd ug·g⁻¹	Cd ug·L⁻¹	Hg ug·g⁻¹	Hg ug·L⁻¹	Cu ug·g⁻¹	Cu ug·L⁻¹	Zn ug·g⁻¹	Zn ug·L⁻¹
MA 1-1 mean¹	18.9	54.5	0.26	10.12	0.19	3145	60	5450	103
MA 2-2 mean	91.9	31.2	0.41	3.36	0.31	1722	158	2805	258
MA 3-3 mean	112	32.6	0.13	0.48	0.05	1305	146	3951	442
MA 4-4 mean	82.9	37.9	0.26	0.94	0.08	1415	117	2689	223
MA 5-5 mean	227	51.2	0.18	0.3	0.07	1513	344	4785	1088
MA 6-6 mean	88.27	20.4	0.09	0.25	0.02	636	56.1	1750	155
MA 7-7 mean	110	8.0	0.13	0.41	0.05	253	27.9	594	65
MA 8-8 mean	113	26.7	0.11	0.35	0.04	989	112	2632	298
MA 9-9 mean	43.4	111.0	0.45	2.09	0.09	3745	163	7126	309

¹ Average calculated from SPM metal concentrations associated with suspended within the water column samples (n=27), which included analysis of 9 grab samples (n=18) that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis in triplicate.

Table 4-14. Average concentrations surveyed at Neck Creek from water column samples collected over a neap tidal cycle (November 2008).

Sample ID	SPM mg·L⁻¹	Cd ug·g⁻¹	Cd ug·L⁻¹	Cu ug·g⁻¹	Cu ug·L⁻¹	Zn ug·g⁻¹	Zn ug·L⁻¹
NC 1-1 mean	91.3	0.09	7.7	0.7	356	32.5	5237
NC 2-2 mean	23.3	0.02	18.9	0.44	593	13.8	16108
NC 3-3 mean	25.2	0.03	9.86	0.25	322	8.11	21092
NC 4-4 mean	8.33	0.01	16.5	0.14	256	2.13	15514
NC 5-5 mean	5.8	0.01	263	1.52	3571	20.7	398151
NC 6-6 mean	6.51	0.01	142	0.92	927	6.03	164615
NC 7-7 mean	14.6	0.01	16.1	0.24	260	3.78	7399
NC 8-8 mean	9.29	0.01	34.3	0.32	609	5.66	23879
NC 9-9 mean	28.8	0.03	15.7	0.45	358	10.3	7254

¹ Average calculated from SPM metal concentrations associated with suspended within the water column samples (n=27), which included analysis of 9 grab samples (n=18) that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis (in triplicate). Hg data from November 2008 survey samples were not reported.

Table 4-15. Average concentrations surveyed at Neck Creek from water column samples collected over a spring tidal cycle (March 2009).

Sample ID	SPM mg·L⁻¹	Cd ug·g⁻¹	Cd ug·L⁻¹	Hg ug·g⁻¹	Hg ug·L⁻¹	Cu ug·g⁻¹	Cu ug·L⁻¹	Zn ug·g⁻¹	Zn ug·L⁻¹
NC 1-1 mean¹	109	17.4	1.88	0.4	0.04	645	70.0	2727	20.0
NC 2-2 mean	81.7	7.55	0.62	0.48	0.04	278	22.7	1468	17.0
NC 3-3 mean	58	6.45	0.37	0.15	0.01	178	10.3	1050	3.09
NC 4-4 mean	45.9	3.68	0.17	0.15	0.01	218	10.0	1303	2.41
NC 5-5 mean	36.3	14.2	0.52	0.4	0.01	688	25.0	2725	3.5
NC 6-6 mean	93.7	13.5	1.26	0.17	0.02	413	38.7	1551	5.5
NC 7-7 mean	57.5	54.4	3.12	0.4	0.02	1775	102.0	5235	6.12
NC 8-8 mean	74.2	28.4	2.11	0.41	0.03	867	64.3	3019	9.71
NC 9-9 mean	79.6	7.52	0.6	0.73	0.06	383	30.5	1460	15.3

¹ Average calculated from SPM metal concentrations associated with suspended within the water column samples (n=27), which included analysis of 9 grab samples (n=18) that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis in triplicate.

Table 4-16. Average concentrations surveyed at Lemon Creek from water column samples collected over an intermediate neap tidal cycle (April 2009).

Sample ID	SS mg·L⁻¹	Cd ug·g⁻¹	Cd ug·L⁻¹	Hg ug·g⁻¹	Hg ug·L⁻¹	Cu ug·g⁻¹	Cu ug·L⁻¹	Zn ug·g⁻¹	Zn ug·L⁻¹
LC1-1 mean	222	0.27	0.06	0.13	0.03	12.2	2.7	38.5	8.5
LC2-2 mean	72	0.69	0.05	2.06	0.15	19.9	1.43	74.6	5.4
LC3-3 mean	260	0.5	0.13	0.1	0.03	31.7	8.24	77.7	20.2
LC4-4 mean	294	0.48	0.14	0.11	0.03	18.8	5.51	58.5	17.2
LC5-5 mean	137	1.07	0.15	0.38	0.05	36.5	5	106	14.6
LC6-6 mean	119	3.19	0.38	0.81	0.1	261	31.13	770	91.9
LC7-7 mean	262	0.23	0.06	0.06	0.02	12.2	3.18	37.3	9.8
LC8-8 mean	252	0.29	0.07	0.04	0.01	30.2	7.61	55.8	14.1
LC9-9 mean	326	0.23	0.08	0.06	0.02	16.9	5.52	46.6	15.2

¹ Average LC SPM metal-specific concentrations (n=27) associated with suspended within the water column samples included analysis of 9 grab samples that were split for Hg and non-Hg metals (Cd, Cu, and Zn) and subsampled for replicate analysis (in triplicate).

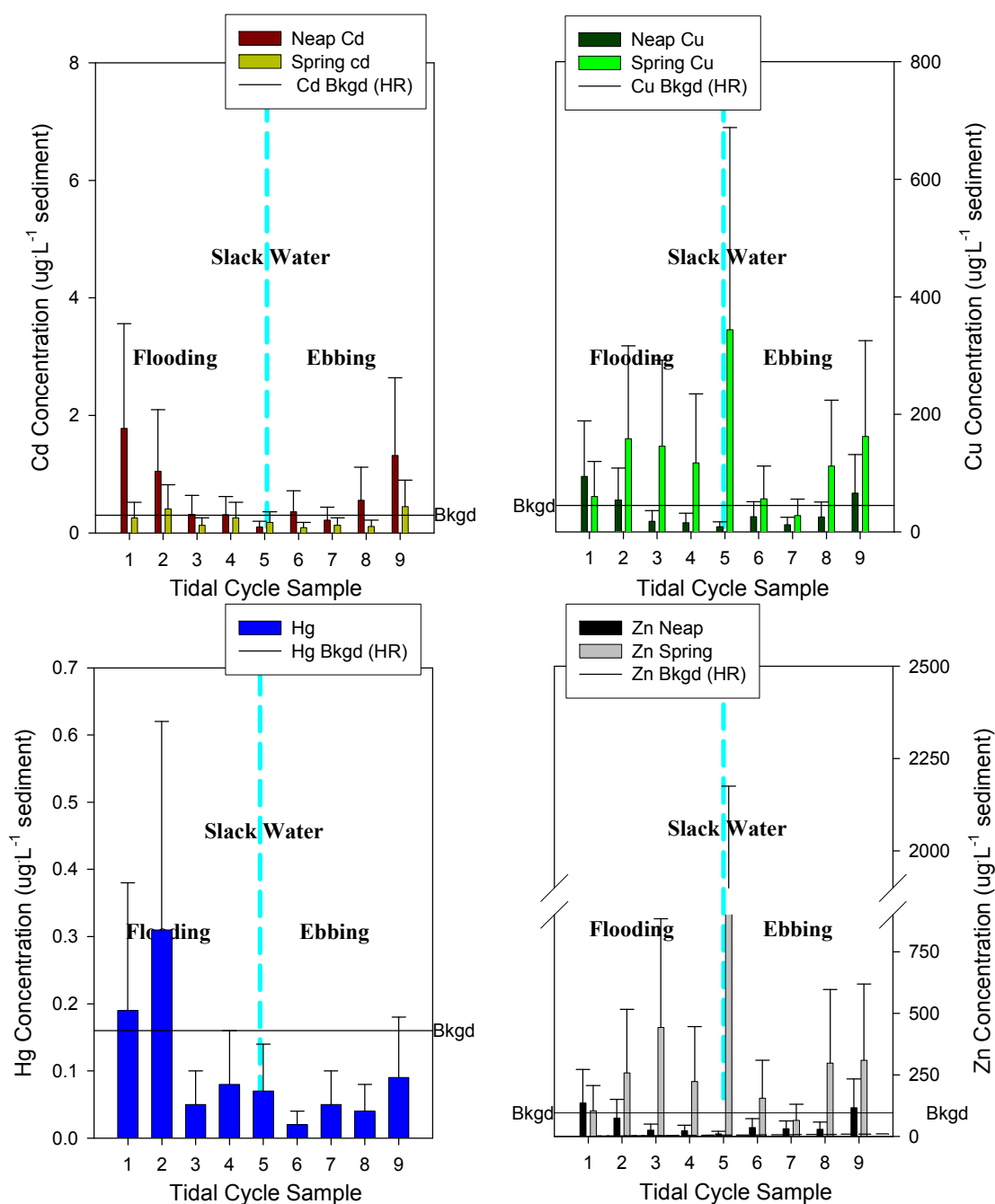


Figure 4-9. Particulate metal concentrations at Main Creek over neap vs. spring tidal cycles.

Graph depicts mean particulate metal concentrations (n=9) over the extent of two complete tidal cycles. For each sampling interval, particulate metal concentrations were calculated via multiplication of mean metal concentrations associated with suspended sediments and mean SPM concentrations (determined from replicate analysis of duplicate suspended particulate matter samples n=4). Temporal SPM metal concentrations used to calculate respective mean particulate values were determined via averages from triplicate metal analysis of sample duplicates (n=6 for the neap tide dataset) and triplicate metal analysis of sample replicates (n=3 for the spring tide dataset). Positive error bars reflect standard deviations of particulate concentration dataset. Literature-based regional background values from Hudson River sediments were used as a proxy for natural concentrations levels and a means for reference (Hirschberg et al. 1996, Bowen et al. 1970).

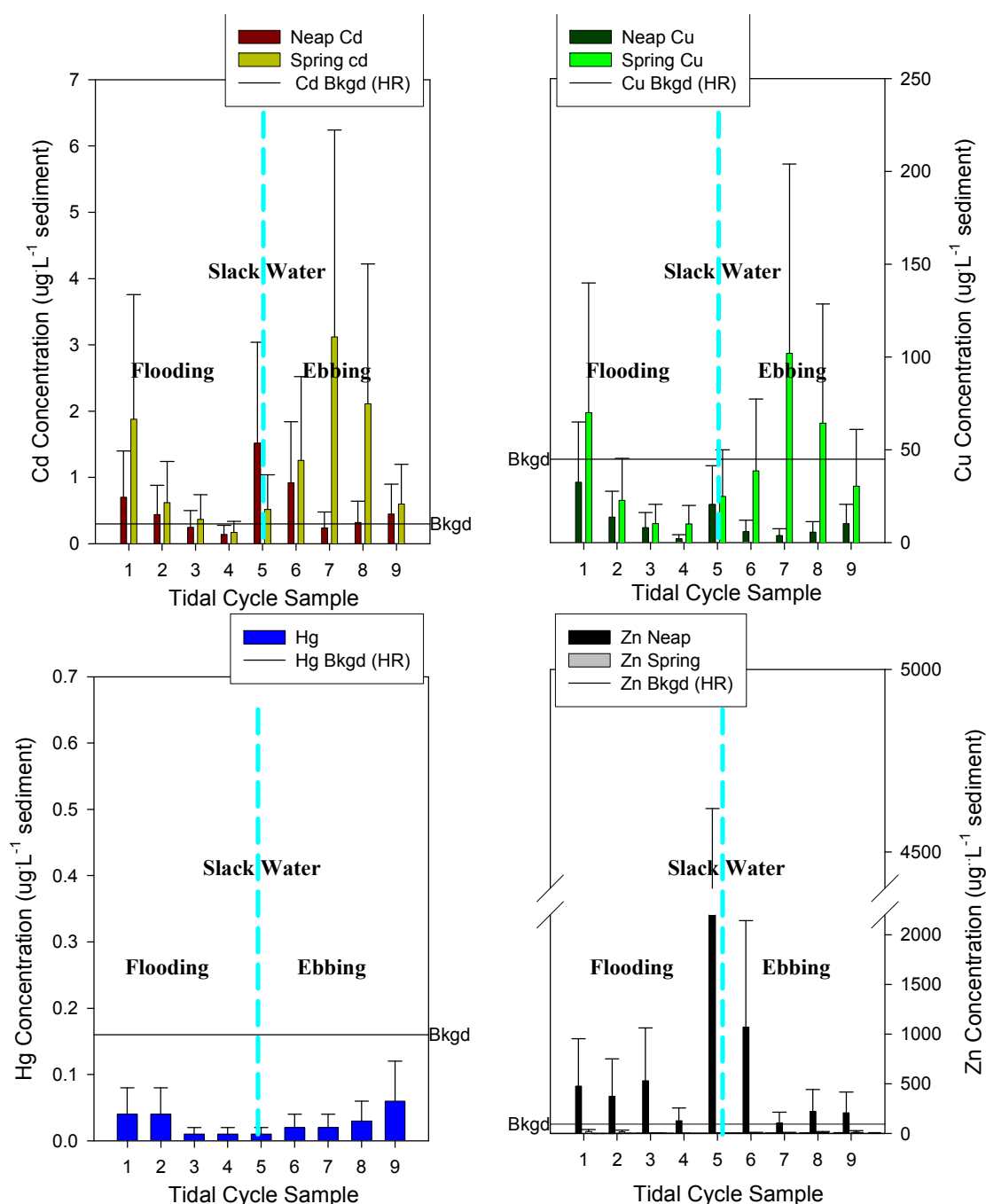


Figure 4-10. Particulate metal concentrations at Neck Creek over neap vs. spring tidal cycles.

Graph depicts mean particulate metal concentrations ($n=9$) over the extent of two complete tidal cycles. For each sampling interval, particulate metal concentrations were calculated via multiplication of mean metal concentrations associated with suspended sediments and mean SPM concentrations (determined from replicate analysis of duplicate suspended particulate matter samples $n=4$). Temporal SPM metal concentrations used to calculate respective mean particulate values were determined via averages from triplicate metal analysis of sample duplicates ($n=6$ for the neap tide dataset) and triplicate metal analysis of sample replicates ($n=3$ for the spring tide dataset). Positive error bars reflect standard deviations of particulate concentration dataset. Literature-based regional background values from Hudson river sediments were used as a proxy for natural concentrations levels and a means for reference (Hirschberg et al. 1996, Bowen et al. 1970).

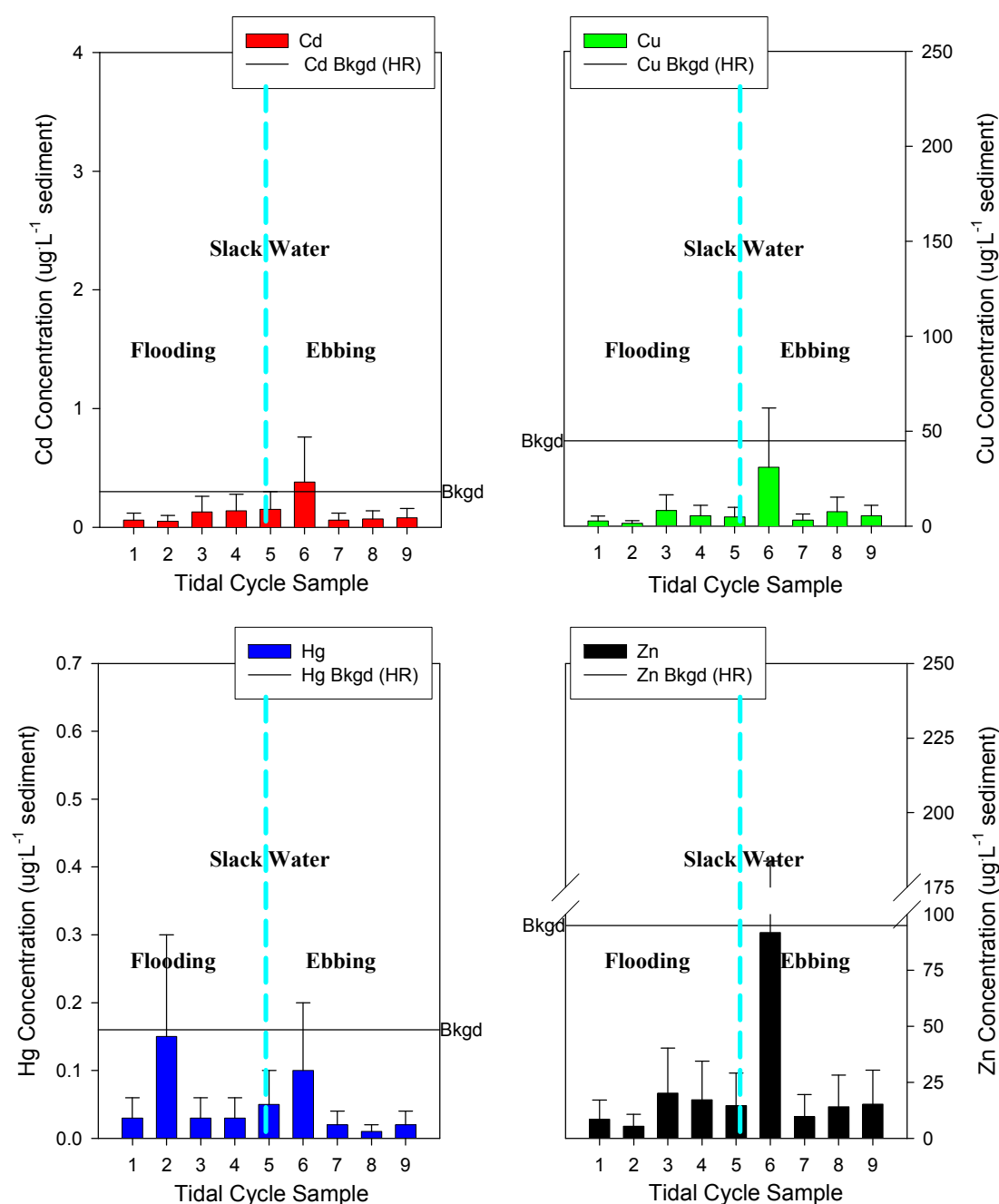


Figure 4-11. Particulate metal concentrations over a median tidal cycle at Lemon Creek.

Graph depicts mean particulate metal concentrations ($n=9$) over the extent of a complete tidal cycle. For each sampling interval, particulate metal concentrations were calculated via multiplication of mean metal concentrations associated with suspended sediments (determined from triplicate metal analysis of sample replicates $n=3$) and mean SPM concentrations (determined from replicate analysis of duplicate suspended particulate matter samples $n=4$). Positive error bars reflect standard deviations of particulate concentration dataset. Literature-based regional background values from Hudson river sediments were used as a proxy for natural concentrations levels and a means for reference (Hirschberg et al. 1996, Bowen et al. 1970).

Table 4-17a. Main Creek neap tide survey import/export tidal calculations November 2008.

MA Neap tide survey	Water volume (m ³)		SPM mg		Cd µg		Hg µg		Cu µg		Zn µg	
Sample/ Tidal Stage	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)
1	2.91	-1.39	139.	-17.8	1.57	-0.49	-	-	83.5	-35.0	120.	-48.6
2	1.64	-0.67	201.	-5.5	2.99	-0.16	-	-	154.5	-8.9	214.	-22.3
3	0.84	-2.57	37.1	-33.1	0.53	-1.47	-	-	30.3	-66.6	42.2	-75.9
4	1.75	-0.63	11.9	-8.3	0.26	-0.86	-	-	13.4	-42.9	19.4	-72.7
Median/Tidal Stage (n=4)	1.70	-1.03	88.1	-13.1	1.05	-0.68	-	-	56.9	-39.0	81.1	-60.7
Average/Tidal Stage (n=4)	1.79	-1.32	97.3	-16.2	1.34	-0.75	-	-	70.4	-38.4	98.9	-54.9
MW U (n ₁ , n ₂ =4)	4		2		5		-	-	6		7	
p-value	0.25	n.s.	0.08	n.s.	0.39	n.s.	-	-	0.56	n.s.	0.77	n.s.
Sum/Tidal Stage (n=4)	7.14	-5.26	389.	-64.7	5.35	-2.98	-	-	282.	-153.	396	-220
Net Difference (Influx-Efflux)	1.88		324.		2.37		-		128.		176.	

Incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete neap spring tidal cycle at Main Creek (November 2008). The significance of tidal stage was tested via Mann-Whitney U analysis, which measured the central tendencies (medians) of respective non-negative fluxes from flood and ebb datasets. The distributions of fluxes from the 2 directional datasets (samples were grouped based on lateral movement of the tide +/-) were compared to determine differences among incoming and outgoing material fluxes. For all parameters tested p values were >0.05 (n.s.), which indicated no significant difference of fluxes with respect to current direction Cd, Cu, Zn, and SPM fluxes. However, the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-)) showed a demonstrable contrast in metal-specific datasets between incoming and outgoing tides.

Table 4-17b. Main Creek spring tide survey import/export tidal calculations March 2009.

MA Spring tide survey	Water volume (m³)		SPM mg*		Cd µg*		Hg µg*		Cu µg*		Zn µg*	
Sample/ Tidal Stage	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)
1	0.68	-7.62	4.2	-676.	0.06	-0.69	0.04	-0.15	13.2	-430.	23	4.2
2	5.54	-2.4	62.5	-261.	0.28	-0.31	0.21	-0.12	108	-66.2	175	62.5
3	9.17	-0.75	614	-83.8	0.71	-0.08	0.27	-0.03	801	-82.9	2425	614
4	6.28	-0.32	770	-15.0	2.41	-0.16	0.74	-0.03	1089	-56.3	2070	770
Median/Tidal Stage (n=4)	5.91	-1.57	338	-172	0.50	-0.24	0.24	-0.08	454	-74.6	1123	5.91
Average/Tidal Stage (n=4)	5.42	-2.77	363	-259	0.87	-0.31	0.32	-0.08	503	-159	1173	5.42
MW U (n₁, n₂=4)	5		0		0		0		0		0	
p-value	0.39	n.s.	0.02	*	0.02	*	0.02	*	0.02	*	0.02	*
Sum/Tidal Stage (n=4)	21.7	-11.1	1451	-1036	3.46	-1.24	1.26	-0.33	2011	-635	4693	21.7
Net Difference (Influx-Efflux)	10.6		415		2.22		0.93		1376		3027	

Incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg were determined from water column samples collected over the extent of a complete spring tidal cycle at Main Creek (March 2009). The significance of tidal stage was tested via Mann-Whitney U analysis, which measured the central tendencies (medians) of respective non-negative fluxes from flood and ebb datasets. The distributions of fluxes from the 2 directional datasets (samples were grouped based on lateral movement of the tide +/-) were compared to determine differences among incoming and outgoing material fluxes. An asterisk (*) denotes a significant difference among the distributions of fluxes entering (+) or leaving (-) the upland marsh habitat ($p \leq 0.05$). For the Main Creek spring tide survey, all particulate metals and SPM showed such significance; the difference among incoming and outgoing water volume flows was considered insignificant ($p > 0.05$). Furthermore, the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-)) showed a net import (+) for all parameters, towards the upland Main Creek marsh-creek habitat.

Table 4-17c. Main Creek calculation summary for tidal exchange of metals and SPM per tidal cycle.

Main Creek Neap Sampling Event, November 2009			
Parameter	Import (flood tide) (n=4)	Export (ebb tide) (n=4)	Net Import/Export (+/-)
Water volume (m³)	7.14	-5.26	1.88
SPM (mg)	389	-64.6	324
Cd (µg)	5.36	-2.97	2.39
Hg (µg)	-	-	-
Cu (µg)	282	-154	128
Zn (µg)	396	-220	176
Main Creek Spring Sampling Event, March 2009			
Parameter	Import (flood tide) (n=4)	Export (ebb tide) (n=4)	Net Import/Export (+/-)
Water volume (m³)	21.7	-11.1	10.6
SPM (mg)	1450	-1036	414
Cd (µg)	3.5	-1.24	2.23
Hg (µg)	1.3	-0.3	0.94
Cu (µg)	2011	-635	1376
Zn (µg)	4693	-1666	3027

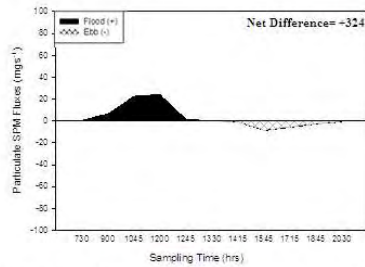
Neap and spring tidal flow conditions demonstrated a net influx of water, SPM and all metals (Cd, Cu, Zn, and Hg) towards inland marsh-creek habitats.

Table 4-17d. Mean tidal exchange of water volume, SPM and metals over 2 Main Creek tidal cycles. Table shows net direction and differences between average import and export terms during neap and spring tides.

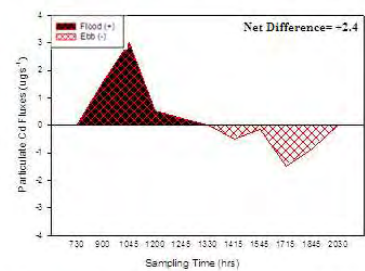
Main Creek Tidal Cycle Average Import			
Parameter	Neap Tide Exchange	Spring Tide Exchange	Averaged Import (+/-)
Water volume (m³)	1.88	10.6	6.24
SPM (mg)	324	414	369
Cd (µg)	2.39	2.23	2.31
Hg (µg)	-	0.94	0.94
Cu (µg)	128	1376	752
Zn (µg)	176	3027	1602

Figure 4-12a. MA neap tide.

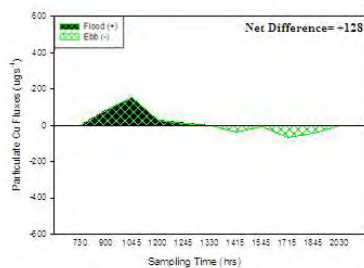
Main Creek Neap Tidal Survey: SPM Fluxes Incoming vs. Outgoing Tidal Currents



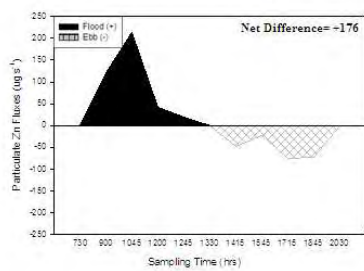
Main Creek Neap Tidal Survey: Cd Fluxes Incoming vs. Outgoing Tidal Currents



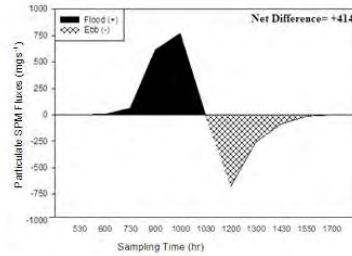
Main Creek Neap Tidal Survey: Cu Fluxes Incoming vs. Outgoing Tidal Currents



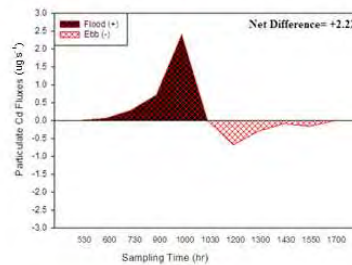
Main Creek Neap Tidal Survey: Zn Fluxes Incoming vs. Outgoing Tidal Currents

**Figure 4-12b. MA spring tide.**

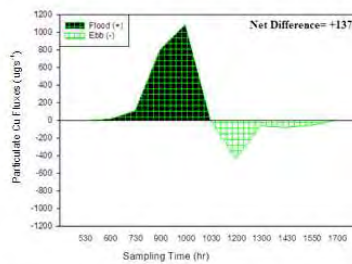
Main Creek Spring Tidal Survey: SPM Fluxes Incoming vs. Outgoing Tidal Currents



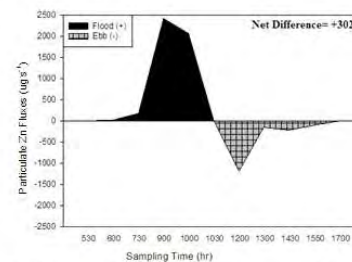
Main Creek Spring Tidal Survey: Cd Fluxes Incoming vs. Outgoing Tidal Currents



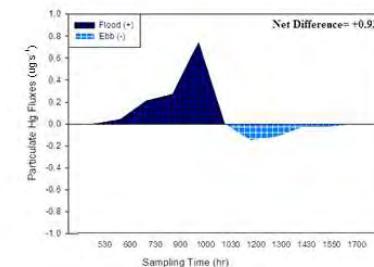
Main Creek Spring Tidal Survey: Cu Fluxes Incoming vs. Outgoing Tidal Currents



Main Creek Spring Tidal Survey: Zn Fluxes Incoming vs. Outgoing Tidal Currents



Main Creek Spring Tidal Survey: Hg Fluxes Incoming vs. Outgoing Tidal Currents

**Figure 4-12a-b. Main Creek net tidal fluxes: import vs. export of SPM and metals.**

Graph depicts mean contaminant fluxes ($n=9$) over the extent of a complete tidal cycle. Particulate fluxes entering and leaving Main Creek via tidal exchange with the Arthur Kill; incoming ($n=4$) and outgoing ($n=4$) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg were determined from water column samples collected over the extent of a complete neap (a) and spring (b) tidal cycle at Main Creek.

Table 4-18a. Neck Creek neap spring tide survey import/export tidal calculations November 2008.

NC Neap tide survey	Water volume (m ³)		SPM mg		Cd µg		Hg µg		Cu µg		Zn µg	
Sample/ Tidal Stage	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)
1	0.01	-0.05	0.21	-0.33	0.00	-0.05	-	-	0.12	-0.31	3.37	-55.0
2	0.27	-1.10	6.84	-16.0	0.07	-0.26	-	-	2.20	-4.15	144.	-118.
3	1.59	-0.43	13.3	-3.99	0.22	-0.14	-	-	3.39	-2.43	206.	-95.
4	1.48	-0.09	8.57	-2.65	2.25	-0.04	-	-	30.60	-0.95	3412.	-19.0
Median/Tidal Stage (n=4)	0.88	-0.26	7.71	-3.32	0.15	-0.10	-	-	2.80	-1.69	175.	-75.0
Average/Tidal Stage (n=4)	0.84	-0.42	7.23	-5.74	0.64	-0.12	-	-	9.08	-1.96	941.	-71.8
MW U (n₁, n₂=4)	6		7		7		-	-	7		4	
p-value	0.57	n.s.	0.77	n.s.	0.77	n.s.	-	-	0.77	n.s.	0.25	n.s.
Sum/Tidal Stage (n=4)	3.35	-1.67	28.9	-23.0	2.54	-0.49	-	-	36.3	-7.84	3765.	-287.
Net Difference (Influx-Efflux)	1.68		5.95		2.05		-		28.5		3478.	

Incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, determined from water column samples collected over the extent of a complete neap tidal cycle at Neck Creek (November 2008). The significance of tidal stage was tested via Mann-Whitney U analysis, which measured the central tendencies (medians) of respective non-negative fluxes from flood and ebb datasets. The distributions of fluxes from the 2 directional datasets (samples were grouped based on lateral movement of the tide +/-) were compared to determine differences among incoming and outgoing material fluxes. For all parameters tested p values were >0.05 (n.s.), which indicated no significant difference of fluxes with respect to current direction Cd, Cu, Zn, and SPM fluxes. However, the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-)) showed a demonstrable contrast in metal-specific datasets between incoming and outgoing tides.

Table 4-18b. Neck Creek spring tide survey import/export tidal calculations March 2009.

NC Spring tide survey	Water volume (m ³)		SPM mg		Cd µg		Hg µg		Cu µg		Zn µg	
Sample/ Tidal Stage	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)
1	0.01	-0.59	0.90	-34.2	0.01	-1.85	0.00	-0.01	0.25	-60.6	0.19	-3.64
2	1.45	-0.21	84.10	-15.9	0.54	-0.45	0.01	-0.01	14.9	-13.8	4.48	-2.09
3	0.25	-0.05	11.50	-4.32	0.04	-0.03	0.00	0.00	2.51	-1.65	0.60	-0.83
4	0.11	-0.02	4.15	-1.65	0.06	-0.03	0.00	0.00	2.86	-0.97	0.40	-0.22
Median/Tidal Stage (n=4)	0.18	-0.13	7.83	-10.1	0.05	-0.24	0.00	-0.01	2.69	-7.73	0.50	-1.46
Average/Tidal Stage (n=4)	0.46	-0.22	25.2	-14.0	0.16	-0.59	0.00	-0.01	5.13	-19.3	1.42	-1.70
MW U (n₁, n₂=4)	7		7		7		6		6		6	
p-value	0.77	n.s.	0.77	n.s.	0.77	n.s.	0.56	n.s.	0.56	n.s.	0.56	n.s.
Sum/Tidal Stage (n=4)	1.83	-0.89	100.7	-56.1	0.65	-2.36	0.01	-0.02	20.5	-77.0	5.67	-6.78
Net Difference (Influx-Efflux)	0.94		44.58		-1.71		-0.01		-56.5		-1.11	

Incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete spring tidal cycle at Neck Creek.

The significance of tidal stage and influence of current direction on fluxes values was tested by comparison of non-negative median values (flood vs. ebb) via Mann-whitney U analysis. An asterisk (*) denotes a significant difference between median fluxes of contaminants entering (+) or leaving (-) the upland marsh habitat ($p \leq 0.05$). Cd, Cu, Zn, Hg, and SPM fluxes were considered insignificant with p values > 0.05 (n.s.). However, the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-)) showed a demonstrable contrast in metal-specific datasets between incoming and outgoing tides.

Table 4-18c. Neck Creek calculation summary for tidal exchange of metals and SPM per tidal cycle.

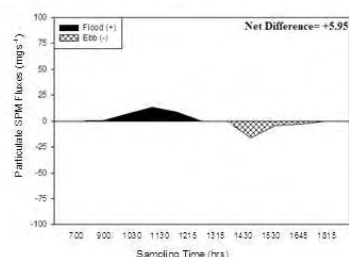
Neck Creek Neap Sampling Event, November 2009			
Parameter	Import (flood tide) (n=4)	Export (ebb tide) (n=4)	Net Import/Export (+/-)
Water volume (m³)	3.35	-1.67	1.68
SPM (mg)	28.9	-23	5.9
Cd (µg)	2.54	-0.49	2.05
Hg (µg)	-	-	-
Cu (µg)	36.3	-7.84	28.5
Zn (µg)	3766	-288	3478
Neck Creek Spring Sampling Event, March 2009			
Parameter	Import (flood tide) (n=4)	Export (ebb tide) (n=4)	Net Import/Export (+/-)
Water volume (m³)	1.83	-0.89	0.94
SPM (mg)	100.7	-56.1	44.6
Cd (µg)	0.65	-2.36	-1.71
Hg (µg)	0.01	-0.02	-0.01
Cu (µg)	20.5	-77	-56.5
Zn (µg)	5.67	-6.78	-1.11

Table 4-18d. Mean tidal exchange of water volume, SPM and metals over 2 Neck Creek tidal cycles. Table shows net direction and differences between average import and export terms during neap and spring tides.

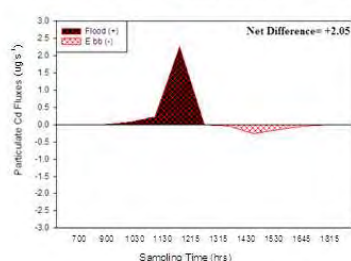
Neck Creek Average Tidal Cycle Average Import/Export			
Parameter	Neap Tide Exchange	Spring Tide Exchange	Averaged Import/Export (+/-)
Water volume (m³)	1.68	0.94	1.31
SPM (mg)	5.9	44.6	25.3
Cd (µg)	2.05	-1.71	0.17
Hg (µg)	-	-0.01	-0.01
Cu (µg)	28.5	-56.5	-14
Zn (µg)	3478	-1.11	1739

Figure 4-13a. NC neap tide.

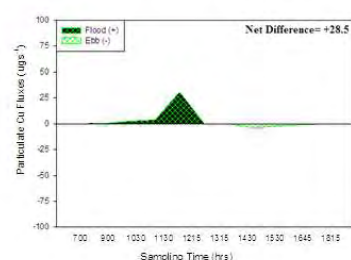
Neck Creek Neap Tidal Survey: SPM Fluxes Incoming vs. Outgoing Tidal Currents



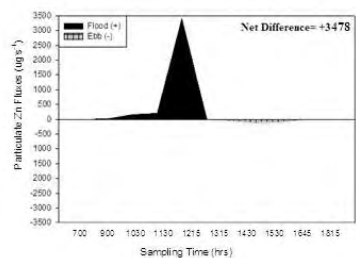
Neck Creek Neap Tidal Survey: Cd Fluxes Incoming vs. Outgoing Tidal Currents



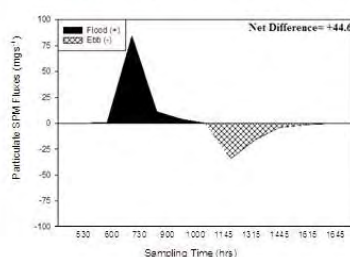
Neck Creek Neap Tidal Survey: Cu Fluxes Incoming vs. Outgoing Tidal Currents



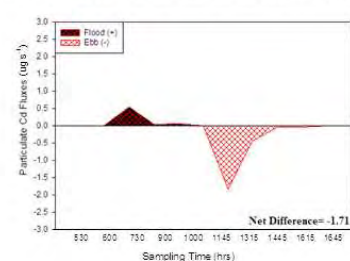
Neck Creek Neap Tidal Survey: Zn Fluxes Incoming vs. Outgoing Tidal Currents

**Figure 4-13b. NC spring tide.**

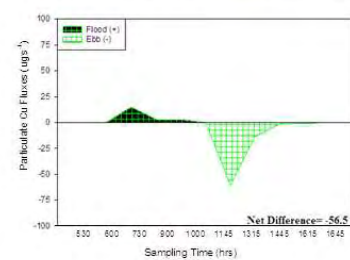
Neck Creek Spring Tidal Survey: SPM Fluxes Incoming vs. Outgoing Tidal Currents



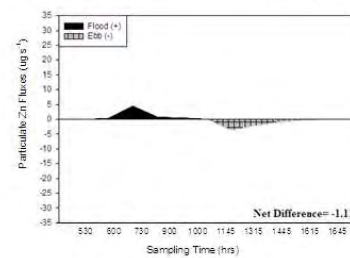
Neck Creek Spring Tidal Survey: Cd Fluxes Incoming vs. Outgoing Tidal Currents



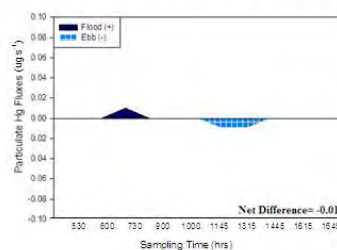
Neck Creek Spring Tidal Survey: Cu Fluxes Incoming vs. Outgoing Tidal Currents



Neck Creek Spring Tidal Survey: Zn Fluxes Incoming vs. Outgoing Tidal Currents



Neck Creek Spring Tidal Survey: Hg Fluxes Incoming vs. Outgoing Tidal Currents

**Figure 4-13a-b. Neck Creek net tidal fluxes: import vs. export of SPM and metals.**

Incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete neap (a) and spring (b) tidal cycle at Neck Creek in 2008, and 2009, respectively. Positive values (y-axis) corresponded to respective sampling intervals during flood tide (n=4) and reflect influxes into Neck Creek. Negative (y-axis) values corresponded to samples collected during ebb tide (n=4) and represented outflow towards the main channel of the Arthur Kill. The net difference between incoming (+) and outgoing (-) contaminant fluxes calculated via the summation of the areas beneath the respective curves produced for each tidal stage (flood vs. ebb) determined the net direction of tidal transport for each parameter studied.

Table 4-19a. Lemon Creek (median tide) survey import/export tidal calculations April 2009.

LC Intermediate Survey	Water volume (m³)		SPM mg		Cd µg*		Hg µg		Cu µg*		Zn µg*	
Sample/Tidal Stage	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)	Flood (+)	Ebb (-)
1	4.30	-4.16	569	-914	0.62	-0.25	0.21	-0.12	20.7	-11.1	60.4	-35.2
2	6.43	-6.48	731	-479	2.33	-0.33	0.61	-1	191	-9.49	563	-35.7
3	8.97	-2.92	2373	-817	0.54	-0.41	0.18	-0.09	28.8	-25.9	88.4	-63.5
4	6.78	-2.61	1695	-952	0.47	-0.23	0.07	-0.06	51.1	-16.1	94.6	-44.4
Median/Tidal Stage (n=4)	6.61	-3.54	1213	866	0.58	0.29	0.2	0.11	40.0	13.6	91.5	40.05
Average/Tidal Stage (n=4)	6.62	-4.04	1342	790.	0.99	0.31	0.27	0.32	72.9	15.65	201.6	44.7
MW U (n₁, n₂=4)	2		6		0		6		1		1	
p-value	0.08	n.s.	0.56	n.s.	0.02	*	0.56	n.s.	0.04	*	0.04	*
Sum/Tidal Stage (n=4)	26.5	-16.2	5368	-3162	3.96	-1.22	1.07	-1.27	292.	-62.6	806.	-179.
Net Difference (Influx-Efflux)	10.3		2206		2.74		-0.2		229		628	

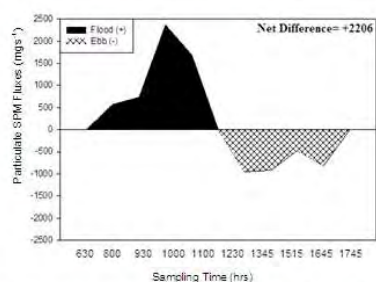
Incoming (n=4) and outgoing (n=4) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete tidal cycle (intermediate flow conditions) at Lemon Creek. The significance of tidal stage and influence of current direction on fluxes values was tested by comparison of non-negative median values (flood vs. ebb) via Mann-Whitney U analysis; an asterisk (*) denotes a significant difference between median fluxes of contaminants entering (+) or leaving (-) the upland marsh habitat ($p > 0.05$). Hg and SPM fluxes did not show significantly different fluxes with respect to current direction (+/-). Analysis of the central tendencies of Cd, Cu, Zn fluxes from each respective tidal stages (ebb vs flood) demonstrated significance differences among incoming and outgoing particulate Cd, Cu, and Zn ($p < 0.05$). This observation was further highlighted in the by the summation of metal-specific fluxes with respect to current direction (flood (+) and ebb (-)), which showed a demonstrable contrast with respect to metal-specific datasets between incoming and outgoing tides.

