

Sediment Quality Characterization for the Forge River, Long Island

A draft report prepared for the
Town of Brookhaven
Long Island, New York

by

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Introduction

The studies undertaken in the Forge River by the School of Marine and Atmospheric Sciences from 2006-2008 were initiated when the environmental agencies of New York State, Suffolk County, and the Town of Brookhaven raised concerns about potential sediment contamination and its impact on the water quality issues in the river. Thus, our reconnaissance survey of June 30, 2006 revealed that the Forge River was experiencing water quality problems other than those associated with sediments. The project expanded considerably beyond its initial focus but sediment characterization remained a major concentration in the overall endeavor. This report summarizes that research.

This report presents the findings of studies conducted to determine the distribution of sediment properties and associated contaminant levels in the Forge River. The sediments were collected with sediment grabs and cores, and provide information on the spatial and temporal distributions of sediment properties around the Forge River, with a focus on the tidal Forge. Most samples were collected on an August 8-9, 2006 sampling cruise conducted aboard a Suffolk County Department of Health Services (SCDHS) vessel. Other grab samples were collected on June 30, 2006, and three surface sediment samples in the upper Forge were collected on December 21, 2006 at sites not accessible by boat. Here we synthesize the results and interpretations presented in three data reports prepared for Suffolk County, which include a report on sediment properties in the Forge River, one on sediment metal concentrations in surficial sediments and sediment core data from the Forge River, and one on organic contaminant distributions in surficial sediments and sediment cores from the Forge River.

Goals of the sampling studies included:

- assessment of sediment enrichment of organic matter as a reflection of water column eutrophication and also as the reservoir of labile organic matter that acts as a sink for oxygen and a source of nutrients back to the water column; that work was then tied to a study of benthic fluxes of nutrients and the role of sediments as a sink for water column oxygen in the Forge;
- assessment of the levels and distributions both aerially and with depth in sediments of potentially toxic trace metals and semivolatile organic contaminants;
- estimation of the thickness and quality of recent mud to support management decisions related to maintenance or remedial dredging.

The sediment coring conducted was not designed to provide precise histories of organic matter and chemical contaminant deposition, although the results obtained shed light on changes over time with respect to pollution in the tidal Forge.

In this report, we further compare metal and organic contaminant data to those sometimes used as sediment quality guidelines during risk assessment efforts, and comment on issues that might arise during consideration of dredging scenarios.

Methods

The methods used to determine sediment properties and chemical concentrations are reported in the aforementioned data reports prepared for the SCDHS. Some of the details of the actual sampling strategy and methods are presented again here to put the results in context. The primary sediment sampling followed a tidal river-wide sediment grab reconnaissance study conducted June 30, 2006, aboard a small boat operated by the SCDHS, where we collected samples at 11 sites corresponding to SCDHS water monitoring sites (Figure 1). From that field trip we gained information about the sediment types and the logistics of sediment sampling approaches required for the shallow Forge River. The locations sampled later were modified based on what we learned on that field trip. For the sake of future studies, it should be noted that sediment sampling is challenging in the Forge River, given the shallow depths, and the draft of vessels large enough to deploy sediment grab and sediment core samplers used.

Sediment grab and core sampling were conducted primarily on August 8-9, 2006, and were largely restricted to deeper areas that have been historically dredged. Grab sampling was completed with the aid of SCDHS on August 8 at 13 sites (Table 1; Figure 1) using a modified Eckman grab sampler, with the same methods (including the 0-5 cm depth interval) used for the U.S. EPA Coastal 2000/National Coastal Assessment Program studies, sampling also supported in part by SCDHS.

Sediment coring methods were chosen based on the shallow water depths and the clearance between the winch on the boat and the water's surface. A standard Benthos gravity corer was used, with acrylic core tubes also from Benthos (2 5/8 in ID x 1.3 m). The sediment core results presented here rely upon 10 cores obtained on August 9. Station locations are provided in Table 2 and Figure 2. Cores were sectioned into discreet depth intervals the same evening (typically, but not always, 0-5, 5-15, 15-30, 30-50 cm, and 50 cm to near the bottom, of cores for those longer than 50 cm). These depth intervals were selected to provide information about the depths of penetration of targeted contaminants of concern into sediments, and not to recreate the history of deposition. In most of the cores, there was a transition in sediment color and texture that typically occurred between 15 cm and 60 cm below the sediment water interface (Table 2). The sediments in the upper layer were generally dark brown to nearly black, and much less consolidated ("soupy" as opposed to stiff). Sediments in lower layers were either gray or light brown transitioning to gray.

Surficial sediments were also collected on December 21, 2006 at a site in the upper tidal Forge along the east bank (termed Upper Forge or UFEB throughout the reports, and one sample each in East and West Ponds (Table 1; Figure 1). As these sites were located in areas inaccessible to boats that could accommodate the grab sampler, a kayak was used and

samples collected by inserting a Benthos tube core into the sediment, and securing the soupy sediment from below with a methanol rinsed plastic cap. These samples were approximately 6-11 cm in length.

It was determined on the June 30 trip that there was a significant thickness of finer grain sediment overlying a sand layer when a 10 foot length of iron rod was inserted into the sediment from the side of the boat (a telltale feeling of hitting grit upon penetration into the sediment bed at some of the sites). On the August 8 sampling, we better defined that depth to sand below the sediment-water interface at each of the sediment grab sample sites: a 15 ft iron bar with a removable T-handle on one end was constructed, inserted into the sediment, and the length recorded if a sand layer was reached. The depth of the finer grain sediment deposit was corrected for the depth of the water. In many cases, sand was not encountered; a minimum thickness of finer grain sediment is listed in Table 1.

Results and Discussion

General Observations from Sediment Grabs and Cores

Muddy organic rich surface sediments were encountered in all of the 40+ samples collected on the four dates. This may have been due in part to our sampling primarily in deeper or formerly dredged channels, where sediment sampling by boat was more feasible. However, it should be noted that there are extensive intertidal mud flats that are seen at lower tides, and they are too soft to safely walk upon. Mud may preferentially accumulate in deeper areas, especially in the Forge where circulation is sluggish. However, visual observations of exposed intertidal sediments at low water on winter tides suggest that fine grained mud may be a pervasive sediment type throughout the tidal Forge. Black suboxic or anoxic mud was observed in the preponderance of samples. Only at sites closest to the mouth of the tidal Forge (stations 12 and 13) and outside the mouth of the Forge in Moriches Bay (station M) was there any evidence of a more oxidized (less dark) sediment water interface. At those three sites, a more oxidized interface was limited to the very surface (on the order of 1 mm). Thus, at all sites, there was evidence of high levels of remineralization of organic matter, and sulfate reduction (black sulfide minerals and smell of sulfide). Low oxygen levels in the overlying water also contribute to the lack of significant penetration of oxygen in the sediments. There was a clear gradient in the darkness and “soupiness” of the mud from north to south along the axis of the Forge, likely reflecting pollution sources of organic matter and greater exchange of cleaner water toward the mouth of the river. Sediment samples from Wills Creek also appeared to have highly excessive levels of organic enrichment.

There were no signs of benthic infauna (from inspection of the entire grab samples and visual inspection of transparent core tubes) at the preponderance of sites on the dates sampled. Benthic organisms were observed at stations M (polychaetes) in Moriches Bay, and UFEB. The latter site was sampled in December when sediment and water column oxygen concentration could have been higher than in summer at the time other samples were collected. Grass shrimp were abundant above shallow tidal Forge sediments south of

Montauk Highway on December 21. At station 13, near the mouth of the Forge, there were mats of amphipod tubes on the surface that appeared to be rotting. This may be the result of colonization of opportunistic, but oxygen sensitive, amphipods earlier in the year, when oxygen conditions were more favorable. This observation is consistent with surveys of populations of benthic organisms conducted that same summer by Chris Gobler's laboratory.

None of the sediments contained visible detritus, with the exception of those in East Pond, where there were abundant twigs and rotted leaf detritus within at least 100 foot radius of the site sampled. We could not find sediment in shallow depths in West Pond that was not covered by algal mats, and therefore we sampled sediment just below the surface of the algae. It was noted that the sediments from East and West Ponds were sandier than those collected in the tidal Forge. The very high sediment organic matter contents of the tidal Forge sediment are thought to be associated with organic mineral particles coated with organic matter rather than "clumps" of detritus or recent animal excrement. This is supported by the benthic flux study results presented in a report to Suffolk County. We believe the source of organic matter enrichment is derived from algal growth in the tidal Forge rather than input of organic matter from the upstream tributaries.

These observations are entirely consistent with sediment sampling of Moriches Bay, the Forge River and other tidal tributaries, conducted in 1959 (Nichols, 1964). Nichols characterized the Forge River, and other duck farm-affected tributaries along Moriches Bay, as "striking in their content of soupy, black, clayey silt that has a rich odor of hydrogen sulfide and are extremely high in organic matter as a result of discharge from duck farms. Because of the anaerobic conditions, benthic invertebrates and foraminifera are absent...." Our coring results described below are similar to the sediment characteristics observed in the tidal Forge five decades ago.

It proved difficult to collect sediment cores greater than 75 cm during our sampling. This was due to the stiffness of sediments (lighter brown proceeding to gray) that existed below the much darker, higher water content sediments above them (Table 2; Figure 3). The approximate depth of this transition is recorded in Table 2. Due to the stiffness of the underlying sediment, it was hypothesized that the deeper sediments were much older clay rich deposits. This proved not to be correct and based on multiple lines of evidence presented below, we believe that the transition layer corresponds to the depth to which sediments were dredged in the time period between 1965 and 1972 (Swanson et al., 2008). The stiffer, deeper portions of the cores are clearly older, and could be much older, than those just above the transition zone, based on profiles of contaminants with known deposition histories.

The depth of finer grain sediment overlying a sand surface is seen in Table 2 and varies between 0.7 and 2.8 m. Only at the most northerly core/grab stations 1 and 7, a grab sample site (station 3) in Wills Creek, and at grab station A was the depth of fine grain sediment less than 2.4 m. The limits to which we could estimate the distance to sand was affected by water depth that had to be subtracted from the length of the rod. Radiochemical dating methods would be useful to help understand the very long term sedimentation and

geology of the tidal Forge, and how it has been influenced by natural and man-made changes in the hydraulic regime.

Water Contents

Water contents were very high as expected in the upper, darker layers of sediment (Figure 3). The differences in average water content between the upper 15 cm of the most northern, and most pollution impacted cores (stations 1, 2, 4, 4B, and 7) was 86.4%, compared to an average water content for all 10 cores (56.3%) measured in sediments below the transition zone. Due to the relatively small number of individual sections of sediment, it is difficult to conclude much about changes in water content below the hypothesized transition zone, although water content was seen to decrease further with depth at station 10, likely due to lower amounts of compaction that could be due to a number of factors (e.g., station 12).