Table 4-19b. Lemon Neck Creek calculation summary for tidal exchange of metals and SPM per tidal cycle.

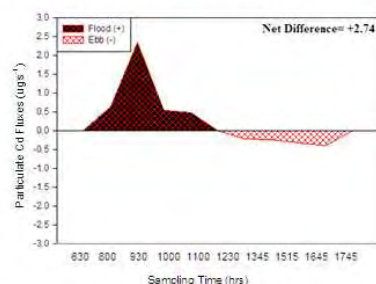
Lemon Creek Sampling Event, April 2009*			
Parameter	Import (flood tide) (n=4)	Export (ebb tide) (n=4)	Net Import/Export (+/-)
Water volume (m³)	26.5	-16.2	10.3
SPM (mg)	5368	-3162	2206
Cd (µg)	3.96	-1.22	2.7
Hg (µg)	1.07	-1.27	-0.20
Cu (µg)	291	-62.64	229
Zn (µg)	806	-179	627

*Survey conducted over tidal cycle with intermediate flow (between spring and neap tidal flows).

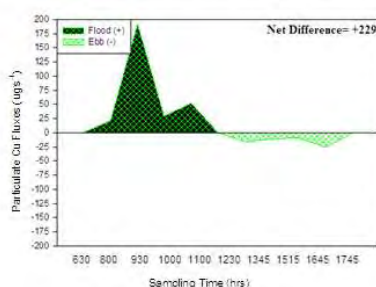
Lemon Creek Median Tidal Survey: SPM Fluxes Incoming vs. Outgoing Tidal Currents



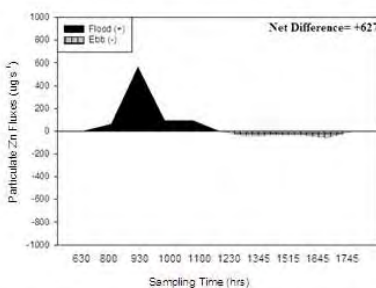
Lemon Creek Median Tidal Survey: Cd Fluxes Incoming vs. Outgoing Tidal Currents



Lemon Creek Median Tidal Survey: Cu Fluxes Incoming vs. Outgoing Tidal Currents



Lemon Creek Median Tidal Survey: Zn Fluxes Incoming vs. Outgoing Tidal Currents



Lemon Creek Median Tidal Survey: Hg Fluxes Incoming vs. Outgoing Tidal Currents

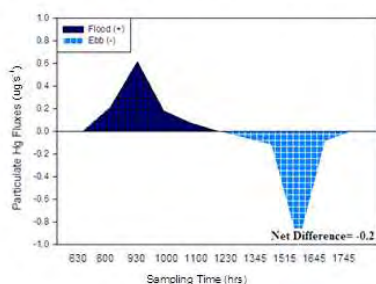


Figure 4-14. Lemon Creek net tidal fluxes: import vs. export of SPM and metals: intermediate tidal survey. Incoming ($n=4$) and outgoing ($n=4$) tidal fluxes of SPM and particulate Cd, Cu, Zn, and Hg determined from water column samples collected over the extent of a complete tidal cycle (intermediate flow conditions) at Lemon Creek. Positive values (y-axis) correspond to respective sampling intervals during flood tide ($n=4$) and reflect influx of particulates into Lemon Creek. Negative (y-axis) values correspond to samples collected during ebb tide ($n=4$) and represent outflow towards the open waters of the NY/NJ HE.

Appendix 4-A: Metal-specific Contamination Factors.

Study Site ¹	Survey/ Sample ²	Metal-Specific Contamination Factors (CF)								Contamination Degree (CD)	
		Cd		Hg		Cu		Zn			
MA	2009 SPM ³	120	Very High	12.7	Very High	36.2	Very High	32.2	Very High	50.2	Very High
	2009 SS	11.5	Very High	7.9	Very High	4.8	Considerable	2.5	Considerable	26.7	Considerable
	2007 SS	18.7	Very High	8.9	Very High	5.7	Considerable	3.1	Considerable	36.3	Very High
	2001 SS	17.3	Very High	-	-	6.5	Very High	3.5	Considerable	27.4	Considerable
NC	2009 SPM ³	125	Very High	2.31	Moderate	15.6	Very High	397.5	Very High	135.2	Very High
	2009 SS	6.4	Very High	7.1	Very High	3.9	Considerable	1.7	Moderate	19.1	Considerable
	2007 SS	15.1	Very High	11.2	Very High	7.7	Very High	2.6	Moderate	36.5	Very High
	2001 SS	9.4	Very High	-	-	5.3	Considerable	1.6	Moderate	16.5	Considerable
LC	2009 SPM ⁴	2.57	Moderate	2.63	Moderate	1.08	Moderate	1.48	Moderate	1.94	Low
	2009 SS	5.4	Considerable	1.5	Moderate	2.9	Moderate	1.85	Moderate	11.6	Moderate
	2007 SS	4.0	Considerable	1.2	Moderate	3.1	Considerable	1.79	Moderate	10.1	Moderate
	2001 SS	7.9	Very High	-	-	2.0	Moderate	1.13	Moderate	11.1	Moderate

Relative extent of anthropogenic metal pollution reflected by Main Creek, Neck Creek, and Lemon Creek SPM and surface sediment samples via Site-specific contamination factors (CF) and contamination degree (CD) determined from Staten Island marsh sediment samples collected from the surface and suspended within the water column at Main Creek, Neck Creek and Lemon Creek.

Appendix 4-B: Hydrological and physiochemical time and tidal data

Appendix 4-B-1.

Main Creek hydrological and physiochemical time and tidal data.

Metal Sample MA Survey 1	Time	Tide
1	900	in flood (+)
2	1045	in flood (+)
3	1200	in flood (+)
4	1245	in flood (+)
5	1330	slack water (prior to ebb)
6	1415	out ebb (-)
7	1545-1600	out ebb (-)
8	1715	out ebb (-)
9	1845	out ebb (-)

Metal Sample MA Survey 2	Time	Tide
1	600	in flood (+)
2	730	in flood (+)
3	900	in flood (+)
4	10:00	in flood (+)
5	10:30	slack water (prior to ebb)
6	1130	out ebb (-)
7	1300	out ebb (-)
8	1430	out ebb (-)
9	1550	out ebb (-)

Appendix 4-B-2.**Neck Creek hydrological and physiochemical time and tidal data.**

Metal Sample NC Survey 1	Time	Tide
1	0700	out ebb (-)
2	0900	in flood (+)
3	1030	in flood (+)
4	1130	in flood (+)
5	1215	in flood (+); high water
6	1315	out ebb (-)
7	1430	out ebb (-)
8	1530	out ebb (-)
9	1645	out ebb (-); low water

Metal Sample NC Survey 2	Time	Tide
1	0600	in flood (+)
2	0730	in flood (+)
3	0900	in flood (+)
4	1000	in flood (+)
5	1100	slack (prior to ebb); high water
6	1145	out ebb (-)
7	1315	out ebb (-)
8	1445	out ebb (-)
9	1615	out ebb (-)

Appendix 4-B-3.**Lemon Creek hydrological and physiochemical time and tidal data.**

Sample LC Survey	Time	Tide
1	0630	out ebb (-)
2	0800	out ebb (-)
3	0930	out ebb (-)
4	1000	slack water (prior to flood)
5	1100	in flood (+)
6	1230	in flood (+)
7	1345	in flood (+)
8	1515	in flood (+); high water
9	1745	out ebb (-)

Appendix 4-C: Tidal survey data.

Appendix4-C-1.

Main Creek neap tidal survey November 19, 2008.

Time (hrs)	Metal Sample	Time (hr)	Tidal current/direction ebb (-); flood (+)	Velocity (m·s ⁻²)	ΔTide	Temp. °C	pH (psu)	Salinity (ppt)	Dissolved oxygen (mg·L ⁻¹)	X-sectional area (m ²)	Water Flow (m ³ ·s ⁻¹)
0	-	730	slack (prior to flood)	0.06		2.4	7.42	-	7.82	15.28	0.92
1.5	1	900	in flood (+)	0.14 ¹		2.5	7.74	7	8.41	20.78	2.91
2.75	2	1045	in flood (+)	0.06		4.8	7.59	14	8.12	27.38	1.64
4.5	3	1200	in flood (+)	0.03		4.8	7.47	-	8.22	27.93	0.84
5.25	4	1245	in flood (+)	0.06	High	5.5	7.66	-	8.28	29.13	1.75
6	5	1330	slack (prior to ebb)	0		-	-	-	-	28.38	Slack
6.75	6	1415	out ebb (-)	-0.07		5.6	7.72		8.78	19.83	-1.39
8.25	7	1545-1600	out ebb (-)	-0.04		3.9	7.78	8.5	8.76	16.76	-0.67
9.75	8	1715	out ebb (-)	-0.16 ²		3.5	7.78	8.8	8.85	16.05	-2.57
11.25	9	1845	out ebb (-)	-0.04	Low	3.3	7.49	8.9	7.83	15.83	-0.63
	-	2030	slack	0		-	-	-	-	-	Slack

¹Maximum flood tidal current (named for direction that set flows)

²Maximum ebb tidal current (named for direction that set flows)

Appendix 4-C-2.**Main Creek spring tidal survey March 27, 2009.**

Time (hrs)	Metal Sample	Time (hr)	Tidal current /direction ebb (-); flood (+)	Velocity (m·s ⁻²)	ΔTide	Temp . °C	pH (psu)	Salinity (ppt)	Dissolved oxygen (mg·L ⁻¹)	X-sectional area (m ²)	Water Flow (m ³ ·s ⁻¹)
0	-	530	slack (prior to flood)	0.03	Low	-	-	-	-	8.08	0.24
1	1	600	in flood (+)	0.05		6.8	8.08	4.4	9.68	13.52	0.68
2.5	2	730	in flood (+)	0.22		6.9	7.99	5.1	8.18	25.18	5.54
3	3	900	in flood (+)	0.31 ¹		7.4	7.91	7.1	12.04	29.58	9.17
4.5	4	10:00	in flood (+)	0.20		7.7	8.05	7.1	16.18	31.38	6.28
5	5	10:30	slack (prior to ebb)	0	High	-	-	-	-	-	Slack
6	6	1130	out ebb (-)	-0.27 ²		10.1	7.96	6.9	14.49	28.23	-7.62
7.5	7	1300	out ebb (-)	-0.14		9.3	7.98	7	14.76	17.13	-2.40
9	8	1430	out ebb (-)	-0.10		11.1	8.01	6.5	13.08	7.47	-0.75
10.3	9	1550	out ebb (-)	-0.05		13.5	7.96	7.5	13.13	6.32	-0.32
11.25	-	1645	slack (prior to flood)	0.01		9.1	7.99	7.0	12.69	13.74	Slack

¹Maximum flood tidal current (named for direction that set flows)

²Maximum ebb tidal current (named for direction that set flows)

Weather conditions: 42-65° F. heavy rainfall previous 12hrs; Travis Avenue culvert upstream flowing through afternoon.

0% of moon visible 3/27/2009 www.saltwatertides.com/cgi-local/newjersey.cgi accessed 3/19/2009

High 9:15 am; low 3:39am; 3:44pm

Appendix 4-C-3.
Neck Creek neap tidal survey November 19th, 2008.

Time	Sample	Time (hrs)	Tidal current /direction ebb (-); flood (+)	Velocity (m·s ⁻²)	ΔTide	Temp. °C	pH (psu)	Salinity (ppt)	Dissolved oxygen (mg·L ⁻¹)	X-sectional area (m ²)	Water Flow (m ³ ·s ⁻¹)
0	1	0700	out ebb (-)	-0.17		1.2	7.53	15.3	8.04	0.11	-0.02
1.5		0830	slack (prior to flood)	0		-	-	-	-	-	
2	2	0900	in flood (+)	0.10		1.7	7.47	7.6	7.89	0.09	0.01
3.5	3	1030	in flood (+)	0.33		3.5	7.52	6.3	7.92	0.83	0.27
4.5	4	1130	in flood (+)	0.58 ¹		8.4	7.6	15.8	8.03	2.75	1.59
5.25	5	1215	in flood (+)	0.47	High	8.5	7.67	13.2	8.42	3.13	1.48
5.75		1245	slack (prior to ebb)	0		-	-	-	-	-	Slack
6.25	6	1315	out ebb (-)	-0.02		9.7	7.79	11	8.09	3.0	-0.05
7.5	7	1430	out ebb (-)	-0.53 ²		7.3	7.63	11.6	7.78	2.08	-1.10
8.5	8	1530	out ebb (-)	-0.38		5.1	7.47	15.8	7.82	1.14	-0.43
9.25	9	1645	out ebb (-)	-0.14	Low	3.6	7.46	13	7.02	0.66	-0.09
11.25		1815	slack water	0.08		-	-	-	-	-	Slack

¹Maximum flood tidal current (named for direction that set flows)

²Maximum ebb tidal current (named for direction that set flows)

Weather conditions: clear, sunny 26-37° F. 60% Moon visible, neap tidal state. www.saltwatertides.com accessed 11/10/2008

Appendix 4-C-4.
Neck Creek spring tidal survey March 27, 2009.

Time (hrs)	Sample	Time (hr)	Tidal current/direction ebb (-); flood (+)	Velocity (m·s ⁻²)	ΔTide	Temp. °C	pH (psu)	Salinity (ppt)	Dissolved oxygen (mg·L ⁻¹)	X-sectional area (m ²)	Water Flow (m ³ ·s ⁻¹)
0	-	0530	slack (prior to flood)	0.03		4.6	7.58	11	7.83	0.10	0.00
.5	1	0600	in flood (+)	0.07		4.8	7.63	11	7.71	0.15	0.01
2	2	0730	in flood (+)	0.52 ¹		8.7	7.59	11	11	2.80	1.45
3.5	3	0900	in flood (+)	0.11		8.8	7.79	8.7	11	2.28	0.25
4.5	4	1000	in flood (+)	0.03		8.9	7.17	19	9.83	4.13	0.11
5.5	5	1100	slack (prior to ebb)	-0.26	High	9	7.18	19	10.3	4.91	1.27
6.25	6	1145	out ebb (-)	-0.61 ²		9	7.23	19	15.4	0.98	-0.59
7.75	7	1315	out ebb (-)	-0.43		12.6	7.79	15	14.7	0.50	-0.21
9.25	8	1445	out ebb (-)	-0.27		13.8	7.31	15.2	15.15	0.20	-0.05
10.75	9	1615	out ebb (-)	-0.21		12.6	7.76	15.3	15.27	0.11	-0.02
11.25	-	1645	Slack (prior to flood)	0.16	Low	12.7	-	13.1	-	0.08	0.01

¹Maximum flood tidal current (named for direction that set flows)

²Maximum ebb tidal current (named for direction that set flows)

Weather conditions: 42-65° F. heavy rainfall previous 12hrs.

0% of moon visible 3/27/2009 www.saltwatertides.com/cgi-local/newjersey.cgi accessed 3/19/2009

High 9:15 am; low 3:39am; 3:44pm

Appendix 4-C-5.

Lemon Creek intermediate tidal survey April 3, 2009.

Time (hrs)	Sample	Time (hr)	Tidal current /direction (ebb (-); flood (+))	Velocity (m·s ⁻²)	ΔTide	Temp. °C	pH (psu)	Salinity (ppt)	Dissolved oxygen (mg·L ⁻¹)	X-sectional area (m ²)**	Water Flow (m ³ ·s ⁻¹)
0	1	0630	out ebb (-)	0.06		10.5	7.38	7.9	9.6	69.4	4.16
1.5	2	0800	out ebb (-)	0.121		10.5	7.41	7.4	9.33	54	6.48
3	3	0930	out ebb (-)	0.05	Low	10.6	7.65	7.2	8.56	58.4	2.92
4.5	4	1000	slack (prior to flood)	0.04		-	7.67	-	-	61.7	2.47
4.75	5	1100	in flood (+)	0.06		10.5	7.54	1.7	10.06	71.6	4.30
6	6	1230	in flood (+)	0.08		10.6	7.51	1.8	9.54	80.4	6.43
7.25	7	1345	in flood (+)	0.11 ²		10.7	7.41	3.4	9.99	81.5	8.97
8.75	8	1515	in flood (+)	0.08	High	10.7	7.49	2.4	9.98	84.8	6.78
10.25	-	1645	slack (prior to ebb)	0.00		-	-	-	-	-	
11.25	9	1745	out ebb (-)	0.03		10.7	7.65	11.8	13.73	87	2.61

¹Maximum flood tidal current (named for direction that set flows)

²Maximum ebb tidal current (named for direction that set flows)

Weather conditions: Overcast; light rain/mist. 48 F-54°F. Variable East Winds at 10-14MPH. 0.05inches preceding 24hrs. 41% moon visible Mid-neap-spring tidal conditions.

**Wet weather runoff and stormwater discharges via culverts underneath Hylan Blvd. may have increased Lemon Creek flows.

Appendix 4-D Main Creek Data

Appendix 4-D-1.

Main Creek neap tidal survey mean calculations.

Sample ID	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Cd ug·L ^{-1*}	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Cu ug·L ^{-1*}	Zn ug·g ⁻¹	Zn ug·L ⁻¹	Zn ug·L ^{-1*}
MA1	100.28	10.32	1.04	1.01	533.47	53.50	52.32	706.87	70.89	69.33
MA1A	95.88	12.43	1.19	1.22	670.77	64.31	65.79	1024.35	98.22	100.5
MA 1 -1mean ¹	156.73	11.37 ²	1.78	-	602.12	94.37	-	865.61	135.66	-
Mean ²	98.08	11.37 ²	1.11	1.12	602.12	58.91	59.06	865.61	84.55	84.9
MA2	78.12	8.21	0.64	0.50	446.86	34.91	27.09	558.41	43.62	33.85
MA2A	43.12	21.53	0.93	1.31	1089.59	46.98	66.05	1569.42	67.67	95.14
MA 2-2 mean ¹	70.59	14.87	1.05	-	768.23	54.23	-	1063.92	75.10	-
Mean ²	60.62	14.87	0.79	0.90	768.23	40.95	46.57	1063.92	55.65	64.49
MA3	10.36	19.14	0.20	0.37	993.08	10.29	19.18	1235.36	12.80	23.85
MA3A	28.26	9.55	0.27	0.18	636.47	17.99	12.29	1036.21	29.28	20.01
MA 3-3 mean ¹	22.26	14.35	0.32	-	814.78	18.14	-	1135.79	25.28	-
Mean ²	19.31	14.35	0.23	0.28	814.78	14.14	15.73	1135.79	21.04	21.93
MA4	15.89	9.51	0.15	0.12	722.60	11.48	9.32	1243.78	19.77	16.04
MA4A	9.89	35.38	0.35	0.46	1539.93	15.24	19.85	2018.70	19.97	26.03
MA 4-4 mean ¹	13.95	22.44	0.31	-	1131.26	15.78	-	1631.24	22.75	-
Mean ²	12.89	22.44	0.25	0.29	1131.26	13.36	14.59	1631.24	19.87	21.03
MA5	16.44	6.34	0.10	0.10	516.22	8.49	8.49	635.09	10.44	10.44
MA 5-5 mean ¹	16.44	6.30	0.10	-	516.22	8.49	-	635.09	10.44	-
Mean ²		6.30	0.10	0.10	516.22	8.49	8.49	635.09	10.44	10.44
MA6	3.25	44.40	0.14	0.73	3201.50	10.42	25.36	4396.52	14.30	34.82
MA6A	12.59	11.21	0.04	0.09	743.29	9.36	5.89	1079.89	13.59	13.59
MA 6-6 mean ¹	13.06	27.81	0.36	-	1972.40	25.77	-	2738.20	35.77	8.55
Mean ²	7.92	27.81	0.09	0.41	1972.40	9.89	15.62	2738.20	8.55	8.55
MA7	12.11	19.64	0.25	0.16	1146.66	13.88	9.95	5018.54	60.76	43.56
MA7A	5.25	37.23	0.45	0.32	2107.66	11.07	18.29	3144.67	16.52	27.30
MA 7-7 mean ¹	7.66	28.43	0.22	-	1627.16	12.46	-	4081.60	31.25	-
Mean ²	8.68	28.43	0.35	0.24	1627.16	12.48	14.12	4081.60	38.64	35.43
MA8	22.27	9.06	0.05	0.08	500.07	11.14	6.32	583.30	12.99	7.38
MA8A	3.02	80.30	1.79	1.02	3526.49	10.65	44.59	4006.35	12.10	50.66
MA 8-8 mean ¹	12.65	44.68	0.56	-	2013.28	25.46	-	2294.82	29.02	-
Mean ²	-	44.68	0.92	0.55	2013.28	10.89	25.46	2294.82	12.54	29.02
MA9	24.06	10.81	0.03	0.14	514.34	12.38	6.55	1374.69	33.08	17.51
MA9A	1.42	197.18	2.51	2.51	9838.03	13.97	125.34	16154.93	22.94	205.81
MA 9-9 mean ¹	12.74	103.99	1.32	-	5176.18	65.94	-	8764.81	111.66	-
Mean ²	-	103.99	1.27	1.32	5176.18	13.17	65.94	8764.81	28.01	111.66

* indicates filter SPM concentration determined from Hg subsample

^A indicates duplicate water sample

¹calculated from the mean concentrations of SPM (n=4) and SPM metals (n=6) yielded from analysis of duplicate water samples, each split for duplicate SPM analysis and triplicate Cd, Cu, and Zn determination.

²calculated from the mean concentrations of SPM (n=2) and SPM metals (n=6) yielded from analysis of duplicate water samples (replicates analyzed in triplicate for Cd, Cu, and Zn determination).

Appendix 4-D-2.

Instantaneous fluxes of water, SS and metals imported and exported through Main Creek cross-section on flooding (+) and ebbing (-) tidal phases during November 2008 neap tide survey.

MA Neap	SPM (mg·s⁻¹)	Cd (µg·s⁻¹)	Cu (µg·s⁻¹)	Zn (µg·s⁻¹)
Flood 1	138.6	1.57	83.5	120.0
Flood 2	201.1	2.99	154.5	214.0
Flood 3	37.1	0.53	30.3	42.2
Flood 4	11.9	0.26	13.4	19.4
Sum	388.8	5.36	281.7	395.6
Ebb 1	-17.8	-0.49	-35.0	-48.6
Ebb 2	-5.5	-0.16	-8.9	-22.3
Ebb 3	-33.1	-1.47	-66.6	-75.9
Ebb 4	-8.3	-0.86	-42.9	-72.7
Sum	-64.6	-2.97	-153.5	-219.6
Import	388.8	5.36	281.7	395.6
Export	-64.6	-2.97	-153.5	-219.6
Difference	+324	+2.4	+128	+176

Appendix 4-D-3

Summary Main Creek spring tidal flow survey March 2009.

Sample ID	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
MA 1	9.33	54.5	0.51	10.1	0.09	3145	29.4	5450	51
MA1*	28.5	-	0.01	-	0.29	-	89.7	-	155
mean	18.9	54.5	0.26	10.1	0.19	3145	59.6	5450	103
MA 2	22.8	31.2	0.71	3.36	0.08	1722	39.3	2805	64
MA2*	161	-	0.11	-	0.54	-	277	-	452
mean	91.9	31.2	0.41	3.36	0.31	1722	158	2805	258
MA3	6.60	32.6	0.22	0.48	0.003	1305	8.61	3951	26
MA3*	217	-	0.05	-	0.10	-	283	-	858
mean	112	32.6	0.13	0.48	0.05	1305	146	3951	442
MA4	12.00	37.9	0.46	0.94	0.011	1415	17	2689	32
MA4*	154	-	0.07	-	0.15	-	218	-	414
mean	82.9	37.9	0.26	0.94	0.08	1415	117	2689	223
MA5	4.98	51.2	0.26	0.30	0.001	1513	7.53	4785	24
MA5*	450	-	0.11	-	0.13	-	680	-	2152
mean	227	51.2	0.18	0.30	0.07	1513	344	4785	1088
MA6	7.73	20.4	0.16	0.25	0.002	636	4.92	1750	14
MA6*	169	-	0.03	-	0.04	-	107	-	295
mean	88.3	20.4	0.09	0.25	0.02	636	56.1	1750	155
MA7	26.7	8.02	0.21	0.41	0.011	253	6.75	594	16
MA7*	194	-	0.04	-	0.08	-	49	-	115
mean	110	8.02	0.13	0.41	0.05	253	27.9	594	65
MA8	6.50	26.7	0.17	0.35	0.002	989	6.43	2632	17
MA8*	220	-	0.04	-	0.08	-	218	-	579
mean	113	26.7	0.11	0.35	0.04	989	112.	2632	298
MA9	7.60	111	0.84	2.09	0.016	3745	28.5	7126	54
MA9*	79.2	-	0.07	-	0.17	-	297	-	564
mean	43.	111	0.45	2.09	0.09	3745	163	7126	309

*Determined from SPM subsample for Hg analysis.

Appendix 4-D-5.

Instantaneous fluxes of water, SPM and metals imported and exported through Main Creek cross-section on flooding (+) and ebbing (-) tidal phases during March 2009 spring tide survey.

MA Spring	SPM (mg·s⁻¹)	Cd (µg·s⁻¹)	Hg (µg·s⁻¹)	Cu (µg·s⁻¹)	Zn (µg·s⁻¹)
Flood 1	4.19	0.06	0.04	13.2	22.9
Flood 2	62.5	0.28	0.21	107.6	175
Flood 3	614	0.71	0.27	801.1	2425
Flood 4	770	2.41	0.74	1089	2070
Sum	1450	3.5	1.3	2011	4693
Ebb 1	-676	-0.69	-0.15	-430	-1183
Ebb 2	-261	-0.31	-0.12	-66.2	-155
Ebb 3	-83.8	-0.08	-0.03	-82.9	-221
Ebb 4	-15	-0.16	-0.03	-56.3	-107
Sum	-1036	-1.24	-0.33	-635	-1666
Import	1450	3.5	1.3	2011	4693
Export	-1036	-1.2	-0.3	-635	-1666
Difference	414	2.23	1	1376	3027

Appendix 4-E Neck Creek Data

Appendix 4-E-1.

Neck Creek neap tidal survey mean calculations.

Sample ID	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Cd ug·L ^{-1*}	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Cu ug·L ^{-1*}	Zn ug·g ⁻¹	Zn ug·L ⁻¹	Zn ug·L ^{-1*}
NC1	37.5	13.2	0.49	602.5	22.6	8254	309	37.5	13.2	0.49
NC1A	73.2	2.2	0.16	110.4	8.08	2220	163	73.2	2.2	0.16
NC 1-1 mean ¹	91.3	7.7	0.7	357	32.53	5237	478	91.3	7.7	0.7
Mean ²	55.4	7.7	0.43	357	19.73	5237	290	55.4	7.7	0.43
NC2	32.5	28.9	0.94	855.8	27.8	23730	771	32.5	28.9	0.94
NC2A	23.1	8.9	0.21	330.3	7.62	8487	196	23.1	8.9	0.21
NC 2-2 mean ¹	23.3	18.9	0.44	593.1	13.8	16108	376	23.3	18.9	0.44
Mean ²	27.8	18.9	0.52	593.1	16.5	16108	447	27.8	18.9	0.52
NC3	28.8	9.5	0.27	336.6	9.7	33403	962	28.8	9.5	0.27
NC3A	32.7	10.2	0.33	308.0	10.1	8781	287	32.7	10.2	0.33
NC 3-3 mean ¹	25.2	9.9	0.25	322.3	8.11	21092	531	25.2	9.9	0.25
Mean ²	30.7	9.9	0.3	322.3	9.91	21092	648	30.7	9.9	0.3
NC4	9.6	23.9	0.23	180.0	1.73	22008	211	9.6	23.9	0.23
NC4A	4.2	9.1	0.04	332.0	1.41	9020	38	4.2	9.1	0.04
NC 4-4 mean ¹	8.3	16.5	0.14	256.0	2.13	15514	129	8.3	16.5	0.14
Mean ²	6.9	16.5	0.11	256.0	1.77	15514	107	6.9	16.5	0.11
NC5	0.7	262.6	0.19	3570.8	2.61	398151	291	0.7	262.6	0.19
NC5A	10.9	262.6	2.85	3570.8	38.81	398151	4328	10.9	262.6	2.85
NC 5-5 mean ¹	5.8	262.6	1.52	3570.8	20.71	398151	2309	5.8	262.6	1.52
Mean ²	5.8	-	-	-	-	-	-	5.8	-	-
NC6	12.8	12.4	0.16	153.3	1.96	4827	62	12.8	12.4	0.16
NC6A	11.8	270.8	3.2	1700.8	20.11	324403	3836	11.8	270.8	3.2
NC 6-6 mean ¹	6.5	142	0.92	927.1	6.03	164615	1071	6.5	142	0.92
Mean ²	12.3	142	1.74	927.1	11.41	164615	2027	12.3	142	1.74
NC7	9.7	26.0	0.25	406.6	3.95	12617	122	9.7	26.0	0.25
NC7A	2.1	6.3	0.01	112.9	0.23	2181	5	2.1	6.3	0.01
NC 7-7 mean ¹	14.6	16.1	0.24	259.7	3.78	7399	108	14.6	16.1	0.24
Mean ²	5.9	16.1	0.1	259.7	1.53	7399	44	5.9	16.1	0.1
NC8	7.1	41.4	0.29	846.6	5.98	21945	155	7.1	41.4	0.29
NC8A	11.1	27.2	0.3	372.4	4.14	25814	287	11.1	27.2	0.3
NC 8-8 mean ¹	9.3	34.3	0.32	609.5	5.66	23879	222	9.3	34.3	0.32
Mean ²	9.1	34.3	0.31	609.5	5.54	23879	217	9.1	34.3	0.31
NC9	35.1	15.4	0.54	395	13.8	7028	246	35.1	15.4	0.54
NC9A	14.6	16.0	0.23	322	4.69	7481	109	14.6	16.0	0.23
NC 9-9 mean ¹	28.8	15.7	0.45	358	10.3	7254	209	28.8	15.7	0.45

* indicates filter SPM concentration determined from Hg subsample

^A indicates duplicate water sample¹calculated from the mean concentrations of SPM (n=4) and SPM metals (n=6) yielded from analysis of duplicate water samples, each split for duplicate SPM analysis and triplicate Cd, Cu, and Zn determination.²calculated from the mean concentrations of SPM (n=2) and SPM metals (n=6) yielded from analysis of duplicate water samples (replicates analyzed in triplicate for Cd, Cu, and Zn determination).

Appendix 4-E-2.

Instantaneous fluxes of water, SPM and metals imported and exported through Neck Creek cross-section on flooding (+) and ebbing (-) tidal phases during November 2008 neap tide survey.

NC Neap	SPM (mg·s⁻¹)	Cd (µg·s⁻¹)	Cu (µg·s⁻¹)	Zn (µg·s⁻¹)
Flood 1	0.21	0	0.12	3.37
Flood 2	6.84	0.07	2.2	144
Flood 3	13.3	0.22	3.39	206
Flood 4	8.57	2.25	30.6	3412
Sum	28.9	2.54	36.3	3766
Ebb 1	-0.33	-0.05	-0.31	-55
Ebb 2	-16	-0.26	-4.15	-118
Ebb 3	-3.99	-0.14	-2.43	-95
Ebb 4	-2.65	-0.04	-0.95	-19
Sum	-22.97	-0.49	-7.84	-288
Import	28.9	2.54	36.3	3766
Export	-23	-0.49	-7.84	-288
Difference	5.9	2.05	28.46	3478

Appendix 4-E-3.

Summary Neck Creek Spring tidal flow summary March 2009.

Sample ID	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
NC1	12.20	17.35	0.21	0.40	0.08	645.08	7.87	2726.64	33.27
NC1*	204.80	17.35	3.55	-	0.00	-	132.11	-	6.81
mean	108.50	17.35	1.88	0.40	0.04	645.08	69.99	2726.64	20.04
NC2	20.20	7.55	0.15	0.48	0.07	278.22	5.62	1467.95	29.65
NC2*	143.20	7.55	1.08	-	0.01	-	39.84	-	4.25
mean	81.70	7.55	0.62	0.48	0.04	278.22	22.73	1467.95	16.95
NC3	5.30	6.45	0.03	0.15	0.02	177.52	0.94	1050.47	5.57
NC3*	110.60	6.45	0.71	-	0.00	-	19.63	--	0.62
mean	57.95	6.45	0.37	0.15	0.01	177.52	10.29	1050.47	3.09
NC4	3.40	3.68	0.01	0.15	0.01	218.38	0.74	1302.94	4.43
NC4*	88.40	3.68	0.33	-	0.00	-	19.31	-	0.39
mean	45.90	3.68	0.17	0.15	0.01	218.38	10.02	1302.94	2.41
NC5	2.40	14.24	0.03	0.40	0.03	687.85	1.65	2725.00	6.54
NC5*	70.20	14.24	1.00	-	0.00	-	48.29	-	0.46
mean	36.30	14.24	0.52	0.40	0.01	687.85	24.97	2725.00	3.50
NC6	6.00	13.47	0.08	0.17	0.03	413.06	2.48	1550.97	9.31
NC6*	181.40	13.47	2.44	-	0.00	-	74.93	-	1.69
mean	93.70	13.47	1.26	0.17	0.02	413.06	38.70	1550.97	5.50
NC7	2.10	54.37	0.11	0.40	0.04	1775.40	3.73	5234.92	10.99
NC7*	112.80	54.37	6.13	-	0.00	-	200.26	-	1.24
mean	57.45	54.37	3.12	0.40	0.02	1775.40	102.00	5234.92	6.12
NC8	5.63	28.42	0.16	0.41	0.06	867.08	4.88	3018.65	17.00
NC8*	142.70	28.42	4.06	-	0.00	-	123.73	-	2.43
mean	74.17	28.42	2.11	0.41	0.03	867.08	64.31	3018.65	9.71
NC9	18.40	7.52	0.14	0.73	0.10	382.88	7.05	1459.87	26.86
NC9*	140.80	7.52	1.06	-	0.01	-	53.91	-	3.78
mean	79.60	7.52	0.60	0.73	0.06	382.88	30.48	1459.87	15.32

* indicates filter SPM concentration determined from Hg subsample.

Appendix 4-E-4.

Instantaneous fluxes of water, SPM and metals imported and exported through Neck Creek cross-section on flooding (+) and ebbing (-) tidal phases during March 2009 spring tide survey.

NC Spring	SPM (mg·s⁻¹)	Cd (μg·s⁻¹)	Hg (μg·s⁻¹)	Cu (μg·s⁻¹)	Zn (μg·s⁻¹)
Flood 1	0.9	0.01	0	0.25	0.19
Flood 2	84.1	0.54	0.01	14.9	4.48
Flood 3	11.5	0.04	0	2.51	0.6
Flood 4	4.15	0.06	0	2.86	0.4
Sum	100.65	0.65	0.01	20.52	5.67
Ebb 1	-34.2	-1.85	-0.01	-60.6	-3.64
Ebb 2	-15.9	-0.45	-0.01	-13.8	-2.09
Ebb 3	-4.32	-0.03	0	-1.65	-0.83
Ebb 4	-1.65	-0.03	0	-0.97	-0.22
Sum	-56.07	-2.36	-0.02	-77.02	-6.78
Import	100.7	0.65	0.01	20.5	5.67
Export	-56.1	-2.36	-0.02	-77	-6.78
Difference	44.6	-1.71	-0.01	-56.5	-1.11

Appendix 4-G Lemon Creek Data

Appendix 4-F-1.**Lemon Creek intermediate tidal flow summary April 2009.**

Sample ID	SPM mg·L ⁻¹	Cd ug·g ⁻¹	Cd ug·L ⁻¹	Hg ug·g ⁻¹	Hg ug·L ⁻¹	Cu ug·g ⁻¹	Cu ug·L ⁻¹	Zn ug·g ⁻¹	Zn ug·L ⁻¹
LC1	272	0.27	0.07	0.13	0.04	12.2	3.31	38.5	10.49
LC1*	171	0.27	0.05	0.13	0.02	12.2	2.08	38.5	6.59
mean	222	0.27	0.06	0.13	0.03	12.2	2.70	38.5	8.54
LC2	129	0.69	0.09	2.06	0.27	19.88	2.57	74.6	9.66
LC2*	15	0.69	0.01	2.06	0.03	19.88	0.29	74.6	1.10
mean	72	0.69	0.05	2.06	0.15	19.88	1.43	74.6	5.38
LC3	236	0.50	0.12	0.10	0.02	31.72	7.49	77.7	18.34
LC3*	284	0.50	0.14	0.10	0.03	31.72	9.00	77.7	22.03
mean	260	0.50	0.13	0.10	0.03	31.72	8.24	77.7	20.18
LC4	286	0.48	0.14	0.11	0.03	18.76	5.38	58.5	16.77
LC4*	301	0.48	0.14	0.11	0.03	18.76	5.65	58.5	17.63
mean	294	0.48	0.14	0.11	0.03	18.76	5.51	58.5	17.20
LC5	147	1.07	0.16	0.38	0.06	36.46	5.36	106.2	15.62
LC5*	127	1.07	0.14	0.38	0.05	36.46	4.64	106.2	13.51
mean	137	1.07	0.15	0.38	0.05	36.46	5.00	106.2	14.56
LC6	49	3.19	0.16	0.81	0.04	260.74	12.82	769.5	37.84
LC6*	190	3.19	0.60	0.81	0.15	260.74	49.44	769.5	145.89
mean	119	3.19	0.38	0.81	0.10	260.74	31.13	769.5	91.87
LC7	323	0.23	0.08	0.06	0.02	12.17	3.93	37.3	12.03
LC7*	201	0.23	0.05	0.06	0.01	12.17	2.44	37.3	7.48
mean	262	0.23	0.06	0.06	0.02	12.17	3.18	37.3	9.75
LC8	190	0.29	0.05	0.04	0.01	30.16	5.73	55.8	10.59
LC8*	315	0.29	0.09	0.04	0.01	30.16	9.49	55.8	17.54
mean	252	0.29	0.07	0.04	0.01	30.16	7.61	55.8	14.07
LC9	365	0.23	0.09	0.06	0.02	16.90	6.18	46.6	17.03
LC9*	287	0.23	0.07	0.06	0.02	16.90	4.86	46.6	13.39
mean	326	0.23	0.08	0.06	0.02	16.90	5.52	46.6	15.21

*Determined from SPM subsample for Hg analysis

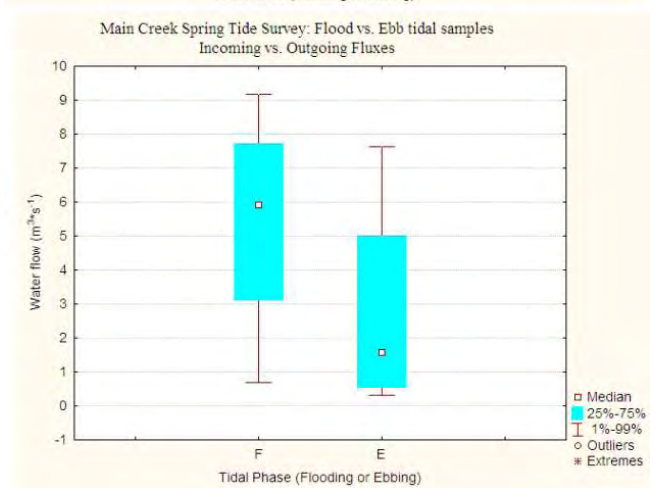
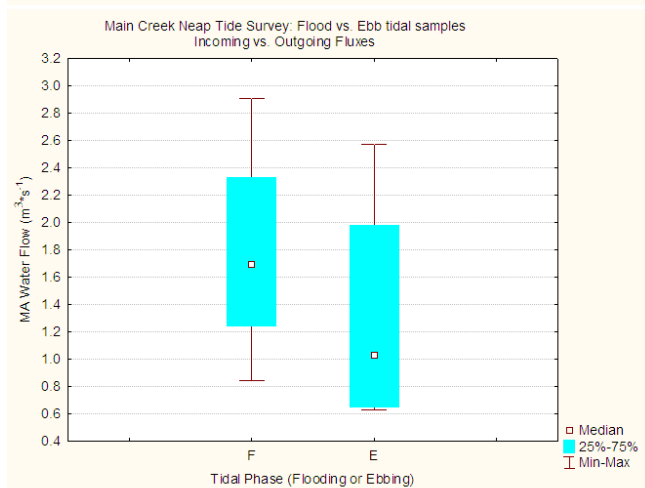
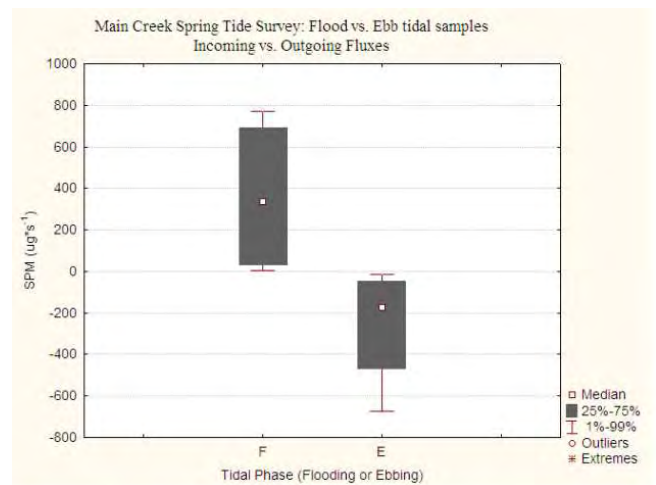
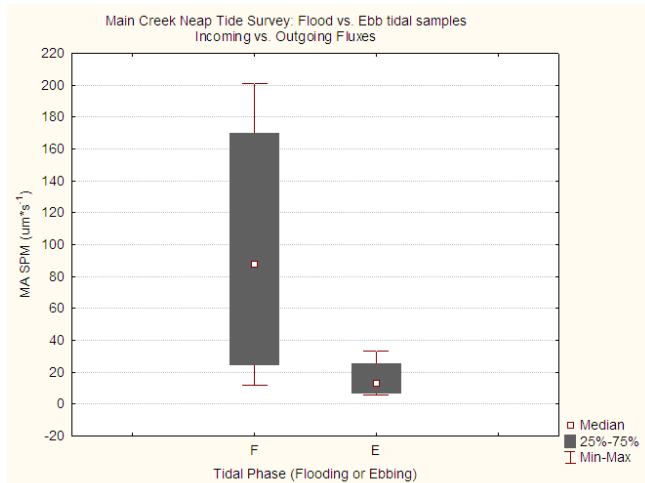
Appendix 4-F-2.

Instantaneous fluxes of water, SPM and metals imported and exported through Lemon Creek cross-section on flooding (+) and ebbing (-) tidal phases during April 2009 intermediate tide survey.

LC Intermediate survey	SPM (mg·s⁻¹)	Cd (µg·s⁻¹)	Hg (µg·s⁻¹)	Cu (µg·s⁻¹)	Zn (µg·s⁻¹)
Flood 1	569	0.62	0.21	20.7	60.4
Flood 2	731	2.33	0.61	191	563
Flood 3	2373	0.54	0.18	28.8	88.4
Flood 4	1695	0.47	0.07	51.1	94.6
Sum	5368	3.96	1.07	291.6	806.4
Ebb 1	-914	-0.25	-0.12	-11.1	-35.2
Ebb 2	-479	-0.33	-1	-9.49	-35.7
Ebb 3	-817	-0.41	-0.09	-25.91	-63.5
Ebb 4	-952	-0.23	-0.06	-16.1	-44.4
Sum	-3162	-1.22	-1.27	-62.64	-178.8
Import	5368	3.96	1.07	291.6	806.4
Export	-3162	-1.22	-1.27	-62.6	-178.8
Difference	2206	2.74	-0.20	229	628

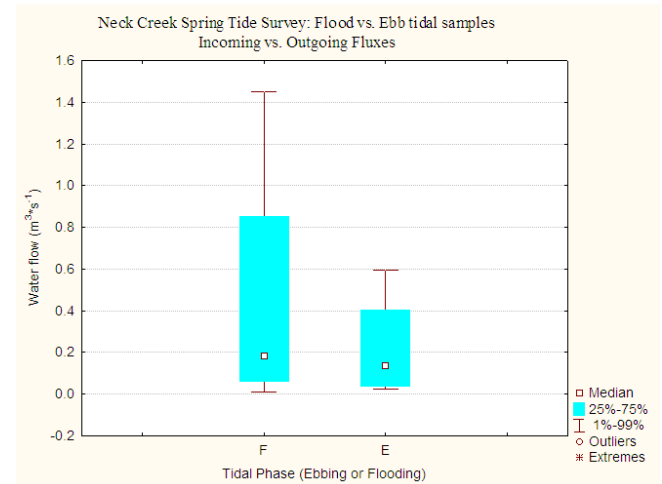
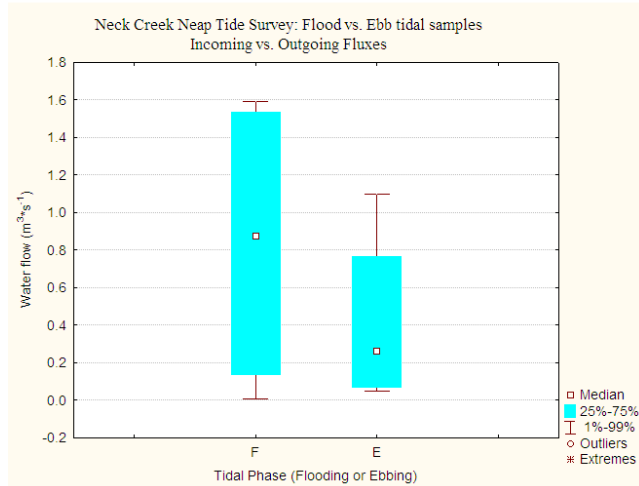
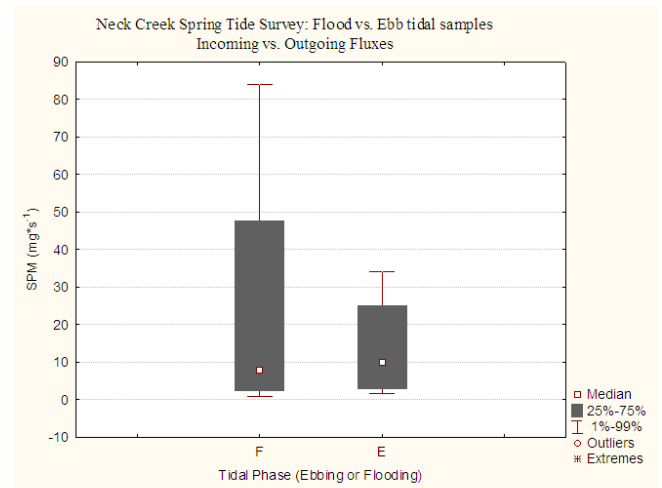
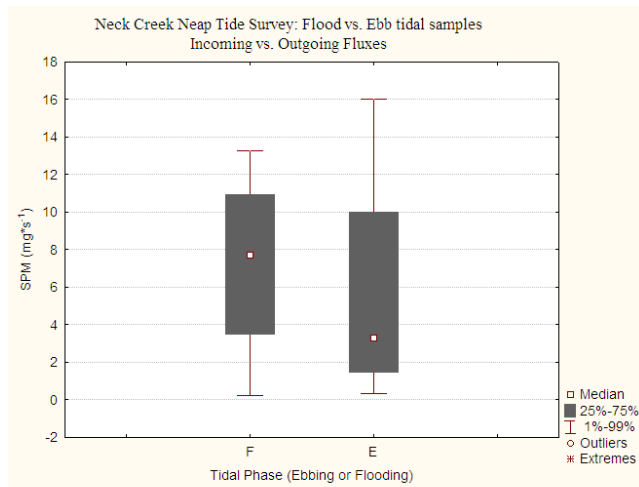
Appendix 4-G: Site-specific tidal survey box plots.

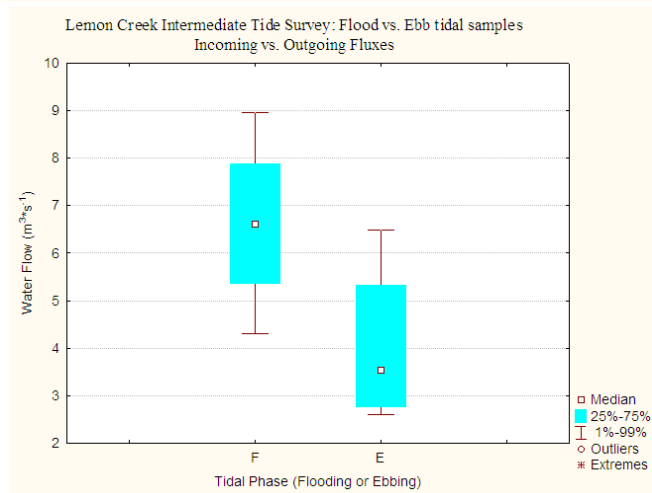
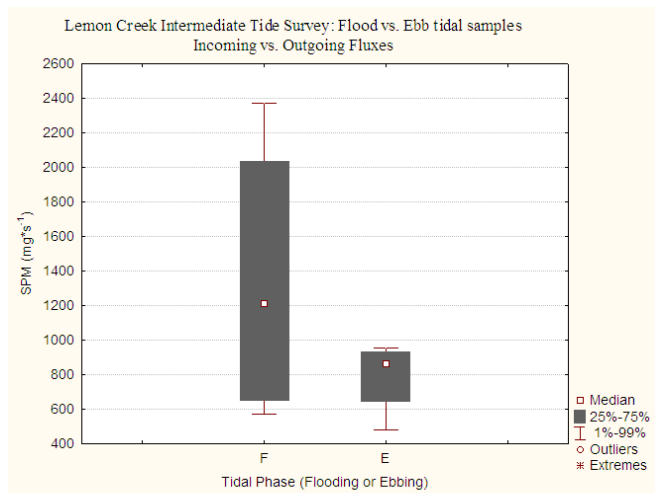
Appendix 4-G-1. Main Creek incoming vs. outgoing fluxes of SPM and water flows.



Appendix 4-G-2.

Neck Creek incoming vs. outgoing fluxes of SPM and water flows.

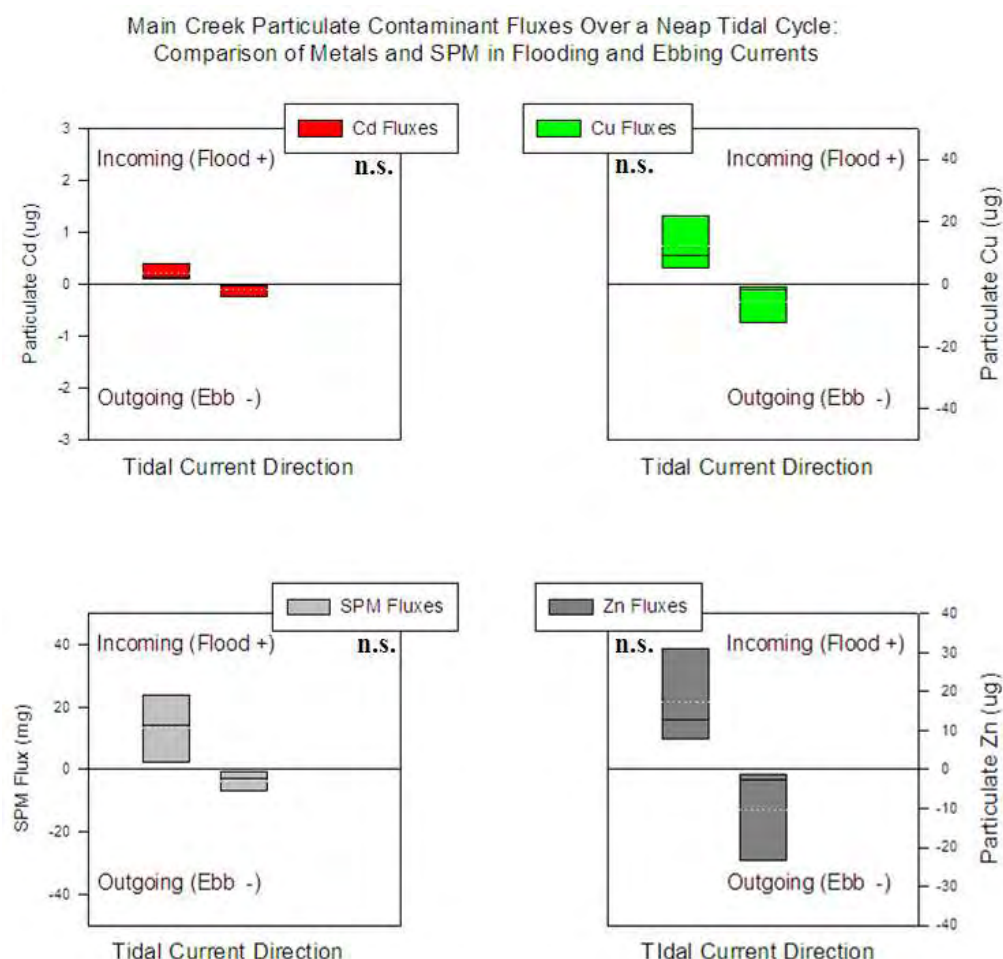


Appendix 4-G-3.**Lemon Creek incoming vs. outgoing fluxes of SPM and water flows.**

Appendix 4-H. Comparison of metals and SPM within the water column of Main Creek during flooding and ebbing currents.

Appendix 4-H-1.

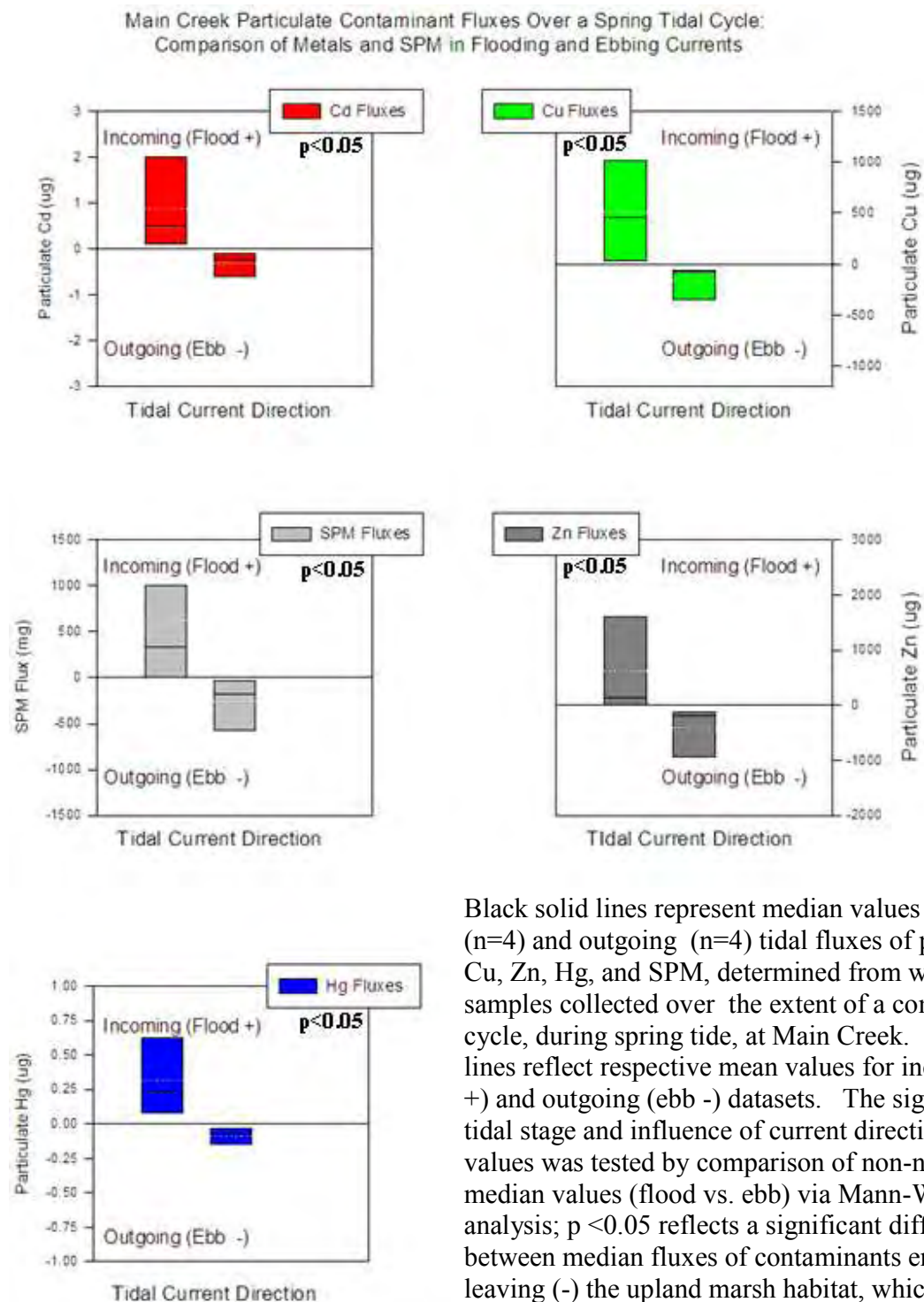
Main Creek incoming vs. outgoing fluxes over a neap tidal cycle.



Black solid lines represent median values of incoming (n=4) and outgoing (n=4) tidal fluxes of particulate Cd, Cu, Zn, and SPM determined from water column samples collected over the extent of a complete tidal cycle, during neap tide, at Main Creek. Dotted lines reflect respective mean values for incoming (flood) and outgoing (ebb) datasets. The significance of tidal stage and influence of current direction on fluxes values was tested by comparison of non-negative median values (flood vs. ebb) via Mann-Whitney U analysis; n.s. denotes no significant difference between median fluxes of contaminants entering (+) or leaving (-) the upland marsh habitat ($p > 0.05$), which was shown by all metals in the neap tidal survey dataset.

Appendix 4-H-2.

Main Creek incoming vs. outgoing fluxes over a spring tidal cycle.



Black solid lines represent median values of incoming ($n=4$) and outgoing ($n=4$) tidal fluxes of particulate Cd, Cu, Zn, Hg, and SPM, determined from water column samples collected over the extent of a complete tidal cycle, during spring tide, at Main Creek. White dotted lines reflect respective mean values for incoming (flood +) and outgoing (ebb -) datasets. The significance of tidal stage and influence of current direction on fluxes values was tested by comparison of non-negative median values (flood vs. ebb) via Mann-Whitney U analysis; $p < 0.05$ reflects a significant difference between median fluxes of contaminants entering (+) or leaving (-) the upland marsh habitat, which was shown by all constituents in the spring tidal survey dataset.

Chapter 5

Large Scale Comparative Assessment of Marsh Sediment Quality over Time: Spatial and Temporal Extent of Metal Contamination and Potential for Toxicity in Arthur Kill versus Raritan Bay Watersheds

CHAPTER SUMMARY

Main Creek, Neck Creek and Lemon Creek temporal and spatial metal distributions were compared with literature-based reference values to describe sediment quality in terms of magnitude of marsh sediment contamination and benthic impacts, including potential toxicity and habitat/community degradation. Theoretical and empirical assessment methods, based on the background sediment and toxicity screening approaches, were used to rank sites in terms of contamination magnitude (pollution load) and potential for toxicity (effect-based benchmarks, toxicity impacts).

The two-fold approach provided multiple lines of evidence in order to establish a comprehensive framework to comparatively assess geographic variability between sites in terms of sediment quality and associated biological effects. The combination of sediment evaluation techniques (series of theoretical and empirical methodologies) applied to analyze Main Creek, Neck Creek and Lemon Creek geochemical datasets collected over the past decade, established a temporal context of marsh-specific sediment pollution. This study design provided the necessary temporal and spatial context to assess past and present conditions (i.e. contamination levels and potential impacts) within marsh-creek habitats along a longitudinal gradient of the study area; and thereby characterize the current status of sediment quality and possible ecological implications within different geographic reaches of the NY/NJ Harbor Estuary. Specific

objectives were to discern intra-marsh differences and characterize large-scale spatial trends with respect to occurrence, extent, and toxic potential of metal contaminated sediments, over time.

The intent of this study was to integrate and further examine previous and acquired datasets from surficial sediment studies conducted over the past decade in order to establish a comprehensive temporal and spatial context necessary to provide a suitable and effective framework to assess sediment quality.

INTRODUCTION

In addition to providing many essential ecosystem services, including biological habitats supporting high species diversity, buffers for natural flood/storm control and groundwater recharge areas salt marshes are further recognized for their ecological value as sediment traps and filters for toxic contaminants (Hung, et al., 2006).

Particle-reactive properties cause metals to adsorb to sediments and accordingly, the majority of metals introduced into receiving waterways become associated, and subsequently transported, with sediments (Sanudo-Wilhelmy, et al., 1999). The ability of sediments to incorporate and accumulate particle-reactive contaminants from the water column is problematic considering that the most distinguishing feature of metals from other toxic pollutants is their inability to biodegrade, which can cause deleterious ecosystem effects (Rozan, et al., 1999; Sanudo-Wilhelmy, et al., 1999; Harikumar, et al., 2009). Resident biota may feed directly upon these suspended particles, or indirectly once they become part of the bed load. Associated contaminants would then be available for possible bioaccumulation and trophic transfer (Luoma, 1989; Hornberger, et al., 1999; Seebaugh, et al., 2005; Audry, et al., 2006).

Although contaminated sediments can settle and become buried, sediment bound metals can become resuspended in the water column via scouring, dredging activities, bioturbation, increased water velocities, wave action and/or currents. Subsequently, they re-enter the system. This redistribution is an important factor in determining the mobility and the toxicity of trace metals within estuaries (Audry, et al., 2006). Once sediment is remobilized, complexation processes and particle chemistry partition and cycle metals between dissolved and particulate phases and thus influence metal fate and bioavailability (Censi, et al., 2006). Therefore, favorable physic-chemical conditions can release [metals can repartition between the particulate and dissolved phases] and supply sediment-bound metals to surrounding ecosystems (Sanudo-Wilhelmy, et al., 1999; Rozan, et al. 1999; Harikumar, et al., 2009).

Collecting water quality data can help provide information regarding the environmental condition of an ecosystem (Rozan, et al., 1999; Sanudo-Wilhelmy, et al., 1999). However, even if water quality monitoring results demonstrate attainment concerning specific measures of health, this single approach may fail to account for poor sediment quality adversely affecting exposed biota (Gurrieri, et al., 1998). Alternatively, assessments of sediments via surficial distributions and core profiles from either mudflats or salt marsh areas can provide better insight into the extent of site-specific metal contamination and yield information on the environmental quality of an ecosystem (Weis, et al., 2005; Strong, et al., 2008).

Prior trace metal studies have determined that marshes buffering the western and southern Staten Island shoreline demonstrate large-scale geographic variability regarding the concentration and distribution of pollutants (Ward, 2001; Nichols, 2004). Vertical and lateral sediment profiles constructed from the three marsh-creek systems depict demonstrable site-specific spatial and temporal metal contamination. In general, this research component will

further examine the extent of site-specific anthropogenic metal contamination (Cd, Hg, Cu, and Zn) and determine the potential sediment toxicity of Main Creek, Neck Creek and Lemon Creek sediments to characterize the quality of sediments in marsh-creek habitats. Accordingly, this study will utilize site-specific acquired (small and large-scale) metal datasets derived from analysis of Main Creek, Neck Creek and Lemon Creek surface and core sediments to consider site-specific biological effects and to facilitate understanding of the environmental integrity of the region.

Study goals included a comprehensive assessment of sediment quality on different scales to identify localized environmental impacts and possible regional ecological implications. Primary objectives were to evaluate the site-specific temporal and spatial metal distributions, with respect to baseline/background levels and toxicity indices, and to describe magnitudes of sediment contamination and potential toxicity throughout the study area over time. This twofold approach established a suitable framework to characterize the quality of Main Creek, Neck Creek and Lemon Creek sediments in order to consider how the magnitude of site-specific anthropogenic metals may illicit toxic impacts in benthic species and affect critical ecological habitats within these marsh-creek systems.

METHODS

In general, this research component will further examine sediment chemistry datasets compiled over the past decade from Staten Island marsh sediments to facilitate a better understanding of the environmental integrity of the region. This study primarily focused on acquired surficial datasets, which provided a comprehensive spatial and temporal context to

characterize sediment quality and habitat impacts based on based on multiple metal contamination and toxicity indices.

To fulfill the study objectives, metal concentrations in core and surface sediments (Appendix A; Chapter 2 and 3, respectively) were evaluated with respect to baseline data (local and national), regional and global background values, sediment benchmarks and toxicity indices to establish a comprehensive framework to further characterize the temporal and spatial marsh contamination identified throughout the study area. Collectively these measures will consider how anthropogenic metal pollution affect Main Creek, Neck Creek and Lemon Creek marsh habitats by describing each site in terms of sediment quality and potential toxicity implications that may result from the site-specific level of contamination.

Study sites

In general, the overall geographic context was described as the center the New York Bight habitat study area, otherwise defined as the New York - New Jersey Harbor Estuary Core Area (NY/NJ HE). Specifically, the study area focused on two sub-regions of the New York Bight watershed, the Arthur Kill and Raritan Bay. Main Creek (MA) and Neck Creek (NC), which are located along the western shore of Staten Island, are within adjacent sub watersheds of the Arthur Kill; whereas Lemon Creek (LC), a Raritan Bay sub watershed, is situated along the southern shore.

The Fresh Kills Landfill Complex and William T. Davis Wildlife Refuge border Main Creek. Main Creek upland marsh and creek habitats are hydrologically-connected to the Arthur Kill Proper via Fresh Kills Creek. Main Creek and Neck Creek are parallel tidal wetland systems that extend from the Arthur Kill. Neck Creek is approximately 1.5 miles north of Main

Creek and extends directly from the main channel of the Arthur Kill towards upland marsh habitat, covering 60-acres of land (OASIS NYC, 2011). In contrast, Lemon Creek is external to the Arthur Kill Complex reaches in a northern direction from the Raritan Bay (Ward, 2002; Nichols, 2004).

Regardless of geography, Main Creek, Neck Creek and Lemon Creek are tidal wetland systems that provide unique creek and upland marsh habitats and various essential ecosystem services, which are critical for sustenance and survival of many important benthic and threatened species. All study sites have been recognized for habitats that have been described as significant with respect to the NY/NJ Harbor Estuary Core Complex (USFWS, 1997) (Fig. 2). Each study site represents a diversity of wetland habitat types, primarily tidal and non-tidal emergent salt, brackish, and fresh marshes, mudflats, ponds and creeks, dominated by cord grasses (*Spartina alterniflora* and *S. patens*), spike grass (*Distichlis spicata*), marsh elder (*Iva frutescens*), common reed and cattail (*Typha latifolia*).

The Arthur Kill complex consists of four major habitat categories: colonial wading bird breeding sites or heronries; water bird foraging areas; freshwater marshes and wooded swamps; and upland forests. In addition to three island heronies (Shooters Island, Prall's Island and Isle of Meadows), Neck Creek Marsh, Fresh Kills, Main and Richmond Creeks are considered among the main foraging areas along the western shore of Staten Island. Lemon Creek flows through Lemon Creek Park, which has been regarded as one of the largest and most pristine salt marshes in Staten Island; the marsh-creek system provides spawning and nursery grounds for many fish and shellfish species, and serves as a habitat for many migratory birds, including one of the only purple martin bird colonies in New York City (NYC Dept. Parks, 2007).

Furthermore, the NY/NJ Harbor Estuary Program (HEP) Habitat Workgroup, which has developed watershed-based priorities for acquisition, protection and restoration, and the United States Army Corps of Engineers, have identified Neck Creek as a tidal wetland for priority habitat acquisition and preservation (NY/NJ HEP Habitat Work Group, 2001; USACE, 2010). Neck Creek, classified as “AK 13” or Comprehensive Restoration Plan (CRP) 17, is highly prioritized due to its importance and ecological value to the NY/NJ Harbor Estuary.

Accordingly, initiatives aim to save and protect the remaining habitats surrounding the area (NY/NJ HEP Habitat Work Group, 2001; Suszkowski, et al., 2006). Lemon Creek is also included as a NY/NJ Harbor Estuary Program (HEP) restoration site (RB1) and a Comprehensive Restoration Plan site (CRP 109). The site, which is earmarked for a possible anadromous fish passage ladder project, covers 10 acres of land that is currently owned by New York City Department of Parks and Recreation (NYCDPR) and National Park Service (NPS) (OASIS NYC, 2011).

Monitoring activities consisted of collection of surface sediments at locations along longitudinal gradients. Surface sediment samples were analyzed for metal concentrations (Cd, Cu, Zn, and Hg) along transects upstream and downstream of where sediment cores were recovered from the three Staten Island marsh sites: Main Creek (40°35'53.13"N; 74°10'32.62"W), Neck Creek (40°35'51.24"N; 74°11'19.56"W), and Lemon Creek (40°31'8.94"N; 74°12'10.98"W) (Fig. 2).(see Chapter 3 for sediment processing and metal chemistry analysis).

The intent of this study was to integrate and further examine previous and acquired datasets from surficial sediment studies conducted over the past decade, in order to provide a

comprehensive temporal and spatial context, which was necessary for establishing an effective framework to assess sediment quality.

Sediment Quality Evaluation/Contamination Assessment

Newly acquired surface sediment (0-2 cm) datasets (2007, 2009), along with surficial data (0-2cm) collected in 2001, (which established “baseline” conditions for the study sites targeted in this dissertation) were analyzed via several “sediment quality guideline” (SQG) methodologies. SQGs represent derived tables of numeric values, which can be classified as either theoretical or empirical. This study utilized both theoretical and empirical sediment evaluation methods to assess sediment quality throughout the study area, discern the spatial extent/occurrence and magnitude of metal-specific contamination, and subsequently rank sites accordingly. In general, background metal concentrations and biological effects-based toxicity indices were included in the two-fold descriptive approach of this research component. This aimed to characterize sediment quality across the study area in terms of the extent of metal contamination and potential for toxic impacts, in order to discern if large-scale trends or variability among sites reflect or are indicative of an impact gradient. (Ward, 2002; Nichols, 2004; Bopp, et al., 2006). Metal analysis of sediments collected from marsh surfaces (2001, 2007, 2009) and at depth (2001 and 2007), provided concentrations for a suite of elements. However, this study focused on a subset of metals (Cd, Hg, Cu, and Zn) which have been identified as contaminants of concern to the NY/NJ Harbor Estuary (NY/NJ HE) because of their potential toxicity (Kennish, 1992; NY/NJ HEP, 1996; Church, et al., 1998).

Evaluation of Cd, Hg, Cu, and Zn detected within transect samples (2009) and previous surface sediments (2001 and 2007), characterized a range of values to assess the extent of site-specific surficial pollution. This approach provided a context to describe sediment quality and

toxicity that accounts for variations attributable to temporal and spatial differences (i.e. different sampling events, locations, and time), and places them into perspective. An aggregate of reference values and sediment quality values were used to further examine the anthropogenic signature (previously identified) throughout the study area to consider the extent that localized or endemic human-induced impacts affect sediment quality and toxicity and subsequently compromise the ecological integrity of marsh habitats. Comparison of sediment chemistry datasets with multiple indices provided the most suitable means to consider possible ecological implications in marsh habitats that may result from metal contamination and sediment toxicity.

Theoretical Sediment Evaluation Methodology

Acquired datasets were evaluated in terms of natural background metal concentrations to establish a context in which to assess the degree of contamination exhibited by marsh cores and surface sediments (Schropp, et al., 1988; Hwang, et al., 2006). Given that background concentrations for the immediate study area are not available, literature-based regional (Hudson River sediment) and global (mean shale) metal concentrations were used as proxies. To assess the extent to which the environmental integrity/health of marsh habitats across the study area has declined due to anthropogenic metal contamination (legacy inputs and present-day loadings), enrichment and anthropogenic contamination indices, including Enrichment Factor (EF), Contamination Factor (CF) and Contamination Degree (CD), were determined for Main Creek, Neck Creek and Lemon Creek.

Prior chapters calculated the sediment enrichment factor (EF) of each element studied based on comparison with regional background values derived from uncontaminated sediments previously collected within the vicinity of the study area (O'Reilly Wiese 1995). The literature-based values used to represent local background levels are as follows: $0.11\mu\text{g Cd}\cdot\text{g}^{-1}$, $0.18\mu\text{g}$

Hg·g⁻¹, 14 µg Cu·g⁻¹, and 81µg Zn·g⁻¹ (Hirschberg et al.1996, Bowen et al. 1979). An enrichment factor (EF) was determined for each metal via computation of the ratio of the reported concentration with respect to the element's regional background concentration (Alexander, et al., 1993; Valette-Silver, 1993; Hornberger, et al., 1999; Strong, et al., 2008).

The EF is expressed below as:

$$EF = C_o / C_r$$

Equation 1

where:

C_o = metal concentration observed in sediment sample

C_r = regional background metal concentration (Hirschberg et al.1996, Bowen et al. 1979).

With an understanding that using regional baseline values as a proxy for natural background concentrations may not absolutely assess data with respect to unpolluted sediments, world shale average trace metal concentrations served as another appropriate set of reference values in which to assess sediment quality. Estimates of preindustrial metal concentrations based upon average world shale values are similar for Hg (0.16 µg Hg·g⁻¹), but notably higher than Hudson River background levels for Cd (0.30 µg Cd·g⁻¹), Cu (45 µg Cu·g⁻¹), and Zn (95µg Zn·g⁻¹) (Wedepohl, et al., 1971; Tomlinson, et al., 1980; Ray, et al., 2006). Accordingly, background enrichment indices, including contamination factor (CF) and contamination degree (CD) supplemented EF values analyzed in prior research components, in order to characterize Cd, Hg, Cu, and Zn contamination within Main Creek, Neck Creek and Lemon Creek (Hakanson, et al., 1980).

The contamination factor (CF) is defined as the metal-specific ratio of observed mean contents in surface and core sediments and respective mean shale values (Eq. 2a), whereas the degree of contamination (CD) is described as the collective sum of all metal-specific contamination factors (Eq. 2b) ((Hakanson, et al., 1980; Angulo, et al., 1996; Gibbs, et al., 1997; Mooraki, et al., 2009):

$$CF = C_{0-1}^i / C_n^i \quad \text{Equation 2a}$$

$$CD = \sum_{i=1}^7 C_f^i \quad \text{Equation 2b}$$

where:

C_{0-1}^i is the mean concentration of the metal measured in the sediment sample

C_n^i is the metal-specific natural background concentration (pre-industrial) as per global mean shale reference values.

Although ratios of detected versus background metal concentrations provide a common means to depict sediment enrichment, no universal ranking schema classifies the extent of metal pollution based upon calculated EF or CF values (Huntley, et al., 1995; Kabir et al. 2009). However, proposed classes and associated sediment quality descriptions (metal-specific risk level of contaminants and overall anthropogenic pollution degree) for ranges of respective CF and CD values displayed in table 4 were adopted from Mooraki et al. 2009 (Hakanson, 1980; Asku, et al., 1997; Nasr, et al., 2006; Dehgan ,et al., 2008; Mooraki, et al., 2009).

Metal-specific CF values were classified accordingly to indicate low to very high risk levels respectively: $CF < 1$ was considered a low contamination factor; $1 < CF < 3$ represented a moderate contamination factor, $3 < CF < 6$ a considerable contamination factor, and $CF \geq 6$

represented a very high contamination factor (Hakanson, 1980; Asku, et al., 1997; Nasr, et al., 2006; Dehgan, et al., 2008; Mooraki, et al., 2009). Likewise, CD values, which measured the collective impact of all metals studied, were aligned with one of four categories representative of successively greater degrees of contamination: low ($CD < 7$), moderate ($7 < CD < 14$), considerable ($14 < CD < 28$), and very high ($CD \geq 28$), which described, in relative terms as indicative of minimal to serious anthropogenic pollution (Hakanson, 1980; Asku, et al., 1997; Nasr, et al., 2006; Dehgan, et al., 2008; Mooraki, et al., 2009).

Pollution Load Index (PLI) - Pollution Load Assessment

The CFs calculated for each metal were used to determine the Pollution Load Index (PLI) using the equation below (Ray, et al., 2006; Tomlinson, et al., 1980) (Eq.3).

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)} \quad \text{Equation 3}$$

Where:

CF = contamination factor

n = number of metals

The PLI method [(product of n number of CF values)^{1/n}] served as a measure to assess the extent of sediment pollution among and within marsh study sites. Accordingly, the PLI represents the overall pollution load at each sampling location; generally, a PLI value of > 1 is indicative of sediment contamination whereas < 1 does not (Satyanarayana, et al., 1994). The extent to which sediment samples varied from these reference values served to comparatively assess site-specific temporal and spatial metal contamination and characterize variability on both large and small spatial scales (Wedepohl, et al., 1971; Tomlinson, et al., 1980; Gurrierri, et al., 1998; Ray, et al., 2006;).

Empirical Sediment Evaluation/Toxicity Indices

To further assess the sediment quality of habitats throughout the study area and examine the toxic potency of contaminated Main Creek, Neck Creek and Lemon Creek sediments, average surficial metal concentrations were compared to reference guidelines used to benchmark toxicity (Long, et al., 1990; NOAA, Bonnevie, et al., 1993;). This study focused on the surficial layer (0-2 cm) because it is often considered the most biologically relevant, since most benthic organisms tend to assemble proximal to the surface (Councell and Bell, 1979; Barrett, et al., 2007).

An initial ecotoxicological sense of metal contamination in sediments was determined using sediment quality guidelines developed for marine and estuarine ecosystems (Bakan et al. 2007). Mean surficial contents determined from Main Creek, Neck Creek and Lemon Creek samples were compared with sediment quality values derived from NOAA's toxicity screening gradient, which categorizes metal-specific concentrations based on likelihood of bioeffects to benthic species, i.e. ERL, ERM, TEL, PEL (Long, et al., 1990; Buchman, 1999; Spencer, et al., 2002; Mil-Homens, et al., 2006; Praveena et al. 2008). "Effects range low" (ERL) and "effects range median"(ERM), which denote concentrations at which negative biological effects were found to occur in 10% and 50% of studies respectively, are often used to characterize the potential toxicity of polluted estuarine sediments (Long, et al., 1990). An alternate or supplemental series of ecological hazard indices includes threshold effects level (TEL), the maximum concentration at which no effects are observed, and probable effects level (PEL) the lower limit of the concentration range at which adverse effects are always observed (Buchman, 1999).

ERL and TEL are concentrations below which adverse effects upon benthic/sediment dwelling fauna would infrequently be expected, whereas, ERM and PEL represent chemical concentration above which adverse effects are likely to occur (Long, et al., 1995; Barrett, et al., 2000; NOAA 2001). These measures will characterize Main Creek, Neck Creek and Lemon Creek in terms of sediment quality and Cd, Hg, Cu, and Zn toxicity to consider how the magnitude of site-specific anthropogenic metal pollution may affect the integrity of habitats within these marsh-creek systems.

In order to collectively examine the efficacy of the aforementioned metal-specific benchmarks (ERL, ERM, PEL), mean sediment quality guideline quotients (mSQGQ) provided an additional context to assess sediment quality impacts. Mean SQGQ values were derived from the Toxic Unit (TU) and Toxic Unit Sum (Sum TU). The quotient of each individual sediment contaminant observed by its respective effects-based SQG value (ERM, PEL, or ERL) yielded a metal-specific TU. Subsequently, the TU for each contaminant (individual quotient with respect to ERM, PEL or ERL) are summed to calculate the TU Sum, and then averaged by the number of study metals (3 in 2001, 4 in 2007 and 2009) to calculate the mean SQGQ (mERMQ, mPELQ, or mERLQ, respectively) (Long, et al., 1998; Fairey, et al., 2002; Thompson, et al., 2009).

Specific ranges of mERMQ values have been identified to correspond to various levels of potential risk for acute toxicity and sub-lethal/chronic benthic toxicity impacts on benthic species (Table 9a). Accordingly, this study further examined mERMQ to categorize values in terms of successively greater potential for acute toxicity to benthic organisms. In order to provide a qualitative description of site-specific mERMQ values four corresponding levels were established as follows: Level I/low (<0.1), Level II/low-moderate (0.11-0.5), Level III/moderate-high (0.51-1.50), and Level IV/high (>1.5) (Long, et al., 1998). In general, in terms of chronic

toxicity, the ranges of ERM Q values that correspond to low, moderate and high risk of stress to benthic organisms are considerably lower, by an order of a magnitude (Thompson, et al., 2009). An ERMQ less than 0.02 is associated with a low risk, while values within the range of 0.02-0.058 suggest a moderate risk, and values above 0.058 represents a high risk of benthic impacts (Hyland, et al., 2002).

RESULTS

Mean metal concentrations and ranges detected in 2009, 2007 and 2001 sediment datasets from Main Creek, Neck Creek and Lemon Creek are shown in Table 1 and Table 2. Metal analysis of Main Creek samples yielded concentration ranges of: 1.28-5.24 $\mu\text{g Cd}\cdot\text{g}^{-1}$, 0.03-2.52 $\mu\text{g Hg}\cdot\text{g}^{-1}$, 41.23-370.72 $\mu\text{g Cu}\cdot\text{g}^{-1}$, and 116.57-322.22 $\mu\text{g Zn}\cdot\text{g}^{-1}$. Concentration values detected in Neck Creek surface sediments varied from 0.82-2.76 $\mu\text{g Cd}\cdot\text{g}^{-1}$, 0.63-1.59 $\mu\text{g Hg}\cdot\text{g}^{-1}$, 60.92-248.62 $\mu\text{g Cu}\cdot\text{g}^{-1}$, and 70.89-184.70 $\mu\text{g Zn}\cdot\text{g}^{-1}$. Metal values reported in Lemon Creek surface sediments 1.36-2.08 $\mu\text{g Cd}\cdot\text{g}^{-1}$, 0.06-0.35 $\mu\text{g Hg}\cdot\text{g}^{-1}$, 101.09-161.93 $\mu\text{g Cu}\cdot\text{g}^{-1}$, and 158.35-227.73 $\mu\text{g Zn}\cdot\text{g}^{-1}$.

It was noteworthy that site-specific mean and median concentrations were markedly similar, and in most instances both values accurately represented the central tendency in Main Creek, Neck Creek and Lemon Creek surficial sediment data acquired from 2001, 2007, and 2009 surveys. Therefore, to remain consistent with previous research components, average sediment concentrations were used for descriptive purposes; which in this study included theoretical and empirical assessments based on comparison to SQGs.

Mean metal concentrations (Cd, Cu, and Zn in 2001, and Cd, Hg, Cu, and Zn in 2007 and 2009) studied in Main Creek, Neck Creek and Lemon Creek surface sediments, using theoretical and empirical sediment quality guidelines (regional and global background sediment reference values derived from Hudson River and world average shale and effect-based toxicity benchmarks from NOAA's screening gradient) are shown in Table 5.

Theoretical Sediment Quality Evaluation

At all three marsh study sites mean Cd, Hg, Cu and Zn concentrations were greater than regional background values of these metals (Table 2, Figure 4). Although average Hg (0.19 and $0.24 \mu\text{g}\cdot\text{g}^{-1}$) detected in Lemon Creek surface sediments was only slightly above regional ($0.18 \mu\text{g}\cdot\text{g}^{-1}$) and ($0.16 \mu\text{g}\cdot\text{g}^{-1}$) global background values, for both years analyzed (2007 and 2009), mean surface concentrations significantly exceeded regional baseline levels for all metals studied (*all p values* <0.00 and *regression line slope*; LC Hg *p value* = 0.009). In addition to background enrichment indices (Appendix A), contamination factor (CF), contamination degree (CD) and Pollution Load Index (PLI) were used to assess the status/conditions throughout the study area based on Cd, Hg, Cu and Zn contents of the sediments.