Organic Carbon and Nitrogen Contents

The total organic carbon (TOC) and nitrogen contents of the sediments (Figure 4) are incredibly high. Maximum TOC contents vary between 7.7 and 12.1% at stations 1, 2, 3, 4, 4B, 7, 8, and 10. These levels are much higher than levels encountered in more moderately eutrophied estuaries (Mayer, 1994). For example, in a system-wide survey of 113 surface sediments in the highly urbanized lower Hudson Basin/New York/New Jersey Harbor complex (Adams and Benyi, 2003), TOC contents of fine grain sediments were typically between 2 and 4% with higher levels (7% in highly sewage-impacted and eutrophied, restricted flushing areas of Jamaica Bay with especially low flushing), near a sewage treatment plant and combined sewer overflow (10%). The very high TOC levels in the tidal Forge River area are likely controlled by the “hyper-eutrophication” of the Forge, which combined with the poor flushing of the river, results in immense delivery and retention of organic matter to the sediments from phytoplankton and algae; the depletion of oxygen in the sediments and overlying water limits to an extent the rate at which bacteria can oxidize that loading of organic matter, and coupled with sediment burial, lead to tremendous preservation of organic matter. Some of the organic matter loading into the tidal Forge is derived from the East and West Ponds as suspended particulate organic matter. The present study was not designed to estimate the relative contribution of this source of organic matter, although extensive monitoring of chlorophyll and TOC at East and West Pond sites could be used to put some limits on those inputs. Wills (stations 3, 4, 4B) and Poospatuck (station 10) Creeks are less affected by the East and West Ponds than are upstream station 1 and 7 sites. The very high and deeply buried TOC levels at sites 3, 4, 4B, 7 and 10 provide evidence that local plankton/algal sources of organic matter within the tidal portions of the Forge act as the major source of organic matter enrichment in the Forge River.

The very high TOC levels measured in East Pond are the result of leaf litter detritus, a conclusion consistent with the higher TOC to organic nitrogen ratio at that site. The lower

TOC levels measured at sites in the upper tidal Forge and West Ponds may have been due to grain size.

Organic nitrogen levels are also highly elevated throughout the Forge River. Thus organic nitrogen has been well preserved and serves as a large reservoir of nutrients that has been shown in our other studies to be released at relatively high rates back into the water column as a result of microbial degradation of sediment organic matter. That microbially-mediated remineralization of organic matter and release of nutrients back to the water column, and corresponding rate of oxygen utilization, are fastest during warmer summer months, unfortunately, when eutrophication is at its worst.

There is a good correlation between the spatial (site to site) and depth profiles of TOC and sediment organic nitrogen with the aforementioned water contents (Figures 3 and 4). This is most likely the result of water content being controlled by recent deposition of more organic rich sediments.

It is of interest to note that the TOC and organic nitrogen levels (the latter not shown here) in deeper sections of the cores (Figure 4) are appreciably lower than at the surface, but are still quite elevated above those typically found in fine grain estuarine sediments not affected by intense eutrophication (typically on the order of 1-2%; Mayer, 1994). The tidal Forge, with its restricted tidal flushing, estuarine circulation, and location within the Moriches Bay lagoon, is naturally susceptible to accumulation of nutrients, organic rich sediments, and eutrophication. Unfortunately, we do not know the ages of the deeper sediment sections of our cores to determine whether organic enrichment started to occur before human's activities on the Forge, especially duck farming. It is seen below that there are essentially no DDT residues or PCBs present and only background levels of PAHs and many trace metals below the transition zone in the sediments. Given the absence of DDT residues below the transition suggests that this sediment predates the 1950s and that more surficial sediments may have been removed during the dredgings between 1965 and 1972. It would be extremely useful to collect additional high resolution sediment cores at selected sites in the Forge River for radiochemical dating to determine whether organic enrichment of sediments occurred before the 20th century and further understand the history of man's effects on the Forge.

The depth profiles of TOC and other contaminants (below) indicate that the excessive organic enrichment of sediments preceded the most recent deterioration of Forge River water quality that led to studies of the river starting in 2005. There are sub-surface maxima of contaminants like DDE and lead in the sediment cores, contaminants whose inputs peaked in the late 1960s/early 1970s. These and other contaminants and sediment properties decrease rapidly at depths that correspond to the transition zone in sediments, further supporting the hypothesis that this surface marks a discontinuity in sediment records as a result of dredging during that time. More compelling are the data of Nichols (1964) that show very high organic matter contents in Forge River sediments collected in 1959. Note that Nichols estimated organic matter contents (up to 21% in the Forge) by loss of weight following

peroxide treatment; as the conversion between TOC and total organic matter approaches a factor of two, the agreement between the data (collected nearly 47 years apart) is consistent. Furthermore, Nichols showed that TOC in muddier Moriches Bay sediments were approximate one fourth of that in the upper tidal Forge, again consistent with the results of this work. We conclude that intense eutrophication in the Forge has occurred at least since before 1950 and maybe for much, much longer.

Sediment Sulfur Contents

The concentrations of sulfur determined by the CHNS analyzer are high and evidence suggests it is largely pyrite. Pyrite levels are indicative of consistently high rates of sulfate reduction (i.e., near zero oxygen and an abundance of labile organic matter for microbial respiration). The reported levels of sulfur/pyrite are very high compared to those measured in estuarine sediments (Bob Aller, personal communication) and like elevated TOC levels, high pyrite concentrations extend to the bottom of the sediment cores.

Grain Size

The grain size data for surface grab and sediment core data were equivocal, but little difference in grain size (or aluminum or iron content as seen below) above and below the transition zone in sediment cores suggests that the source of sediment to the Forge has not changed greatly over time. Nichols (1964) also characterized Forge River sediments as organic rich silt.

Metals and Organic Contaminants in Sediments

The concentrations and spatial distributions of metal and organic contaminants in Forge River sediments are controlled by a number of factors:

- 1) proximity to point sources, or watershed-wide sources of contaminants that may exist.
- 2) changes in history of point and non-point sources (e.g., atmospheric deposition of contaminants directly to the Forge or through runoff from the watershed).
- 3) the high organic carbon content and fine grain nature of the sediment that results in higher sorption and enrichment of contaminants and background metals to be present in the sediments. This is important, for example, when we tried to compare the concentrations of contaminants measured here to sediment data for samples from Great South Bay, or Moriches Bay, collected during Coastal 2000 or the National Coastal Assessment Program, we found the comparisons inappropriate given the coarse grain, low aluminum and iron, sandy nature of the sediments consistently analyzed in those studies. Coarse grain sediments will sorb less contaminant and are less likely to be reflective of depositional areas where the record of load contamination is recorded.

- 4) the high amount of sediment and water column sulfide levels that appear to scavenge selected metals from seawater when it enters the Forge. This is especially important for explaining the levels of molybdenum (Mo) and cadmium (Cd) in the tidal Forge, and may affect the concentrations of other metals including copper (Cu), silver (Ag) and even potentially the elements zinc (Zn), and lead (Pb).
- 5) the concentrations of contaminants in fine grain fractions of sediments in Moriches Bay that then get flushed into and deposited in the Forge.
- 6) other factors such as the relative amounts of sediment burial and mixing, and potential dilution of contaminants by inputs of cleaner sediments.

Below we present again data and data interpretation that is found in reports to Suffolk County and expand on interpretation of that data.

Metals in sediment grab and core samples

Metal concentrations in grab sediment samples are shown in Table 3. Concentrations (in $\mu\text{g/g}$ dry weight) of the major carrier elements, iron (Fe) and aluminum (Al), ranged from 25,300-38,900, and 38,800-60,800 (average Fe and Al = 35,500 and 54,400, respectively). The vast preponderance of Fe and Al in sediment is natural, and the levels present are consistent with that of fine grain muddy sediment; the concentrations of Fe and Al are somewhat lower near the mouth of the Forge (station 13) and outside the mouth at station M, indicating a coarser grain sediment. The average levels for the other trace metals were several orders of magnitude lower (Mo (molybdenum) = 8.99, Ag = 0.79, Pb = 65.6, Cd = 1.22, Co (cobalt) = 9.8, Cu = 86.6, Ni (nickel) = 27.9, V (vanadium) = 117, Zn = 203, Ti (titanium) = 0.631 and Mn (manganese) = 389). For most of the metals, there is relatively little spatial variability in concentrations when the effect of lower aluminum content at stations 13 and M is considered. The biggest exception is for Mo, followed by Cd. These metals decreased from the upper Forge River to the lower portions of the river, with the highest metal accumulation in or near the tributaries of the river and at station 1, the station sampled farthest up the river near the end of the boat channel. Molybdenum concentrations in the lower Forge River were almost an order of magnitude lower than the values measured in the upper river locations (2-3 $\mu\text{g/g}$ versus 10-25 $\mu\text{g/g}$), and Cd levels increased two to three fold going up the river. Finally, Cu concentrations also tended to increase by almost a factor of two going up the river, with the exception of somewhat elevated levels of Cu at station B, sampled proximate to the Old Neck marina pier. This latter observation is consistent with the elevated dissolved Cu measured at that site and may be associated with the use of Cu-containing boat bottom paints. However, such a hypothesis should be viewed as tenuous and in need of much more testing.

The elevations of Mo and Cd (and perhaps to some extent Cu) are likely the result of these redox sensitive metals or sulfur seeking metals being scavenged from the dissolved

phase from highly reducing and sulfidic sediments in the upper Forge. In oxic seawater, Cd, and particularly Mo, are not very particle reactive, although Cd enrichment in sediment can also be related to anthropogenic inputs. Molybdenum, and even relatively particle-reactive Cu, have been observed to be enriched in sulfide-rich sediments (Nameroff et al., 2002; Morford et al., 2005; Adelson et al., 2001). Much, but not all, of the work on utilizing redox-sensitive metals as indicators of bottom sediment or bottom water redox status has been conducted in anoxic estuarine fiords (Anderson et al., 1989), and in oxygen-minimum areas of the continental slope, as well as deep sea paleo-oceanography applications (Nameroff et al., 2002). Molybdenum enrichments in dated sediment cores have been used to reconstruct the history of coastal anoxia in Chesapeake Bay sediments (Adelson et al., 2001). Thus, the enrichment of Mo in sediments, as well as most of the enrichment of Cd, are due to the low oxygen and high sulfur content of sediments and waters in up-river and tributary sediments. These findings are consistent with the high level of organic enrichment at these sites; the same areas have the lowest oxygen concentrations in water (Wilson et al., 2009); the greatest amounts of sulfate reduction and sulfide production in sediments (Benthic Flux Report for SCDHS), and other unpublished data and observations. Whether more modest increases in Cu at some of these sites are also due to redox driven processes or to other local inputs is uncertain.