Large-scale assessment of marsh contamination by calculating EF, CF, CD, and PLI

With an understanding that using regional baseline values as a proxy for natural background concentrations may not absolutely assess data with respect to unpolluted sediments, trace metals in world shale average were used as an additional set of reference values to calculate the Contamination Factor (CF), Contamination Degree (CD) and Pollution Load Index (PLI) of previously collected field sediments (Eq. 2a-b, 3) (Angulo, et al., 1996; Gibbs, et al., 1997). Notably, estimates of preindustrial metal concentrations based upon average world shale values were lower than Hudson River background levels for Cd and Hg ($0.30 \mu\text{g Cd}\cdot\text{g}^{-1}$, $0.16 \mu\text{g Hg}\cdot\text{g}^{-1}$)

and higher for Cu and Zn ($45 \mu\text{g Cu}\cdot\text{g}^{-1}$, $95\mu\text{g Zn}\cdot\text{g}^{-1}$) (Wedepohl, et al., 1971; Tomlinson, et al., 1980; Ray, et al., 2006).

Contamination Factors and Contamination Degree

Background concentrations derived from world mean concentrations reported for shale (Table 6), were used to record CFs for each metal measured in Lemon Creek sediment samples (Table 3, 4, and Appendix C). Metal-specific CFs, which reflects the ratio of observed mean contents in surface and core sediments, respective mean shale values and CD values representative of the total, or collective sum of CFs, (Eq. 2a-b) are given in Table 4. Accordingly, Table 4 lists the terminologies used to describe site-specific determinations of contamination factor and contamination degree (Hakanson, 1980; Dehgan, et al., 2008; Mooraki, et al., 2009).

For each element, respective CF values were calculated from sediments samples collected at each intra-marsh surficial location and were averaged to determine mean 2009 Cd, Hg, Cu, and Zn CFs, and collectively were used to determine the overall site-specific CD for each study site (7-9a-b, Appendix C, Table 4.) Calculation of contamination factors (CF) from mean sediment concentrations recorded for Main Creek surficial transect samples showed the highest values of Cd (11.5), Hg (7.9), Cu (4.77), and Zn (2.53) (Table 3, Figure 6). CFs determined from mean Cd, Hg, Cu, and Zn contents in Neck Creek surface sediments were 6.35, 7.13, 3.89, and 1.65, respectively (Table 3, Figure 6). Mean surficial CFs of Cd, Hg, Cu, and Zn calculated for Lemon Creek of the most recent mean surface sediments corresponded to 5.35, 1.53, 2.89, 1.89 (Table 3, Figure 6).

Temporal CF values calculated from 2001 and 2007 datasets for Main Creek, Neck Creek and Lemon Creek are summarized in Table 4. Both Main Creek and Neck Creek demonstrated very-high CF values with respect to Cd and Hg and showed either considerable or very high Cu CF values for all years. In contrast, Lemon Creek CFs were lower, particularly with respect to Hg, but were greater than 1 (1.21-1.53), and thereby reflected values within the moderate range. With the exception of Cd, which measured 7.9 in 2001, all elements at Lemon Creek reflected either moderate or considerable CFs. For all years, Main Creek and Neck Creek CFs were lowest for Zn, although CFs were categorized as considerable at Main Creek (2.53-3.06), and moderate at Neck Creek (1.65-2.58); Lemon Creek demonstrated lower Zn CF values (1.13-1.85), but levels were also classified as moderate.

For all years CD values determined at Lemon Creek were relatively constant (10.1-11.6) and suggested moderate contamination, whereas respective CFs at Main Creek and Neck Creek collectively demonstrated similar CD values indicative of very high contamination in 2007 (36.3 and 36.5) and considerable contamination in 2009 (26.7 and 19) and 2001 (27.4 and 16.5) (Table 4a-b).

Pollution Load Index (PLI)

The extent of contamination/load of metal pollution was assessed in Main Creek, Neck Creek and Lemon Creek sediments via the PLI equation (Tomlinson, et al., 1980; Satyanarayana et al., 1994). Metal-specific CFs were collectively used to calculate the PLI values for each site, which are summarized in Table 4 and depicted in Figs. 10,11a-d. PLI values recorded for Main Creek, Neck Creek and Lemon Creek using mean surface sediment concentrations analyzed in 2009 were 5.76, 4.13, and 2.57, respectively (Table 4). However, the mean PLI value calculated

from the average of all PLI values determined from Main Creek, Neck Creek and Lemon Creek lateral surficial metal distributions were 4.32, 4.10, and 2.37, consecutively (7-9b). It was apparent that Lemon Creek 2009 PLI values (2.57) were generally in agreement with PLI values reported in 2007 and 2001 (2.28 and 2.63), regardless of whether or not Hg was analyzed (Table 4, Appendix C, 11a-d). In contrast, both Main Creek and Neck Creek values were far less consistent, but overall all, each site showed obviously higher PLIs for all years than Lemon Creek (10, 11a-d).

Empirical Results

Small-scale Empirical Assessment of Toxicity Potential via Site-specific Mean Cd, Hg, Cu and Zn Concentrations Relative to Effect-based SQVs (2009)

Comparisons of Main Creek, Neck Creek and Lemon Creek mean surficial metal concentrations calculated from 2009 intra-marsh lateral metal distributions are summarized with respect to effect-based empirical sediment quality guidelines (Table 1, Appendix A). Detectable Cd and Cu concentrations were greater than both TEL and ERL values in 100% surface samples collected along longitudinal transects spanning each study site. Of all marshes mean value for Cd was greatest at Main Creek, 3.57 (vs. 1.6 At Lemon Creek), which was comparatively lower than relatively similar surface values measured in 2007 and 2001, which were 5.62 and 5.18, respectively (Table 1).

In contrast to Neck Creek and Lemon Creek, Cd concentrations reported in surface sediments from 1/3 of Main Creek locations were higher than the PEL value (4.21) and Cu concentrations in 1/2 of Main Creek surface samples were greater than the ERM (270) value. However, in most Neck Creek and Lemon Creek surface samples, Cu levels were evidently higher than the respective PEL value (108).

Hg concentrations were greater than TEL (.696) and ERL (.71) values at sampling sites 4/6, 6/6, 5/6 of the sampling locations in which surface sediments were collected within Main Creek, Neck Creek and Lemon Creek, respectively. Furthermore, PEL and ERM values were exceeded in 50% of Main Creek and 5/6 of Neck Creek surface transect locations (Table 1).

With the exception of a singular surface sample within Main Creek and Neck Creek, Zn concentrations generally exceeded TEL and ERL values. Furthermore, Zn concentrations detected in 1/3 of Main Creek transect samples were found at levels above the PEL value (270). Surface sediments over the lateral extent studied at Lemon Creek exhibited levels of Zn that were slightly greater than Zn TEL and ERL values (Table 1).

Large-scale Empirical Assessment of Toxicity Potential via Site-specific Mean Cd, Hg, Cu and Zn Concentrations Relative to Effect-based SQVs (2009, 2007, 2001)

Comparisons between site-specific mean temporal metal concentrations and each of set of numerical toxicity benchmarks applied in this study (effect range low (ERL)/effect range median (ERM) and threshold effect level (TEL)/probable effect level (PEL) values), are summarized in Tables 6. Surface sediment samples from all three sites showed 4/4 metals (Cd, Hg, Cu, and Zn) above TEL and ERL in 2009 and 2007, and 3/3 metals (Cd, Cu, and Zn) above TEL and ERL in 2001 (Fig. 12).

Figures 14-16 depict temporal Main Creek, Neck Creek and Lemon Creek mean surface Cd, Hg, Cu, and Zn values relative to respective effect-based benchmarks, which show large-scale geospatial variability regarding potential (metal specific) incidence of toxicity among marsh-creek habitats. The number of metals that exceeded PEL varied among sites and years (Table 6-7). Overall, Main Creek exhibited the most metals with concentrations that reached

PEL (4/4 in 2009 and 2007, and 3/3 in 2001), and Lemon Creek had the least (1/survey year). The number of metals detectable at concentrations above PEL at Neck Creek differed, depending on the year; ranging from 4/4 to 1/3 in 2007 and 2001, respectively (Figs-14-16). Although all sites showed at least maximum Cu concentrations above PEL, Lemon Creek was the only site where detectable Cu was not observed to approach the ERM range and no additional metals reflected concentrations higher than PEL (Figs.14b, 15b, 16.).

The number of metals with concentration values greater than ERM varied temporally and spatially, among study sites and year of sample collection. For example, the number of incidences where metal-specific values exceeded ERMs ranged from 0 to 2, at Lemon Creek and Main Creek, respectively (Table 6). Neck Creek and Main Creek sediments consistently exceeded the Hg ERM level (Table 6). Hg was the only metal that demonstrated surface sediment concentrations that exceeded ERM values at both Main Creek and Neck Creek in 2009 and 2007 (Figs. 14a, 15a). Cu levels detected in surface sediments collected in earlier studies at Main Creek and Neck Creek (2001 and 2007, respectively) exceeded ERMs (Figs. 15b, 16). In contrast, no study metals were elevated above respective ERMs at Lemon Creek (Figs. 14-16).

Collective Empirical Assessment Results

Toxic Units and TU sum

Calculation of Toxic Units (TU), the ratio of individual concentration (mean Cd, Hg, Cu, and Zn contents) to respective toxicity reference value (i.e. PEL, ERM, ERL) are displayed in Figs. 7, 8, and Appendix C. At Main Creek and Neck Creek, Hg measured the largest TU value of all study metals, while Lemon Creek sediments depicted the greatest TU for Cu. Site-specific TU values depended on the element and respective benchmark category applied (i.e. PEL, ERM, or ERL) which, in turn, influenced the combined metric. Accordingly, TU sum also varied

according to site and reflected the number of metals (4 in 2009 and 2007; 3 in 2001), type of benchmark (i.e. PEL, ERM, ERL) and elements included in surficial datasets (Cd, Cu, and Zn measured in all datasets, Hg not analyzed in 2001).

The summation of Main Creek, Neck Creek and Lemon Creek TU values from 2001, 2007, and 2009 datasets derived the toxic unit sum (TU Sum) (Fig. 7- 8, Appendix C). Hg accounted for the largest fraction of total toxic units at both Arthur Kill sites, whereas, Cu mainly contributed the majority at Lemon Creek. Site-specific 2009 and 2007 TU sum values derived from Cd, Hg, Cu, and Zn TUs (based on PEL), respectively, ranged from 5.67- 5.20 at Main Creek and 2.78-4.78 at Neck Creek. For the same years the Lemon Creek values were substantially lower and demonstrated more temporal consistency (1.42-1.33). Based on ERM, the greatest TU Sum was identified at either Main Creek or Neck Creek; 2009 and 2007 values at these sites ranged from 3.59-4.24 and 2.78-4.87, respectively, whereas, in the same consecutive years, Lemon Creek TU sum ranged from 1.42-1.33.

Mean Sediment Quality Guideline Quotients (mSQGQ)

Recent and temporal surficial datasets from Main Creek, Neck Creek and Lemon Creek were also evaluated using the mean sediment quality guideline quotient (SQGQ) approach. Calculated values for “mean PEL quotient” (mPEL Q), “mean ERM quotient” (mERM Q), and “mean ERL quotient” (mERL Q) are exhibited in Tables 7-8 and Appendix C, respectively. Table 9 presents the combined results the above-mentioned SQGQs, derived from the mean of individual ratios of metal-specific concentrations normalized to respective bioeffects benchmarks (PEL, ERM, and ERL). Of all sites, Main Creek reflected the highest mean SQGQs, with respect to PEL Q, ERM Q, and ERL Q, in 2009 and 2001, whereas these values were highest at

Neck Creek in 2007. Among all sites and years, Lemon Creek showed the lowest SQGQs for all benchmarks (Table 9).

The lowest site-specific mERMQ values (0.82, 0.53, and .21) were calculated for Main Creek, Neck Creek and Lemon Creek respectively, in 2001 (Table 8). In order to provide a qualitative description that corresponded to the level/degree of acute toxicity reflected by site-specific mERMQ values four categories were used: Level I/low (<0.1), Level II/low-moderate (0.11-0.5), Level III/moderate-high (0.51-1.50), and Level IV/high (>1.5) (Long et al. 1998). No sites exhibited mERMQ values that were greater than Level IV/High (>1.5). However, both Main Creek (.82-1.06) and Neck Creek (.53-0.69) demonstrated values within the Level III/Moderate-High acute toxicity range (0.51-1.5) for all years (Table 9a). In contrast, over the past decade, analysis of Lemon Creek sediments demonstrated mERM Q values which varied from 0.21-0.36 (2001 vs.2009), indicative of Level II (0.11-0.5) in terms of acute toxicity (Table 9a). With respect to chronic toxicity implications, all Main Creek, Neck Creek and Lemon Creek mERMQ values were >0.058 , which suggested sediments represented a high risk of stress/impacts to benthic organisms (Table 9a).

DISCUSSION

Urbanized coastal regions remain vulnerable to anthropogenic stressors that have altered the function and destroyed many shoreline areas and tidal wetland systems which provide critical ecosystem services, including habitat for fish and wildlife (Steinberg, et al., 2004). Although legislation now mandates the protection of wetlands, inputs and accumulation of persistent pollutants, such as metals associated with past and present land use activities, have contributed to degradation and loss of estuarine habitats (Kennish, 2002). In addition, water quality regulations

have reduced the magnitude of contaminants discharged from point sources (i.e. wastewater effluents, CSOs). However, decreased sediment quality may be expected to persist in many estuarine areas on account of widespread coastal and urban development for residential, commercial and/or industrial uses, and infrastructure initiatives (Schaffelke, et al., 2005). Furthermore, present-day contaminant loadings in marshes within urbanized environments may become excessive because of the impact of numerous point and non-point pollutant sources.

In addition to high volumes of storm water runoff laden with sediments and toxic pollutants, poor tidal flushing further propagates degradation of sediment quality and benthic habitats in many areas of the NY/NJ Harbor Estuary (Steinberg, et al., 2004; USASCE HRE, 2010). Accordingly, the New York/New Jersey Harbor Estuary Program (NY/NJ HEP) has included “Management of Toxic Contamination” as a current priority in terms of a number of relevant goals and objectives. Applicable actions to achieve this include: reduce continuing discharges of the chemicals of concern to the estuary; remediate selected contaminated sediments; better understand the problem and take additional actions as more is learned (NY/NJ HEP CCMP, 2010). Meanwhile, the presence of toxic chemicals in water and sediments throughout New York-New Jersey Harbor has resulted in reduced water quality, fisheries restrictions/advisories, and general adverse impacts to the estuarine and coastal ecosystems.

Metals are of specific concern in the protection and management of estuarine systems because of their persistence and potential toxicity. Elevated metal concentrations can also serve as a proxy for other pollutants, signaling the presence of additional contaminants (Schropp, et al., 1988). Contaminated regional sediments and benthic biota may contain high concentrations of metals (Adams, et al., 1998; Adams, et al., 2003; Bopp, et al., 2006; USASCE HRE, 2010). Particular areas within the NY/NJ HE, including the Arthur Kill, identified as “hot spots” of

contamination since the early 1990s, remain a regional issue (Long, et al., 1990; NOAA, 2001; Steinberg, et al., 2004; HEP, 2006). Evidence of Arthur Kill sediment toxicity (i.e. metals and other contaminants) on account of poor tidal flushing, in combination with both century/decades-old legacy contamination and present-day loadings, may also pose a threat to bordering coastal environments via tidal flux /transport and advection; a multifaceted problem with respect to the Arthur Kill (Olsen, et al., 1982; Long, et al., 1990; Bonnevie et al., 1992, USFWS, 1997; USACE HRE, 2010). In addition to monitoring and sediment toxicity studies within the Arthur Kill proper, which noted the presence of biological effects was likely due to sediments that contained toxic metals, complementary studies have demonstrated that metals in adjacent marsh systems (including Main Creek and Neck Creek) reached levels above background sediment concentrations, implicating anthropogenic enrichment (Cd, Hg, Cu, and Zn) has affected benthic infaunal community dynamics (Bonnevie, 1993; NOAA, 1999; Long, 1996; Ward, 2001; Nichols, 2004; Chapter 2; Goto, 2009; Seebaugh, 2010).

Given that human activities often elevate natural elemental concentrations inherent within sediment, it was not a revelation that anthropogenic metals were prevalent environmental components in marsh-creek systems throughout the study area (Chapter 2, 3). In general, marshes along the Arthur Kill (Main Creek and Neck Creek) demonstrated comparatively greater levels of temporal and spatial enrichment relative to Lemon Creek, a tidal marsh-creek hydraulically connected to the Raritan Bay. The greater contamination associated with the Arthur Kill marshes was to be expected, as increased levels often occur in areas zoned and historically predominated by industrial and manufacturing activities. Therefore, it was likely that anthropogenic activities in surrounding watersheds directly and indirectly subjected Main Creek and Neck Creek to greater metal loads via a combination of sustained and intermittent terrestrial,

atmospheric and estuarine inputs associated with historical and contemporary land uses (Thorton 1991, Franco 2005).

The intent of this study was to collate and further analyze surficial results from geochemical studies conducted within the study reach over the past decade (2001, 2007 and 2009) in order to establish a suitable and effective framework to accurately assess sediment quality. Integration of previous and recently acquired datasets provided a comprehensive temporal and spatial context in which to determine the environmental significance of metals detected within Main Creek, Neck Creek and Lemon Creek marsh-creek habitats. In general, this research component examined how sediment quality and associated impacts vary across the study area by characterizing extent of site-specific anthropogenic metal pollution (Cd, Hg, Cu, and Zn) and large-scale variability in magnitude and potential toxicity of contaminated sediments over time. Study goals included a comprehensive assessment of metal contamination on different scales to identify localized environmental impacts and possible regional ecological implications. Primary objectives were to evaluate the concentration of metals in surface and core sediments with respect to baseline/background levels and toxicity indices to describe the environmental significance of temporal and spatial marsh contamination identified throughout the study area. This approach will establish a comprehensive framework to characterize the quality of Main Creek, Neck Creek and Lemon Creek sediments in terms of the degree of site-specific anthropogenic sediment contamination and potential biological effects to consider how the magnitude of metals may affect the severity and occurrence of toxicity incidences and overall integrity of habitats within these marsh-creek systems.

Collectively, the series of sediment evaluation techniques (combination of theoretical and empirical methodologies) applied to analyze Main Creek, Neck Creek and Lemon Creek

geochemical datasets collected over the past decade, established a temporal context of marsh-specific sediment pollution. This approach provided the necessary temporal and spatial framework to assess past and present conditions (i.e. contamination levels and potential impacts) within marsh-creek habitats along a longitudinal gradient of the study area; and thereby, characterize the current status of sediment quality and possible ecological implications within in different geographic reaches of the NY/NJ Harbor Estuary. Specific objectives were to discern intra-marsh variability and characterize large-scale spatial trends along a with respect to occurrence, extent, and toxic potential of metal contaminated sediments over time.

Although intra-specific temporal conditions were analyzed, this research component aimed to discern inter-marsh differences with respect to occurrence, extent, and potential toxicity of metal contaminated sediments in order to describe sediment quality along a geographic gradient. An additional objective of this research component was to emphasize the present status of each site via characterizing the ecological significance of surficial metals distributions over a greater reach of the tidal portion of each marsh-creek system compared to more localized sampling strategies used in earlier studies. The goal of this approach was to account for small-scale variations and consider the affect of potential intra-marsh fluctuations in describing site-specific conditions. Based on previously defined large-scale pollution gradients, which definitively ranked sites in terms of metal distributions and anthropogenic enrichment levels (MA > NC > LC), secondary objectives were to determine evidence of temporal changes in site-specific sediment quality, measured in terms of contamination magnitude (pollution load) and potential for toxicity (effect-based benchmarks, toxicity impacts). Likewise, secondary objectives were to determine the role of this factor and if it is reflected in temporal changes in

site-specific condition (i.e. contamination magnitude, pollution load, toxicity impacts) and/or previously defined large-scale pollution gradients.

The intent/purpose of emphasizing the most recent sampling design, which collected samples laterally over a greater area extent of each site compared to more localized sampling strategies in earlier studies, was to depict the present status of each site. The goal of this approach was to account for small-scale metals distributions and consider the affect of potential intra-marsh variations. Likewise, secondary objectives were to determine the role of this factor and if it is reflected in temporal changes in site-specific condition (i.e. contamination magnitude, pollution load, toxicity impacts) and/or previously defined large-scale pollution gradients.

Spatial and Temporal Context

Since the majority of metals introduced into receiving waterways systemically become associated with sediments, analysis of paleoecological pollution trends has been the focus of many marsh studies (Sanudo-Wilhelmy, et al., 1999; Rozan, et al. 2001; Christiansen, et al., 2002; Bopp, et al., 2006). This approach is useful in assessing temporal contamination, evaluating modern improvements in contaminant levels and assessing the effectiveness of recent pollution control programs implemented to reduce loadings (Christiansen, et al., 2002; Bopp, et al., 2006). Over the past decade two coring studies, conducted in 2001 and 2007, focused on the temporal metal distributions of Cd, Cu, and Zn in part of Main Creek, Neck Creek and Lemon Creek. Sediment core profiles depicted site-specific metal enrichment and variability among Staten Island marshes, which provided initial insight and prompted further investigation regarding the environmental integrity of these ecosystems (Weis, et al., 2005; Strong, et al., 2008).

Sediment chronologies established that metal distribution trends were site-dependent. However, cores from environments within the Arthur Kill Complex (Main Creek and Neck Creek) exhibited elevated metal concentrations that were similar in magnitude and demonstrably greater than values observed in sediments from an external marsh (Lemon Creek). Core profiles illustrated that although Main Creek, Neck Creek and Lemon Creek reflected variable degrees of recovery and attenuation within contemporary sediments, all study sites demonstrated temporal metal enrichment that steadily exceeded background levels. Although notably greater in marshes along the western versus southern margins of Staten Island, the extent of Cd, Cu, and Zn enrichment described for all sites indicated anthropogenic metals have degraded sediment quality throughout the study area.

Analysis of core datasets in terms of the vertical distribution of Cd, Cu, and Zn concentrations demonstrated Main Creek, Neck Creek and Lemon Creek sediments are important repositories of metals, regardless of depth. However, in contrast to greater depths, contaminants compartmentalized within surface sediments undergo rapid mixing and are available for exchange within the ecosystem (Rozan, et al., 2001; Harikumar, et al., 2009). Furthermore, compared with overlying surface water and deeper sediments, surficial sediments contain the majority of the metals supply within marine ecosystems (Rozan, et al., 2001). Accordingly, supplemental studies, which analyzed Main Creek, Neck Creek and Lemon Creek surface sediments along lateral transects that extended bi-directionally from prior coring locations, substantiated that all sites remain susceptible to modern metal pollutants as anthropogenic impacts continue to compromise these important marsh-creek habitats (Strong, et al., 2008). Furthermore, examination of surficial metals along longitudinal transects confirmed the apparent site-specific and inter-spatial variability that was evident in earlier coring studies. Thereby, large-

scale pollution trends derived from small-scale assessments of metal distributions at depth and in surface sediments were consistent. Regardless of any site-specific (vertical or lateral) temporal or spatial variations, marshes along the Arthur Kill exhibit a greater magnitude of anthropogenic contamination than Lemon Creek, demonstrating greater pollution on the western margin than the southern border of Staten Island. In general, considerably different surficial metal concentrations were apparent throughout the study area. However the greatest mean metal concentrations were mainly observed at Main Creek, Neck Creek and Lemon Creek, consecutively. Although Main Creek consistently ranked the highest in terms of all metals studied, only the mean value for Cd ($3.46 \mu\text{g}\cdot\text{g}^{-1}$) was significantly greater than Neck Creek ($1.9 \mu\text{g}\cdot\text{g}^{-1}$), which was slightly above Lemon Creek ($1.61 \mu\text{g}\cdot\text{g}^{-1}$).

Given that the surface layer dually acts as an important sink and source of metals, this research component focused on surficial distributions of Cd, Hg, Cu, and Zn to further examine the extent of sediment quality impacts associated with marsh contamination throughout the study area. Analysis of sediments collected along longitudinal gradients at Main Creek, Neck Creek and Lemon Creek characterized a range of Cd, Hg, Cu, and Zn values to determine current levels of surficial enrichment. Evaluation of the mean concentration of metals detected in transect samples (2009), in conjunction with previously collected surface sediments (2001 and 2007), also added further insight regarding site-specific temporal assessments. This approach provided a context to describe Main Creek, Neck Creek and Lemon Creek surficial pollution that accounted for variations attributable to different sampling events, locations and time. In the past decade, surface sediments from marsh habitats around Staten Island exhibited variable scales of elevated metal concentrations (Ward, 2002; Nichols, 2004).

Evaluation of environmental significance of metals in marsh sediment by comparison with theoretical SQGs

Previous chapters accounted for intra-marsh variations of metals at depth and in surface sediments, which provided a temporal and spatial context of sediment contents within each marsh-creek system to examine metal distributions and fate of metals on both small and large-scales. Accordingly, this approach established the necessary framework to assess the quality of marsh sediments throughout the study area, in terms of the extent of metal contamination and potential toxicity. Thereby, this research component was integral to address the significance of widespread metal inputs and related environmental stress due to the prevalent anthropogenic signature, which may compromise ecological integrity of valuable marsh-creek habitats throughout the study area.

Background Sediment Approach

Thus far, the sediment background approach (BSA) was used to identify anthropogenic metal enrichment, and thereby further characterize temporal and spatial metal distributions and variability on large and small scales. For the purposes of this study, the background sediment approach served as an initial means to identify site-specific contamination and determined if study sites necessitated further examination to investigate extent and potential for toxic implications. Subsequently, the BSA also served to discern large-scale variability among marsh sediment quality across longitudinal impact gradients over time.

The basis of this approach is to compare observed values from geochemical analyses of study site sediments with reference values from background sediments. Samples that are not significantly greater than reference background values are assumed not hazardous, whereas with those greater it is implicit that conditions may be hazardous (MacDonald, 1994). As previously reported in Chapters 2 and 3, it was evident from metal analysis of Main Creek, Neck Creek and

Lemon Creek marsh cores that for all sites surface sediments were demonstrably greater than background. Accordingly, sediment concentrations that significantly exceed background levels, as evidenced for all sites in 2007 surface sediments (Chapter 2), warrant concern and implicate metal contamination.

Given that background metal concentrations representative of natural elemental constituents in local sediments were unavailable, and that there is no appropriate reference site in the immediate vicinity of the study sites, prior studies (Chapters 1-3) derived “regional background levels” from literature-based values that have been previously reported in the surrounding geographic study area (i.e. within the New York-New Jersey Harbor Estuary Complex) (Appendix) (Bowen, et al., 1979; O’Reilly Wiese, 1995; Hirschberg, et al., 1996).

The abovementioned studies characterized EFs in both vertical and lateral analysis of surface and depth samples and found that in general, Main Creek, Neck Creek and Lemon Creek demonstrated EFs that were considerably greater than 1.0, which is indicative of significant enrichment of anthropogenic metals (Chapter 2 and 3) (Appendix). Intra-marsh differences among calculated EF values were attributed to metal-specific inputs that contribute inconsistent levels of elements in sediments and/or variable transport and/or removal rates of each metal from marsh sediments (Chapter 3) (Lu, et al. 2005).

Considering the enormity of available background sediment values referenced in literature and the extensive range of metal-specific concentrations, there within, and the intent to further use the background sediment approach as it applies to sediment quality, this research component included an additional source of relevant proxy data, world mean shale. With an understanding that neither regional nor global background reference values may absolutely assess data with respect to unpolluted sediments, both Hudson River sediments and mean world

shale baseline metal datasets were used as proxies of natural concentrations (Angulo, et al.1996; Gibbs, et al., 1997). Estimates of preindustrial metal concentrations based upon average world shale values are similar for Hg ($0.16 \mu\text{g Hg}\cdot\text{g}^{-1}$), but notably higher than Hudson River background levels for Cd ($0.30 \mu\text{g Cd}\cdot\text{g}^{-1}$), Cu ($45 \mu\text{g Cu}\cdot\text{g}^{-1}$), and Zn ($95\mu\text{g Zn}\cdot\text{g}^{-1}$) (Wedepohl, et al., 1971; Tomlinson, et al., 1980; Ray, et al., 2006).

Accordingly, background enrichment indices, including contamination factor (CF) and contamination degree (CD), supplemented EF values analyzed in prior research components in order to characterize Cd, Hg, Cu, and Zn contamination within Main Creek, Neck Creek and Lemon Creek (Hakanson, et al., 1980). Normalization of observed metal contents with both sets of regional (Hudson River sediment) and global (world mean shale) background reference values supplemented prior studies, which focused on evaluation of anthropogenic vs. natural metal components to emphasize (small and large-scale) enrichment trends and discern spatial and temporal variations and not attributable background sources. Furthermore, the extent of variation between site-specific metal distributions and respective Cd, Hg, Cu, and Zn concentrations also served as a theoretical means to measure sediment quality, and thereby extended the applicability of the sediment background approach to determine the environmental significance of Cd, Hg, Cu, and Zn levels detected with Main Creek, Neck Creek and Lemon Creek and over time.

Small and large-scale assessment of spatial and temporal sediment contamination by calculating the (EF, CF, CD, PLI)

In an effort to put the metal concentrations into context in terms of pollution levels, the mean values for cores and surface sediment transects at each site were compared to world shale averages to determine the Concentration Factor (CF), which were utilized to calculate the

Tomlinson Pollution Load Index (PLI) as expressed in Eq. 1 (Tomlinson et al. 1980; Ray et al. 2006). Previous chapters analyzed total metals in Main Creek, Neck Creek and Lemon Creek in cores and surficial transect samples to discern intra-marsh differences of sediment concentrations and anthropogenic enrichment at depth and in surface sediments in order to examine the probable influence of both natural and anthropogenic factors (i.e. disturbances). Accordingly, collective evaluation and comparative assessment site-specific vertical and lateral distribution trends characterized the spatial and temporal extent and occurrence of contaminants (i.e. Cd, Hg, Cu, and Zn) within and throughout the study area on small and large scales. CFs and PLIs were calculated to further describe the degree of metal contamination reported in surface sediments and cores (Hakanson et al. 1980). The CF for each metal and the PLI value for each intra-marsh surficial location were used to determine the mean 2009 Cd, Hg, Cu, and Zn CFs, and collectively, the overall site-specific PLI for each study site (7-9a-b, Appendix C, Table 4.)

Large-scale assessment of marsh contamination by calculating the (EF) and (CF)

Metal-specific background enrichment indices, including Enrichment Factor and Contamination Factor established/provided the initial framework to assess the extent to which pervasive anthropogenic metal inputs have compromised the environmental integrity/health of marsh habitats across the study area due to legacy contamination and present-day loadings. Subsequently, CFs determined for Main Creek, Neck Creek and Lemon Creek, collectively, via the degree of contamination (CD) and pollution load index (PLI), characterized sediment quality in terms of the magnitude of contamination.

At each site the enrichment and contamination factor was calculated for Cd, Hg, Cu, and Zn in 2007 and 2009, and for all the same metals except for Hg in 2001 (Tables 3-4). In general, Cd demonstrated the highest metal-specific CFs at all sites, with the exception of Neck

Creek in 2009, which showed a slightly greater Hg CF value (7.13 vs. 6.35) (Table 4). Overall, Zn CFs were the most comparable among sites. In contrast to Main Creek and Neck Creek, Lemon Creek demonstrated greater metal-specific values in 2009 than in earlier surveys. However, Lemon Creek also showed only minor temporal variability for most pollutants, perhaps with the exception of Cd, which, ranged from 7.90, 4.02, and 5.35 times greater than global background in 2001, 2007, and 2009, respectively.

Overall, EF and CF results demonstrated that Cd was the greatest contaminant in sediments throughout the study area (Table 3; Appendix A). However, EF values showed that second to Cd, Cu contributed the most in polluting sediments in all sites. However, CF results clearly showed that Cd and Hg were respectively the major sediment contaminants at Main Creek and Neck Creek, but at Lemon Creek Cu was second to Cd regardless of background reference value used. These finding suggested the widespread impact of Cd and Cu, however, implicated Hg inputs were localized and may affect Arthur Kill sites to a greater degree than observed at Lemon Creek. In contrast, Zn posed the least pollution impact among all elements throughout the study area. Likewise, these findings were confirmed by the degree of contamination (CD) and pollution load index (PLI), which reflected the collective effect of all metals studied.

Contamination Degree (CD)

In accordance with large-scale interspatial variability and temporal trends reflected by site-specific CFs, the degree of contamination (CD) calculated from contemporary (2009) and baseline (2001) geochemical datasets from Main Creek was higher than measured for the other study sites. However, CD values for Main Creek and Neck Creek were comparable in 2007, at which time both sites demonstrated peak CD values that were indicative of very high contamination (36.3 and 36.5, respectively). The consecutively higher CD values in 2007 (10.1)

and 2009 (11.6) at Lemon Creek suggested a temporal decline in sediment quality. Conversely, over the same timeframe, both Arthur Kill sites exhibited lower contamination degree by a factor of 1.4 at Main Creek and 1.9 at Neck Creek. Accordingly, both sites reflected very high contamination in 2007, and considerable contamination in both 2001 and 2009. In contrast, Lemon Creek sediments yielded lower CD values that fluctuated slightly over time. Although the maximum value (11.62) was derived from contemporary (2009) sediments, the temporal range of CD values (10.14-11.62) exhibited by Lemon Creek sediments consistently characterized a moderate degree of contamination over the past decade. Therefore, the greater presence and temporal extent of metals enrichment detected within Main Creek and Neck Creek sediments, attributable to prior inputs and current loadings, implied these sites have experienced greater sediment quality degradation and associated ecological impacts than Lemon Creek. Although the higher degree of contamination, considerable to very high, may have more adversely compromised the health of Arthur Kill benthic habitats, the moderate degree of contamination sustained by Lemon Creek sediments over ten years, may also have affected the environmental integrity of this system (Mooraki, et al., 2009)

Pollution Load Index (PLI) Method

Comparisons of site-specific sediment concentrations to natural background elemental values collectively established PLI index values. These are indicative of the quality of marsh sediments in terms of the contamination level, based on the number and/or extent to which natural elemental concentrations (mean shale) were exceeded. Pollution load index characterized site-specific sediment quality in terms of magnitude of sediment contamination and provided a proxy value, with which to comparatively assess and rank marsh conditions. As an extension of the background sediment approach, PLI values qualitatively demonstrated sediment contamination

and potential ecological risk. Site-specific PLI values ranked highest either at Main Creek and Neck Creek for all years and consistently lowest at Lemon Creek. Consequently, the Arthur Kill sites (based on theoretical assumptions associated with PLI value) were anticipated to incur greater sediment quality impacts (i.e. incidences of toxicity). Main Creek, Neck Creek and Lemon Creek PLI values illustrated a demonstrable large-scale variability across a longitudinal gradient that extends from the Arthur Kill to the Raritan Bay; depicting an evident geographic sediment contamination gradient, which was consistent over time, among marshes along the western and southern margins of Staten Island.

Downcore Pollution Load Indices

As expected by the consistency in Lemon Creek vertical and lateral metal distributions and enrichment shown at depth and surface sediments (Chapters 2 and 3), metal-specific CFs collectively demonstrated limited spatial and temporal variability of PLI values. PLI values of 2007 sub-core samples indicate anthropogenic metal loadings in Main Creek, Neck Creek and Lemon Creek sediments over time. In this study, Main Creek and Neck Creek clearly demonstrate the lowest PLI values in the uppermost core sections (0-2 cm, 2-4 cm, respectively). In contrast to respective minimums (6.9, 4.7) and to a lesser extent, mean values (7.8, 6.1), the maximum PLIs (8.8, 8.9) detected at Main Creek and Neck Creek, were relatively similar. The narrow range (2.4-4.1) of evidently lower downcore PLI values reflects the comparatively greater consistency and lesser degree of temporal pollution at Lemon Creek.

Calculations based on datasets from earlier coring studies (2001) within these systems show PLI values in 60% of Lemon Creek samples were less than 1. In contrast, PLI values were greater than 1 at all depths in Main Creek and Neck Creek cores collected in 2001 and all sites in 2007. In contrast to the present study, the greatest PLI value was detectable in the surface layer

of Main Creek and downcore PLIs were generally less variable (6.2-7.4). Main Creek and Neck Creek cores (2001) demonstrated comparatively lower (6.7) and higher (8.5) mean PLI values.

The different levels and invariably high PLI values that were apparent throughout the length of Main Creek, Neck Creek and Lemon Creek confirmed the site-specific temporal and surficial contamination and large-scale pollution gradients. However, the surficial layer of all marsh cores demonstrated lower PLI values than bottom sediments.

Lateral Surficial PLIs

This study focused on the extent of metal pollution in Main Creek, Neck Creek and Lemon Creek sediments and its impact on these marsh-creek systems via examination of surface datasets (2001, 2007, and 2009) via the pollution load index (PLI) method. The evaluation of individual and mean EFs, CFs and PLI values confirmed that Main Creek, Neck Creek and Lemon Creek are contaminated by Cd, Hg, Cu, and Zn. However, either Main Creek or Neck Creek showed the greatest PLI values, which were considerably higher than Lemon Creek in all survey years.

It was noteworthy that currently high pollution loads (>1) were calculated throughout the areal extent of all marsh-creek systems; PLI values varied from 2 to 7.3, 3 to 5.4, and 2 to 2.9 for Main Creek, Neck Creek and Lemon Creek surficial sediments, respectively. These ranges align with the successively greater small-scale spatial and temporal variability of metal distributions reported at Lemon Creek, Neck Creek, and Main Creek (Chapter 2 and 3). PLI values calculated from 2009 mean Main Creek, Neck Creek and Lemon Creek surface sediments (5.76, 4.13, and 2.57, respectively), were lower at the Arthur Kill sites, and higher at Lemon Creek than reported in 2007 (7.32, 7.60, 2.28). Although the evident lateral variability of Main Creek surface

distributions did affect the PLI value, determined from the site-specific mean of all samples vs. mean PLI from individual surficial locations (5.76 and 4.32, respectively), there was little difference apparent at Neck Creek (4.10) and Lemon Creek (2.37) in 2009, 2007 or 2001 at all sites.

Mean Surficial PLIs

Compared to the Arthur Kill sites, metal-specific mean CFs were generally lower at Lemon Creek and in certain instances (i.e. Hg and Cu), only slightly greater than 1. All Lemon Creek individual ratios depicted Cd, Hg, Cu, and Zn enrichment, which collectively established successively greater PLI values (2.63, 2.82, 3.06) in 2001, 2007, and 2009, respectively. In contrast to both Main Creek and Neck Creek, accounting for Hg enrichment in Lemon Creek surface sediments in 2007 and 2009 reflected lower respective PLI values (2.27 vs. 2.82 in 2007 and 2.57 vs. 3.06 in 2009), than determined without incorporating Hg. This was due to the determination of the lower Hg CFs (0.19 and $0.24 \mu\text{g}\cdot\text{g}^{-1}$) detected in Lemon Creek surface sediments, which were only slightly above regional ($0.18 \mu\text{g}\cdot\text{g}^{-1}$) and ($0.16 \mu\text{g}\cdot\text{g}^{-1}$) global background values for both years analyzed (2007 and 2009), opposed to the comparatively greater levels observed for both Arthur Kill sites. In 2007 and 2009 mean Hg contents at Main Creek measured $1.42 \mu\text{g}\cdot\text{g}^{-1}$ and $1.26 \mu\text{g}\cdot\text{g}^{-1}$ whereas, in the same years, Neck Creek reached $1.77 \mu\text{g}\cdot\text{g}^{-1}$ and $1.14 \mu\text{g}\cdot\text{g}^{-1}$, successively. Although PLI values exhibited an increasing trend over time, the limited extent of temporal variability reflected minimal effect on the relatively consistent magnitude of sediment contamination demonstrated over the past decade at Lemon Creek.

Overall, theoretical assessment methodologies characterized marsh-specific magnitudes of metal contamination and discernable geographic variability across the study area. The

multiplicity of indices utilized to rank study sites reflected consistency among large-scale temporal and spatial sediment quality trends. Accordingly, metal-specific background enrichment indices (i.e. EFs and contamination factors) and respective degree of contamination and pollution load, derived a longitudinal impact gradient (Arthur Kill marshes/Lemon Creek). Therefore, based on the background sediment approach, initial theoretical assessment methodologies established a correlation between metal distributions and sediment quality, which is relative to site-specific magnitudes of anthropogenic contamination. Furthermore, additional understanding regarding temporal contamination on a variety of spatial scales substantiated prior observations discerned from coring studies (Chapter 2).

Evaluation of environmental significance of metals in marsh sediment by comparison with empirical SQGs

Given the prevalent anthropogenic contamination throughout study area ($PLI > 1$), site-specific metal concentrations detected at Main Creek, Neck Creek and Lemon Creek were compared with effect-based SQGs to assess the quality of respective marsh sediments in terms of potential ecological impacts. Rather than representing metal-specific criteria or acceptable levels that future restoration/remediation initiatives should target/attain; the intended use for applying numerical sediment quality guidelines (SQGs) in this study, and arguably the most appropriate purpose, was for toxicological screening of surficial sediment datasets. Two sets of SQ values from NOAA's gradient served as empirical toxicity benchmarks in an effort discern the environmental significance of metal-specific sediment contents observed on small and large spatial scales and identify the relative degree of biological effects that contaminated marsh sediments may pose to benthic species across the study area over time. This study component focused on the surficial layer (0-2 cm) and is most important biologically relevant, since most

benthic organisms tend to assemble proximal to the surface (Councell and Bell, 1979; Barrett, et al., 2007).

Over the past decade, periodic sampling and analysis of Main Creek, Neck Creek and Lemon Creek surface sediments established a temporal and spatial context in which to evaluate occurrence, spatial extent and magnitude of anthropogenic metal contamination, and established a comprehensive framework assess and characterize sediment quality throughout the study area. Sediment samples were collected from multiple areas within each study site to determine recent concentration levels and distributions of surficial metals. Cd, Cu, and Zn were in all datasets (2001, 2007, and 2009), while Hg analysis was included for the latter two years (2007 and 2009). Generally, sediments throughout the study area contain elevated levels of metals associated with anthropogenic activities (i.e. development and land use). Albeit on different scales, surficial sediments of marsh-creek habitats over the extent of Main Creek, Neck Creek and Lemon Creek are subject to Cd, Hg, Cu, and Zn that may be potentially toxic to estuarine organisms.