Another redox sensitive metal is Mn. It is seen in Table 3 that Mn is lowest at the sites (stations 3 and 7) where Mo is highest. Manganese is preferentially mobilized from sediments relative to otherwise geochemically similar Fe under reduced sedimentary conditions due to the precipitation of Fe with sulfide (see Morford et al., 2005). A lower Mn/Fe ratio has been recognized as an indicator of sediment reducing conditions in Long Island Sound (LIS) (Varekamp et al., 2003), where the median ratios of Mn/Fe in “depositional” LIS surface sediments are modestly (about 30%) lower than those in otherwise very similar LIS sediments that are classified as more “unsorted and reworked” (Mecray et al., 2000). The former sediments might be expected to be more reducing than the latter population of sediments.

The sediment core profiles of each metal are shown in Figures 5-17. The profiles of the metals vary among sites, but there are consistent trends observed for individual metals.

- The major elements Al and Fe, and both V and the conservative element Ti all track each other well; variations with depth are modest at most sites. The drop in concentrations of these elements with depth at sites 4, 4B and 7 is also seen in organic carbon at these sites, and likely reflects a decrease in both grain size and surface area of the sediments in those deeper layers.
- The metals Co and Ni generally track Al with depth, with the exception of enrichments at stations 8 and 11 near the surface. Cobalt, Ni, and Mn are all enriched on the surfaces of iron oxide or iron/manganese oxide coatings of particles -- this may be why there is a greater amount of minerals with these more oxidized phases in the more surficial sediments at these sites. Consistent with this hypothesis are the

correspondingly low values of Mo in these samples, a metal that is not accumulated under increasing oxidizing conditions.

- Metals with strong top-down vertical gradients of Ag, Pb, Cu, and Zn indicate more recent anthropogenic inputs of these metals as are generally seen in coastal and estuarine sediments along the North Atlantic seaboard of the United States. The input of Ag has often been associated with sewage inputs, but can come from a variety of other sources. The source of Pb has most likely been from automobile exhaust and atmospheric deposition in the watershed of the Forge River and Moriches Bay region, sources that have decreased for over 30 years, but may still be running off into local waters. The subsurface maxima of Pb concentrations observed at stations 1, 2, 4, 4B, 7, and 8 are telling, as these are the sites with the greatest amount of recent sediment accumulation. The maximal levels are all just above the apparent discontinuity in sediment type and correspond to maximal levels of DDT as a function of depth in the same sediments. Once again, these data are consistent with the hypothesis that sediments at these sites are not very well mixed and preserve some of the historical information about past contamination in the Forge. At other sites, such as stations 10, 11, 12 and A, the maximal levels are near the surface, which may indicate that the sediment accumulation is too slow, or mixing is too rapid, to preserve recent changes over the past 35-40 years at these sites. With few exceptions, the metal levels measured at the bottom of the different cores are relatively uniform and suggest that they approximate background levels, or levels before extensive development of the area. Cores at stations 4 and 4B did not penetrate deeply enough for background levels to be measured.
- When metal concentration between the tops and bottoms of the cores is compared, it is seen that Cu is more enriched than Zn, and there is little evidence that the input of either metal has changed dramatically in recent years.
- The concentrations of Mo and Cd are also greater in the upper parts of the sediment cores than near the bottom, especially for Cd. However, the redox-sensitive element Mo is also enriched compared to background levels deep in the cores, with levels near 5 ppm below the discontinuity depths (e.g., at stations 2, 8 and 11). These high Mo values suggest that the Forge River was characterized by sediments very low in oxygen farther back in time. Unfortunately, the age of the sediments below the discontinuity is unknown. Such knowledge would provide insight into the timing of hypoxia occurrences in the Forge (Adelson et al., 2001).

It is useful to compare the concentrations of metals measured in surface sediments to those measured in other New York coastal waters, most proximate to highly urbanized areas. The mean and median concentrations of metals in surface sediments measured in the Forge are compared in Table 4 to larger studies throughout Long Island Sound (LIS; 96 sites classified as muddy and depositional; Mccray et al., 2001) and in the New York/New Jersey Harbor complex study conducted by EPA (111 sites with most of them muddy; Adams and

Benyi, 2003). Molybdenum and Co were not measured in either study; nor were V and Ni sediment concentrations measured in the EPA study. As mentioned before, the levels of redox-sensitive Mo in Forge River sediments are sometimes exceptionally high, higher than the highest levels measured in the more hypoxic areas of the Chesapeake Bay (Adelson et al., 2001).

Al: The levels are slightly lower than those measured in LIS, and about 30% higher than average values from NY/NJ Harbor. The lower levels in the latter study are due to the inclusion of a small fraction of sites that were sandy, especially in Raritan Bay, outer New York Harbor, and parts of Jamaica Bay near its mouth. It is most useful to compare other metal concentrations normalized to Al as an indicator of fine grain sediment (see bottom of Table 4).

Fe: The levels are slightly higher than in LIS, which in turn are higher than in NY/NJ Harbor, even after normalization to Al. This may be the result of differences between the geology of the local watershed in the Forge and in LIS, perhaps also the result of changes in the elemental composition of the sediment source material.

Ag: Concentrations normalized to Al are half of what they are in LIS, but only 30% of what they are in the more sewage-impacted region of NY/NJ Harbor. The lower levels in LIS may be due to the large number of stations far from land and sources of sewage in the area of the East River. However, it is not clear what the source of Ag is in the Forge and Moriches Bay, as there are not significant direct discharges of sewage in the area.

Pb: Levels of lead are intermediate between those in LIS and NY/NJ Harbor. It might be noted that the intensity of local atmospheric deposition in the area is probably intermediate between the two areas as well. Cochran et al. (1998) found that 70-90% of the sediment Pb inventory in LIS could be attributed to direct atmospheric sources.

Cd: Levels are comparable to NY/NJ Harbor, where there are areas of significant Cd inputs, but five times greater than in LIS when normalized to Al. It is hypothesized that the observed enrichment in Cd is due to scavenging highly reduced sediments in the Forge and much less to anthropogenic inputs.

Cu and Zn: When normalized to Al, the levels in the Forge are, respectively, 1.6 to 1.8 times greater than in LIS, but about half of what they are in the NY/NJ Harbor. Cochran et al. (1998) estimated that approximately 30-50% of excess Cu and Zn in LIS could be attributed to direct atmospheric deposition. It is not clear whether there are significant local inputs of Cu and Zn to the Forge River, but some of the observed excess is due to non-point sources into the Forge and Moriches Bay, that would include runoff of atmospheric deposition to the watershed.

Mn: The ratio of Mn/Fe in the Forge is 35-40% of what it is in the other areas (40-60% when normalized to Al). It is hypothesized that some of this difference is due to preferential mobilization of Mn in the strongly seasonally hypoxic/anoxic Forge River.

PAHs in sediment grab and core samples

The concentrations of targeted individual and summed total polycyclic aromatic hydrocarbons (PAHs) in surface grab samples are given in Table 5; the corresponding concentrations of PAHs in sediment cores as a function of depth are provided in Figure 18. The composition of PAHs did not vary dramatically among sites, nor does it vary much with depth, at least above the depths where PAHs levels drop to much lower values (as do other anthropogenically derived metals and DDT residues in the same cores). Concentrations of PAHs in deeper, older samples at the bottom of some cores are still detectable. Because we do not have dates on the deeper layers of the cores, it can not be determined whether these concentrations correspond to times before or after development of the area. However, there are always natural background levels of PAHs in sediments due to either forest fires or erosion of sedimentary rocks like shales that contain PAHs. As discussed in the Organic Contaminant Report for SCDHS, the PAH composition in sediments is dominated by high molecular weight (HMW, in this case those with four to five rings) PAHs, with significant levels of three-ring phenanthrene as well. There is a general correlation between PAH levels and organic carbon levels. That and the absence of variation in composition are consistent with a single source of PAHs in the area. PAH compositions dominated by HMW PAHs are considered to be an indicator of combustion derived PAH sources (Yan et al., 2006) as opposed to petrogenic sources (e.g., oil, shale). The ratios of methylated phenanthrenes to phenanthrene are expected to be higher than those observed for petrogenic PAH sources, lowest in high temperature combustion sources, and intermediate if the source is low temperature or less complete combustion (e.g., forest fires or some wood burning stoves). The methylphenanthrene to phenanthrene ratio is lower than that expected for petrogenic sources, but higher than if it was dominated by high temperature combustion. It is hypothesized that the source of PAHs is from combustion sources and may include contributions from the wood or coal burning stoves, coal or wood burning trains, historic brush fires, and perhaps less efficient diesel burning vehicles. Further compositional or isotopic analysis of the individual PAHs could be used to narrow these possibilities. The similarity of compositions among those found in tidal Forge samples and those from the fresh water East and West Ponds is consistent with the conclusion that there is a single dominant combustion-derived source of PAHs to the local area. The PAHs that then accumulate in sediments may come from direct atmospheric deposition to the Forge, to deposition in the watershed and runoff into the Forge, and to atmospheric deposition to the greater area of Moriches Bay and the transport of some of the fine grain sediment carrying those PAHs from Moriches Bay into the Forge, deposition characteristic of sediment trapping in estuaries, especially sluggishly mixed water bodies with estuarine circulation like the Forge.

The concentrations of total PAHs (e.g., mean levels in surface grab samples of 1200 ng/g, ranging from 302 to 3330 ng/g; Table 5) are elevated above background coastal

sediments, within the range found in other estuaries in the coastal and estuarine waters close around or near New York. For example, in the 113 samples collected in the general area of the NY/NJ Harbor (including sandier, more flushed areas of Raritan Bay and outer NY Harbor) ranged between 30 and 91,000 ng/g. The above background levels of PAHs in the Forge may be related to several factors; e.g.: 1) a small surface area of the Forge compared to that of the watershed; 2) the high levels of organic matter in the Forge that are both indicative of efficient estuarine trapping, and result in greater sorption of PAHs that in turn affect retention of PAHs in the system; and 3) that the highly reducing (very low oxygen) rapidly buried sediments will greatly favor preservation of PAHs in sediments as they can be readily degraded by bacteria in the presence of oxygen (LeBlanc et al., 2006). A discussion of how these levels compare to estimated toxicological risk is discussed in a separate report to Brookhaven Town. However, it is likely that if the source of PAHs is from combustion sources, then the bioavailability of those PAHs (in comparison to those from oil-derived sources) is greatly diminished by strong sorption to soot particles or charcoal that is associated with combustion.