To further assess the quality of habitats throughout the study area and examine the toxic potency of contaminated Main Creek, Neck Creek and Lemon Creek sediments, average surficial metal concentrations were compared to reference guidelines used to benchmark toxicity (NOAA, Bonnevie et al. 1993). Recovered Cd, Hg, Cu, and Zn concentrations identified in Main Creek, Neck Creek and Lemon Creek surface samples over the past decade (2001, 2007, and 2009), which were evaluated with respect to ERL, ERM, TEL, PEL values, collectively characterized and comparatively assessed site-specific conditions in terms of severity of potential toxicity of marsh sediments, in order to discern geographic variations with respect to the spatial-temporal extent and magnitude of sediment quality degradation and associated impacts. Surface samples

were evaluated with respect to temporal and spatial metal distributions to account for small and large-scale variability.

A key component of this study was to incorporate metal distribution datasets that considered both large and small scale variations in terms of space and time. For example, the different spatial scales accounted for in the study included the geographic extent of study area vs. the site-specific study reach of marsh-creek system. Whereas, long-term to short-term temporal scales ranged from decadal vs. contemporary timeframes, aligning with baseline data from initial studies (2001).

Although on different scales, surficial sediments of marsh-creek habitats over the extent of Main Creek, Neck Creek and Lemon Creek were subject to Cd, Hg, Cu, and Zn inputs that may be potentially toxic to estuarine organisms. In contrast to earlier studies at Main Creek, Neck Creek and Lemon Creek, 2009 datasets likely accounted for greater intra-marsh fluctuations, which provided a more complete framework to describe the present status of sediment quality in marsh-creek habitats and the current potential for toxic impacts and biological effects associated with metal-contaminated sediments of site-specific change over time. To varying extents, sediments from all systems demonstrated metal-specific inconsistencies with respect to surficial distributions over time and/or small-scale intra-spatial variations.

Although, of all study sites, Main Creek demonstrated the most evident intra-spatial variability with respect to small-scale environmental significance of Cd, Hg, Cu, and/or Zn surficial distributions, both Arthur Kill sites depicted a certain extent of site-specific temporal and/or spatial variations. Except for a few evident shifts in metal contents, explanatory factors

were considered relevant/applicable to both sites; and were likely attributable to: the relatively high sediment concentrations that were in-between the range of toxicity benchmark values applied to measure, or be indicative of greater threat of biological effects (i.e. ERM and PEL), and/or due to the more apparent small-scale fluctuations reflected in 2009 metal distributions, in which may have possibly been on account of the greater areal reach studied. In contrast to the Arthur Kill sites, relatively minor and generally consistent environmental significance of metals was identifiable in Lemon Creek sediments from temporal and spatial datasets spanning the past decade, and as recently examined, laterally, extending from the upland marsh to the Raritan Bay).

Given the different primary objectives of localized coring studies (conducted in 2001 and 2007) and the most recent transect study (2009), which aimed to evaluate a larger spatial extent of each marsh-creek system, it was expected that discrepancies among study designs and methods would be reflected as temporal variations, but were considered fundamentally attributed to the different events. Although a possible factor in site-specific temporal comparisons, with respect to past and contemporary conditions, the disparate study designs (i.e. different number of locations and samples analyzed) did not limit or affect comparisons among sites.

With the exception of mean Zn determined at Lemon Creek in 2001, surface sediments from all sites reflected concentrations of all study metals that were above TEL and ERL. Given that mean Cd, Hg, Cu, and Zn values detected in Main Creek, Neck Creek and Lemon Creek surface sediments surpassed ERL guidelines, it was evident that over the past decade, except for 2001 assessments at Lemon Creek, all marsh-creek habitats posed at least a low, if not greater, threat of biological effects on benthic organisms. Furthermore, this finding suggested site-specific likelihood of metal-specific sediment toxicity may be directly correlated with the degree

of anthropogenic metal contamination; which has compromised sediment quality throughout the study area and continues to threaten the ecological integrity of these marsh-creek habitats.

For all years, all metals were within the PEL or ERM range at Main Creek; maximum Cd and Zn were detectable at levels higher greater than PEL, mean Hg was detectable above ERM, and Cu values were found above ERM in 2/3 surveys (2001 and 2009). Of all sites, Neck Creek demonstrated the most temporal variability with respect to the number of metals above PEL or ERM; ranging from 4/4 to 1/3 in 2007 and 2001, respectively. However, similar to Main Creek, mean surficial Hg values were consistently above ERM, and Cu was either greater than PEL or ERM in all surveys. Conversely, Cd and Zn contents greater than PEL were limited to the 2007 dataset.

Contrary to both Main Creek and Neck Creek, no metals were detectable near ERM and Cu was the only metal that reached concentrations above PEL at Lemon Creek. For example, the most recent surveys (2009 and 2007) measured consistent Cu means (130.59 and 140.48, respectively), which were above PEL (108) but, levels were still about half of ERM (270)

Based on PEL/ERM values, with respect to likelihood of potential incidence of toxicity, Hg was consistently high at Main Creek and Neck Creek, moderate to high estimated risk was identified with detectable Cu levels at both Arthur Kill sites. In addition, Main Creek and Neck Creek reflected Cd and Zn within the range of moderate, and low to moderate probability of occurrence, respectively. In contrast, except for a low to moderate level of expected effects for Cu, all other metals (Cd, Hg, and Zn) at Lemon Creek were relatively low according to TEL/ERL values.

Based on potential toxicity with respect to Hg, coastal environments along the Arthur Kill are likely subject to an additional source(s) of Hg (i.e. localized atmospheric, tidal exchange, legacy contamination, and runoff). Given that Cu was the only metal to exceed PEL values at Lemon Creek may be implicative of localized watershed contributions of Cu-specific inputs. However, the temporal consistency of Cu exceedances was suggestive of widespread enrichment due to regional anthropogenic activities (Hwang et al. 2006;).

With the exception of mean surficial Zn concentrations observed at Lemon Creek in baseline studies, average sediment metal contents detected from all sites over time were greater than TEL and ERL.

Altogether, comparisons of Cd, Hg, Cu, and Zn contents to metal-specific toxicity indices estimated the current environmental significance/implications/threat of metals decreased at Main Creek, Neck Creek and Lemon Creek, respectively. In contrast to the significant difference in extent (occurrence and severity) of toxicity observed among Lemon Creek and Arthur Kill marshes (based number of metals above PEL and lack of ERM exceedances), the degree of sediment quality impacts characterized at Main Creek and Neck Creek were relatively similar. Although current condition/quality of sediments throughout the study area suggested ecological risk may be highest at Main Creek, site-specific differences with respect to Neck Creek were limited, generally on account of insignificant temporal variations of metal-specific concentrations. The reverse was apparent in 2007.

In general, empirical assessment of site-specific surficial sediment datasets analyzed from the two coring studies (2001 and 2007) and transect study (2009)], suggested that temporal and spatial variability had minimal affect on the ecological significance of Main Creek, Neck Creek

and Lemon Creek metal concentrations, based on the multiple toxicity benchmarks applied in this study. Despite a few cases, the estimated potential for metal-specific effects to occur at Main Creek, Neck Creek and Lemon Creek, due to respective levels of mean Cd, Hg, Cu, and Zn observable over the past decade, generally remained within the range of values from either set of toxicity benchmarks that are indicative of high-moderate probability (ERM/PEL) or lower-no probability (ERL/TEL). Therefore, intra-spatial temporal and spatial differences had relatively little influence on the overall ecological significance of metals, in terms of sediment quality impacts, measured by extent of contamination and potential for toxicity.

In contrast to the evident difference in the occurrence and severity of toxicity observed between Lemon Creek and both Arthur Kill marshes (based number of metals above PEL and lack of ERM exceedances), the difference between Main Creek and Neck Creek was negligible. Although Cd concentrations did not exceed ERM at Main Creek or Neck Creek, the quantity of elements identifiable at sediment concentrations above PEL, and the relatively higher ratio to applicable SQGs (as reflected by the magnitude of individual and collective metrics) implied that Main Creek and Neck Creek sediments may illicit comparatively greater biological effects in benthic species than Lemon Creek in terms of occurrence and severity of toxicity, which in turn may pose more severe habitat impacts and cascading ecological implications. It follows that toxic units (TU), which reflect the ratio of the observed mean metal concentration and the respective toxicity reference value (i.e. ERL, PEL, ERM value), were considerably higher at the Arthur Kill sites; where they were greatest for all metals at Main Creek or Neck Creek, depending on survey year/dataset and benchmark value applied.

Collective Empirical Sediment Quality Assessment

In order to represent the collective presence of all study metals, individual TUs were totaled to determine TU sum, and averaged to calculate mean sediment quality guideline quotients (mean SQGQs). Accordingly, these combined values (i.e. PEL quotient, ERM quotient, and ERL quotient) incorporated the number and magnitude of which metals exceeded respective SQGs, providing an empirical means to collectively characterize sediment quality, in terms of potential toxicity, and discern large-scale geographic variability over time (Sprague, 1970; Pederson, et al., 1998; Barrett, et al., 2007).

Toxic Unit (TU)

Individual study elements were normalized to respective numerical sediment quality guidelines (SQGs), including ERL (Effects range low), Probable Effect Level (Lower limit of the range of concentrations at which adverse effects are always observed), and ERM (Effects range median) for quantification of metal-specific toxic units (TU). The derivation of Main Creek, Neck Creek and Lemon Creek TU values was achievable via normalization of detectable Cd, Hg, Cu, or Zn concentrations to the sediment quality guideline associated with each metal. Site-specific TU values depended on the element and respective benchmark category applied (i.e. PEL, ERM, or ERL) which in turn, influenced the combined metric. When Hg analysis was included in geochemical examination of surface sediments in 2007, it ranked the highest of all elements in terms of TU at both Main Creek and Neck Creek. Accordingly, it was apparent that for the Arthur Kill sites, TU values for Hg contributed to the majority of collective values that reflected contamination with respect to all study metals. In contrast, Cu demonstrated the greatest TU and measured the largest fraction of the total or sum of toxic units at Lemon Creek.

TU SUM and Mean SQGQ

The potential for surface sediments to illicit toxicity due to the collective impact of all metals studied (Cd, Hg, Cu, and Zn) was determined via Sum TU and mean Sediment Quality Guideline Quotients (SQGQ). The combination of all individual toxic units (TU), or ratio of mean (observed) sediment concentration (Cd, Hg, Cu, or Zn) to an effect-based reference value (i.e. PEL, ERM, or ERL) quantified site-specific values for TU sum and mean SQGQs (ERM Q) and PEL Quotient (PEL Q). These are also used to predict stress in benthic invertebrate communities (Hyland, et al., 2002). Such collective measures further established the geographic and temporal extent of sediment quality and correlated metal contamination and potential toxicity.

Toxic unit sum, (TU Sum) and mean sediment quality guideline quotients (mean SQGQs) were determined via the addition and average of individual TUs recorded for individual metals analyzed at each site. Like TU Sum, mean SQGQ, calculated in terms of PEL (PEL Q), ERM (ERM Q), and ERL (ERL Q), accounted for the presence of multiple contaminants mixed within collected surface sediments. In addition, mean SQGQs, incorporated the number, and severity of SQGs exceedances which, along with type of benchmark, has shown to affect capacity of these metrics to provide an accurate prediction of acute toxicity to amphipods in laboratory and field toxicity studies (Fairey, et al., 2006).

The sum of toxic units (TU), which represents the ratio of individual mean metal concentrations to the respective toxicity reference value (i.e. ERL, PEL, ERM value), was considerably higher at the Arthur Kill sites compared to Lemon Creek. Accordingly, TU Sum also varied according to site and reflected the number of metals (4 in 2009 and 2007; 3 in 2001), type of benchmark (i.e. PEL, ERM, ERL) and elements included in surficial datasets (Cd, Cu,

and Zn measured in all datasets; Hg not analyzed in 2001). Regardless of the benchmark value applied, the greatest TU sum (i.e. PEL or ERM ratio) was identifiable with either Main Creek or Neck Creek, depending on survey year/dataset. For example, although the highest sum of toxic units (TU) (i.e. PEL ratio), was reflected by Main Creek in 2/3 surveys (5.67 and 5.20 in 2009 and 2001, respectively), overall (with respect to all sites and studies), Neck Creek demonstrated the greatest value (7.75) in 2007. In contrast, Lemon Creek consistently reflected the lowest TU sum regardless of the survey year (2.59, 2.49, 1.8 in 2009, 2007, and 2001, respectively) or toxicity value referenced (i.e. TU Sum (ERM ratio) ranged from 1.42- 0.85).

SQGQ Benchmark Quotients

Mean Sediment Quality Guideline Quotients (SQGQ) (i.e. mean PEL quotient and/or mean ERM quotient) (Long, et al., 1990; Long, et al., 1995) were used to evaluate the collective degree of site-specific marsh sediment contamination and empirically determine sediment quality in relation to expected incidence of toxicity and the number and/or degree to which SQGs values were exceeded. It was noteworthy that in general, PEL quotients (1.73- 1.42 at MA; 1.04-1.94 at Neck Creek; and 0.60-0.65 at Lemon Creek) were not significantly different over time; also, with the exception of the 2007 NC ERM Quotient (1.22 compared with 0.69 in 2009 and 0.53 in 2001) site-specific ERM quotients (1.06-0.82 at MA and 0.36-0.21 at Lemon Creek) were generally consistent. This confirmed temporal consistency in terms of the ecological significance of Main Creek, Neck Creek and Lemon Creek metal contamination, despite any inconsistencies in sampling or small-scale/large-scale variability.

Furthermore, SQGQs also demonstrated comparability between the Arthur Kill sites, and significant variability with respect to Lemon Creek, particularly between Main Creek and Lemon Creek. Although Lemon Creek TU Quotients were notably uniform over time, it was apparent

that both the ERM Quotient and PEL Quotient were the highest in 2009, whereas in 2001, these respective parameters were the lowest. In contrast to Lemon Creek, the highest ERM Quotient determined for Main Creek and Neck Creek aligned with the 2007 datasets. However, evident variability with respect to SQGQ calculated at Main Creek and Neck Creek over time resulted in inconsistencies among temporal trends depicted by site-specific values derived for PEL Q and ERM Q. Although, maximum temporal PEL Quotients occurred at Main Creek in 2001 and at Neck Creek in 2007, in 2009 both Arthur Kill sites reflected the minimum PEL Q values.

Mean ERM Quotient Assessment

Although mean SQGQs incorporate both the number of SQGs exceeded and the degree to which they are exceeded, and are used for comparison with observed biological effects in the laboratory or field, the number and type of SQGs used can affect their capacity to predict acute toxicity to marine amphipods in laboratory toxicity tests (Long et al. 2006., Fairey et al. 2001). The most commonly applied measure to assess the presence and extent of sediment quality degradation is the mean ERM Quotient (mERMQ) (Long, et al. 1998). Accordingly, mERMQ values were used to predict and compare sites in terms of the presence and absence of toxicity and benthic community degradation.

Various studies have demonstrated the significance of the relationship between mERMQ and sediment toxicity and thereby validated the use of ERMQ values as an indicator to predicate acute sediment toxicity (Carr, et al., 1996; Thompson, et al., 1999; Thompson, et al., 2004; Fairey, et al., 2002; Thompson, et al., 2009). Accordingly, mERMQ values derived from Main Creek, Neck Creek and Lemon Creek datasets were compared with mERMQ classification ranges (Long, et al. 1998) to classify and describe successive categories of acute toxicity to benthic organisms (i.e. amphipods). Although no sites exhibited mERMQ values that predicted a

high potential for acute toxicity to benthic organisms for all years, a moderate-high risk level of acute toxicity was implicated by both Main Creek (.82-1.06) and Neck Creek (.53-1.22) mERMQ values. In contrast, Lemon Creek surface sediments exhibited mERMQ values within the range indicative of low-moderate acute toxicity. Although Lemon Creek sediments depicted consistency, in that the results were qualitatively described as within the Level II/low-moderate range, temporal mERMQ values increased from 0.21, 0.33, to 0.36 in 2001, 2007, and 2009 respectively, which suggested relatively greater toxicity in over the past decade.

Chronic toxicity impacts have also been associated with mERMQ values. In general, values below 0.02 are indicative of a low risk of stress to benthic organisms. ERMQ values above 0.02 are successively predictive of an increasingly greater incidence of benthic habitat degradation; mERM Q within the range of 0.021- 0.058 suggest a moderate risk, whereas values above 0.058 represent a high risk of benthic impacts (Hyland et al. 2002, Thompson et al. 2004, Thompson et al. 2009). Over the past decade, Main Creek, Neck Creek and Lemon Creek mERMQ values aligned within the following respective ranges: 0.82- 1.06, 0.53-1.22, and 0.21-.36, which were indicative of high risk of benthic impacts. Although for all years Main Creek, Neck Creek and Lemon Creek sediments demonstrated ERMQ values that represented a high risk to benthos.

Given that effect-based empirical sediment quality values were used as intended, for screening potential toxicity, it is important to recognize that objectives of this research component were to fundamentally indicate ecological hazards (necessitating/requiring further study) and not to implicate metal-specific ecotoxicological risk or causative relationships among effects and metal-specific thresholds. Furthermore, environmental threat may be underestimated considering the pervasive contamination associated with Arthur Kill marshes and regionally. [Note that both Raritan Bay and the Arthur Kill are “Impaired 303d listed Waterways” with

respect to metals on the 303b.] (Berger, 1994; USACE, Steinberg, et al., 2004; NOAA ST; NYSDEC 2009, NJDEP 2011).

The potential incidence of sediment toxicity did not account for synergistic interactions among the study metals or consider the combined effects associated with the presence of additional pollutants, including metals and organic contaminants, which are prevalent throughout the NY/NJ Harbor Estuary and are particularly of concern in marshes along the Arthur Kill (Berger, 1994). Therefore, the ecological threat of contaminated sediments and the geographic disparate quality of marsh sediments (characterized by the extent of variation of mean surface metal concentrations relative to background indices (theoretical SQV) and toxicity benchmarks (empirical SQV) may be underestimated. Further biological and chemical tests and analyses are essential for appropriate assessment and management of risks associated with sediment contamination (NYSDEC, 1999). Community structure and function, which may be more sensitive to sediment contamination, should be integrated into future research agendas and should incorporate experimental sediment toxicity studies and consider that community structure and function may be more sensitive to sediment contamination (Delta).

Geographic Impact Gradient

Collective assessment of the quality of Main Creek, Neck Creek and Lemon Creek sediments in terms of all study metals (Cd, Hg, Cu, and Zn) via mean ERM/PEL (TU) Quotients, clearly defined a large-scale/geographic impact gradient with respect to potential for toxic effects, which aligned with assumptions based on large-scale spatial and temporal trends described by site-specific PLI values.

Collectively, metal-specific theoretical (i.e. EF, CF) and empirical sediment quality (i.e. TEL, ERL, PEL, ERM) assessment techniques associated comparatively lower sediment quality in relation to Main Creek and Neck Creek in terms of greater magnitudes of site-specific temporal contamination (PLI) and potential incidence of biological effects/toxicity in sediment dwelling species (mean PEL/ERM Quotient), than characterized at Lemon Creek. Estimated likelihood of exposure to metal contaminated marsh sediments to illicit toxic implications decreased at Main Creek, Neck Creek and Lemon Creek, respectively. However, relative to Lemon Creek, demonstrably greater sediment quality impacts were expected for the Arthur Kill sites with respect to potential occurrence and severity.

The evident large-scale variability of marsh sediment quality, in terms of the relative degree of toxic risks and ecological implications identified with the magnitude of contaminated sediments characterized across the study area, did not change over time, but rather consistently reflected a demonstrable geographic impact gradient. Comparatively, in all years, greater relative threat/risk was associated with Main Creek and Neck Creek due to more severely degraded quality of marsh sediments than observed at Lemon Creek. Thereby, the extensive anthropogenic sediment contamination identifiable with the Arthur Kill marshes was expected to elicit far greater and severe toxic implications than anticipated at Lemon Creek.

Accordingly, large-scale impact gradients were comparatively consistent over time. Based on comparative assessment of site-specific mean element concentrations (2001, 2007 and 2009) to the above-mentioned toxicity benchmarks, the likelihood for biological effects and relative degree of potential risks to benthic species due to contaminated sediments from Main Creek and Neck Creek sediments were expected to be far greater (strong/high probability vs. low probability of toxic impacts) than estimated at Lemon Creek.

CONCLUSION

Large and small-scale metal concentration datasets obtained from chemical analysis of depth and surface samples collected from Main Creek, Neck Creek and Lemon Creek provided a comprehensive spatial and temporal context/framework to examine the current condition of sediment and habitat quality throughout the study area. Although toxicity tests/assays were beyond the scope of the study, an aggregate of reference values (i.e. global and regional background and effect-based biological indices) proved useful for characterizing the extent of anthropogenic contamination, metal pollution loads and potential toxicity of sediments at each site. Accordingly, the environmental significance of metal concentrations and quality of sediments at depth and surface layers was determined via theoretical and empirical assessment methods, in terms of magnitude of contamination and potential toxicity, to assess the severity of human-induced impacts and ecological implications that may affect marsh habitats over the extent of the study area.

ERL exceedances were common throughout the study area on spatial and temporal scales. Specifically, Main Creek, Neck Creek and Lemon Creek surface sediments reflected mean metals (Cd, Hg, Cu, and Zn) concentrations that were at least greater than ERL in all instances except for surficial Zn contents in baseline Lemon Creek sediments (2001). However, it was apparent that while Lemon Creek increased in terms of all sediment quality indices, both Main Creek and Neck Creek decreased. Thereby, the greater contamination and potential incidence and severity of Lemon Creek sediments (mainly Cu pollution) apparent over the past decade implicated a localized, rather than a regional/endemic disturbance (anthropogenic or natural). Beyond the expected intra-marsh temporal variability anticipated on account of differences among surveys (due to necessary modifications to sampling design/methods

according to specific objectives) attributable to variable sample sizes and areal extent examined within Main Creek, Neck Creek and Lemon Creek overall, observed temporal changes were minor with respect to site-specific sediment quality in terms of magnitudes of sediment contamination or potential toxicity.

Although, to a certain degree potentially toxic levels of metals were observable in all marshes, in terms of effects based indices, there was also evident large-scale spatial impact gradient with respect to metal contaminated surface sediments. Lemon Creek, located on Staten Island's south shore along the Raritan Bay, was the "cleanest" site based on empirical SQGs. In contrast to Main Creek and Neck Creek sediments, Lemon Creek sediments did not demonstrate detectable levels of any metals above ERM, and PEL exceedances were limited to Cu. The consistency, extent, and higher frequency in which metals within Main Creek and Neck Creek sediments, particularly Hg and Cu, were observable at concentrations greater than effect-based thresholds, implicated greater incidences of biological effects may occur due to the more severe degradation of sediment quality within the Arthur Kill marshes. Accordingly, occurrence of sediment quality degradation and impacts was associated with geographic proximity to the Arthur Kill, with the farthest/most distal study site, Lemon Creek, reflecting the lowest magnitude of metal contamination and toxicity potential.

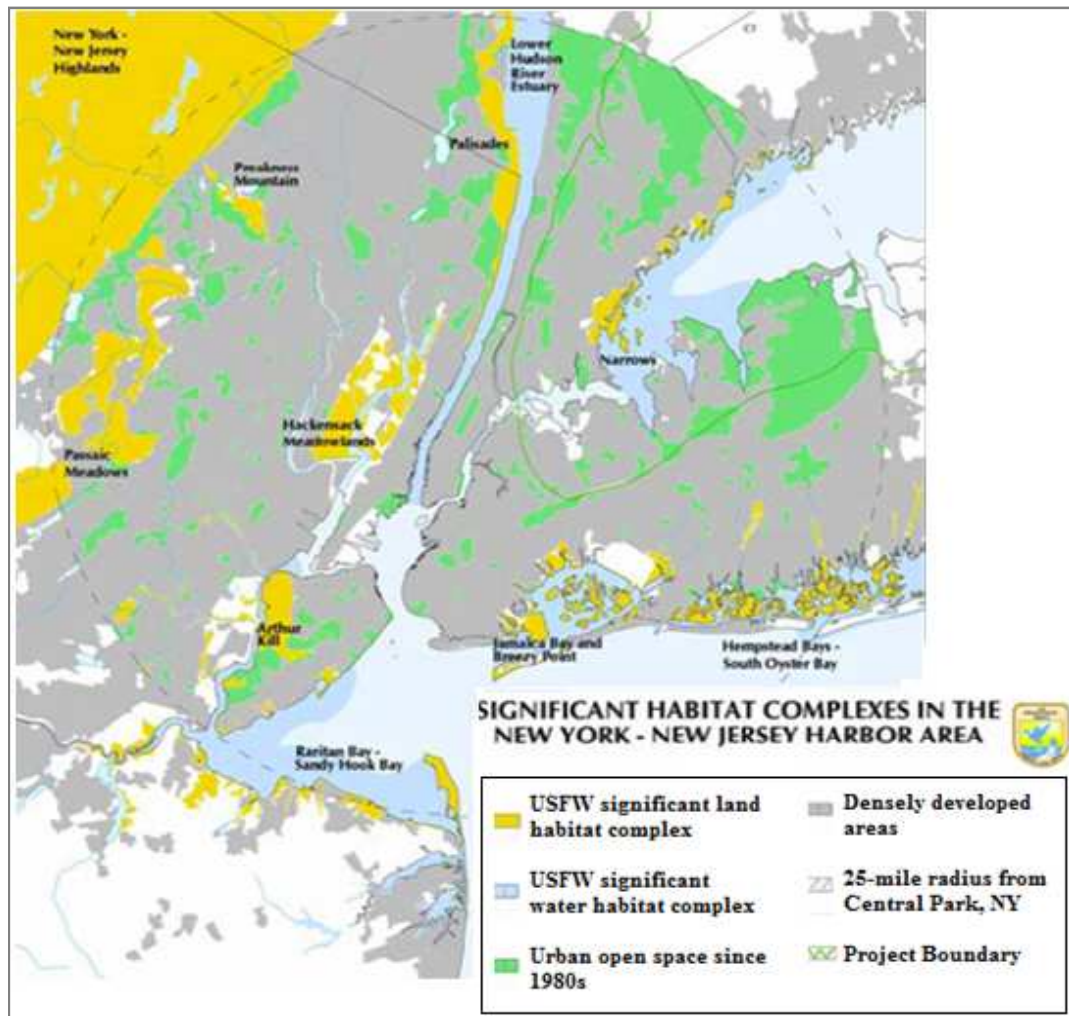


Figure 5-1. Significant habitat complexes within the New York-New Jersey Harbor Estuary (NY/NJ HE). Map depicts present-day urban open space and significant water and land habitat complexes (NFWS 2007, USACE 2009).

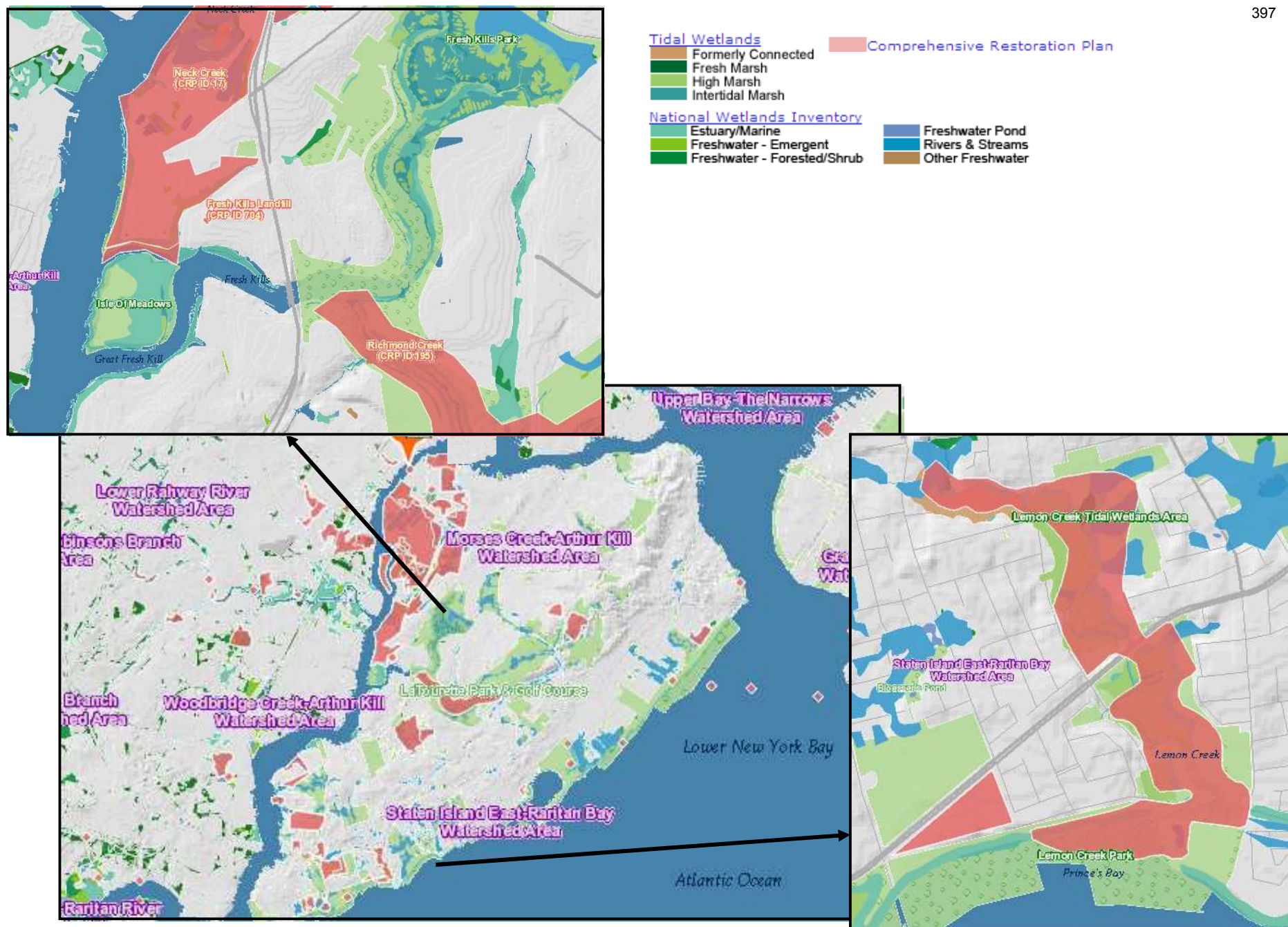


Figure 5-2. Marsh study sites and NY/NJ HE Comprehensive Restoration Management Plan sites (CCMP 2010, Oasis NYC 2011).

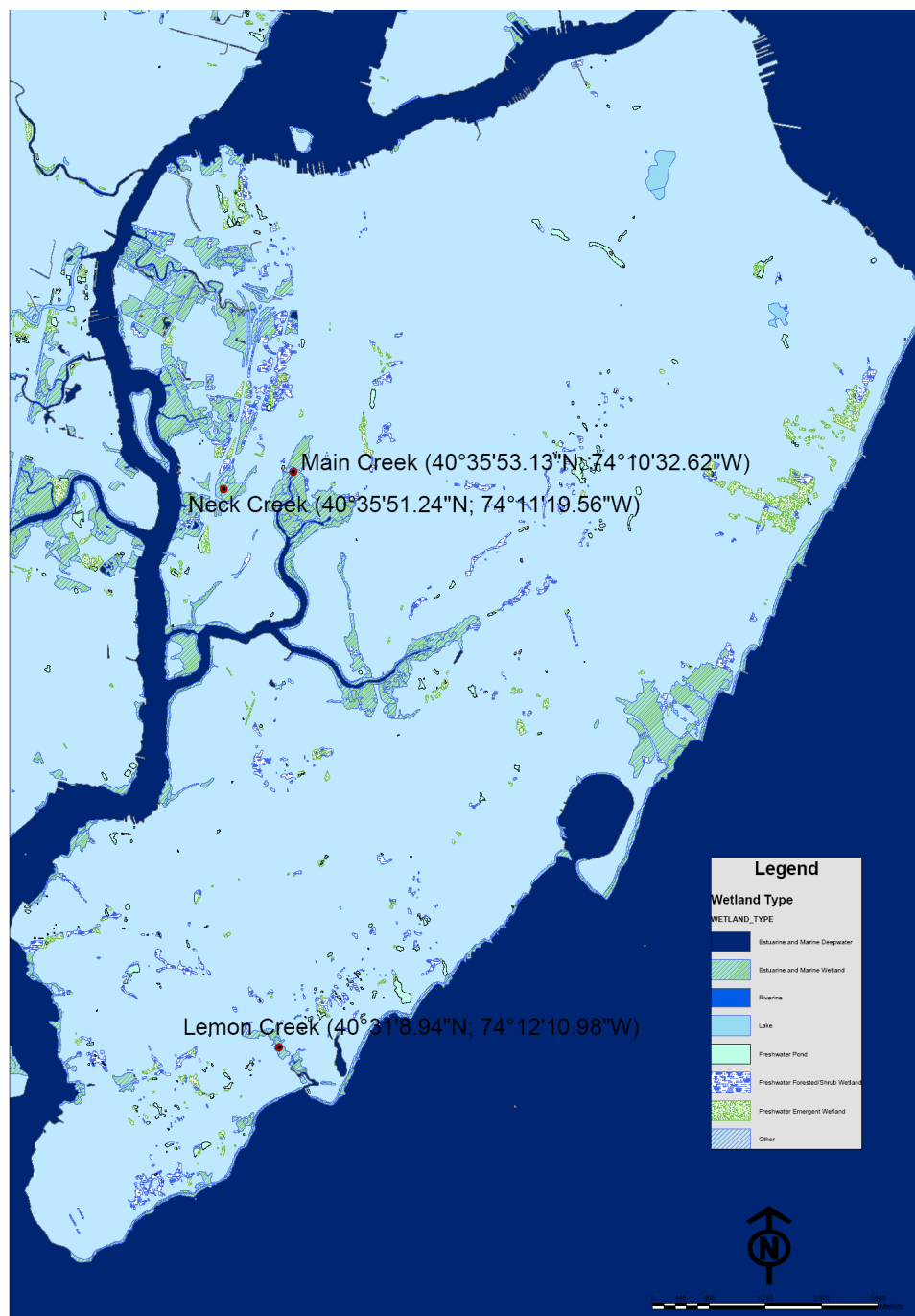


Figure 5-3. Geographic extent of study area and marsh locations. Situated along the western (MA and NC) and southern (LC) shores of Staten Island, all three marsh-creek systems are classified as estuarine wetlands and exchange water with open waters of the New York/New Jersey Harbor Estuary (NY/NJ HE). MA and NC are tidally influenced by the Arthur Kill, located in the mid-western portion of the NY/NJ HE system, and LC drains into the Eastern Raritan Bay watershed.

Table 5- 1a. Mean and range of Cd, Hg, Cu, and Zn in MA, NC and LC surficial sediment samples (2009).

	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)		Hg ($\mu\text{g}\cdot\text{g}^{-1}$)		Cu($\mu\text{g}\cdot\text{g}^{-1}$)		Zn($\mu\text{g}\cdot\text{g}^{-1}$)	
Study Site/ Year	Range	Mean	Range	Mean	Range	Mean	Range	Mean
MA 2009	1.30 $\pm$ 0.03-5.04 $\pm$ 0.29	3.57	0.03 $\pm$ 0.0-2.44 $\pm$ 0.08	1.26	44.8 $\pm$ 4.99-353 $\pm$ 22.1	229	119 $\pm$ 4.06-322 $\pm$ 0.08	243
NC 2009	2.41 $\pm$ 0.41-1.82 $\pm$ 0.06	1.84	0.64 $\pm$ 0.01-1.55 $\pm$ 0.04	1.14	100 $\pm$ 54.6-249 $\pm$ 0.0	165	105 $\pm$ 45.2-185 $\pm$ 0.0	152
LC 2009	1.37 $\pm$ 0.01-1.99 $\pm$ 0.04	1.62	0.07 $\pm$ 0.0-0.34 $\pm$ 0.0	0.24	112 $\pm$ 8.8-151 $\pm$ 2.8	131	161 $\pm$ 1.97-191 $\pm$ 29.2	177

Metal-specific concentrations reflect minimum and maximum $\pm$ standard error (S.E.). For each study site, mean Cd, Cu, and Zn concentrations were determined from the average of lateral surficial metal concentrations (n=54). Mean metal contents for Main Creek, Neck Creek, and Lemon Creek transects were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure

Table 5-1b. Mean and range ($\pm$ S.E.) of metal concentrations in 2001 and 2007 surface sediments.

Study Site/Year	Range	Mean	Study Site/ Year	Range	Mean
Main Creek 2001	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)		Main Creek 2007	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	
	4.57-6.02 $\pm$ 0.34	5.18		5.08-6.27 $\pm$ 0.35	5.62
	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)			Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	
	N/A	N/A		1.41-1.43 $\pm$ 0.01	1.42
	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)			Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	
	275-333 $\pm$ 13.5	294		265-250 $\pm$ 5.22	255
	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)			Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	
	320-366 $\pm$ 10.6	337		280-301 $\pm$ 5.99	291
Neck Creek 2001	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)		Neck Creek 2007	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	
	2.33-3.21 $\pm$ 0.2	2.82		3.92-4.46 $\pm$ 0.36	4.52
	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)			Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	
	N/A	N/A		1.77-1.84 $\pm$ 0.02	1.79
	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)			Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	
	223-253 $\pm$ 6.15	239		316-402 $\pm$ 28.63	345
	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)			Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	
	157-178 $\pm$ 5.09	167		208-294 $\pm$ 25.6	245
Lemon Creek 2001	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)		Lemon Creek 2007	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	
	2.01-2.58 $\pm$ 0.12	2.37		0.92-1.47 $\pm$ 0.16	1.21
	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)			Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	
	N/A	N/A		0.19-0.20 $\pm$ 0.001	0.19
	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)			Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	
	41.5-137 $\pm$ 25.2	91.3		101-193 $\pm$.0	141
	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)			Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	
	54.2-163 $\pm$ 23	108		141-219 $\pm$ 24.7	170

Metal-specific concentrations reflect minimum and maximum $\pm$ standard error (S.E.). For each study site, mean Cd, Cu, and Zn concentrations were determined from the average of mean surface (0-2cm) metal concentrations (n=3). Table reflects acquired datasets from 2001 and 2007 sampling at Main Creek, Neck Creek, and Lemon Creek, which included sediment samples collected from localized coring locations within each site (n=3) that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

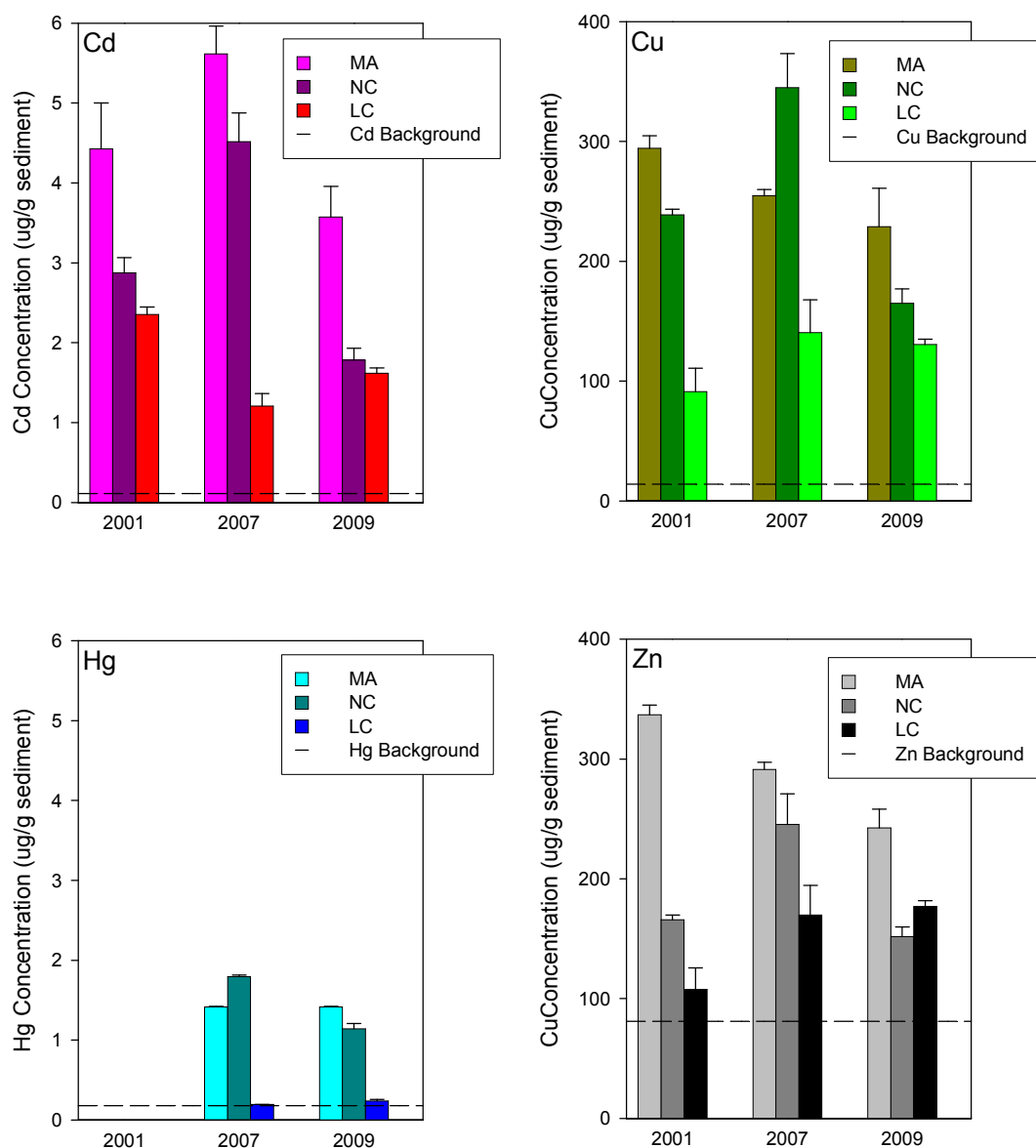


Figure 5-4. Metals in surface sediments at Staten Island marsh sites: 2001, 2007, 2009. Figure reflects inter-marsh variability of temporal Cd, Hg, Cu, and Zn concentrations. Vertical bars represent mean metal-specific surface sediment concentrations ($\pm$ S.E.) at Main Creek, Neck Creek, and Lemon Creek from 2001, 2007, and 2009 datasets, respectively.

Table 5-2. Regional Enrichment Factors (EF) in Main Creek, Neck Creek, and Lemon Creek surface sediments 2001, 2007, 2009.

Main Creek	EF Cd	EF Hg	EF Cu	EF Zn		Neck Creek	EF Cd	EF Hg	EF Cu	EF Zn		Lemon Creek	EF Cd	EF Hg	EF Cu	EF Zn
2009	31.48	7.02	15.32	2.96		2009	17.31	6.34	12.50	1.93		2009	14.60	1.36	9.28	2.17
2007	51.09	7.87	18.18	3.59		2007	18.73	9.96	22.47	2.91		2007	10.91	1.08	10.03	2.10
2001	47.09	N/A	3.36	4.16		2001	25.64	N/A	17.05	2.05		2001	21.55	N/A	6.52	1.33

Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996 and Bowen et al. 1979). In 2009, site-specific mean Cd, Hg, Cu, and Zn concentrations were determined from the average of lateral surficial metal concentrations (n=54). 2007 and 2001 mean surface sediment values reflect average of surface (0-2cm) samples from each site (n=6).

Table 5-3. Mean surface sediments (2009): Enrichment Factors vs. Contamination Factors for averaged surface sediment transect samples

Site	EF Cd	CF Cd	EF Hg	CF Hg	EF Cu	CF Cu	EF Zn	CF Zn
MA	31.48	11.54	7.02	7.9	15.32	4.77	2.96	2.53
NC	17.31	6.35	6.34	7.13	12.50	3.89	1.93	1.65
LC	14.60	5.35	1.36	1.53	9.28	2.89	2.17	1.85

Relative extent of anthropogenic metal pollution reflected by Main Creek, Neck Creek, and Lemon Creek surface sediment samples (2009). Mean metal contents for 2009 dataset reflects Main Creek, Neck Creek, and Lemon Creek transects were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure. Literature-based regional and global proxies for natural background sediment concentrations were derived from Hudson River (Hirschberg et al. 1996 and Bowen 1979) and worldwide average elemental Cd, Hg, Cu, and Zn contents found in shale (Wedpohl et al. 1968).

Figure 5-5a.

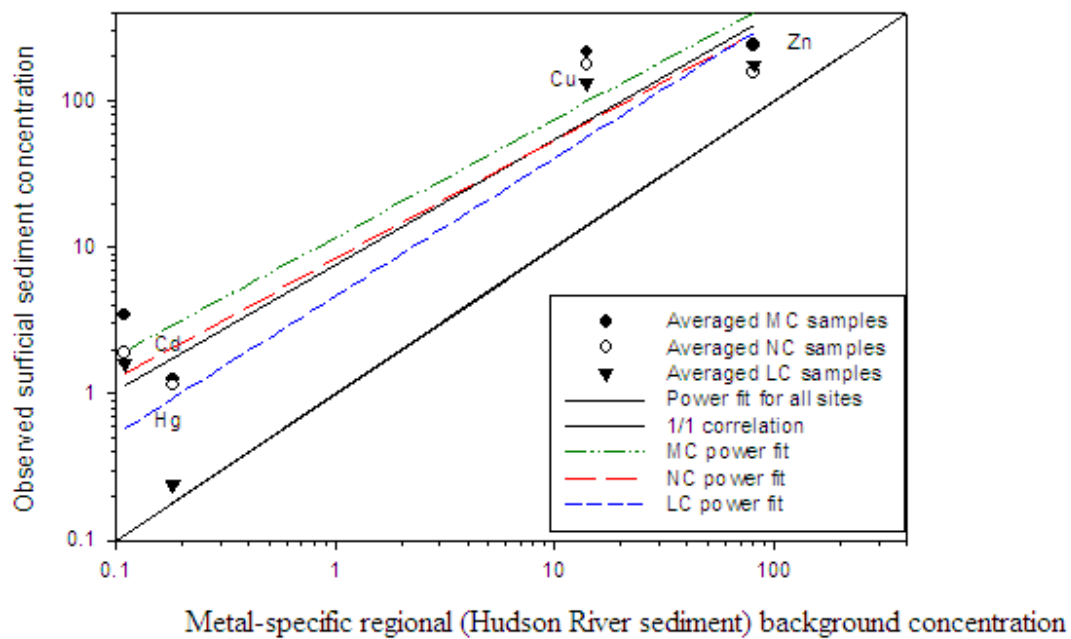


Figure 5-5b.

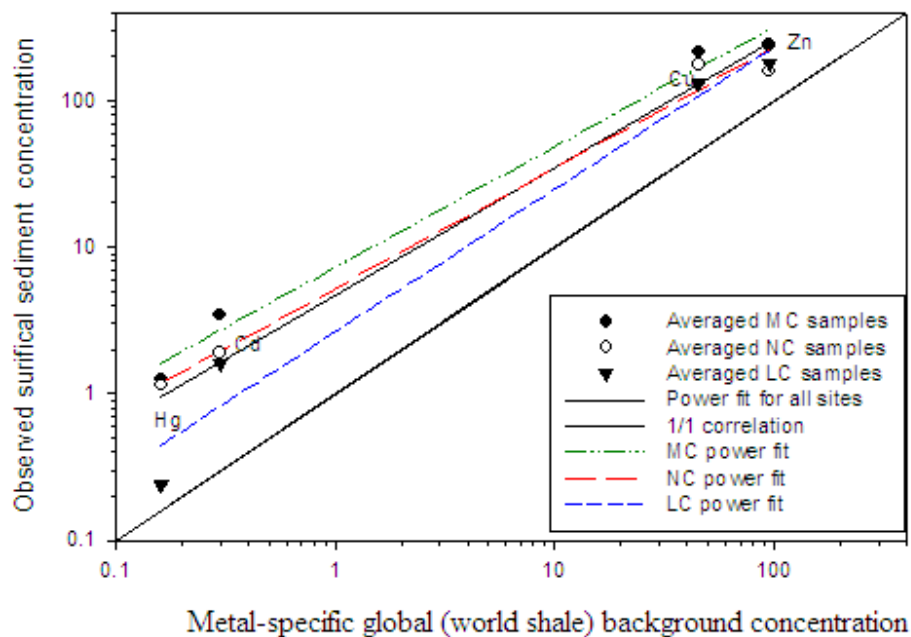
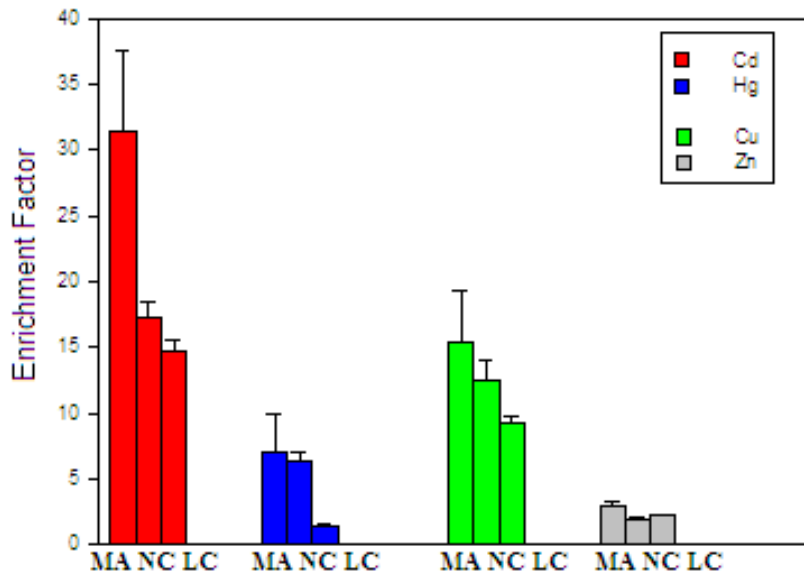


Figure 5-5a-b. MA, NC, and LC mean surface sediment concentrations (log scale) in relation to (a) regional background and (b) global mean shale background concentrations. Literature-based regional and global proxies for background concentrations based on natural levels of Cd, Hg, Cu, and Zn found in Hudson River sediments (Hirschberg et al. 1996 and Bowen 1979) and worldwide average elemental shale contents found (Wedpohl et al. 1968).

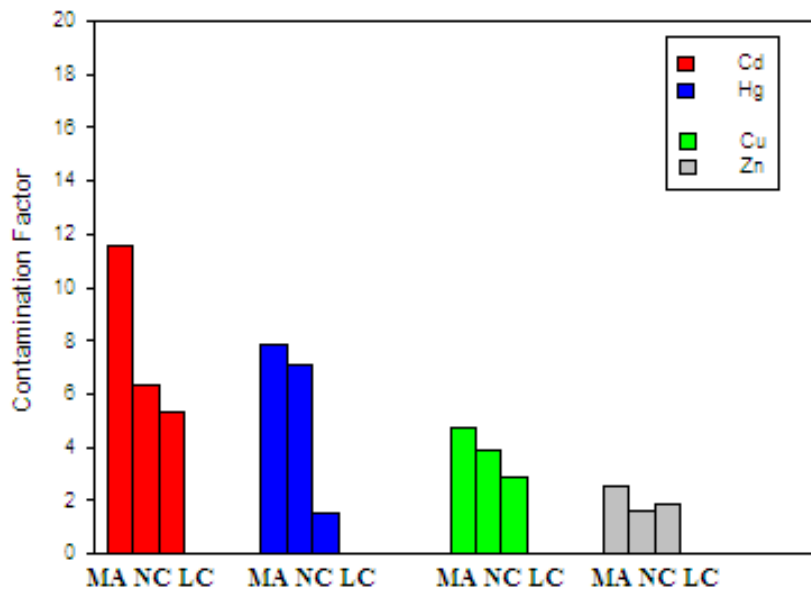
EF of surface sediments at Staten Island marsh sites.



(n=54). Mean metal contents for Main Creek, Neck Creek, and Lemon Creek transects were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

Figure 5-6a. Large-scale variability and extent of present-day (2009) anthropogenic contamination using EFs. Large-scale variability and extent of present-day (2009) metal-specific sediment contamination, in terms of MA, NC, and LC enrichment factors (EF), derived from site-specific mean surficial Cd, Hg, Cu, and Zn distributions relative to respective regional background values (theoretical SQG). Enrichment factors calculated using Hudson River sediment background concentrations (Hirschberg et al. 1996 and Bowen et al. 1979). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations

CF of surface sediments at Staten Island marsh sites.



metal contents for Main Creek, Neck Creek, and Lemon Creek transects were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

Figure 5-6b. Large-scale variability and extent of present-day (2009) anthropogenic contamination using CFs. Graph depicts metal-specific sediment contamination, in terms of MA, NC, and LC contamination factors (CF) derived from site-specific mean surficial Cd, Hg, Cu, and Zn distributions relative to respective global background values (theoretical SQG). Contamination factors calculated using global world shale sediment background concentrations (Wedpohl et al. 1968). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations (n=54). Mean

Table 5-4a. Contamination factor (CF), risk level of contaminants, contamination degree (CD) and pollution degree in MA, NC, and LC (2001, 2007, and 2009).

Contamination factor (CF)		Associated Risk Level of contaminants
CF Range	CF Level	Description
CF<1	Low	indicative of low metal-specific sediment contamination
1<CF<3	Moderate	indicative of moderate metal-specific sediment contamination
3< CF <6	Considerable	indicative of considerable metal-specific sediment contamination
CF ≥ 6	Very High	indicative of very high metal-specific sediment contamination
Contamination degree (CD)		Magnitude of Contamination
CD Range	CD Level	Description
CD<7	Low	unpolluted/minimal degree of anthropogenic contamination
7< CD <14	Moderate	moderate degree of contamination
14< CD < 28	Considerable	considerable degree of contamination
CD ≥ 28	Very High	very high degree of contamination indicating serious anthropogenic pollution

Table 5-4b. Mean contamination factors and contamination degree for surface datasets (2001; 2007; 2009).

Study Site	Survey Year	Metal-Specific Contamination Factors								Contamination Degree (CD)	
		Cd		Hg		Cu		Zn			
Main Creek	2009	11.5	Very High	7.90	Very High	4.77	Considerable	2.53	Considerable	26.7	Considerable
	2007	18.7	Very High	8.86	Very High	5.66	Considerable	3.06	Considerable	36.3	Very High
	2001	17.3	Very High	N/A		6.54	Very High	3.54	Considerable	27.4	Considerable
Neck Creek	2009	6.35	Very High	7.13	Very High	3.89	Considerable	1.65	Moderate	19.0	Considerable
	2007	15.1	Very High	11.2	Very High	7.66	Very High	2.58	Moderate	36.5	Very High
	2001	9.4	Very High	N/A		5.31	Considerable	1.75	Moderate	16.5	Considerable
Lemon Creek	2009	5.35	Considerable	1.53	Moderate	2.89	Moderate	1.85	Moderate	11.6	Moderate
	2007	4.02	Considerable	1.21	Moderate	3.12	Considerable	1.79	Moderate	10.1	Moderate
	2001	7.90	Very High	N/A		2.03	Moderate	1.13	Moderate	11.1	Moderate

Relative extent of anthropogenic metal pollution reflected by Main Creek, Neck Creek, and Lemon Creek SPM and surface sediment samples via site-specific contamination factors (CF) and contamination degree (CD) determined from Staten Island marsh sediment datasets acquired in 200, 2007, and 2009.

Table 5-5 (abbreviated). Contamination Factors and PLI for mean surface sediments (2001; 2007; 2009).

Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	PLI	Mean PLI	PLI w/o Hg
2009	11.5	7.90	4.77	2.53	5.76	4.32	5.18
2007	18.7	8.86	5.66	3.06	7.32	7.32	6.87
2001	17.3	N/A	6.54	3.54		-	7.37
Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	PLI	Mean PLI	PLI w/o Hg
2009	6.35	7.13	3.89	1.65	4.13	4.10	3.44
2007	15.1	11.2	7.66	2.58	7.60	7.59	6.68
2001	9.4	N/A	5.31	1.75		-	4.43
Lemon Creek	CF Cd	CF Hg	CF Cu	CF Zn	PLI	Mean PLI	PLI w/o Hg
2009	5.35	1.53	2.89	1.85	2.57	2.50	3.05
2007	4.02	1.21	3.12	1.79	2.28	2.27	2.81
2001	7.90	N/A	2.03	1.13		-	2.63

Relative extent of anthropogenic metal pollution reflected by Main Creek, Neck Creek, and Lemon Creek SPM and surface sediment samples via site-specific contamination factors (CF) and contamination degree (CD) determined from Staten Island marsh sediment datasets acquired in 200, 2007, and 2009.

Table 5-5a. Contamination Factors and PLI for Mean Surface Sediments (2001; 2007; 2009). Comparison of mean surface sediment metal concentrations with average shale values: sum of metal-specific contamination factors (Contamination Degree) and the Pollution Load Index (PLI).

Study Site	Survey Year	Cd		Hg		Cu		Zn		CD	PLI			
		Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	CF	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	CF	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	CF	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	CF	Sum	Surface Mean	Calculated Mean ⁵	Surface Mean w/o Hg	Calculated Mean ⁵
MA	2009 ¹	3.57	11.5	1.26 ⁴	7.90	229	4.77	243	2.53	26.7	5.76	4.32	5.18	4.70
	2007 ²	5.62	18.7	1.42	8.86	255	5.66	291	3.06	36.3	7.32	7.32	6.87	6.87
	2001 ³	5.18	17.3	-	-	295	6.54	337	3.54	27.4	-	-	7.37	7.36
NC	2009 ¹	1.84	6.35	1.14	7.13	165	3.89	152	1.65	19.0	4.13	4.10	3.44	3.43
	2007 ²	4.52	15.1	1.79	11.2	345	7.66	245	2.58	36.5	7.60	7.59	6.68	6.87
	2001 ³	2.87	9.4	-	-	239	5.31	166	1.75	16.5	-	-	4.42	4.43
LC	2009 ¹	1.62	5.35	0.24	1.53	131	2.89	177	1.85	11.6 ⁴	2.57	2.50	3.05	3.06
	2007 ²	1.21	4.02	0.19	1.21	141	3.12	170	1.79	10.1 ⁴	2.28	2.27	2.81	2.82
	2001 ³	2.35	7.90	-	-	91.3	2.03	108	1.13	11.1 ⁴	-	-	2.63	2.58

¹Reflects mean of 18 samples analyzed in 2009 (3 samples from each of the 6 surface locations across each marsh-creek system).

²Reflects mean of 9 samples analyzed in 2007 (3 samples were analyzed from each of the 3 locations in 2007).

³Reflects mean of 12 samples analyzed in 2001 (4 samples were analyzed from each of the 3 locations in 2001).

⁴Represents Sum of Cd, Cu, and Zn CFs.

⁵Depicts the mean of individual PLIs calculated for each surface location within MA, NC, and LC.

Table 5-5b. Contamination Factors and PLI for mean core and mean surface Cd, Cu, and Zn concentrations (2001; 2007; 2009).

Main Creek (2009)	CF Cd	CF Cu	CF Zn	PLI¹	Neck Creek (2009)	CF Cd	CF Cu	CF Zn	PLI	Lemon Creek (2009)	CF Cd	CF Cu	CF Zn	PLI
Surface Mean (0-2cm)	11.5	4.77	2.53	5.18	Surface Mean (0-cm)	6.35	3.89	1.65	3.44	Surface Mean (0-2cm)	5.35	2.89	1.85	3.05
Main Creek (2007)	CF Cd	CF Cu	CF Zn	PLI	Neck Creek (2007)	CF Cd	CF Cu	CF Zn	PLI	Lemon Creek (2007)	CF Cd	CF Cu	CF Zn	PLI
Core Mean	21.7	6.5	3.36	7.81	Core Mean	11.1	11.1	2.47	6.71	Core Mean	5.13	3.54	1.94	3.28
Surface Mean (0-2cm)	18.7	5.7	3.06	6.87	Surface Mean (0-cm)	15.1	7.66	2.58	6.68	Surface Mean (0-2cm)	4.02	3.12	1.79	2.81
Main Creek (2001)	CF Cd	CF Cu	CF Zn	PLI	Neck Creek (2001)	CF Cd	CF Cu	CF Zn	PLI	Lemon Creek (2001)	CF Cd	CF Cu	CF Zn	PLI
Core Mean	16.6	5.3	3.44	6.71	Core Mean	15.0	6.57	6.21	8.49	Core Mean	5.69	0.59	0.61	1.27
Surface Mean (0-2cm)	17.3	6.5	3.54	7.37	Surface Mean (0-cm)	9.4	5.31	1.75	4.43	Surface Mean (0-2cm)	7.9	2.03	1.13	2.63

¹PLI results do not include Hg CFs.

Figures 5-7a-b. Contamination factors and PLI values per transect location at Main Creek.

Contamination factors and PLI values calculated using world shale as a proxy for natural background concentrations of Cd, Hg, Cu, and Zn (Wedpohl et al. 1968). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations (n=54). Mean metal contents for transect sampling locations were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

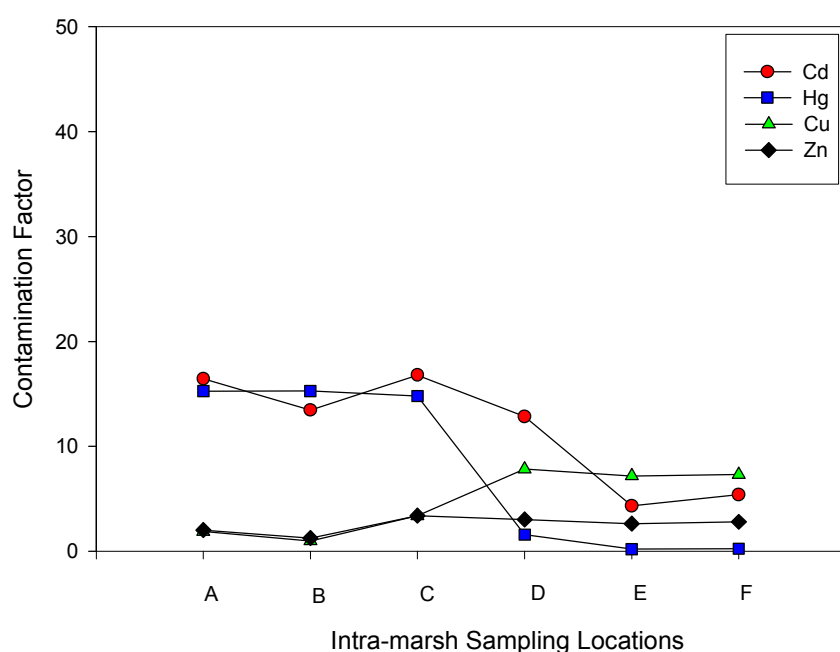


Figure 5-7a. Contamination factors ($CF = C_{\text{observed}}/C_{\text{background}}$) per transect location at Main Creek. Figure reflects lateral surface sediment contamination factors along respective transect locations extending the wadable extent of Main Creek.

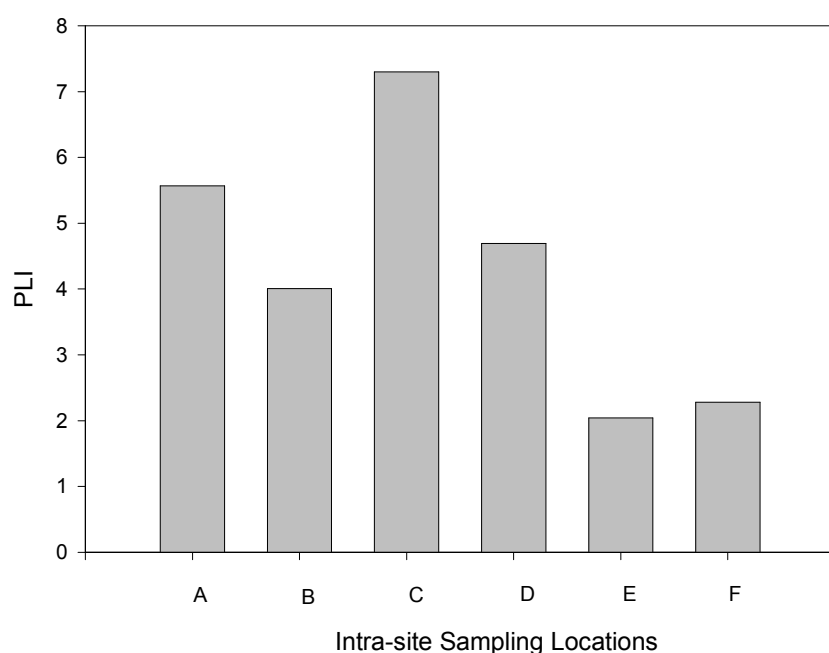


Figure 5-7b. Main Creek intra-spatial variability of pollution load indices (PLI). Figure reflects values per transect location at Main Creek. Lateral surface sediment PLI values determined along respective transect locations extending the wadable extent of the tidal portion of Main Creek.

Figures 5-8a-b. Contamination factors and PLI values per transect location at Neck Creek.

Contamination factors and PLI values calculated using world shale as a proxy for natural background concentrations of Cd, Hg, Cu, and Zn (Wedpohl et al. 1968). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations (n=54). Mean metal contents for transect sampling locations were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

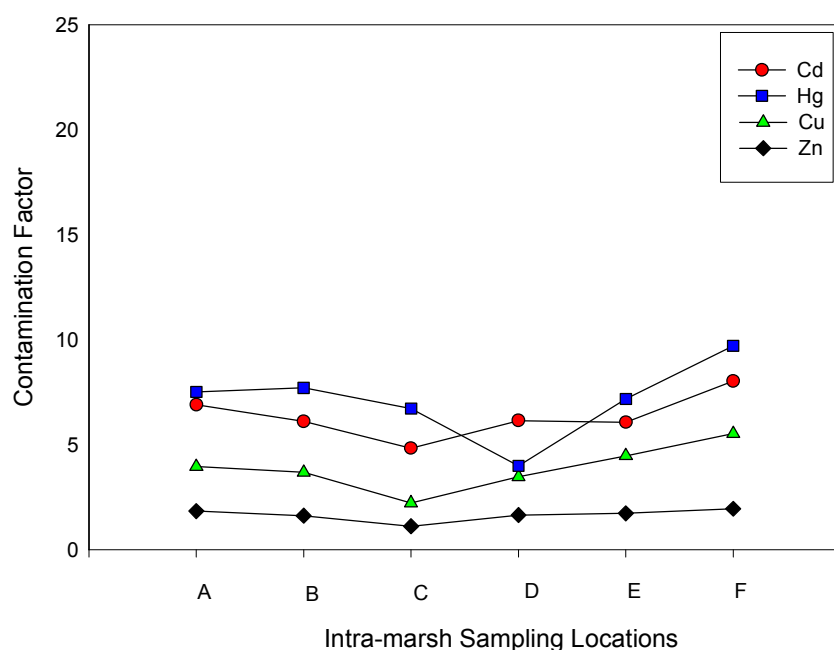


Figure 5-8a. Contamination factors ($CF = C_{\text{observed}}/C_{\text{background}}$) per transect location at Neck Creek. Figure reflects lateral surface sediment contamination factors along respective transect locations extending the wadable extent of Neck Creek.

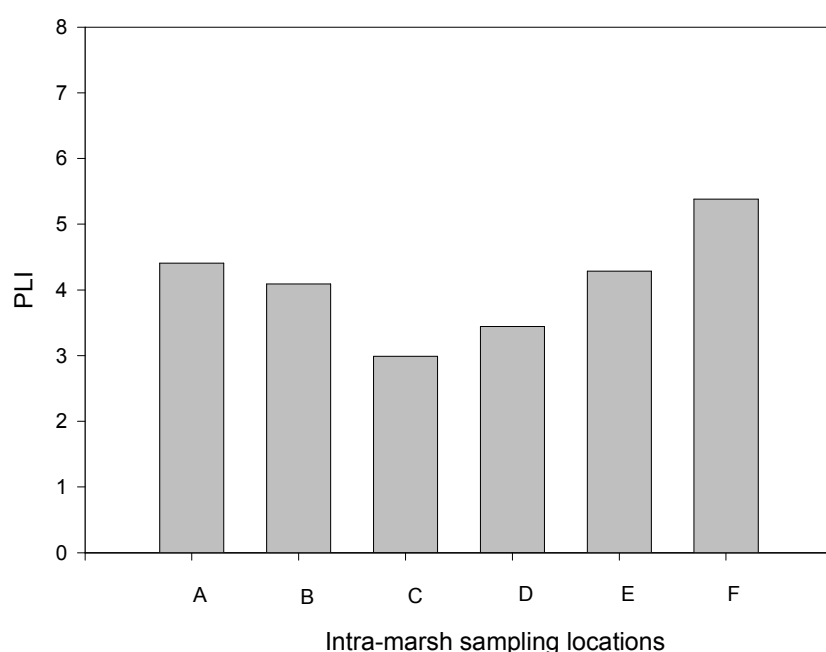


Figure 5-8b. Neck Creek intra-spatial variability of pollution load indices (PLI). Figure reflects values per transect location at Neck Creek. Lateral surface sediment PLI values determined along respective transect locations extending the wadable extent of the tidal portion of Neck Creek

Figures 5-9a-b. Contamination factors and PLI values per transect location at Lemon Creek.

Contamination factors and PLI values calculated using world shale as a proxy for natural background concentrations of Cd, Hg, Cu, and Zn (Wedpohl et al. 1968). Site-specific mean Cd, Cu, and Zn concentrations determined from the average of lateral surficial metal concentrations (n=54). Mean metal contents for transect sampling locations were calculated from site-specific datasets that included concentrations from 3 surface sediment samples from each transect location (n=6), that were each split in triplicate for metal processing and replicate elemental analysis via inductively coupled plasma argon emission spectroscopy (ICP-AES), subsequent to a near total acid digestion procedure.

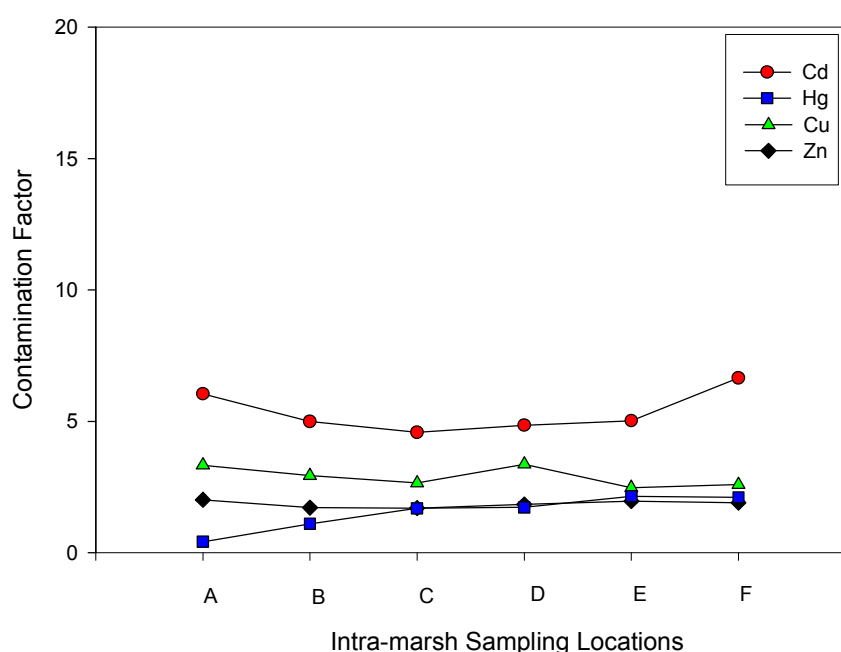


Figure 5-9a. Contamination factors ($CF = C_{\text{observed}}/C_{\text{background}}$) per transect location at Lemon Creek. Figure reflects lateral surface sediment contamination factors along respective transect locations extending the wadable extent of Lemon Creek.

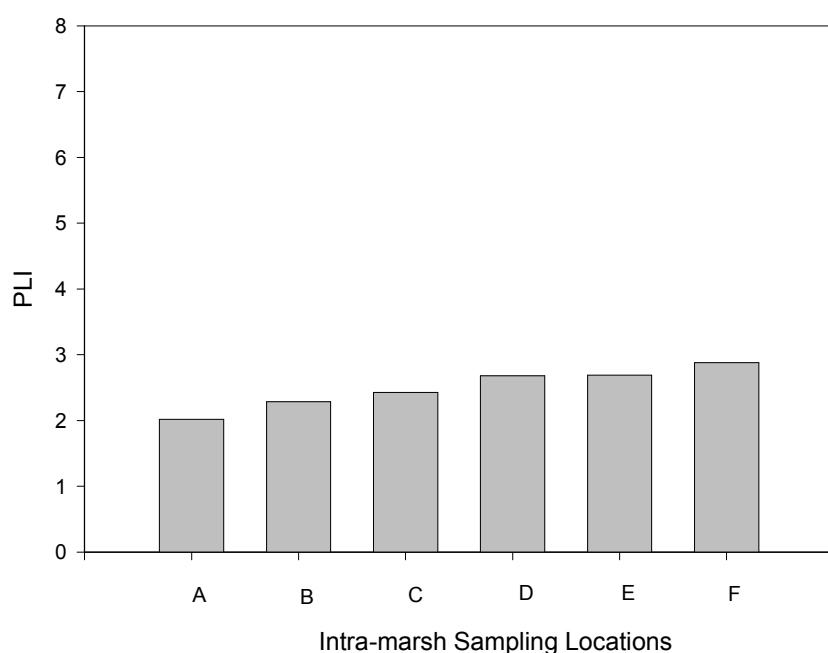


Figure 5-9-b. Lemon Creek intra-spatial variability of pollution load indices (PLI). Figure reflects values per transect location at Lemon Creek. Lateral surface sediment PLI values determined along respective transect locations extending the wadable extent of the tidal portion of Lemon Creek.

Figure 5-10a-d. Large-scale variability and magnitude of marsh sediment contamination. Graphs reflect collective extent of site-specific enrichment via mean surficial PLI values for 2001, 2007, and 2009 datasets.

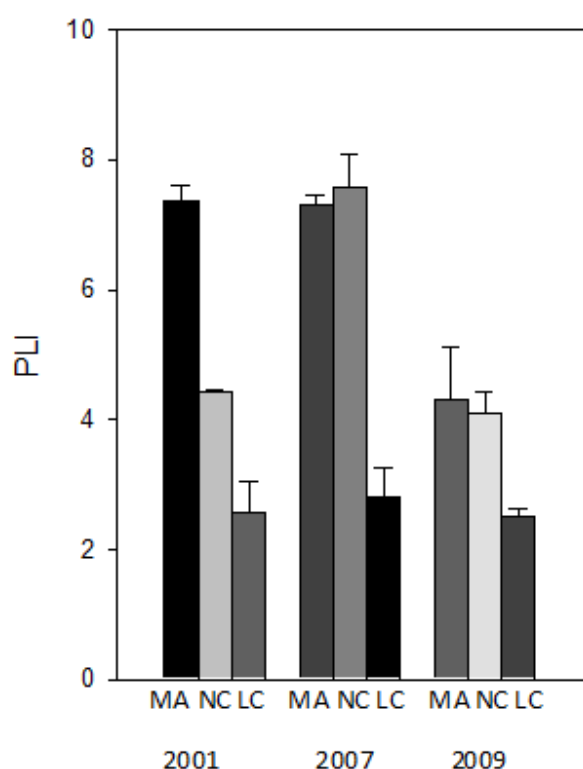


Figure 10a. Large-scale variability of mean temporal pollution load indices. PLI values $\pm$ (S.E.) determined via the collective extent of all metal-specific contamination factors (CF) reflected by MA, NC, and LC surficial distributions (2001, 2007, and 2009).

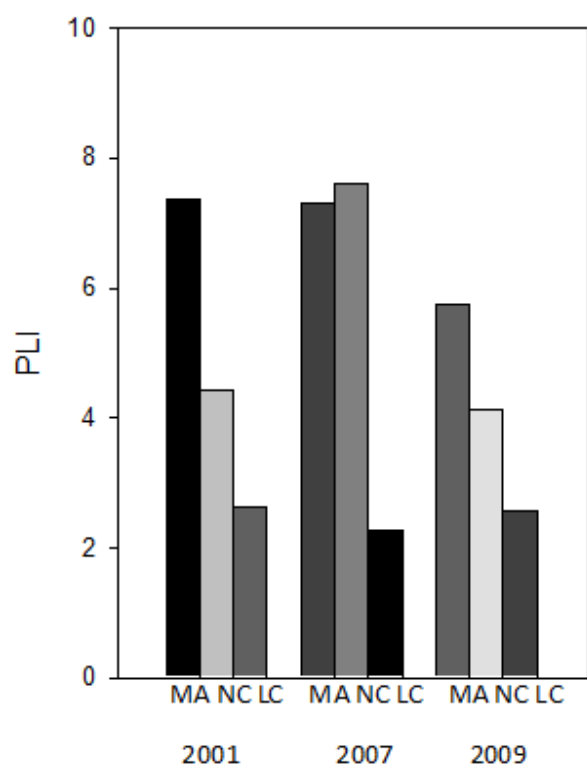


Figure 10b. Large-scale variability of temporal pollution load indices. Average PLI values determined via the collective extent of all metal-specific contamination factors (CF) reflected by MA, NC, and LC mean sediment concentrations (2001, 2007, and 2009).

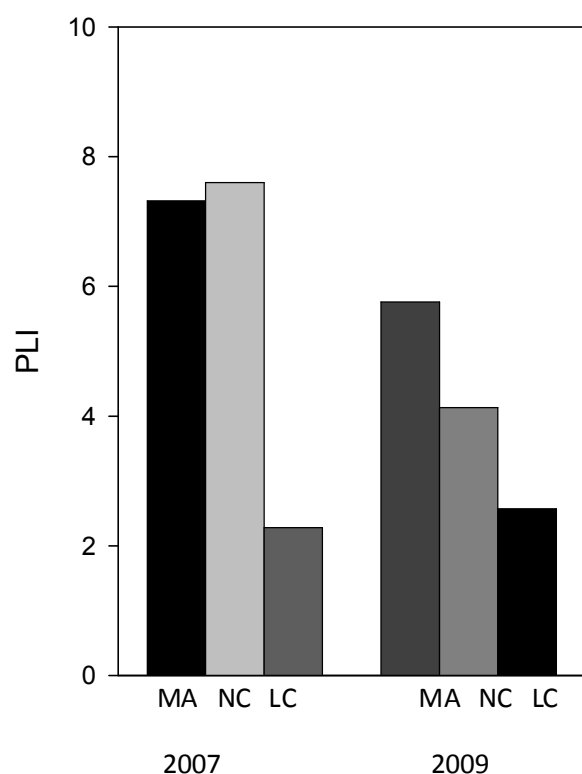


Figure 10c. Large-scale variability of temporal pollution load indices. PLI values determined via the collective extent of all metal-specific contamination factors (CF) reflected by MA, NC, and LC mean sediment concentrations (2007 and 2009); incorporates Hg concentrations in calculation of PLI.

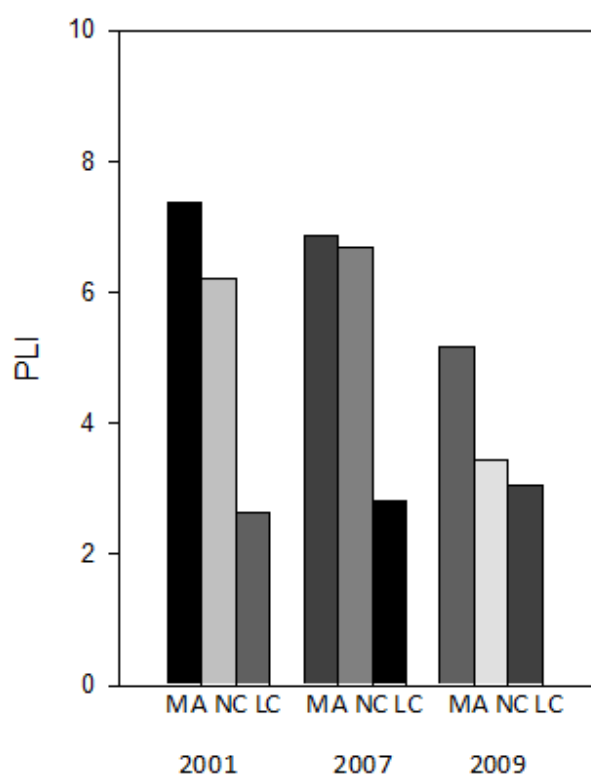


Figure 10d. Large-scale variability of temporal pollution load indices. Values determined via the collective extent of Cd, Cu, and Zn contamination factors (CF) reflected by MA, NC, and LC mean sediment concentrations (2001, 2007, and 2009); does not incorporate Hg data, as concentrations were not determined in 2001 studies.

Figure 5-11a-d. Temporal Variability of MA, NC and LC mean Pollution Load Index (PLI).

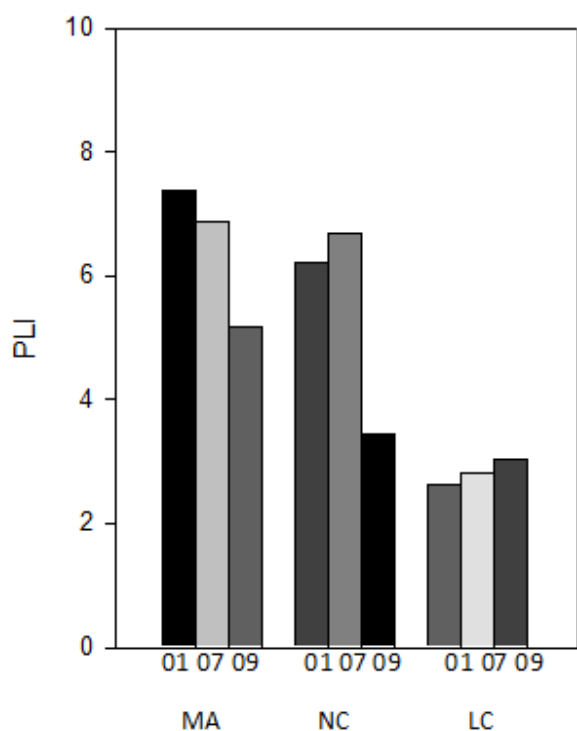


Figure 11a. Temporal variability of MA, NC, and LC mean Pollution Load Index. PLI values determined via the collective extent of all metal-specific contamination factors (CF) reflected by 2007 and 2009 surface metal distributions.