Finally, it should be mentioned that there are additional PAHs that are readily detected in fine grain sediments near urbanized areas. Many of these PAHs are alkylated, similar to the methylphenanthrenes in this analysis. While the sum of PAHs reported in monitoring studies is generally the sum of the compounds reported here, for some ecotoxicological applications a multiplication factor is used to estimate something much closer to a total PAH concentration. That factor estimate and actual measured ratios are typically ≤ 2 (Yan et al., 2006), a number that will be lower given the addition to methylphenanthrenes to our analyses and the fact that combustion sources have lower amounts of PAHs not determined here.

DDT residues and other chlorinated pesticides in sediment grab and core samples

A large number of pesticides were analyzed in each sediment sample, but the only confident detections reported were for DDT residues. Concentrations were dominated by p,p'-DDE and p,p'-DDD, generally the two most persistent metabolites of DDT, widely used prior to 1966-1972 for agricultural and mosquito control applications. The concentrations and vertical profiles (Table 7; Figure 19) and the ratios of DDE to DDD vary greatly throughout the system. The total DDT concentrations are consistently low in almost all of the surficial sediments sampled in the tidal sections of the Forge River. Very high levels are seen in a single sediment sample from East Pond (confirmed qualitatively and quantitatively by subsequent GC/MS analysis), and the most northern stations in the tidal Forge. It is possible that the higher levels found near the head of the tidal Forge are affected by East Pond sources. The level of total DDT in a surface sediment from West Pond is still relatively low, but higher than that measured in most of the tidal Forge. Because of different sampling methods, and possible differences in burial rates, caution is advised in comparing DDT concentrations in West Pond and the tidal Forge.

The subsurface maxima of DDT residues in several sediment cores is consistent with historical inputs of DDT to the area as its use was restricted, then banned, between 1966 and 1972 on Long Island, and with the relatively rapid burial at those sites. This is well exemplified at station 7, one site where the historical record appears to be well preserved, with anoxic sediments and hypoxic waters minimizing the chance of biological mixing by benthic infauna. The profiles agree with those of other indicators, for example the profiles of Pb, whose inputs were greatly reduced when Pb was banned as a gasoline additive in 1972. The depths of penetration at each sediment cores station are consistent with other metals, and also with the PAHs, and with sediment properties like organic carbon and water content. As mentioned above, the penetration of DDT in high sediment accumulation cores is consistent with the observed transition zone, which has been hypothesized to be the result of dredging that occurred in a period close to 1970.

It is difficult to argue whether the primary sources of DDT to the tidal Forge are, or were, affected by local uses, or from atmospheric transport from use outside the watershed of the Forge. However, the high level of DDT residues found in East Pond is almost certainly the result of localized use or direct inputs at some time in history. It should be pointed out that only one sample from East Pond was collected and it may not be representative of conditions in the pond.

The ratio of DDD to DDE varies greatly among sites. The reasons for these differences may result from multiple mechanisms. In the presence of oxygen or with metabolism in animals, DDE is a major metabolite, whereas DDD is the major initial metabolite of DDT under low oxygen sediment conditions. The ratio can depend on how much parent DDT enters directly to reducing areas (much of the sediment in the Forge River), as opposed to primary inputs to the Forge as DDE that does not convert to DDD. It is of interest to note that the ratio of DDD to DDE tends to be much higher in the upper reaches of the tidal Forge where the sediments are essentially anoxic, and expected to be more anoxic for a greater fraction of time, than sediments closer to mouth of the Forge River.

Before detailed screening (see above) for detection of other pesticides in sediments, there were numerous detections of almost half of the pesticides listed in Table 6. However, most of the concentrations were just above detection. After applying all the criteria above, the vast preponderance of possible detections could be discarded. The exceptions were a couple of samples with lindane detection at or near 1 ppb (e.g., at station 1, 0-5 cm), and possible detection of the two chlordane isomers that were targeted analytes (gamma and alpha chlordane, otherwise referred to as trans- and cis-chlordane, respectively). The possible detections of lindane are not reported here because they are close to the detection limit (Table 4) and because there is not a hint of a peak in samples at sediment core depths just below or at a site proximate to it. The possible detections of chlordane (residential termite control was one major use) are less easily dismissed as possible detections (0.6-1.8 ng/g in surface sediments at East Pond, and stations 2, 4, 4B, and 7 and small peaks elsewhere) and an apparent increase in concentration with depth at station 7 to a maximum value of 6.8 ng/g). We do not report these levels, however, for two reasons: 1) the peak

shape of trans-chlordane extends to a longer retention time and tails; and 2) that alpha or cis-chlordane elutes at a retention time nearly identical to PCB 110 (otherwise, co-elution of target compounds was not deemed to be a significant problem in this study). However, technical chlordane is a mixture of many compounds that exist at lower percentages than do the cis and trans-isomers of chlordane. The presence of other chlordane compounds or residues could potentially explain the tailing observed for trans-chlordane. To confirm whether low levels of chlordane are present in these sediments, one would could re-run the samples on another GC column with different mechanism of peak separation or utilize GC-MS systems with more selective or sensitive mass spectrometry - negative ion chemical ionization or high resolution mass spectrometry, where detection limits can approximate that of the very sensitive ECD detector, but with greater selectivity.

PCBs in sediment grab and core samples

Most often the levels of PCB congeners were all very low compared to the lowest standard. In a few cases, blank levels also approached the lowest PCB standard peak height of given congener. It was very rare for a PCB peak height to approach or exceed that of the second lowest standard used in the calibration. The summed concentrations of PCBs reported in Table 7 and in Figure 20, should be viewed as containing significant uncertainty. Only a fraction and not the same fraction of PCB congeners were determined to be detections in the samples. PCB congeners 66, 101, 77 (co-elutes in samples with 110), 118, 153+105, and 138 were detected in more than half of the upper sediment samples, followed by frequent detections of congeners 28 and 52; other congeners were rarely detected, and there were not detections for congeners 8, 206, and 209. The general agreement in the vertical profiles between PCBs and DDTs (the drop in PCBs after 1970 is known to be slower than that for DDT) and absence of detection at the bottom of most sediment cores are consistent with expectations though and provides some measure of confidence in the presence of PCBs in a sample and the magnitude of the concentrations estimated. The range of summed total PCB concentrations reported is significantly similar to or lower than that found in a 1993 survey of samples from 146 sites collected by EPA (same PCB congeners measured) from the NY/NJ Harbor complex and adjacent waters (Adams and Benyi, 2003). While PCB concentrations in surface sediments have decreased over time, the low PCB levels found here are much lower than those found in the lower Hudson River Estuary, where the sum of the concentrations of same PCB congeners averaged 150 ng/g and maximum levels were 2500 ng/g (Adams and Benyi, 2003), and pale in comparison to PCB levels at the PCB Superfund Site in the upper Hudson (exceeding tens and even over 100 µg/g). The most commonly detected congeners in the Forge River are those with 5 or 6 chlorines, which are more characteristic of long range atmospheric sources rather than local inputs. An atmospheric source of PCBs would agree with the low concentrations of total PCBs reported in Forge River sediments.

Comparison of Sediment Contaminant with Sediment Quality Guidelines

There are many ways in which sediment quality assessments for metal and organic contaminants are conducted and tools that are used. Some of these include: comparisons to sediment quality guideline numerical values; toxicity testing, which is often assessed with an acute toxicity test with amphipods such as *Ampelisca abdita*, sediment bioaccumulation tests, and measurements of benthic community structures.

A widely used approach for initial screening of sediments for ecological risk is to compare measured sediment contaminant concentrations to numerical sediment quality guidelines. However, strict comparisons of concentrations should be done with caution, based on the complexity of the underlying science, differences in sediment types, the manner in which the comparisons are made, and the approaches used to generate concentration based numerical sediment quality guidelines. Furthermore, management guidelines or management standards (e.g., in the State of Washington related to marine waters such as Puget Sound) can vary significantly in different jurisdictions and are utilized differently within local management or regulatory frameworks. Generally, there are very few enforceable sediment quality criteria that are used outside of site specific situations, which may be driven by human health risks rather than ecological ones.

Virtually all approaches for establishment of sediment quality guidelines rely on statistical analyses of laboratory based dose response data and empirical correlations between concentrations of individual contaminants and measures of biological responses. Biological endpoints are frequently based on acute amphipod tests. This weight of evidence statistical approach was popularized following the work by Long and Morgan (1990). Often guidance levels are suggested that include a lower concentration level that borders on a no or low probability effects threshold, and a higher concentration level where the probability of association between contaminant and adverse biological effects are greater. As contaminants of potential concern most often co-occur, there are approaches for taking mixtures into effect, but we are not aware of situations when such approaches are utilized in management applications. The most commonly used sediment quality guidelines quoted are still based upon the definitions and values from Long and colleagues (1990; 1995), guidance levels that correspond to effects range low (ERL) and effects range median (ERM).

A problem with setting simple concentration based guidelines or standards is that they do not consider contaminant bioavailability, or sediment properties that clearly affect concentrations and predicted to affect bioavailability (e.g., surface area/grain size, organic matter, or metal sulfide). Some management approaches do try to take this into account; e.g., the State of Washington bases their Sediment Management Standards (Washington State Dept. of Ecology, 2009) for nonpolar organic contaminants (which guide the process used in some management decisions) on organic carbon normalized concentrations (mg/Kg organic carbon). Examples of nonpolar organic contaminants include PAHs, PCB, and chlorinated pesticides. However, a similar approach is not used for metals. If one considers Forge River sediments where sediment organic carbon levels are in the 8-10% range, an approach that that

used dry weight concentration levels would lead to a calculated risk coefficient 4 to 10-fold greater than an organic carbon normalized value if it were estimated from sediments with a mean TOC of 1-2%.

The ERL and ERM from Long et al. (1995), and Sediment Quality Standards from Washington State (very high values used in Puget Sound which has several contamination problems) are compared to the range of values reported in surface sediments of the tidal Forge in Table 8. It is seen that none of the metal or organic contaminant concentrations measured in the Forge (even downcore) exceed the Washington no effect level sediment criteria level. There are exceedances of the ERL values for Pb, Cd, Cu, and Zn, although there are no concentrations measured above ERM levels, which can carry more weight as regulatory triggers. For the sum of PAHs there are a couple of surface sediments where ERL is approached, but no exceedances for PCBs are found. There is a subsurface maximum of total PCBs at station 7 that exceeds the ERL values, but that is not true when averaged over the upper half meter of sediment. However, surficial sediments in the tidal Forge generally have total DDT residue concentrations that often exceed the ERL, but none exceed the ERM. Again DDT concentrations have subsurface maxima that exceed the ERM, but if average concentrations of DDT residues over the upper 0.5–1 m of sediment were homogenized, concentrations would be below ERM at station 7 where concentrations are highest. As discussed above, there is a sample from East Pond where much higher levels of DDT residues were found.