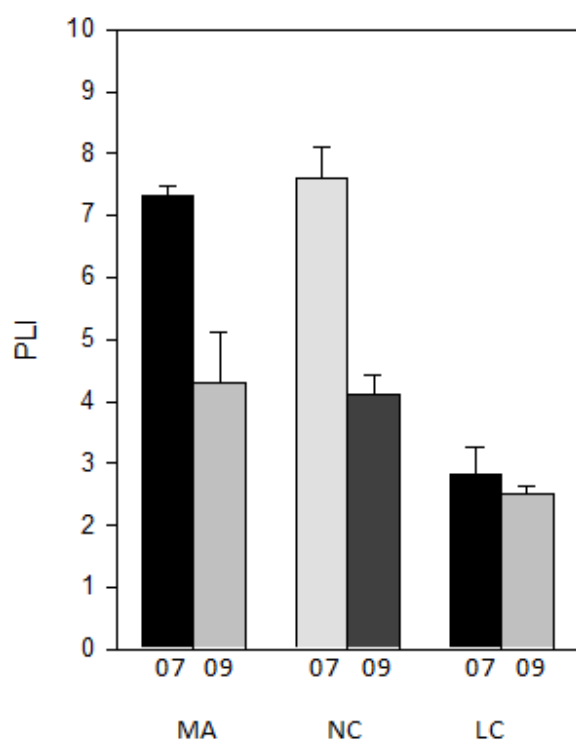


Figure 11b. Temporal variability of MA, NC, and LC Pollution Load Index. PLI values determined via collective extent of all metal-specific contamination factors (CF) reflected by mean surface concentrations measured in 2001, 2007, and 2009

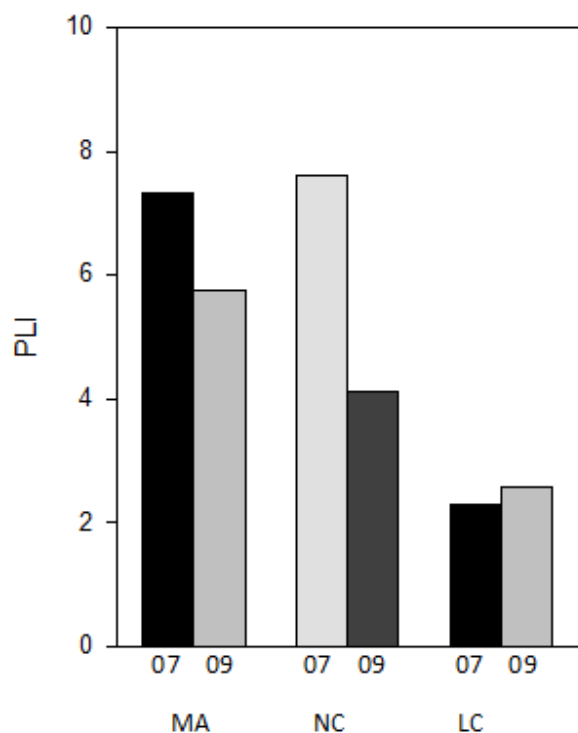


Figure 11c. Temporal variability of MA, NC, and LC Pollution Load Index. PLI values determined via collective extent of all metal-specific contamination factors (CF) reflected by mean surface concentrations measured in 2007 and 2009.

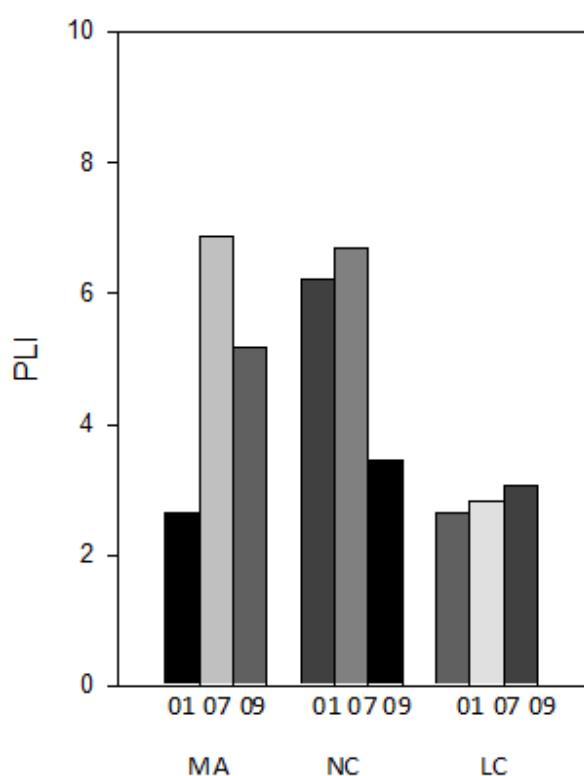


Figure 11d. Temporal variability of MA, NC, and LC Pollution Load Index. PLI values determined via collective extent of site-specific Cd, Cu, and Zn contamination factors (CF) reflected by mean surface concentrations measured in 2001, 2007, and 2009.

Table 5-6. Theoretical and empirical sediment quality guidelines and mean for the studied metals in MA, NC and LC. Regional and global background sediment reference values and effect-based toxicity benchmarks derived from Hudson River, world average shale and NOAA's screening gradient).*

Background/Reference	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)
Regional Baseline/ Background ¹	0.11	0.18	14	81
Mean World Shale /Background ²	0.3	0.16	45	95
Tenth highest reported level ³	2.5	1.7	180	380
Highest reported level ³	11	4.3	320	570
Maximum concentration in 6 contaminated estuaries ⁴	862	1130	2540	16667
Toxicity Benchmarks	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)
Threshold effects level (TEL)	0.676	<i>0.13</i>	18.7	124
Effects range-low (ER-L)	1.2	<i>0.15</i>	34	150
Probable effects level (PEL)	4.21	<i>0.696</i>	108	271
Effects range-median (ER-M)	9.6	<i>0.71</i>	270	410
Main Creek	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)
MA Mean 2009 (n=18)	3.57	1.26	229	242
MA Mean 2007 (n=9)	5.62	1.42	255	291
MA Mean 2001 (n=12)	5.18	-	294	337
Neck Creek	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)
NC Mean 2009 (n=18)	1.84	1.14	165	152
NC Mean 2007 (n=9)	4.52	1.79	345	245
NC Mean 2001 (n=12)	2.87	-	239	166
Lemon Creek	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)
LC Mean 2009 (n=18)	1.62	<i>0.24</i>	131	177
LC Mean 2007 (n=9)	1.21	<i>0.19</i>	140	170
LC Mean 2001 (n=12)	2.35	-	91	108

*E RL: Effects Range Low, ERM: Effects Range Medium, TEL: Threshold Effect Level (Maximum concentration at which no effect are observed), PEL: Probable Effect Level (Lower limit of the range of concentrations at which adverse effects are always observed).

¹Background concentration based on Hudson River sediment data (Hirschberg et al. 1996).

²Background concentration based on Hudson River sediment data (Bowen et al. 1979).

³ERL and ERM sediment quality indices based on biological effects studies (Long et al. 1995). **Bold** indicates greater than ERM.

⁴TEL and PEL effect-based values derived from (MacDonald et al. 2000). *Italics* indicate values greater than PEL.

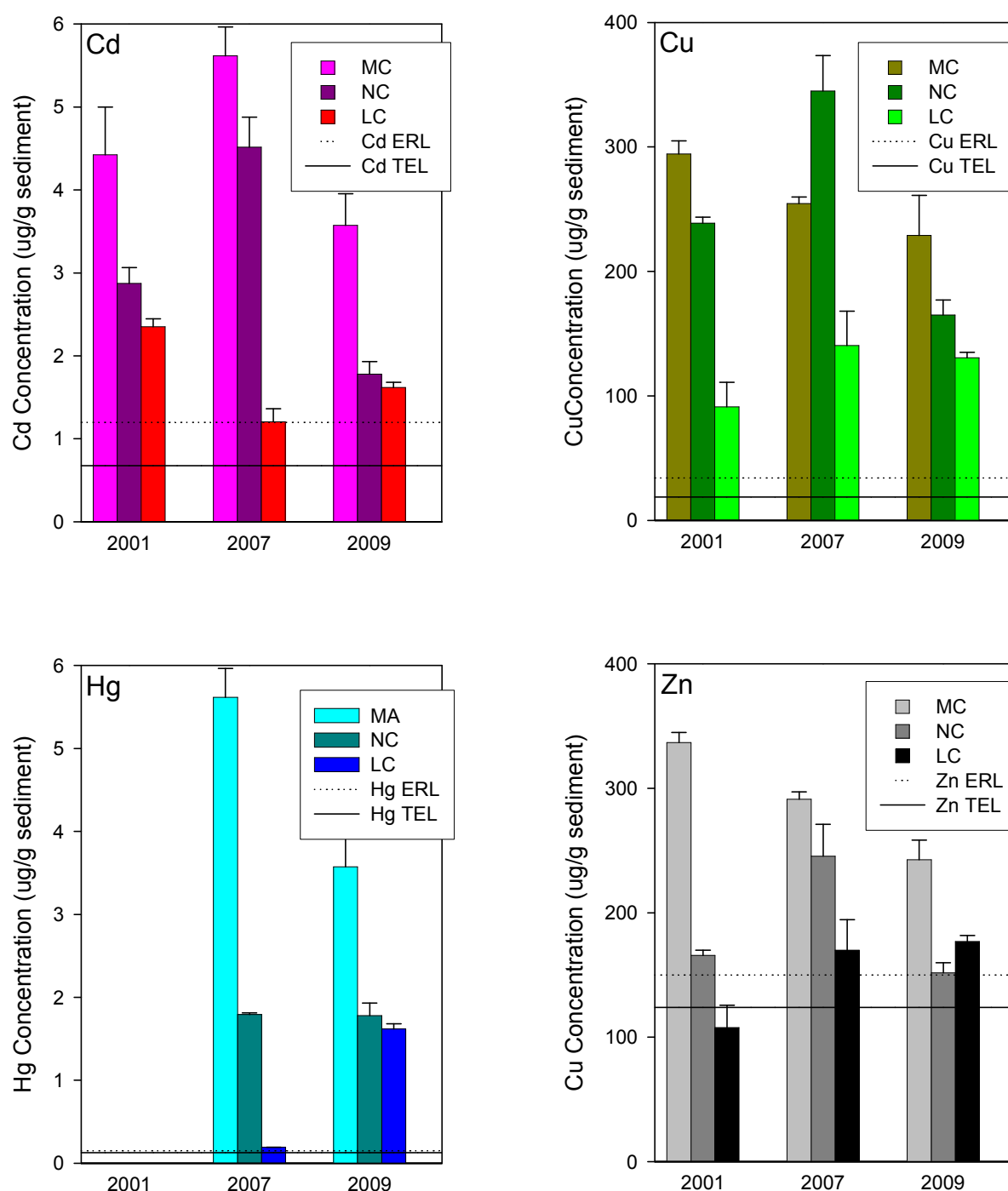


Figure 5-12. Metals in surface sediments at Staten Island marsh sites: 2001, 2007 and 2009. Figure reflects inter-marsh variability of temporal Cd, Hg, Cu, and Zn concentrations with respect to empirical sediment quality guidelines (effect-based values). Vertical bars represent mean ($n=3$) metal-specific surface sediment concentrations ($\pm$ S.E.) at Main Creek, Neck Creek, and Lemon Creek from 2001, 2007, and 2009 datasets, respectively. Dotted lines (---) represent metal-specific effects-range low (ERL) thresholds, based on biological effects studies (Long et al. 1995). Solid lines (—) represent metal-specific Threshold Effect Level (TEL), which depicts the maximum concentration at which no effects are observed (MacDonald et al. 2000).

Table 5-7. Metal-specific TU (ratio of mean Cd, Hg, Cu, and Zn in relation to PEL) and collective sum and of site-specific mean TU Quotient (2001, 2007, 2009).

Study Site	Survey Year	Cd		Hg		Cu		Zn		TU Sum	Mean PEL Quotient
		Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU		
MA	2009 ¹	3.57	0.85	1.26 ⁴	1.81	229	2.12 ⁵	243	0.89	5.67	1.42
	2007 ²	5.62	1.33	1.42	2.04	255	2.36	291	1.07	6.81	1.70
	2001 ³	5.18	1.23	-	-	295	2.73	337	1.24	5.20	1.73
NC	2009 ¹	1.84	0.44	1.14	1.64	165	1.53	152	0.56	4.16	1.04
	2007 ²	4.52	1.07	1.79	2.58	345	3.19	245	0.91	7.75	1.94
	2001 ³	2.87	0.68	-	-	239	2.21	166	0.61	3.50	1.17
LC	2009 ¹	1.62	0.38	0.24	0.34	131	1.21	177	0.65	2.59	0.65
	2007 ²	1.21	0.29	0.19	0.28	141	1.30	170	0.63	2.49	0.62
	2001 ³	2.35	0.56	-	-	91.3	0.85	108	0.40	1.80	0.60

¹Reflects mean of 18 samples analyzed in 2009 (3 samples from each of the 6 surface locations across each marsh-creek system).

²Reflects mean of 9 samples analyzed in 2007 (3 samples were analyzed from each of the 3 locations in 2007).

³Reflects mean of 12 samples analyzed in 2001 (4 samples were analyzed from each of the 3 locations in 2001).

⁴**Bold** indicates concentration exceeds PEL

⁵Shading indicates greatest site-specific TU/survey

Table 5-8. Metal-specific TU (ratio of mean Cd, Hg, Cu, and Zn in relation to ERM) and collective sum and of site-specific mean TU Quotient (2001, 2007, 2009).

Study Site	Survey Year	Cd		Hg		Cu		Zn		TU Sum	Mean ERM Quotient
		Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU	Mean ($\mu\text{g}\cdot\text{g}^{-1}$)	TU		
MA	2009 ¹	3.57	0.37	1.26 ⁴	1.77 ⁵	229	0.85	243	0.59	3.59	0.90
	2007 ²	5.62	0.59	1.42	2.00	255	0.94	291	0.71	4.24	1.06
	2001 ³	5.18	0.54	-	-	294	1.09	337	0.82	2.45	0.82
NC	2009 ¹	1.84	0.19	1.14	1.61	165	0.61	152	0.37	2.78	0.69
	2007 ²	4.52	0.47	1.79	2.53	345	1.28	245	0.60	4.87	1.22
	2001 ³	2.87	0.30	-	-	239	0.88	166	0.40	1.59	0.53
LC	2009 ¹	1.62	0.17	0.24	0.34	131	0.48	177	0.43	1.42	0.36
	2007 ²	1.21	0.13	0.19	0.27	141	0.52	170	0.41	1.33	0.33
	2001 ³	2.35	0.24	-	-	91.3	0.34	108	0.26	0.85	0.28

¹Reflects mean of 18 samples analyzed in 2009 (3 samples from each of the 6 surface locations across each marsh-creek system).

²Reflects mean of 9 samples analyzed in 2007 (3 samples were analyzed from each of the 3 locations in 2007).

³Reflects mean of 12 samples analyzed in 2001 (4 samples were analyzed from each of the 3 locations in 2001).

⁴**Bold** indicates concentration exceeds ERM

⁵Shading indicates greatest metal-specific TU

Table 5-9. Mean ERL; PEL; and ERM Quotients.

Site/ Survey Year	TU Sum (ERL ratio)	ERL Quotient	TU Sum (PEL ratio)	PEL Quotient	TU Sum (ERM ratio)	ERM Quotient
MA Mean 2009	19.7	4.93	5.67	1.42	3.59	0.90 ¹
MA Mean 2007	23.6	5.89	6.81	1.70	4.24	1.06 ¹
MA Mean 2001	15.2	5.07	5.20	1.73	2.45	0.82
NC Mean 2009	15.0	3.75	4.16	1.04	2.78	0.69
NC Mean 2007	27.5	6.87	7.75	1.94	4.87	1.22
NC Mean 2001	10.5	3.51	3.50	1.17	1.59	0.53
LC Mean 2009	7.97	1.99	2.59	0.65	1.42	0.36
LC Mean 2007	7.57	1.89	2.49	0.62	1.33	0.33
LC Mean 2001	5.36	1.34	1.80	0.60	0.85	0.21

Site/Survey Year	ERM Quotient	Acute Toxicity Level	Potential Acute Toxicity Risk	Chronic Toxicity Risk
MA Mean 2009	0.90 ¹	Level III	moderate - high	High
MA Mean 2007	1.06 ¹	Level III	moderate - high	High
MA Mean 2001	0.82	Level III	moderate -high	High
NC Mean 2009	0.69	Level III	moderate - high	High
NC Mean 2007	1.22	Level III	moderate - high	High
NC Mean 2001	0.53	Level III	moderate -high	High
LC Mean 2009	0.36	Level II	low-moderate	High
LC Mean 2007	0.33	Level II	low-moderate	High
LC Mean 2001	0.21	Level II	low-moderate	High

¹ Potential acute toxicity categories: Level I=low, Level II=low-moderate, Level III= moderate to high, Level IV=High; for amphipod mortality (Long *et al.*, 1998)

² Assessment based on benthic community degradation (Hyland *et al.*, 1999)

Table 5-9a. Classification categories for potential acute toxicity and chronic toxicity associated with ERM Q ranges.

Acute Toxicity¹	Level I (< 0.1)	Level II (0.11-0.5)	Level III (0.51-1.5)	Level IV (>1.5)
Chronic Toxicity²	Low (≤0.020)	Moderate (0.021-0.058)	High (>0.058)	

¹ (Long *et al.*, 1998)

² Hyland *et al.*, 1999)

Figure 5-13.a-b. Spatial and temporal variability of MA, NC, and LC mean PEL Quotients (Mean Toxic Unit (TU) Sum) of total metal-specific (Cd, Hg, Cu, and Zn) TUs (2001, 2007, and 2009).

Fig. 13a. Large-scale Variability of Mean PEL Quotients determined via the collective extent of potential metal-specific toxic-effects reflected by Total Sum of TUs determined in 2001, 2007, and 2009.

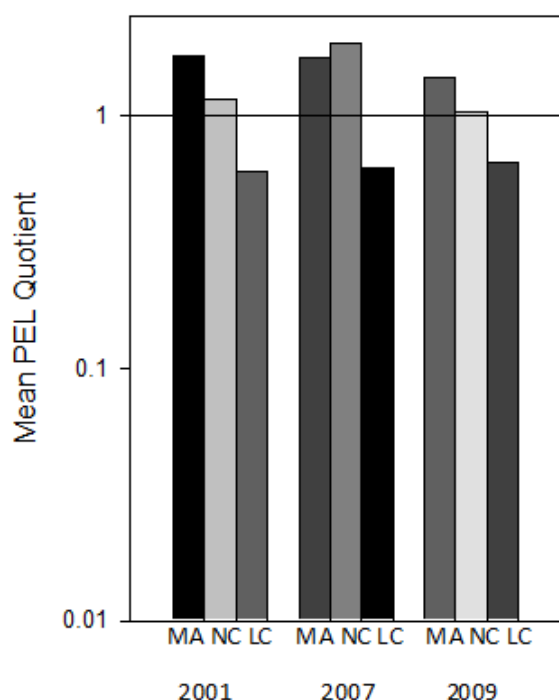


Fig. 13 b. Temporal Variability of Site-specific Mean PEL Quotients determined via the collective extent of potential metal-specific toxic-effects reflected by Total Sum of TUs determined in 2001, 2007, and 2009.

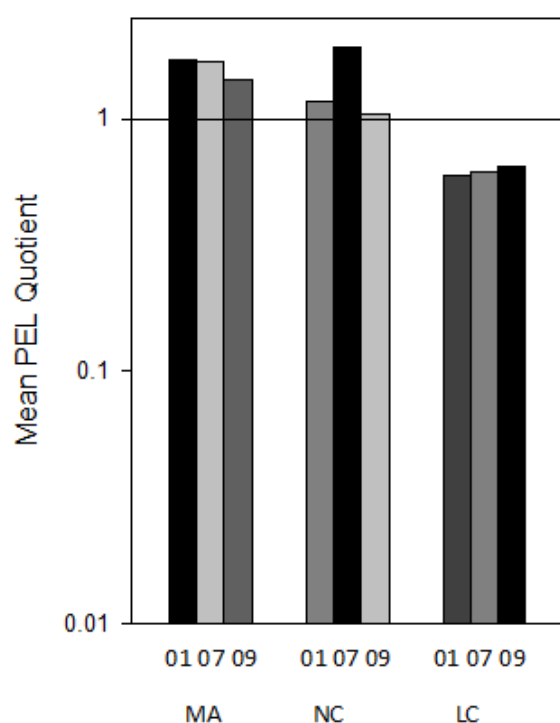


Figure 5-13c-d. Spatial and temporal variability of site-specific mean PEL Quotients (Mean Toxic Unit (TU) Sum) of all metal-specific TUs at MA, NC, and LC (2007 and 2009).

Fig. 13c. Large-scale Variability of Mean PEL Quotients determined via the collective extent of potential of metal-specific toxic-effects reflected by the sum of metal-specific TU totals determined in 2007, and 2009.

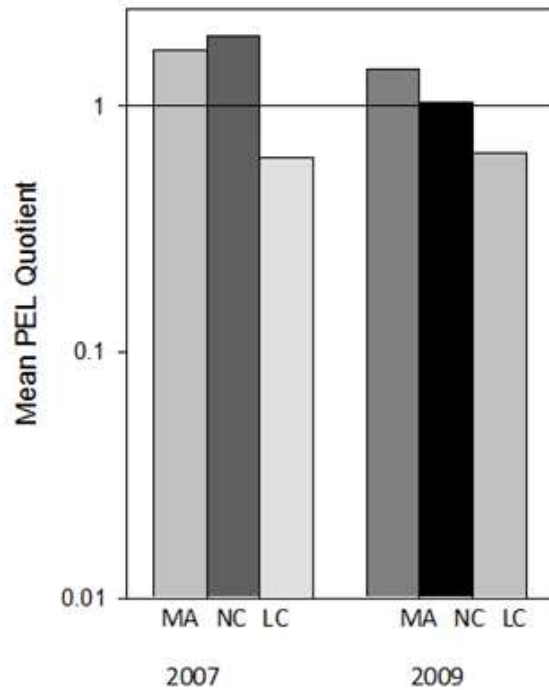


Fig. 13d. Temporal Variability of Site-specific Mean PEL Quotients determined via the collective extent of potential of metal-specific toxic-effects reflected by the sum of metal-specific TU totals determined in 2007 and 2009.

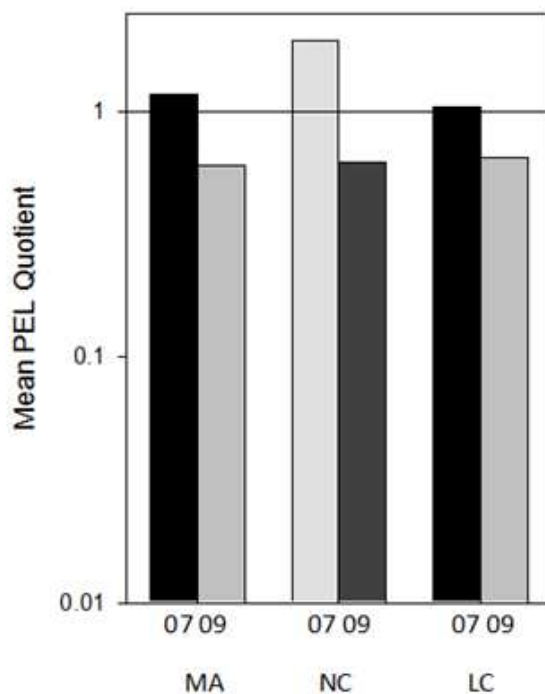


Figure 5-14a-b. Spatial and temporal variability of MA, NC, and LC Mean ERM Quotients (Mean Toxic Unit (TU) Sum) of total metal-specific (Cd, Hg, Cu, and Zn) TUs (2001, 2007, and 2009).

Fig. 14a. Large-scale Variability of Mean ERM Quotients determined via the collective extent of potential metal-specific toxic-effects reflected by Total Sum of TUs determined in 2001, 2007, and 2009.

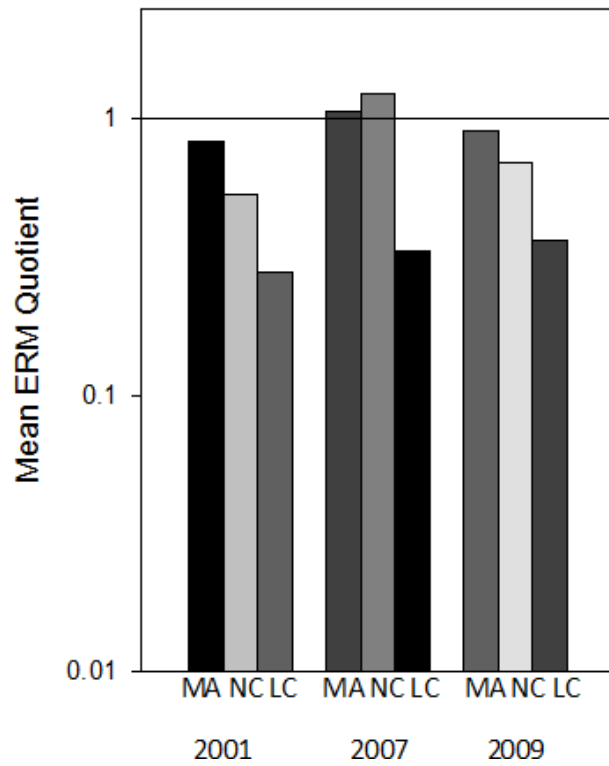


Fig. 14b. Temporal Variability of Site-specific Mean ERM Quotients determined via the collective extent of potential metal-specific toxic-effects reflected by Total Sum of TUs determined in 2001, 2007, and 2009.

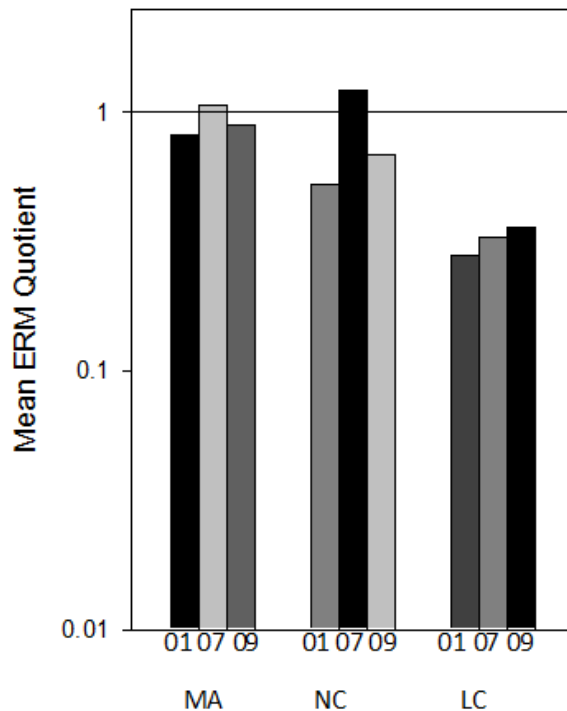


Figure 5-14c-d. Spatial and temporal variability of site-specific mean ERM Quotients (Mean Toxic Unit (TU) Sum) of all metal-specific TUs at MA, NC, and LC (2007 and 2009).

Fig. 14c. Large-scale Variability of Mean ERM Quotients determined via the collective extent of potential of metal-specific toxic-effects reflected by the sum of metal-specific TU totals determined in 2007, and 2009.

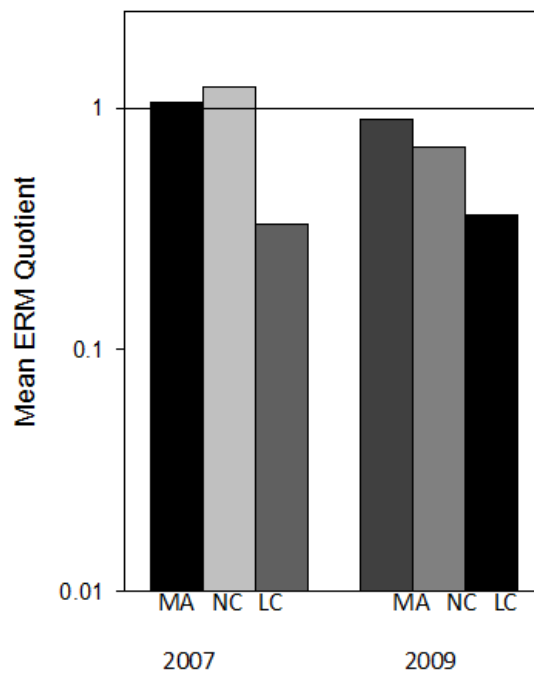
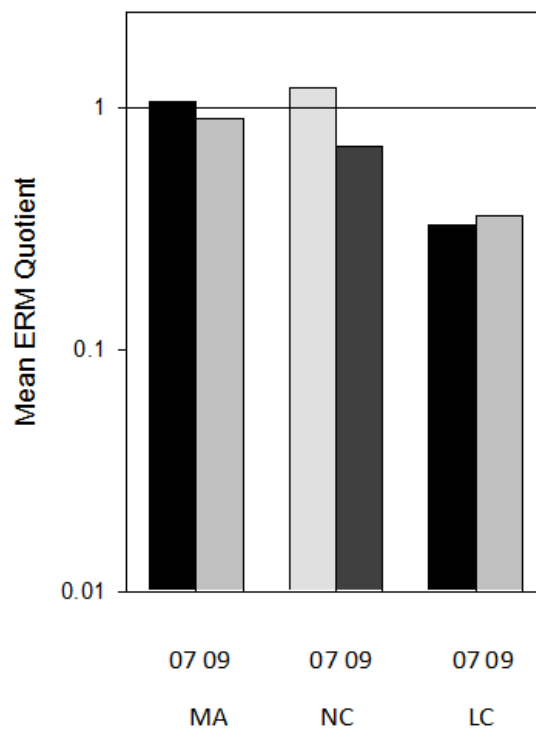
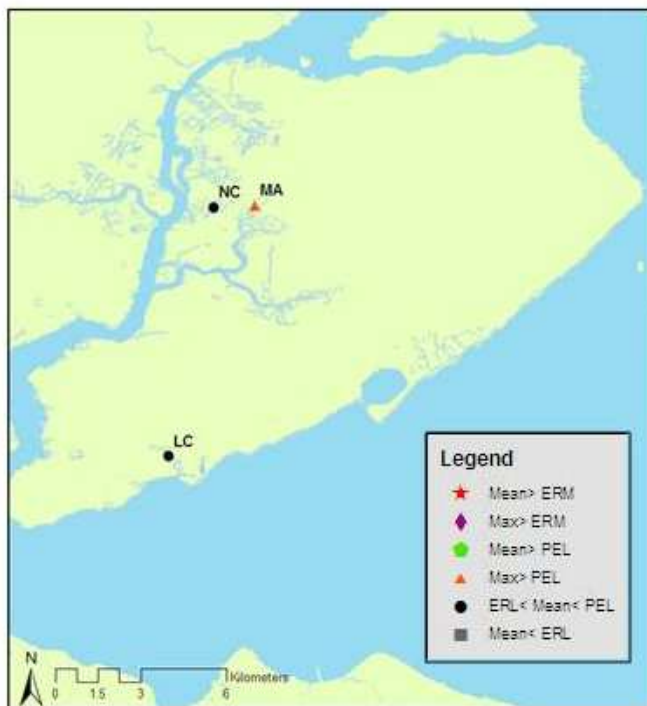
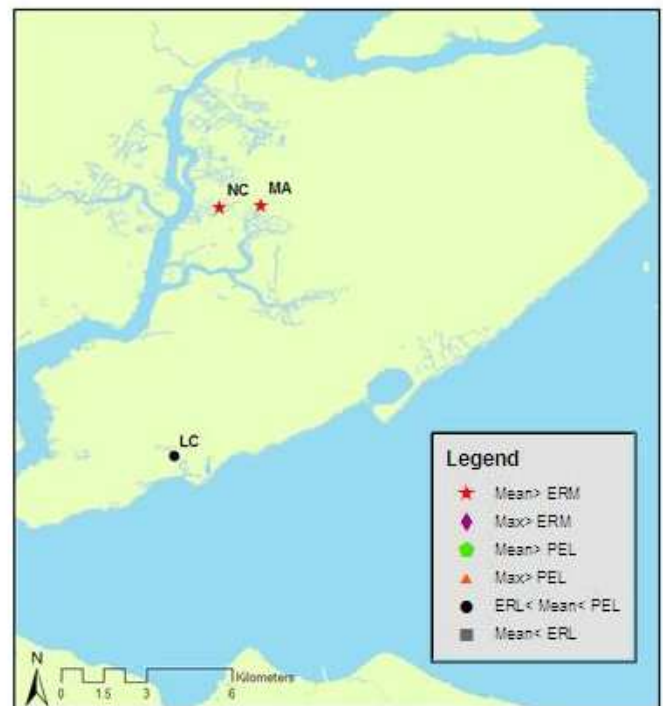


Fig. 14d. Temporal Variability of Site-specific Mean ERM Quotients determined via the collective extent of potential of metal-specific toxic-effects reflected by the sum of metal-specific TU totals determined in 2007 and 2009.



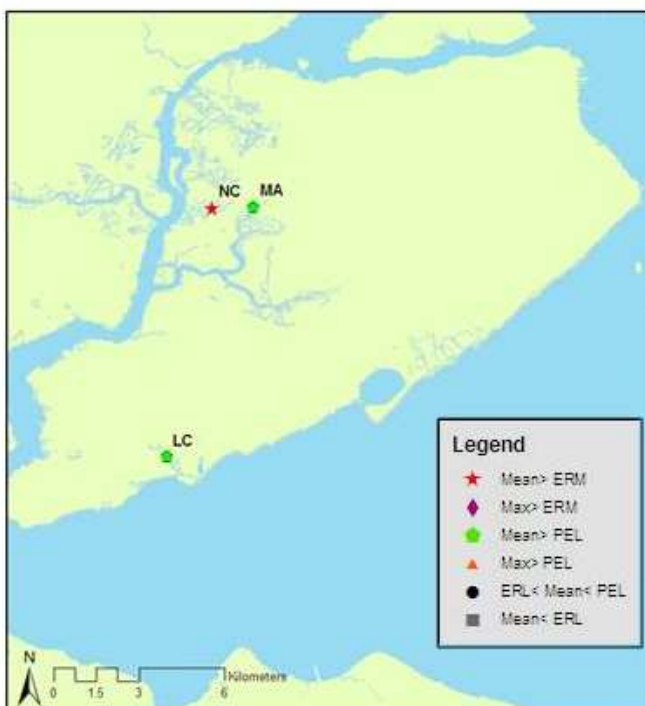


Potential for toxic effects associated with Cd in MA, NC, and LC sediments

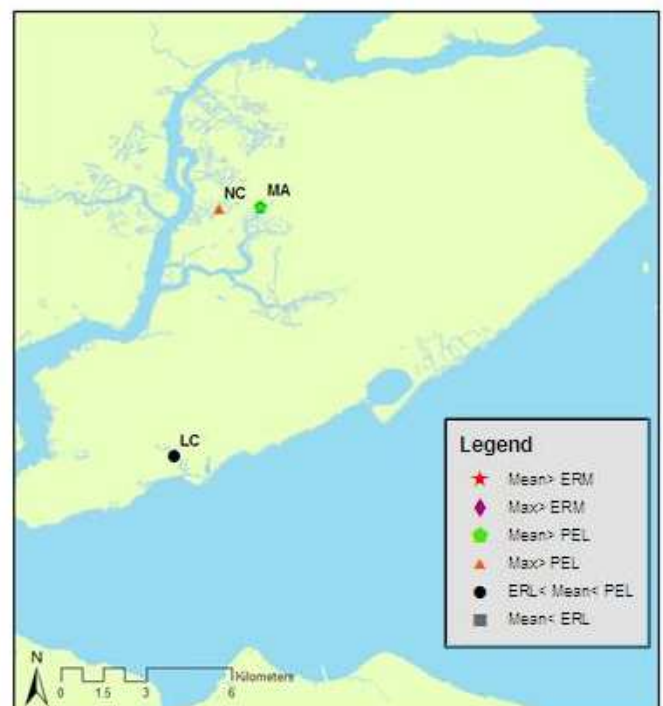


Potential for toxic effects associated with Hg in MA, NC, and LC sediments

Figure 5- 15a. Occurrence, variability, and potential extent of toxic effects associated with Cd, and Hg sediment contamination in Staten Island marshes (2009).

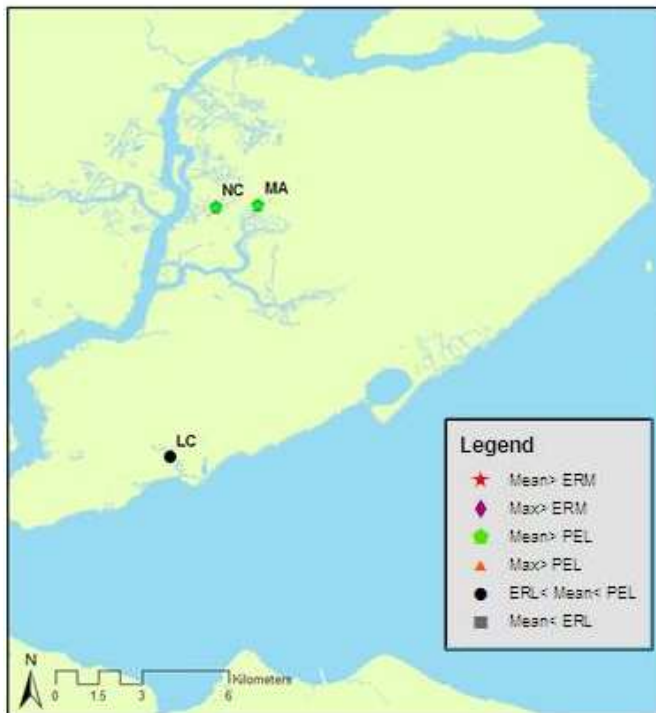


Potential for toxic effects associated with Cu in MA, NC, and LC sediments

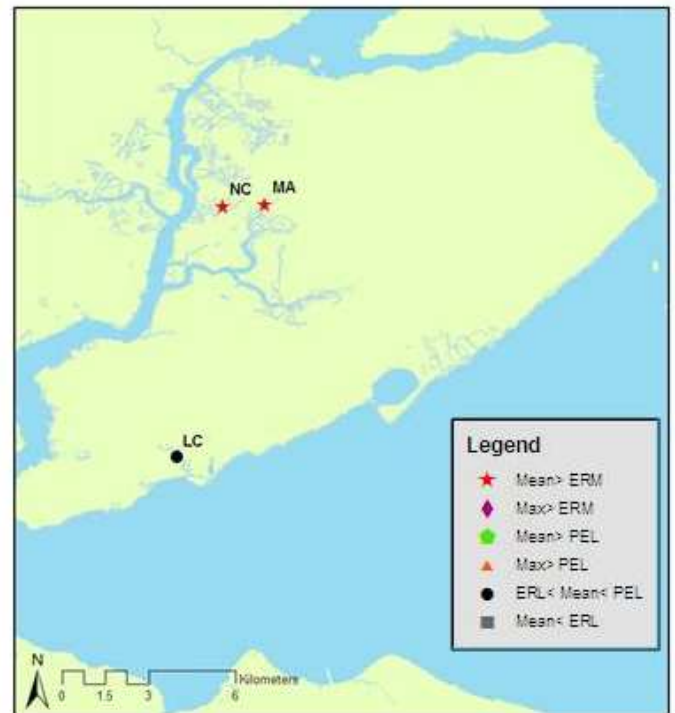


Potential for toxic effects associated with Zn in MA, NC, and LC sediments

Figure 5- 15b. Occurrence, variability, and potential extent of toxic effects associated with Cu, and Zn sediment contamination in Staten Island marshes (2009).

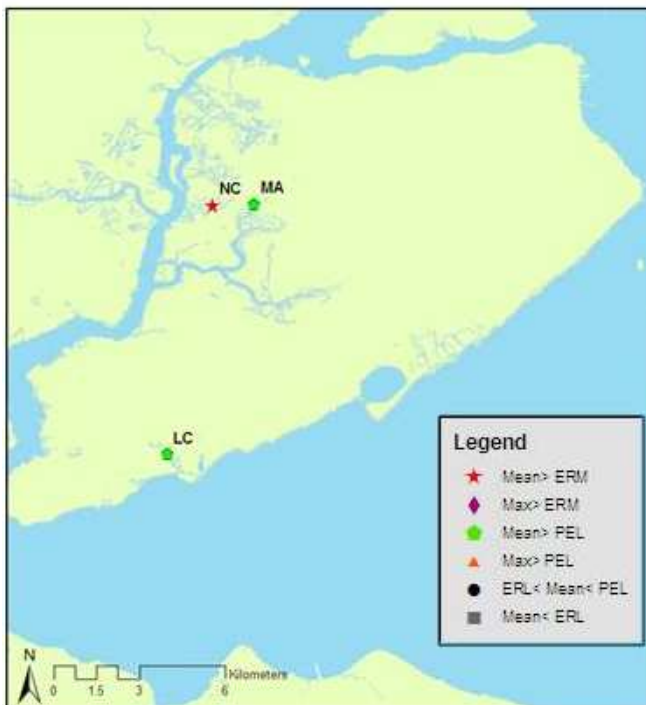


Potential for toxic effects associated with Cd in MA, NC, and LC sediments

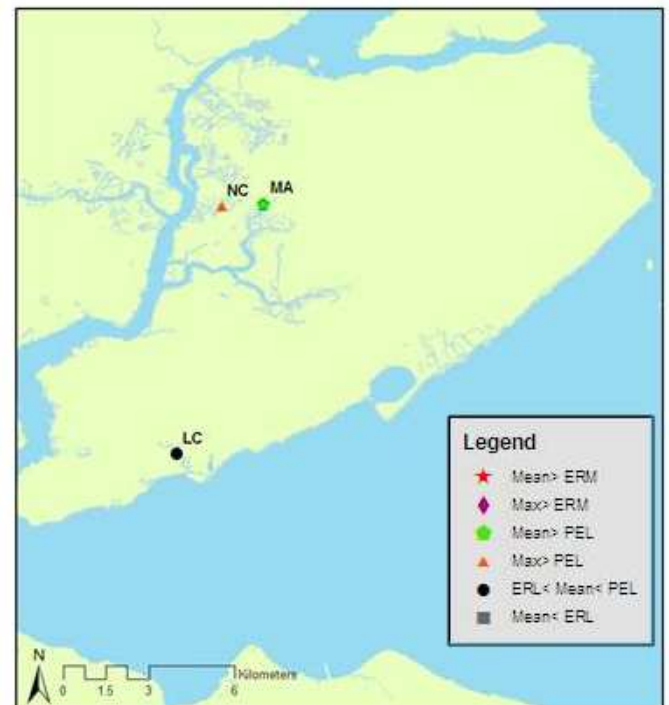


Potential for toxic effects associated with Hg in MA, NC, and LC sediments

Figure 5-16a. Occurrence, variability, and potential extent of toxic effects associated with Cd, and Hg sediment contamination in Staten Island marshes (2007).

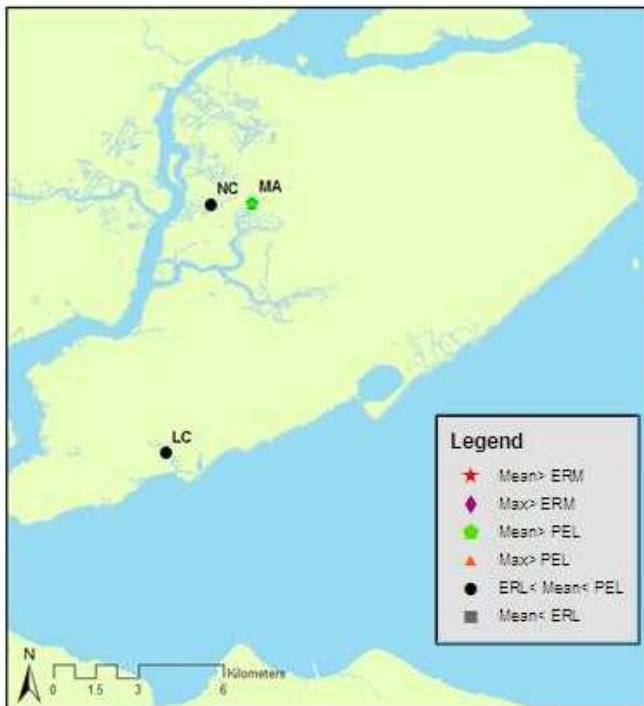


Potential for toxic effects associated with Cu in MA, NC, and LC sediments

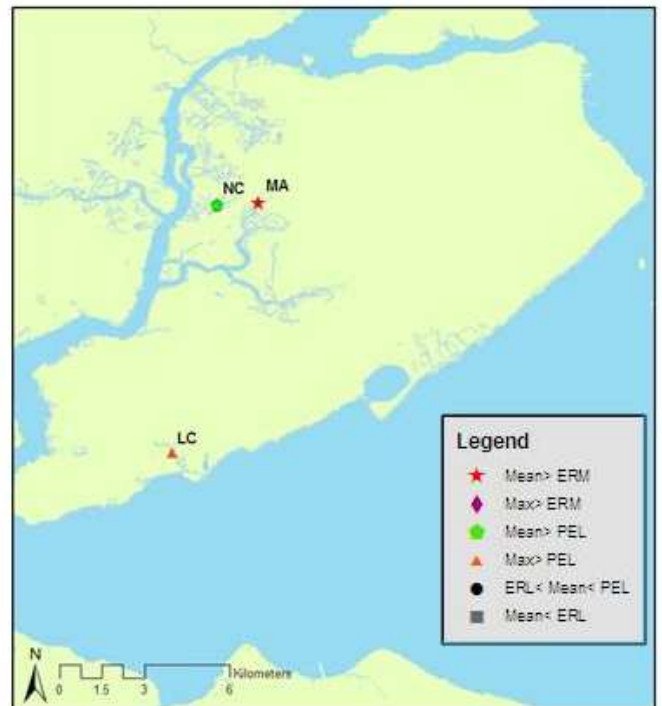


Potential for toxic effects associated with Zn in MA, NC, and LC sediments

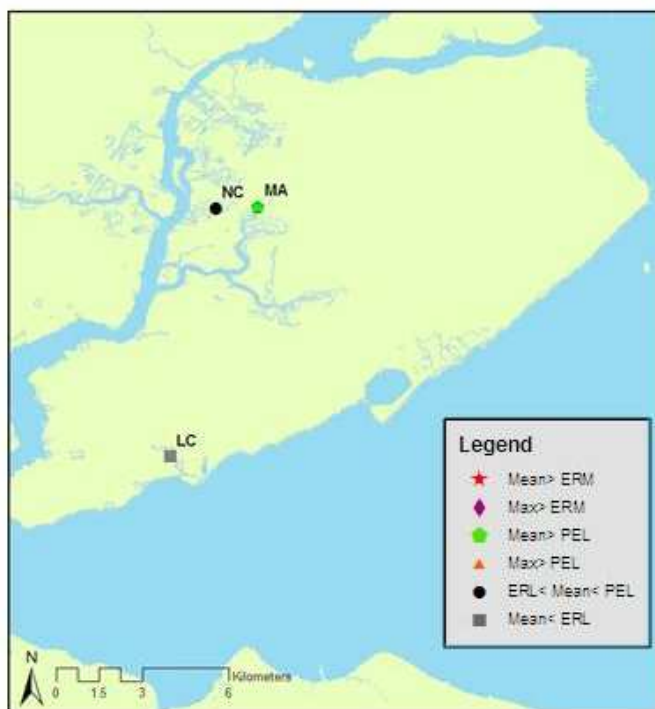
Figure 5-16b. Occurrence, variability, and potential extent of toxic effects associated with Cu, and Zn sediment contamination in Staten Island marshes (2007).



Potential for toxic effects associated with Cd in MA, NC, and LC sediments



Potential for toxic effects associated with Cu in MA, NC, and LC sediments



Potential for toxic effects associated with Zn in MA, NC, and LC sediments

Figure 5-17. Occurrence, variability, and potential extent of toxic effects associated with Cd, Cu, and Zn sediment contamination in Staten Island marshes (2001).

Appendices

Appendix 5-A. Summary of metal concentrations in surface sediment transects recovered from marsh study sites in 2009.

Location	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)			Hg ($\mu\text{g}\cdot\text{g}^{-1}$)			Cu ($\mu\text{g}\cdot\text{g}^{-1}$)			Zn ($\mu\text{g}\cdot\text{g}^{-1}$)		
MA	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE
A ¹	4.66-5.23	4.93±0.29	0.17	2.40-2.50	2.44±0.05	0.03	79.6-92.0	85.4±6.25	3.61	185-201	192±8.09	4.67
B	3.93-4.10	4.04±0.10	0.06	2.36-2.52	2.44±0.08	0.04	41.2-48.3	44.8±4.99	3.53	117-122	119±4.06	2.87
C	4.71-5.24	5.04±0.29	0.16	2.33-2.39	2.37±0.03	0.02	151-153	152±1.03	0.73	322-322	322±0.08	0.06
D	3.84-3.86	3.85±0.02	0.01	0.26-0.25	0.25±0.0	0.00	328-371	353±22.10	12.76	275-299	289±12.7	7.31
E	1.28-1.32	1.30±0.03	0.02	0.03-0.03	0.03±0.0	0.00	307-360	331±26.99	15.58	245-254	2505±4.55	2.62
F	1.54-1.66	1.62±0.07	0.04	0.04-0.04	0.04±0.0	0.00	298-328	317±16.56	9.56	253-279	267±13.6	7.88
NC	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE
A ¹	2.03-2.11	2.07±0.05	0.04	1.19-1.22	1.20±0.01	0.01	177-179	178±1.46	1.04	168-181	174±9.09	6.43
B	1.76-1.88	1.83±0.07	0.04	1.22-1.24	1.23±0.01	0.01	162-169	166±3.57	2.06	152-156	154±2.29	1.32
C	0.82-2.08	1.45±0.89	0.63	1.06-1.10	1.07±0.02	0.01	60.9-163	100±54.58	31.51	70.9-156	105±45.23	26.11
D	1.71-1.95	1.84±0.12	0.07	0.63-0.65	0.64±0.01	0.01	146-163	156±9.01	5.20	147-163	157±8.63	4.98
E	1.78-1.89	1.82±0.06	0.04	1.12-1.19	1.15±0.04	0.02	199-206	201±4.41	2.55	162-169	165±3.52	2.03
F	2.18-2.76	2.41±0.41	0.41	1.50-1.59	1.55±0.04	0.03	249-249	249±0.00	0.00	185-185	185±0.00	0.00
LC	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE	Range	Mean	SE
A ¹	1.41-2.08	1.81±0.36	0.21	0.06-0.07	0.07±0.00	0.00	132-162	150±16.0	9.21	158-215	191±29.2	16.9
B	1.48-1.52	1.50±0.02	0.01	0.17-0.18	0.18±0.00	0.00	123-137	132±7.92	4.57	159-165	163±3.05	1.76
C	1.36-1.38	1.37±0.01	0.01	0.27-0.27	0.27±0.00	0.00	117-121	119±2.61	1.85	159-162	161±1.97	1.40
D	1.41-1.49	1.45±0.04	0.02	0.27-0.28	0.28±0.00	0.00	148-153	151±2.75	1.58	174-176	175±0.87	0.50
E	1.49-1.52	1.51±0.01	0.01	0.34-0.35	0.34±0.00	0.00	101-117	111±8.77	5.06	166-228	186±35.85	20.7
F	1.96-2.04	1.99±0.04	0.02	0.33-0.34	0.34±0.00	0.00	113-120	117±3.39	1.96	179-181	180±1.53	0.88

¹ All individual locations within MA, NC, and LC reflects the average of 3 samples, each replicated for triplicate metal analysis.

Appendix 5-A-1. Regional Enrichment Factors (EF) in Main Creek, Neck Creek, and Lemon Creek surface sediments 2001, 2007, 2009.

Main Creek	EF Cd	EF Hg	EF Cu	EF Zn		Neck Creek	EF Cd	EF Hg	EF Cu	EF Zn		Lemon Creek	EF Cd	EF Hg	EF Cu	EF Zn
2009	31.5	7.02	15.3	2.96		2009	17.3	6.34	12.5	1.93		2009	14.6	1.36	9.28	2.17
2007	51.1	7.87	18.2	3.59		2007	18.7	9.96	22.5	2.91		2007	10.9	1.08	10.0	2.10
2001	47.1	N/A	3.36	4.16		2001	25.6	N/A	17.1	2.05		2001	21.6	N/A	6.52	1.33

Appendix 5-B. Site-specific CF, CD, PLI mean and median values (2001, 2007, 2009).

Appendix 5-B-1. Main Creek CF, CD, and PLI calculations.

Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2009 Mean	11.5	7.90	4.77	2.53	26.7	5.76
A	16.4	15.3	1.90	2.02	35.6	5.57
B	13.5	15.3	0.99	1.26	31.0	4.00
C	16.8	14.8	3.37	3.39	38.4	7.30
D	12.8	1.59	7.83	3.04	25.3	4.69
E	4.33	0.21	7.18	2.64	14.4	2.04
F	5.39	0.24	7.32	2.81	15.8	2.28
Median	13.2	8.19	5.28	2.73	28.1	4.35
Calculated Mean						4.32
Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2007 Mean	18.7	8.86	5.66	3.06	36.3	7.32
1	20.9	8.93	5.89	3.08	38.8	7.63
2	16.9	8.85	5.54	3.17	34.5	7.16
3	18.3	8.78	5.54	2.95	35.6	7.16
Median	18.3	8.85	5.54	3.08	35.6	7.16
Calculated Mean						7.32
Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2001 Mean	17.3	N/A	6.54	3.54	27.4	7.37
1	15.6	N/A	6.52	3.56	25.7	7.13
2	15.3	N/A	6.12	3.39	24.8	6.81
3	20.1	N/A	6.13	3.37	29.6	7.45
4	18.2	N/A	7.40	3.85	29.4	8.03
Median	16.9		6.33	3.48	27.5	7.29
Calculated Mean						7.36

Appendix 5-B-2. Neck Creek CF, CD, and PLI calculations.

Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2009 Mean	6.35	7.13	3.89	1.65	19.0	4.13
A	6.90	7.51	3.96	1.84	20.2	4.40
B	6.10	7.70	3.68	1.62	19.1	4.09
C	4.83	6.72	2.23	1.11	14.9	2.99
D	6.15	3.99	3.47	1.65	15.3	3.44
E	6.07	7.17	4.47	1.73	19.5	4.29
F	8.03	9.71	5.52	1.94	25.2	5.38
Median	6.13	7.34	3.82	1.69	19.3	4.19
Calculated Mean						4.10
Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2007 Mean	15.1	11.2	7.66	2.58	36.5	7.60
1	13.1	11.1	7.01	2.46	33.7	7.08
2	17.2	11.5	8.93	3.10	40.7	8.60
3	14.9	11.0	7.04	2.19	35.1	7.09
Median	14.9	11.1	7.04	2.46	35.1	7.09
Calculated Mean						7.59
Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2001 Mean	9.41	N/A	5.31	1.75	16.5	4.43
1	7.78	N/A	5.62	1.80	15.2	4.28
2	10.7	N/A	4.96	1.65	17.3	4.44
3	10.3	N/A	5.37	1.67	17.3	4.51
4	8.92	N/A	5.27	1.87	16.1	4.45
Median	9.59		5.32	1.73	16.7	4.44
Calculated Mean						4.42

Appendix 5-B-3. Lemon Creek CF, CD, and PLI calculations.

Lemon Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2009 Mean	5.35	1.53	2.89	1.85	11.6	2.57
A	6.04	0.41	3.33	2.01	11.8	2.02
B	4.99	1.10	2.93	1.71	10.7	2.29
C	4.57	1.69	2.65	1.69	10.6	2.43
D	4.85	1.72	3.36	1.84	11.8	2.68
E	5.02	2.15	2.47	1.96	11.6	2.69
F	6.64	2.11	2.59	1.90	13.2	2.88
Median	5.00	1.70	2.79	1.87	11.7	2.55
Calculated Mean						2.50
LC Sample	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2007 Mean	4.02	1.21	3.12	1.79	10.1	2.28
1	4.90	1.22	4.29	2.30	12.7	2.77
2	4.08	1.21	2.82	1.57	9.69	2.16
3	3.07	1.21	2.25	1.48	8.02	1.88
Median	4.08	1.21	2.82	1.57	9.69	2.16
Calculated Mean						2.27
LC Sample	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI
2001 Mean	7.90	N/A	2.03	1.13	11.0	2.63
1	8.61	N/A	2.93	1.71	13.3	3.51
2	8.18	N/A	3.05	1.28	12.5	3.18
3	6.71	N/A	0.92	0.57	8.20	1.52
4	8.12	N/A	1.21	0.97	10.3	2.12
Median	8.15		2.07	1.13	11.4	2.65
Calculated Mean						2.58

Appendix 5-B-4. Main Creek, Neck Creek, and Lemon Creek PLI calculations with and without Hg CFs.

Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)	Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)	Lemon Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)
2009 Mean	11.5	7.90	4.77	2.53	26.7	5.76	5.18	2009 Mean	6.35	7.13	3.89	1.65	11.6	4.13	3.44	2009 Mean	5.35	1.53	2.89	1.85	11.6	2.57	3.05
A ¹	16.4	15.3	1.90	2.02	35.6	5.57	3.98	A ¹	6.90	7.51	3.96	1.84	11.8	4.40	3.69	A ¹	6.04	0.41	3.33	2.01	11.8	2.02	3.43
B	13.5	15.3	0.99	1.26	31	4.00	2.56	B	6.10	7.70	3.68	1.62	10.7	4.09	3.31	B	4.99	1.10	2.93	1.71	10.7	2.29	2.92
C	16.8	14.8	3.37	3.39	38.4	7.30	5.77	C	4.83	6.72	2.23	1.11	10.6	2.99	2.28	C	4.57	1.69	2.65	1.69	10.6	2.43	2.74
D	12.8	1.59	7.83	3.04	25.3	4.69	6.74	D	6.15	3.99	3.47	1.65	11.8	3.44	3.27	D	4.85	1.72	3.36	1.84	11.8	2.68	3.11
E	4.33	0.21	7.18	2.64	14.4	2.04	4.35	E	6.07	7.17	4.47	1.73	11.6	4.29	3.61	E	5.02	2.15	2.47	1.96	11.6	2.69	2.90
F	5.39	0.24	7.32	2.81	15.8	2.28	4.80	F	8.03	9.71	5.52	1.94	13.2	5.38	4.42	F	6.64	2.11	2.59	1.90	13.2	2.88	3.20
PLI Mean						4.32	4.70	PLI Mean						4.10	3.43	PLI Mean						2.50	3.06
Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)	Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)	Lemon Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)
2007 Mean	18.7	8.86	5.66	3.06	36.3	7.32	6.87	2007 Mean	15.1	11.2	7.66	2.58	10.1	7.60	6.68	2007 Mean	4.02	1.21	3.12	1.79	10.1	2.28	2.81
1 ¹	20.9	8.93	5.89	3.08	38.8	7.63	7.23	1 ¹	13.1	11.1	7.01	2.46	12.7	7.08	6.09	1 ¹	4.90	1.22	4.29	2.30	12.7	2.77	3.65
2	16.9	8.85	5.54	3.17	34.5	7.16	6.67	2	17.2	11.5	8.93	3.10	9.69	8.60	7.81	2	4.08	1.21	2.82	1.57	9.69	2.16	2.63
3	18.3	8.78	5.54	2.95	35.6	7.16	6.69	3	14.9	11.0	7.04	2.19	8.02	7.09	6.12	3	3.07	1.21	2.25	1.48	8.02	1.88	2.17
PLI Mean						7.32	6.87	PLI Mean						7.59	6.87	PLI Mean						2.27	2.82
Main Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)	Neck Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)	Lemon Creek	CF Cd	CF Hg	CF Cu	CF Zn	CD	PLI	PLI (w/o Hg)
2001 Mean	17.3	N/A	6.54	3.54	27.4		7.37	2001 Mean	9.41	N/A	5.31	1.75	16.5		4.43	2001 Mean	7.90	N/A	2.03	1.13	11.1		2.63
1 ¹	15.6		6.52	3.56	25.7		7.13	1 ¹	7.78		5.62	1.80	15.2		4.28	1 ¹	8.61		2.93	1.71	13.3		3.51
2	15.3		6.12	3.39	24.8		6.81	2	10.7		4.96	1.65	17.3		4.44	2	8.18		3.05	1.28	12.5		3.18
3	20.1		6.13	3.37	29.6		7.45	3	10.3		5.37	1.67	17.3		4.51	3	6.71		0.92	0.57	8.20		1.52
4	18.2		7.40	3.85	29.4		8.03	4	8.92		5.27	1.87	16.1		4.45	4	8.12		1.21	0.97	10.3		2.12
PLI Mean							7.36	PLI Mean							4.42	PLI Mean							2.58

¹Each individual location within MA, NC, and LC reflects the average of 3 replicated samples analyzed in triplicate.

Appendix 5-C. Metal-specific TU (ratio of mean Cd, Hg, Cu, and Zn in relation to ERL) and collective sum of site-specific Mean TU Quotient (2001, 2007 and 2009).

Site/Survey Year	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	Cd TU	Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	Hg TU	Cu ($\mu\text{g}\cdot\text{g}^{-1}$)	Cu TU	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	Zn TU	Sum TU	Mean ERL Quotient
MA Mean 2009	3.57¹	2.98	1.26	8.40²	229	6.73	243	1.62	19.7	4.93
MA Mean 2007	5.62	4.68	1.42	9.47	255	7.49	291	1.94	23.6	5.89
MA Mean 2001	5.18	4.32	-	0.00	294	8.66	337	2.24	15.2	5.07
NC Mean 2009	1.84	1.53	1.14	7.60	165	4.85	152	1.01	15.0	3.75
NC Mean 2007	4.52	3.77	1.79	12.0	345	10.1	245	1.64	27.5	6.87
NC Mean 2001	2.87	2.39	-	0.00	239	7.02	166	1.11	10.5	3.51
LC Mean 2009	1.62	1.35	0.24	1.60	131	3.84	177	1.18	7.97	1.99
LC Mean 2007	1.21	1.01	0.19	1.30	140	4.13	170	1.13	7.57	1.89
LC Mean 2001	2.35	1.96	-	0.00	91.3	2.68	108	0.72	5.36	1.79

¹Bold indicates concentration exceeds ERL

²Shading indicates greatest metal-specific TU

Chapter 6. Conclusion

Ultimately, this study provides critical data needed to develop a systemic and effective ecosystem perspective for future conservation and restoration efforts. Such scientific data on temporal and spatial scales is essential for establishing a solid foundation for planning and tracking success of both site-specific and ecosystem-scale restoration projects (National Research Council, 2001, 2002; USACE HRE, 2010).

Both natural and anthropogenic sources contribute to sediment enrichment. Primary pathways in which metal pollutants reach marsh ecosystems include point and non-point sources (i.e. industrial and municipal facilities, land runoff, atmospheric deposition, erosion and weathering) (Hare, 1992; Helgen, et al., 1996; Herut, et al., 1997; Rozan, et al., 2001; Weis, et al., 2006; Harikumar, et al., 2009). Increased regulation and treatment advances targeting anthropogenic effluents have enhanced the environmental integrity of estuaries nationwide. However, characterizations of region-wide progress may over-generalize and misrepresent the condition of individual waterways within these systems. For example, overall sediment and water quality improvements recognized in the New York/New Jersey Harbor Estuary misconstrues the recovery status of the Arthur Kill, which remains severely impaired by legacy and contemporary contaminant loadings (Steinberg, et al., 2004). Ecosystems along the Arthur Kill have long been vulnerable to deleterious impacts of various industrial and manufacturing facilities sited along this urban waterway (Huntley, et al., 1995) (see Chapter 1 for more information). Currently, many of these operations have been marginalized, displaced or no longer exist, which has consequently reduced anthropogenic metal loadings and minimized residual impacts from point sources. However, contaminant-laden sediments within the Arthur Kill complex may remain a threat to neighboring ecosystems (Vitaliano, et al., 2002).

The presence of toxic chemicals in water and sediments throughout the New York-New Jersey Harbor estuary (NY/NJ HE) has resulted in an enormity of extensive ecological and economic implications. In addition to general adverse impacts for estuarine and coastal ecosystems, the ubiquity and toxicity potential of persistent contaminants (i.e. metals) has led to systemic effects including reduced water and sediment quality, habitat degradation/loss, fisheries restrictions, recreational use advisories, species-specific reproductive impairments. Thereby, much like a negative feedback loop, in turn, the important interdependence of the NY/NJ HE between ecological and economic interests/needs, which makes it challenging to strike a balance between intrinsic and extrinsic values associated with natural and human interests. For instance, ecological and economic consequences linked to the omnipresent persistent pollutants and legacy contamination of sediments (i.e. the management of contaminated dredged material) has resulted in uncertainty regarding planned construction and future maintenance of the maritime infrastructure that supports shipping in the Harbor.

Restoration efforts can strive to meet a variety of goals, especially given the heavy past and future anthropogenic influence in the dynamic urban setting of the New York/New Jersey Metropolitan area. Regionally, the fundamental approach to ecosystem restoration encompasses a ‘renaturing’ approach. This manner of restoration aims for ecosystem improvements and development of habitats for the benefit of estuarine species and for new and increased (intrinsic and extrinsic) use of the estuary environment by humans (NYNJHEP, 1996; HREP, 1996; HREP, 2002; HREP, 2005; Bain, et al., 2006; USACE HRE, 2010).

Large scale ecosystem restoration projects have gained attention as they promise potential solutions to complex issues by employing a systems approach that bridges multiple issues and demonstrates a collaborative effort involving public, government and private

interests and institutions, while leveraging funding for a common goal. However, the long term track record of successfully implemented restoration projects of this scale remains to be seen; and the causes of success and failure are, as of yet, undetermined. Nonetheless data of the type reported in this study is fundamental for establishing attainable and measurable goals and for monitoring progress, success and evaluating failures (USCE HRE 2010).

A regional Contaminant Assessment Reduction Program (CARP) monitoring and mass balance modeling study has recently been completed for the NY-NJ Harbor and adjoining waters (HydroQual, 2007; NJDEP, 2008), which will help evaluate the progress of various regional efforts for long-term contaminant reduction of sediments. Nonetheless, it is recognized that additional sampling data of finer spatial resolution is required in proximity to specific localized areas to identify finer-scale sediment dynamics, transport, and fate, and current toxic contaminant distributions in sediment (USACE HRE, 2010).

Previous monitoring activities in Staten Island marshes included collection and analysis of cores and surface sediments to examine spatial and temporal distributions of chemical constituents (i.e. metals and radionuclides). Collectively, evaluation of vertical and lateral profiles constructed for each marsh helped to determine a number of characteristics, including: site-specific enrichment, temporal and spatial variations, small and large-scale trends and pollution gradients, while also investigating regional and localized influences, historic and contemporary loadings. Although Main Creek, Neck Creek and Lemon Creek demonstrated site-specific variations and enrichment of metals, sediment concentrations at depth and in surficial layers of all marshes generally indicated anthropogenic pollution.

On both spatial and temporal scales, comparative pollution assessments at Main Creek, Neck Creek and Lemon Creek were consistent. Evaluation of cores and surface sediments established large-scale distribution patterns and enrichment trends that described a pollution gradient over the extent of the study area (AK sites > LC). The variable levels of metals are likely a result of the different types and duration of anthropogenic activities that have been associated with the watersheds surrounding Main Creek, Neck Creek and Lemon Creek (Suskowski, 2006). Frequently, identifying and detecting the magnitude of individual sources, and subsequent transport, distribution and tracking of metal mobility is technically difficult (Rozan, et al., 2001). It proved to be particularly complicated in this study due to the multiplicity of point and non-point sources affecting the study area. The possible contribution and plausible cycling of metals linked to both historical and current anthropogenic activities added complexity to distinguishing between local and endemic sources (as well as the role of tidal exchange within the Arthur Kill complex) and ascertaining downstream vs. upstream (terrestrial vs. estuarine) impacts (Loska and Wiechula, 2002).

Although metal inputs attributable to certain suspected sources (i.e. legacy contamination and stormwater runoff) are difficult to assess and trace because volumes and frequencies can vary, it is critical to consider their potential impact on receiving environments. Accordingly, it is necessary to recognize that collectively, intermittent and/or consistent loadings from a combination of point and non-point sources may result in synergistic effects and ecological consequences (Franco, 2005). Furthermore, with Staten Island development initiatives continuing to rise, the natural ability of marshes to filter runoff and control stormwater have been compromised, making discrete pollution sources (i.e. runoff and stormwater pollution) an increasing threat to marsh ecosystems (Livingston, 1989).

Large and small-scale metal concentration datasets obtained from chemical analysis of depth and surface samples collected from Main Creek, Neck Creek and Lemon Creek provided a comprehensive spatial and temporal framework to examine the current condition of sediment and habitat quality throughout the study area. Although toxicity assays were beyond the scope of the study, an aggregate of reference values (i.e. background and contamination indices) proved useful for characterizing the extent of anthropogenic contamination, metal pollution loads and potential toxicity of sediments at each site. Accordingly, metal concentrations in cores and surface sediments were evaluated in terms of sediment quality and toxicity benchmarks to assess human-induced impacts and ecological implications that may affect marsh habitats over the extent of the study area.

Assessments of the lateral distribution of metals along spatial gradients at Main Creek, Neck Creek and Lemon Creek provided a better context to understand sediment quality throughout the study area in order to identify toxicity implications and site-specific marsh habitat impacts. Such indices and measures are commonly used to detect structural and functional impairment of threatened habitats and to prioritize restoration initiatives to ameliorate the toxic condition and restore ecosystem integrity (USACE HRE, 2010). It has been determined that NY/NJ Harbor Estuary sediments are repositories of many toxic chemicals; accordingly, the effects of contaminated sediments on ecological function and human use maybe significant (NY/NJ HEP, 1996; HREP, 1996; Bain, et al., 2006; USASCE HRE, 2010).

Nevertheless, this study provided additional critical data needed to articulate a systemic ecosystem perspective in future conservation and restoration planning. It also resulted in much needed scientific data on temporal and spatial scales for establishing a foundation for planning

and tracking success of site-specific and region wide projects (National Research Council 2001, 2002; USASCE HRE, 2010).

Sediment Cores

Metal and radionuclide analyses established that coring locations within all marshes (MA, NC, and LC) acted as repositories for fine-grained particles and associated contaminants on long (<10yrs.) and short-term (<1yr.) scales. For all sites, the levels of Cd, Cu and Zn found throughout the temporal extent of all sediment cores were indicative of anthropogenic pollution.

Main Creek, Neck Creek and Lemon Creek coring datasets demonstrate evidence indicative of site-specific temporal variations of chemical distributions (metals [2001; 2007] and short-lived radionuclides such as Be⁷ [2007]) in downcore sediments from localized areas of each site. Although higher radionuclide activities were identifiable in recent sediments (deposited within a year) from Main Creek and Lemon Creek, marshes adjacent to the Arthur Kill (MA and NC) demonstrated a comparatively greater metal pollution than Lemon Creek, which opens into the Raritan Bay. Regardless of site-specific metal concentrations and radionuclide activities within Main Creek, Neck Creek and Lemon Creek sediment columns, comparable metal enrichment was measurable within the bottom and top layers. This suggested insignificant attenuation of past metal inputs derived from natural and anthropogenic sources. An assessment of metal contamination and sediment quality via surficial metals datasets acquired over the past decade, further confirmed that sustained anthropogenic contamination is likely attributable to a combination of ubiquitous and acute localized pollution sources that contribute metal-specific inputs (i.e. Cu and Zn) linked to past and present-day loadings (i.e. legacy discharges, current non-point sources).

Geochemical results of Lemon Creek sediment enrichment at depth and surface sediments increased demonstrably over time (2001 vs. 2007), with respect to metals concentrations relative to regional and global background levels. This temporal trend was apparent through 2009. However, it did not affect the potential toxicity of contaminated sediments over time.

Surface Sediment Transects

This research component first determined metal concentrations in sediments along longitudinal transects spanning a larger extent within Main Creek, Neck Creek and Lemon Creek to characterize small-scale distributions and enrichment patterns, which together with vertical/downcore distributions established a more complete context in which to describe site-specific spatial and temporal sediment contamination. Subsequently, comparative assessments of site-specific surface sediment enrichment provided a comprehensive context to describe large-scale contaminant trends/spatial gradients throughout the study area. Furthermore, these results demonstrated that greater metals concentrations may reflect the greater contamination of marshes along the western margin of Staten Island.

On both spatial and temporal scales, comparative pollution assessments at Main Creek, Neck Creek and Lemon Creek were consistent. Evaluation of cores and surface sediments established large-scale distribution patterns and enrichment trends that described a pollution gradient over the extent of the study area (AK sites > LC). The variable levels of metals are likely a result of the different types and duration of anthropogenic activities that have been associated with the watersheds surrounding Main Creek, Neck Creek and Lemon Creek.

Although prior core assessments established Main Creek, Neck Creek and Lemon Creek sediments act as repositories of chemical constituents, analyses were limited to a specific area within each marsh system. Therefore, longitudinal transects assessed the spatial distribution of metals throughout the areal extent of each study site. Moreover, the degree to which small-scale spatial variations occurred in another integral environmental compartment, the water column, was examined over a tidal cycle at Main Creek, Neck Creek and Lemon Creek to examine contribution to site-specific spatial and temporal trends. Accordingly, additional research components aimed to determine the degree to which small-scale spatial variability of metals in surficial sediments and suspended particles/solids (SS) contributed to the site-specific spatial and temporal longitudinal (lateral transects) and vertical (downcore) patterns.

Evaluation of Main Creek, Neck Creek and Lemon Creek cores demonstrated the sediments acted as a repository of metals. However, geochemical analyses focused on cores collected from particular marsh flat locations, targeting sites that were previously sampled or exhibited optimal conditions for reconstructing sediment chronologies (slow-currents, fine-grained sediments dominated by silt and clay fractions) (Bopp, et al., 2006). Thereby, site-specific characterizations of intra-spatial metal distributions were limited to the spatial extent examined within each study site.

Primary study objectives of Chapter 3 rectified small-scale influences via examination of Main Creek, Neck Creek and Lemon Creek longitudinal surface sediment transects in order to characterize intra-marsh fluctuations and consider site-specific spatiotemporal variability on finer resolution scales. In addition to analyzing metal contents of surficial marsh bed deposits, this research component also analyzed Cd, Hg, Cu, and Zn associated with the particulate

(opposed to dissolved) fractions of total solids suspended within the water column to determine the presence and elemental distributions among these two major environmental compartments.

A secondary goal comparatively assessed relative magnitude of metal concentration and enrichment levels exhibited by sediments in suspension in the water column and “biologically active” surface deposits. Accordingly, this approach effectually tested the applicability of the premise that sampling marsh bed sediments, and particularly environmentally relevant surface layers, can be considered representative of fine-grained suspended matter transported with the overlying flow of creek conduits within marshes and alternatively, the predicative ability of water column samples analyzed on dry weight basis (mass·mass).

Although site-specific temporal distribution trends characterized via geochemical assessments were based on sediment cores from localized areas of each marsh system in Chapter 2, Chapter 3 presented an examination of surface sediment metal concentrations along longitudinal transects within Main Creek, Neck Creek and Lemon Creek to characterize small-scale variations, distribution trends and surficial contamination. Chapter 3 considered and accounted for intra-marsh spatial variability and suggests that the examination of a greater study area is not likely to largely affect prior observations showing site-specific depth profiles of metals and temporal distributions trends. Therefore, it is clear that, beyond differences among sampling surveys attributable to variable sample sizes and areal extents characterized within each system, large-scale spatial variability among sites and trends are consistent with those characterized by prior marsh assessments.

Examining the vertical and lateral distribution of metals and level of enrichment and pollution loads at depth and in surficial sediments demonstrated that all marshes are subject to

metal contamination and finally, at current at levels, can result in toxic biological effects that may deleteriously affect marsh-creek habitats and cause cascading ecological implications.

Particulate Metals and Tidal Flux of Suspended Sediments

Previous research components (Chapters 2 and 3) assessed intra-site metal distributions at depth and in surface sediments in Main Creek, Neck Creek and Lemon Creek, collectively depicted site-specific levels of enrichment. These findings showed large-scale variations of anthropogenic Cd, Hg, Cu, and Zn, and established a geographic pollution gradient with respect to spatial and temporal contamination of marsh sediments.

The intent the intent of Chapter 4 was to examine suspended sediment metals distributions and tidal variations within the study sites. This complimented the examinations performed in Chapter 3. Lemon Creek demonstrated the lowest magnitude, and greatest consistency, both temporally and spatially in terms of anthropogenic contamination, which may indicate proximity to the Arthur Kill, and tidal connectivity, affects the quality of marsh sediments. Likewise, marsh-creek habitats adjacent to Arthur Kill may be susceptible to greater impacts and more severe ecological implications than ecosystems external to the Arthur Kill proper. Although further study is required, tidal exchange may contribute to the large-scale contamination gradient demonstrated by temporal and spatial datasets. Therefore it was obvious that land use in surrounding watershed areas, and subsequent runoff from predominately industrial areas, resulted in greater impact to Arthur Kill marsh-creek habitats than observed at Lemon Creek.

In general, site-specific differences between and among sites (and surveys) may be due to a variety of natural and anthropogenic factors, including spatial and temporal dynamics on both

large and small scales. Regardless of tidal phase (i.e. spring/neap) or stage (i.e. ebb, flood) tidal flows effectively served to (re)suspend and transport sediments laterally among open water and inland wetland systems. In relation to LC, both MA and NC showed significantly lower concentrations of SPM and higher levels of all particulate (and SPM) metals. The greater magnitudes of metals within the water column (AK sites > LC) aligned with findings from prior coring and transect studies. However, this contrast between parameters (SPM concentrations and metals) shown by the study sites within the Arthur Kill and Raritan Bay watersheds implicated localized hydrodynamics and land-use are largely attributable to the evident geographic variability of water column constituents.

Tidal flow conditions, but rather site-specific creek morphology and localized dynamics, and geography, may play an ancillary role in the cyclic (re)distribution, transport, and fate of metals via deposition (of particulate metals suspended within the water column) or conversely, the remobilization of metal contaminated particles deposited on surficial bed sediments. Compared to the Arthur Kill sites, Lemon Creek clearly showed a higher tidal prism value. Although, only one survey was used to characterize a tidal prism at Lemon Creek, it is likely that the site showed the maximum value of water volume exchanged on account of localized creek morphology, including the greater surface area ratio of the Raritan Bay, in conjunction with site-specific hydraulic factors that influenced greater tidal forcing and increased velocity measurements over the tidal cycle survey.

In general, anthropogenic modifications to channel morphology, characteristic of all marshes, likely affected localized velocity gradients and generated current asymmetries due to respective dynamics such as, shear flow dispersion and tidal trapping. The evident contrast

among flood and ebb tidal flows at all sites, which demonstrated greater import (influx) relative to export (efflux) of water, was reflected by calculation of MA, NC, and LC tidal prisms. Upstream of MA, NC, and LC cross-sectional sampling locations, ancillary channels (i.e. mosquito channels) and diking of upland wetlands likely impacted net flux and movement of water parcels entering and draining the sites (on flood and ebb tides). The asymmetrical tidal prisms measured at all sites and surveys indicated the relative importance of marsh geometry. Thereby, localized marsh geometry likely affected hydrodynamics, and ultimately, scalar transport of metals within all systems. Accordingly, both natural geochemical and anthropogenic disturbances affected metal distributions in MA, NC, and LC sediment compartments and were considered important dynamics controlling sedimentation and resuspension of metal-bound sediments.

The significance of tidal stage was tested by comparison the central tendencies (medians) of respective non-negative fluxes from flood and ebb datasets. The distributions of fluxes from the 2 directional datasets (samples were grouped based on lateral movement of the tide +/-) were compared to determine differences among incoming and outgoing material fluxes entering (+) or leaving (-) the upland marsh habitat. The neap tide survey conducted at Main Creek showed insignificant differences between flood and ebb tide instantaneous fluxes with respect to Cd, Cu, Zn, and SPM fluxes. However, similar to Neck Creek and Lemon Creek, the summation of metal-specific flux curve areas with respect to current direction (flood (+) and ebb (-)) showed a demonstrable contrast in metal-specific datasets between incoming and outgoing tides.

The difference between incoming (+) and outgoing (-) contaminant fluxes, calculated via the summation of the areas beneath the respective curves produced for each tidal stage (flood vs. ebb), determined the net direction of tidal transport for each parameter studied. In general, Neck

Creek surveys contrasted in terms of the net direction of tidal transport of Cd, Cu, Zn, and Hg on particles suspended within the water column during neap and spring tidal flow conditions.

Conversely, both Main Creek surveys demonstrated a net positive term (influx) for all constituents studied. The positive value determined for both Main Creek surveys indicated a net import of Cd, Cu, Zn, and Hg on particles suspended within the water column during both minimum (neap) and maximum (spring) tidal ranges and low and high flow conditions characteristic of neaps and springs. In general, Lemon Creek showed a net import for all parameters except for Hg (i.e. Cd, Cu, Zn, and SPM). Although the net difference between ebb and flood area curves reflected a negative value for particulate Hg, the net export term was negligible.

Sediment Quality

Present-day conditions were examined with consideration of the intra-spatial variability of small-scale surficial metal distributions (via determination of CF and PLI values) along lateral transects that extended away from prior coring locations; reaching either towards, or away from, upland marsh habitats. However, neither presence of anthropogenic contamination, nor magnitude of enrichment levels is necessarily indicative of greater potential of toxic response. Opposed to the obvious endemic presence of Cu and Zn, the relative signature of certain metals (i.e. Hg and perhaps Cd) identified within marshes in the Arthur Kill watershed, demonstrated a relatively greater environmental impact in terms of potential illicit toxic effects in benthic organisms and habitat degradation.

Collective assessments of intra-marsh metal distributions in Main Creek, Neck Creek and Lemon Creek surface and core sediments depicted site-specific levels of enrichment, which

discerned large-scale spatial variability of anthropogenic enrichment, theoretically implying greater sediment contamination in marshes along the western margin of Staten Island. Intra-marsh variability of sediment quality, in terms of magnitude of site-specific metal contamination of marsh sediments, was determined by theoretical assessment methods.

Contamination Factors (CFs) were used initially to further illustrate previous findings of the background sediment approach, in which regional reference values were used to describe Enrichment Factors (EFs), or metal-specific contamination extents at depth and in surface sediments. These measures were used collectively to determine the Pollution Load Index (PLI) of Main Creek, Neck Creek and Lemon Creek cores and surface sediments, which was used to represent site-specific mean magnitude of temporal and spatial sediment contamination.

This research component used an aggregate of reference values and benchmarks to further examine the anthropogenic metals signature and establish if temporal and spatial variability among marsh sediment quality reflected previously defined large-scale pollution gradients. Given that sediment quality measurements used to assess spatial and temporal extent of contamination and toxicity potential throughout the study area demonstrated consistent large-scale trends over time, this study confirmed/defined a demonstrable impact gradient, which was directly correlated with pollution load and metal concentrations. Although, not affected by spatial/areal small-scale distribution or toxicity variations examination of small-scale distributions provided additional insight on large-scale distributions and comparisons among sites in terms of potential for sediment toxicity and habitat degradation, which was integral in order to further consider the extent that [localized or endemic] natural and human-induced factors/disturbances affected metal distribution and enrichment levels throughout the study area.

Conclusion

Temporal variations in downcore chronologies of particle-reactive contaminants (radionuclides and metals) and inter-spatial differences between Main Creek, Neck Creek, and Lemon Creek, in terms of lateral distributions and magnitude of metal concentrations (Cd, Hg, Cu, and Zn) suggested that on both local and regional scales, natural environmental dynamics (i.e. biogeochemical interactions and hydrodynamics (currents and waves) and anthropogenic stressors (i.e. dredging, human-induced physical habitat disturbance and pollution via point and diffuse sources) influenced site-specific depositional context and enrichment levels.

In terms of metal distributions and enrichment, intra-marsh spatial and temporal differences in metal contents were site-specific. Generally, Lemon Creek showed the most consistency among elements analyzed within each dataset, and also among all metal compartments studied (i.e. sediment cores, marsh surface sediments, SPM and particulates suspended within the water column. Conversely, Main Creek showed the least, in terms of inter-elemental consistency; metals did not show temporal or spatial constancy at depth, in surface layers, nor suspended as particulates

Given the dynamic contribution and partitioning of metals among environmental compartments, sediments were found as repository and source of pollutants throughout the study area. Further studies are recommended, including a continuous monitoring of study metals considering both biotic and abiotic compartments. Further monitoring of study metals with respect to biotic and abiotic compartments would help to examine causative effects related to actual environmental exposure of metal contaminated sediments. In addition to sediment chemistry, future studies might include community composition measurements (i.e. indices

benthic diversity and abundance) and additional data for biological effects (observed toxicity, histopathology).

Various human activities and mixed land-uses have compromised the quality of Main Creek, Neck Creek and Lemon Creek sediments. Accordingly, marsh-creek habitats throughout the study area are subject to considerable stress due to anthropogenic impacts, including chemical and manufacturing industries, dredging, drilling and urban development and re-development. Moreover, anthropogenic stressors, known to cascade through ecosystems via food webs, may result in adverse ecological effects (Goto, 2009).

Degradation of habitat quality in urban tidal salt marshes can adversely affect resident fishes, potentially disrupting trophic connectivity and energy flow in coastal ecosystems (Goto, 2009). Although species specific impacts are beyond the scope of this study, benchmarks and toxicity indices enhanced the overall understanding of the environmental integrity of urban marsh habitats. Since certain areas are slated for restoration and/or acquisition there is a need to evaluate past and current levels metal pollution and examine the potential toxicological effects of contaminated sediments to establish a comprehensive assessment framework to measure future restoration initiatives.

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