As an illustration of how difficult it is to set and agree upon sediment quality screening levels, we have also included in Table 8 some of the “Sediment Criteria” values recommended in a NY DEC “Technical Guidance for Screening Contaminated Sediments” (NY DEC, 1999) document prepared by the Division of Fish, Wildlife, and Marine Resources (a revision of earlier documents) that also provides suggested prescriptions and advice for further studies that might be done when sediments exceed these guidance levels. These values and those of Washington State provided represent likely end-members for the range of concentration based guidelines that are available. Application of the NY DEC values would result in more exceedances of low effects concentrations and a couple of exceedances of Cu and Zn in surficial sediments, as well as for Pb when below surface maximum levels are considered at sediment core stations 1, 7 and 8. It is very unclear whether the DEC still uses this document for guidance, as we can not find any reference to that or any other DEC sediment quality guideline levels over the ten years since that document was prepared, nor can it be found on a search of the NY DEC website. The values provided in the 1999 DEC document illustrate how difficult it is to set standards that are useful or provide an assessment of risk and benefit. To provide more conservative environmental protection, NY DEC recommended values for sediment metals that relied more heavily on a 1992 Report (Persuad et al., 1992) prepared for the Ontario Ministry of the Environment. The values provided are lower than those used by other governmental bodies. Applications of these guidelines would lead to the vast preponderance of muddy sediments found in depositional environments (such as channels) anywhere in New York coastal waters, failing at least some of the screening or guidance levels (e.g., Cu, Ni, and Pb at the Moriches Bay station M sites). This is true for

sediments very far from pollution point sources (e.g., central and eastern Long Island Sound; Table 5). It is important to note that sediment quality guidelines for Fe, Mn, and Ni are at background/natural levels for these metals in fine grain sediments -- this illustrates the problem of numerical values that average across sediment types. These points are raised not so much to criticize the assessments made by NY DEC, but to show that there is both great uncertainty in determining sediment quality screening levels, and that one should use caution when interpreting their meaning or best use.

In summary, if one considers that the Forge River sediments are fine grained (have high Al and Fe), the concentrations of metals and organic contaminants are well within an expected range, based on local urbanization and the atmospheric inputs that derive from the west (see Table 5 and discussions in the text). One would also expect even greater enrichment of organic contaminants and some metals (e.g., Cu) due to the very high organic carbon content of the sediments. The exceptions to this observation are primarily for Cd and Mo, metals that are not highly adsorbed to sediments, but can be scavenged from seawater under very low oxygen conditions that prevail in areas of the Forge. DDT levels likely reflect local spraying for mosquitoes that were especially prevalent in wetland areas, or other pest control uses. More sampling of East Pond should be done to evaluate the potential for it to act as a continuing source to the tidal Forge.

Toxicity Assessments of Forge River Sediments -- Other Considerations

Other approaches for assessing the ecological risks from Forge River sediments or dredged materials from the Forge River could include toxicity testing (usually with amphipods) and sediment bioaccumulation studies using test bivalve or polychaete species. While these tests are used routinely to assess highly contaminated harbor sediments, there is a reasonable likelihood based on personal experience that test organisms would either die, or in the case of bioaccumulation species, not ingest or burrow in sediments that are as high in ammonia, sulfide, and demand as much oxygen as do many surficial sediments from the tidal Forge. There are procedures to be followed when ammonia levels rise in amphipod tests, but it would be extremely difficult to separate out toxicity from potentially toxic metal or organic contaminants from the effects of having such highly reducing muds, muds that presently do not provide a habitat for any macrofaunal benthic organisms. These concerns do not suggest that dredged materials from the Forge would present any toxicological/ecological risk if either marine or upland disposal were considered; that would depend on many factors related to how the material was disposed. We simply bring up this issue if local management decisions concerning Forge River sediments will be dependent on regulatory approaches that might involve testing with benthic organisms.

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Table 1. Sediment Grab Samples (0-5cm) + Sediments Collected above the Railroad Track

<u>Station No.</u>	<u>Date</u>	<u>Time</u>	<u>Water Depth (ft)</u>	<u>Mud Thickness (ft)</u>	<u>Latitude</u>	<u>Longitude</u>
1	8/8/2006	14:28	4	4.4	40.797633	-72.830117
2	8/8/2006	13:20	4.5	8.6	40.79515	-72.830717
3	8/8/2006	14:05	4.5	5.6	40.79505	-72.833250
7	8/8/2006	9:37	5	5	40.800433	-72.830567
8	8/8/2006	10:14	3.4	8.1	40.794533	-72.827200
9	8/8/2006	13:02	5	>9.1	40.79185	-72.826483
10	8/8/2006	12:47	6	8	40.78765	-72.830517
11	8/8/2006	12:25	5	>9.8	40.788317	-72.823267
12	8/8/2006	11:40	5	>9.2	40.78245	-72.817100
13	8/8/2006	11:23	6	>9.1	40.775417	-72.810533
A	8/8/2006	10:35	4.5	2.3	40.789283	-72.821517
B	8/8/2006	12:07	6	>9.4	40.786417	-72.817667
M	8/8/2006	10:57	6	>8	40.776483	-72.796350
UFEB	12/21/2006	9:00			40.8053	-72.832183
E Mill Pond	12/21/2006	10:22			40.8075	-72.831667
W Mill Pond	12/21/2006	10:50			40.807767	-72.835467

Table 2. Sediment Core Samples (collected 8/9/2006)

<u>Station No.</u>	<u>Time</u>	<u>Upper Layer Thickness (cm)</u>	<u>Latitude</u>	<u>Longitude</u>
7	9:12	35	40.800733	-72.830733
8	10:00	36	40.794517	-72.827150
A'	10:20	19	40.788717	-72.821333
12	10:29	14	40.782833	-72.817100
11	10:45	15	40.788167	-72.824217
10	11:11	20	40.7875	-72.830400
4	11:35	>34	40.795	-72.836017
4B	11:41	>30	40.79505	-72.836033
2	11:58	52	40.795167	-72.830733
1	12:21	36	40.797633	-72.830200

**Table 3. Trace Metal Concentrations in Sediment Grab Samples (ppm)
(August 8, 2006)**

<u>Station</u>	<u>Mo</u>	<u>Ag</u>	<u>Pb</u>	<u>Cd</u>	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Ni</u>	<u>V</u>	<u>Zn</u>	<u>Ti</u>	<u>Mn</u>	<u>Al</u>
1	7.34	0.72	78.61	1.21	9.80	87.60	37098	29.70	110	204	576	341	60842
2	14.93	0.85	66.27	1.60	11.00	121.70	37781	30.00	131	258	621	334	58198
3	25.36	0.78	64.95	1.61	9.83	121.91	38880	27.82	127	209	597	275	55491
7	13.73	0.75	80.90	2.13	8.45	130.81	31778	27.66	108	249	557	240	55986
8	10.82	0.89	90.81	2.28	13.37	99.27	38434	31.04	122	303	502	392	57429
9	10.01	0.90	67.03	1.21	11.32	95.28	37059	30.00	127	201	629	347	56744
10	8.27	0.73	71.24	1.15	9.66	69.29	38184	27.94	107	171	586	366	59208
11	3.36	0.87	58.26	0.87	9.79	70.26	34988	25.51	110	156	676	741	50677
12	2.86	0.86	63.12	0.63	9.45	64.32	38782	26.75	121	146	697	535	55624
13	2.69	0.47	35.22	0.55	7.02	37.87	28010	27.52	85	282	602	461	42425
A	6.76	0.84	65.25	0.84	10.14	71.13	38251	28.39	126	171	842	396	55808
B	8.58	0.96	67.32	1.18	10.56	116.09	37200	30.71	151	197	701	335	60374
M	2.14	0.60	43.67	0.54	6.61	39.59	25269	20.34	90	96	611	291	38801

Table 4. Comparison of metal concentrations in the Forge River to Long Island Sound and the NY/NJ Harbor Complex

	Mo	Ag	Pb	Cd	Co	Cu	Fe	Ni	V	Zn	Ti	Mn	Al
Forge River (n=13)													
Av	9.0	0.79	66	1.2	9.8	87	36000	28	120	200	0.63	390	54000
STD	6.4	0.13	15	0.56	1.8	31	4400	2.8	18	58	0.084	130	6700
Median	8.3	0.84	66	1.2	9.8	88	37000	28	120	200	0.61	350	56000
LIS (n=96)													
Av	n.d.	0.44	48	0.25	n.d.	60	33000	32	89	130	0.39	1000	61000
STD	n.d.	0.32	21	0.26	n.d.	29	8600	21	15	31	0.12	490	12000
Median	n.d.	0.42	42	0.17	n.d.	57	33000	30	92	120	0.39	900	63000
NY/NJ Harbor Complex (n=111)													
Av	n.d.	1.8	97	0.97	n.d.	80	20000	28	n.d.	190	n.d.	520	41000
STD DEV	n.d.	1.3	81	0.99	n.d.	82	11000	14	n.d.	130	n.d.	210	16000
Median	n.d.	1.9	88	0.75	n.d.	62	19000	30	n.d.	170	n.d.	480	45000
Me/Al													
Forge	n.d.	1.4E-05	1.2E-03	2.2E-05	1.8E-04	1.6E-03	6.5E-01	5.1E-04	2.1E-03	3.7E-03	1.2E-05	7.1E-03	1.0E+00
LIS	n.d.	7.2E-06	7.8E-04	4.1E-06	n.d.	9.8E-04	5.4E-01	5.3E-04	1.5E-03	2.1E-03	6.4E-06	1.7E-02	1.0E+00
NYNJ	n.d.	4.4E-05	2.3E-03	2.3E-05	n.d.	1.9E-03	4.9E-01	6.9E-04	n.d.	4.6E-03	n.d.	1.2E-02	1.0E+00

Table 5. Cocentrations of PAHs in surface grab sediment samples (ng/g)

Station No.	NAP	1-MeN	2-MeN	ACEY	FLU	ACE	PHEN	ANTH	ΣMePH	FLA	PYR	BAA	CHRY	BBKF	BAP	IND	DBA	BGHP	total PAH
1	13.85	11.72	5.87	8.76	8.23	2.90	68.84	16.16	93.90	397.07	281.25	87.10	131.72	285.42	107.00	148.89	19.78	130.13	1819
2	6.32	7.46	3.93	6.12	6.54	2.84	53.33	15.24	50.83	197.00	144.35	74.66	101.23	248.02	91.43	83.93	20.29	74.87	1188
3	20.92	14.73	8.45	12.06	13.41	6.25	149.62	33.20	146.33	806.67	560.36	180.40	226.90	501.87	174.41	237.32	29.32	208.93	3331
7	9.49	9.96	5.05	7.91	8.68	4.38	66.43	17.86	75.58	265.56	216.04	92.46	140.66	273.16	113.60	91.73	16.86	83.96	1499
8	10.37	8.61	4.25	6.14	5.06	1.09	41.16	12.33	44.76	163.40	119.10	72.72	93.39	229.95	117.50	108.86	20.25	91.27	1150
9	11.50	11.25	5.14	6.21	5.55	2.29	49.90	11.43	60.56	214.46	134.02	47.98	82.28	184.50	69.95	86.61	11.08	73.57	1068
10	8.74	8.35	4.33	5.62	6.71	3.53	57.28	12.73	49.08	163.86	118.28	62.62	77.76	199.25	98.98	99.52	20.65	81.03	1078
11	11.57	16.54	7.45	8.03	8.66	5.39	64.48	18.64	68.51	172.96	158.34	99.84	120.81	278.38	110.83	95.89	19.47	80.63	1346
12	9.25	7.70	3.14	3.10	3.64	0.55	22.07	8.30	25.62	77.64	58.22	29.99	36.63	95.43	44.23	44.35	9.71	37.86	517
13	4.78	4.28	1.31	1.81	2.67	0.92	15.56	5.22	19.35	49.37	41.60	19.05	26.13	51.05	21.53	18.26	2.54	16.37	302
A	19.14	14.66	6.96	5.81	10.33	6.06	130.19	10.38	83.57	303.12	19.67	49.18	89.42	190.10	67.78	87.45	11.00	69.75	1175
B	8.36	5.83	2.52	5.01	3.01	0.33	22.97	10.47	23.53	85.58	63.50	38.62	56.41	141.50	64.44	61.58	12.35	48.50	655
M	12.74	9.65	4.65	5.68	5.27	2.25	48.94	14.03	47.49	126.39	94.15	44.02	70.61	146.04	59.86	62.64	8.77	48.93	812
Upper Forge	3.68	4.21	3.35	4.80	4.27	2.25	53.02	9.50	45.73	184.85	163.15	68.87	112.83	179.29	72.36	50.42	9.93	49.30	1022
E Mill Pond	31.45	42.75	17.31	11.67	18.91	10.63	248.86	45.90	301.63	600.97	478.45	176.27	281.42	461.14	203.28	150.94	22.70	112.48	3217
W Mill Pond	2.19	2.56	1.09	1.80	4.49	2.60	85.04	10.73	77.98	270.30	205.95	92.61	123.67	199.03	93.09	52.14	11.71	53.89	1291

Table 6. List of PAH analytes and standards	
<i>PAH Analytes:</i>	<i>MDL (ng/g)</i>
naphthalene	0.40
1-methylnaphthalene	0.40
2-methylnaphthalene	0.40
acenaphthylene	0.40
fluorene	0.40
acenaphthene	0.40
phenanthrene	0.40
anthracene	0.40
sum of methylphenanthrenes	>0.40
fluoranthene	0.40
pyrene	0.40
benz(a)anthracene	0.40
chrysene	0.40
benzo(b)fluoranthene	0.40
benzo(b)fluoranthene	0.40
benzo(a)pyrene	0.40
indeno(1,2,3-cd)pyrene	0.40
dibenz(a,h)anthracene	0.40
benzo(g,h,i)perylene	0.40
<i>Surrogates:</i>	
d12 chrysene	
d10 phenanthrene	
<i>Internal Standard:</i>	
p-terphenyl	

Table 6 continued. Chlorinated pesticide analyte list	
<i>Pesticide Analytes:</i>	<i>MDL (ng/g)</i>
2,4,5,6-tetrachloro-m-xylene	0.80
triflurilin	1.00
a-BHC	0.40
di-allate	1.25
pentachloronitrobenzene (PCNB)	0.50
b-BHC	0.40
lindane (g-BHC)	0.40
dichlone	0.50
d-BHC	0.40
heptachlor	0.40
aldrin	0.40
isodrin	0.50
heptachlor epoxide	0.40
captan	1.00
g-chlordane	0.40
endosulfan I	0.40
a-chlordane	0.40
dieldrin	0.80
4,4' DDE	0.80
endrin	0.80
endosulfan II	0.80
chlorobenzilate	2.50
4,4' DDD	0.80
endrin aldehyde	0.80
endosulfan sulfate	0.80
carbophenothion (trithion)	5.00
4,4' DDT	0.80
captafol	1.00
endrin ketone	0.80
4,4'-methoxychlor	4.00
mirex	0.50
decachlorobiphenyl (PCB 209)	1.60
<i>Surrogates:</i>	
DBOFB	
e-BHC	
<i>Internal Standard:</i>	
Octachloronaphthalene	

Table 6 continued. PCB congener standards (IUPAC numbers)		
<i>PCB Congeners:</i>		<i>MDL (ng/g)</i>
2,4'-Dichlorobiphenyl	PCB 8	0.50
2,2',5-Trichlorobiphenyl	PCB 18	0.50
2,4,4'-Trichlorobiphenyl	PCB 28	0.50
2,2',5,5'-Tetrachlorobiphenyl	PCB 52	0.50
2,2',3,5'-Tetrachlorobiphenyl	PCB 44	0.50
2,3',4,4'-Tetrachlorobiphenyl	PCB 66	0.50
2,2',4,5,5'-Pentachlorobiphenyl	PCB 101	0.50
3,3',4,4'-Tetrachlorobiphenyl	PCB 77	0.50
2,3',4,4',5-Pentachlorobiphenyl	PCB 118	0.50
2,3,3',4,4'-Pentachlorobiphenyl	PCB 105	0.50
2,2',4,4',5,5'-Hexachlorobiphenyl	PCB 153	0.50
2,2',3,4,4',5'-Hexachlorobiphenyl	PCB 138	0.50
3,3',4,4',5-Pentachlorobiphenyl	PCB 126	0.50
2,2',3,4',5,5',6-Heptachlorobiphenyl	PCB 187	0.50
2,2',3,3',4,4'-Hexachlorobiphenyl	PCB 128	0.50
2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB 180	0.50
2,2',3,3',4,4',5-Heptachlorobiphenyl	PCB 170	0.50
2,2',3,3',4,4',5,6-Octachlorobiphenyl	PCB 195	0.50
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	PCB 206	0.50
Decachlorobiphenyl	PCB 209	0.50
<i>Surrogates:</i>		
2,4,5-Trichlorobiphenyl	PCB 29	
2,2',3,4,5,6'-Hexachlorobiphenyl	PCB 143	
<i>Internal Standard:</i>		
Octachloronaphthalene	OCN	

Table 7. DDT residue and Σ PCB concentrations (ng/g) in sediment Grab Samples (0-5cm); all DDT residues are the p,p' isomers

<u>Station No.</u>	<u>DDT</u>	<u>DDE</u>	<u>DDD</u>	<u>ΣDDT</u>		<u>ΣPCB</u>
1	0	6.9	3.7	10.6		7.7
2	0	1.5	3.6	5.1		3.3
3	0	6.8	8.5	15.3		16
7	1.0	12.3	24.9	38.2		7.8
8	0	0	0	0		
9	0	2.7	0.3	3.0		15
10	0	2.6	2.8	5.4		5.5
11	0	1.3	0	1.3		6.4
12	0	1.0	1.0	2.0		3.9
13	0	1.0	0	1.0		2.3
A	0	1.2	0	1.2		11
B	0	1.1	1.3	2.4		2.1
M	0	0.6	0	0.6		7.5
UFEB	0.95	14.1	39.0	54.1		9.3
E Mill Pond	40.5	721	1590	2350		0
W Mill Pond	6.6	34.8	72.6	114		2.3

Table 8. Comparison of contaminant concentrations in surficial tidal Forge River Sediments to three sets of sediment quality guidelines; see text for data sources – ranges of concentrations for organic contaminant levels have converted to TOC normalized concentrations (Wash. State and NY DEC benthic chronic aquatic tox) to dry weight concentrations assuming TOC levels of 5 and 10%. Pyrene and Fluorene are chosen as representative PAH as they were found in all sources of data. Concentrations in ug/g for metals and PAHs and ng/g for total DDTs and PCBs.

	Zn	Ag	Pb	Cd	Mn	Cu	Fe	Ni	Fluorene	Pyrene	DDTs	PCBs
Forge River												
surface sediments	150-300	0.47-0.96	35-91	0.55-2.3	240-740	38-122	25000-39000	26-31	0.003-0.013	0.020-0.56	0-38	2.3-16
Long et al. 1995												
ERL	150	1.0	47	1.2		34		21	0.019	0.665	1.6	23
ERM	410	3.7	218	9.6		270		52	0.54	2.6	46	180
NY DEC, 1999												
lowest effect	120	1.0	31	0.6	460	16	20000	16				
severe effect	270	2.2	110	9.9	1100	110	40000	50				
Chronic benthic seawater									1.9-3.8	17-35	50-100	2100-4200
Wash. State, 2009												
no effect	410	6.1	450	5.1		390			8-16	50-100		600
adverse effects	960	6.1	530	6.7		390			60-120	70-140		1200

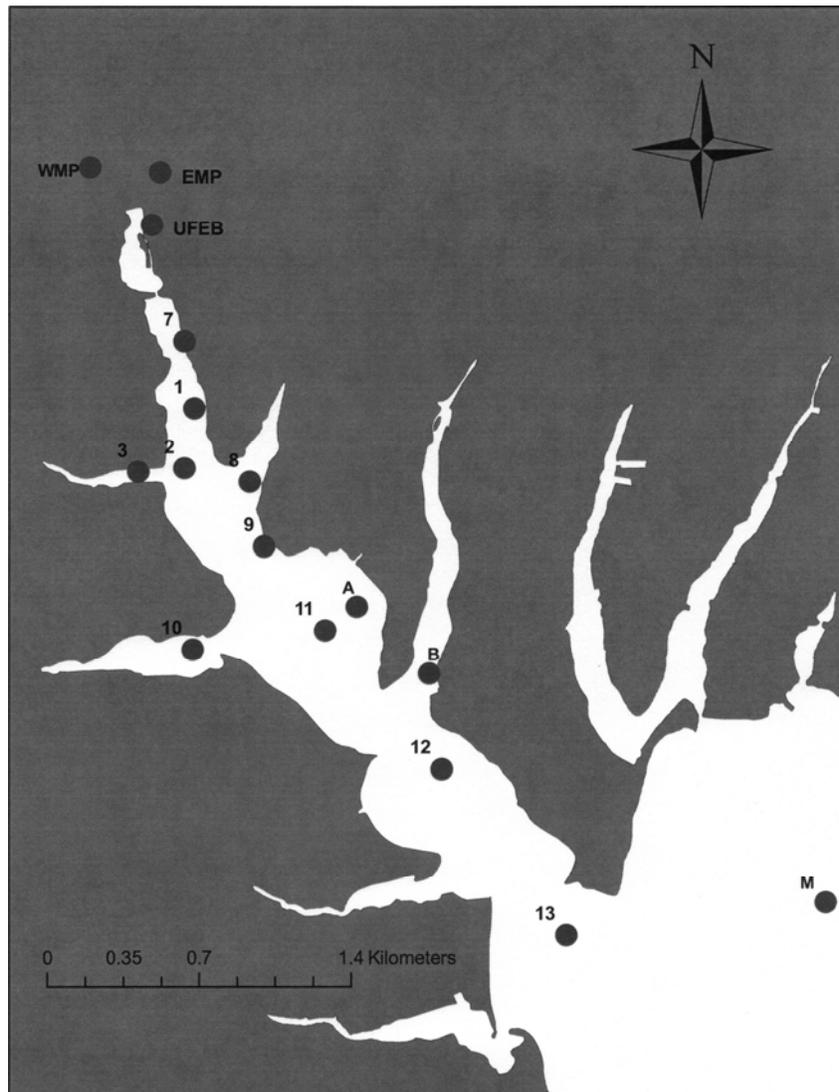


Figure 1. Surface sediment station locations (coordinates in Table 1). The West Mill Pond (WMP), East Mill Pond (EMP), and Upper Forge East Bank (UFEB) samples were collected by hand from a Kayak, and all other samples represent 0-5 cm sediment grab samples.



Figure 2. Locations of Sediment Cores (Coordinates in Table 2). Stations 4 and 4B were nearby each other. The actual positions of stations 4 and 7 appear too close to shore and represent minor miscalibration of the map coordinates.

Figure 3. Sediment Core Water Contents.

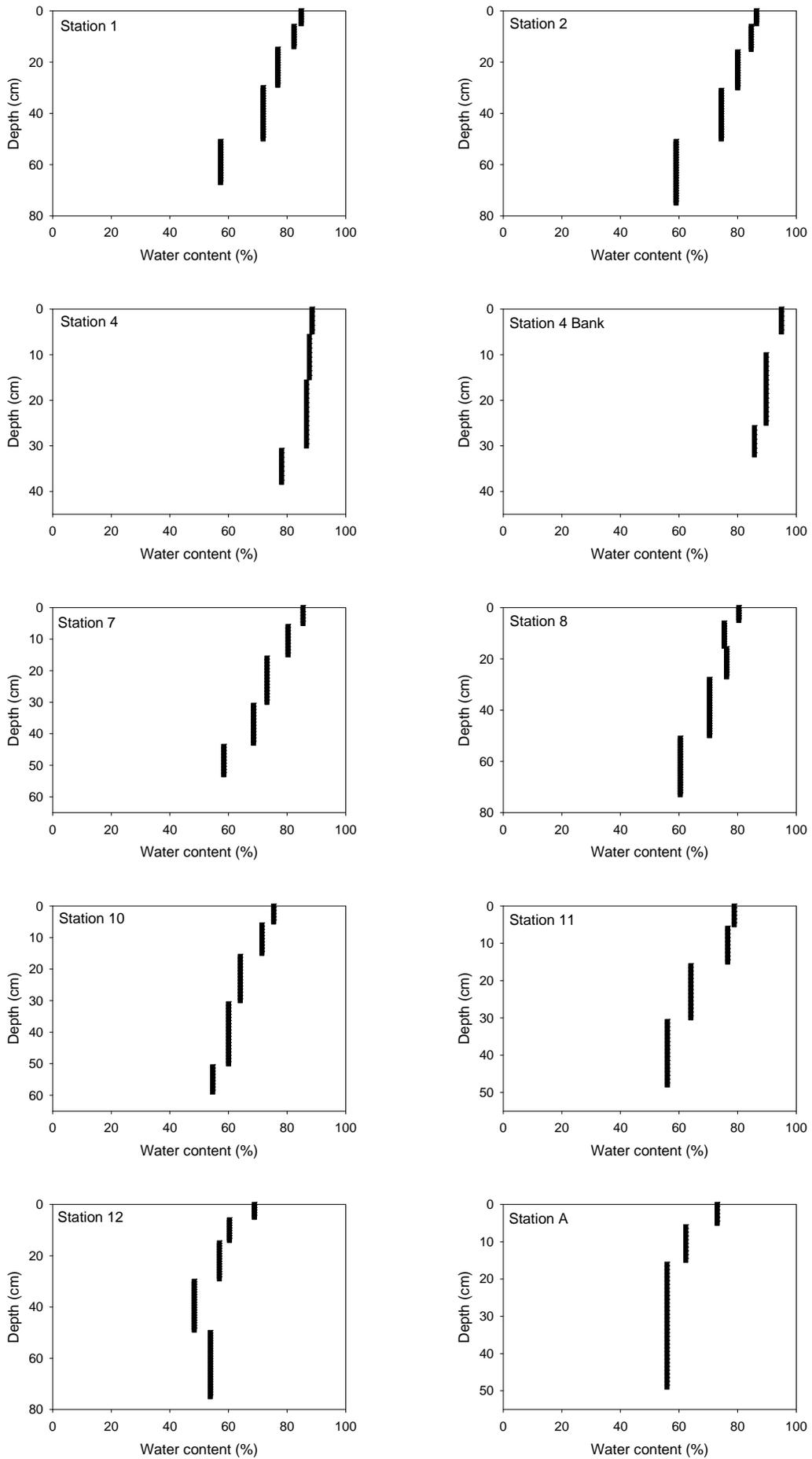


Figure 4. Sediment Core Total Organic Carbon (TOC) contents.

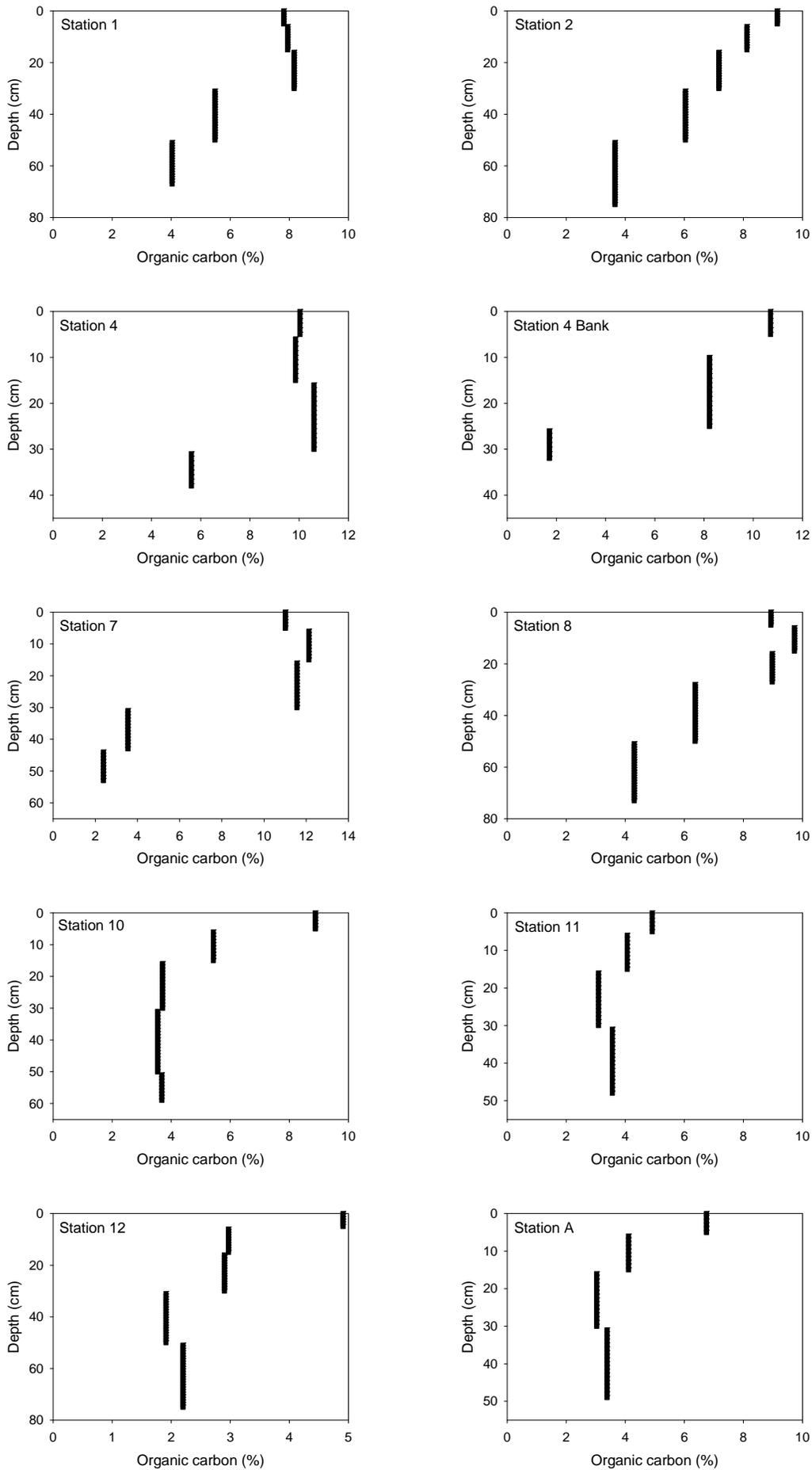


Figure 5. Mo concentration profiles in 10 sediment cores

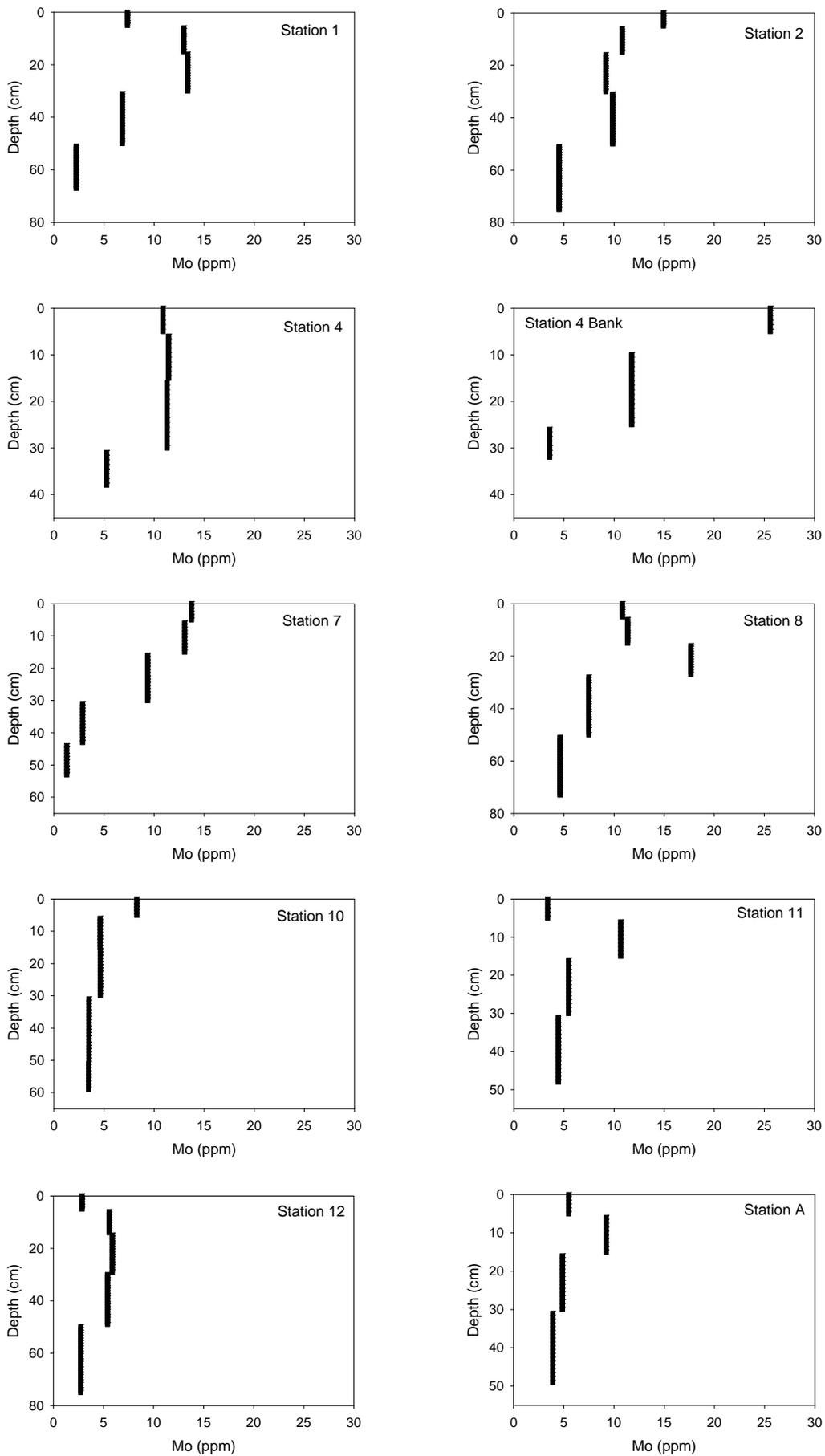


Figure 6. Ag concentration profiles in 10 sediment cores

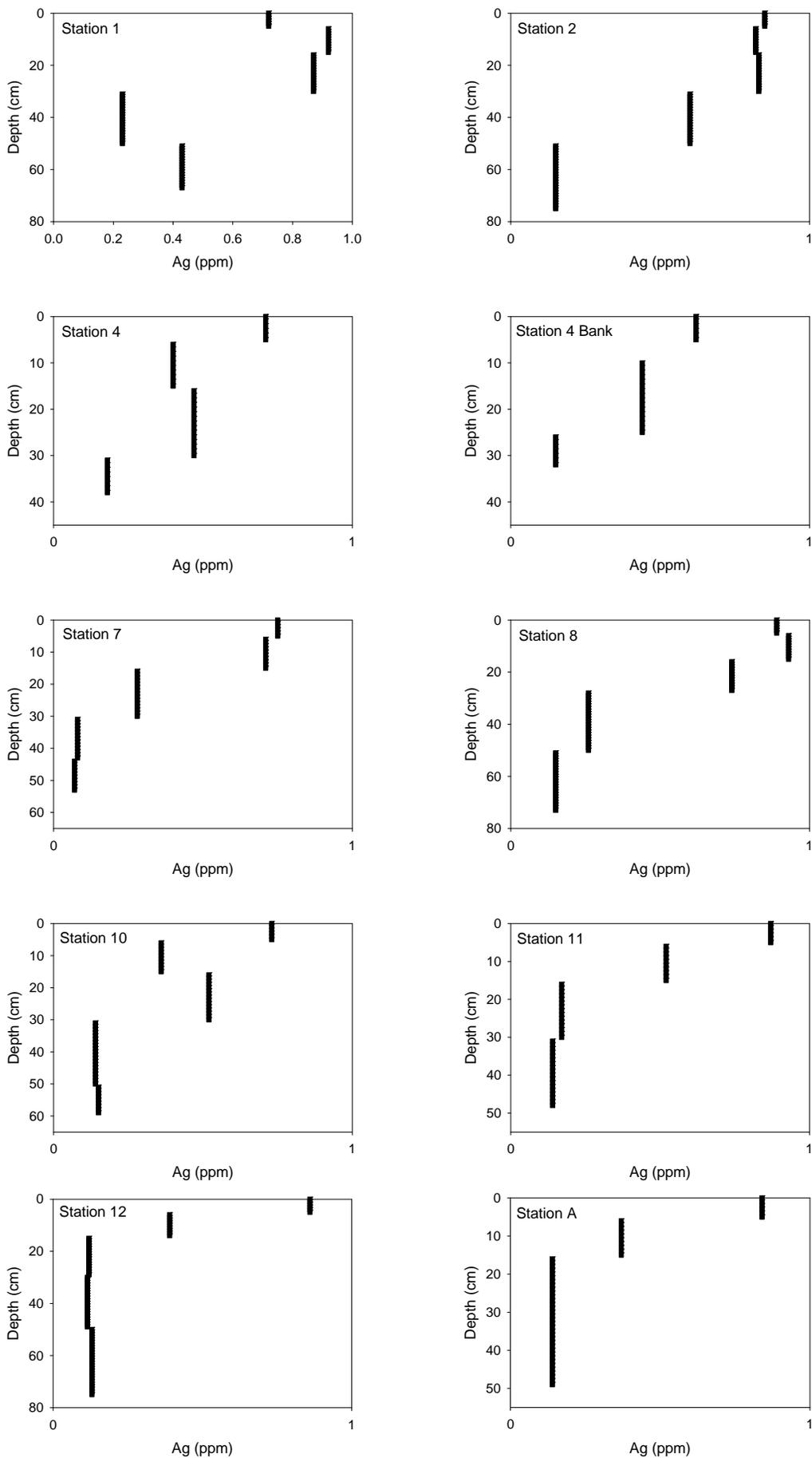


Figure 7. Figure 3. Pb concentration profiles in 10 sediment cores

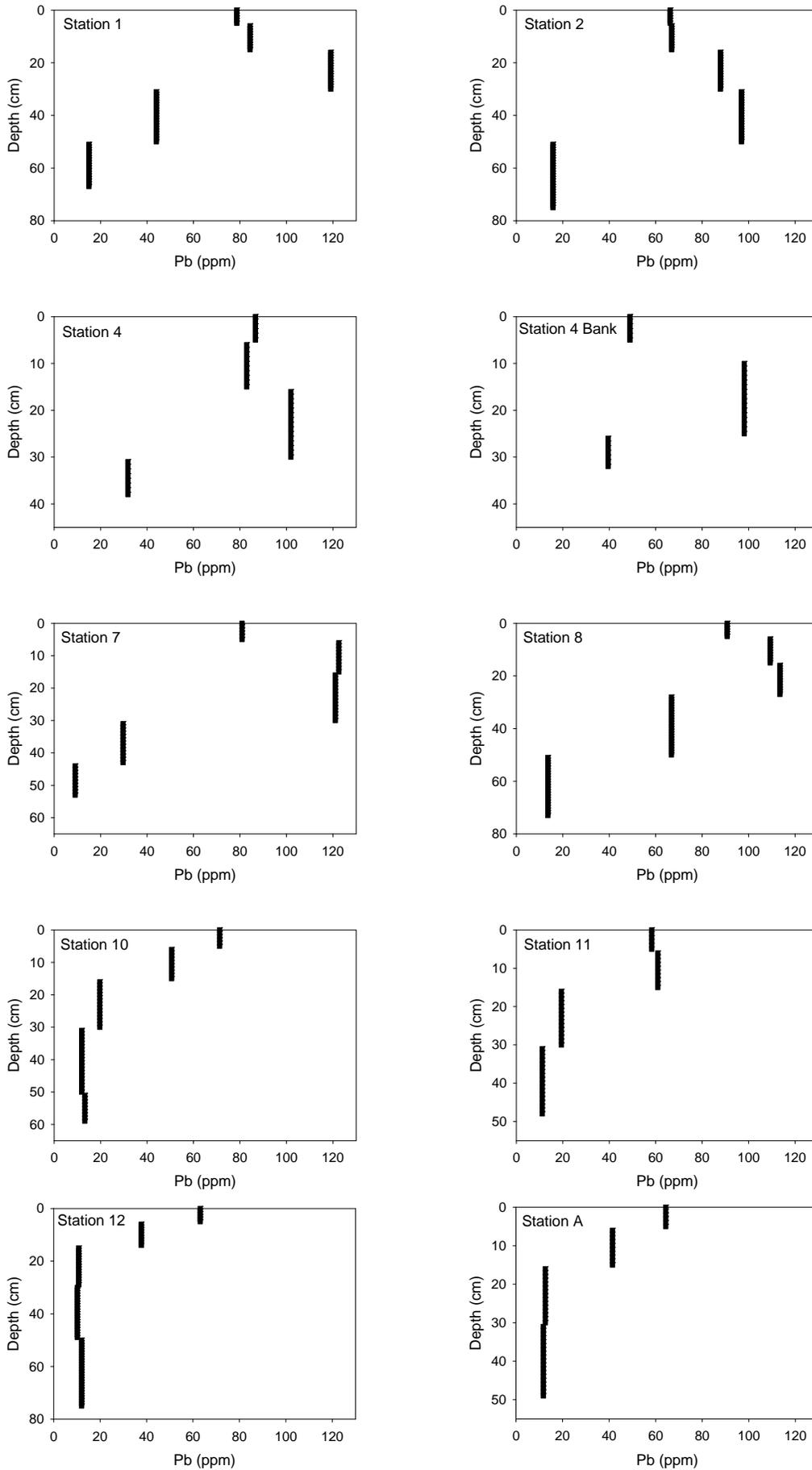


Figure 8. Cd concentration profiles in 10 sediment cores

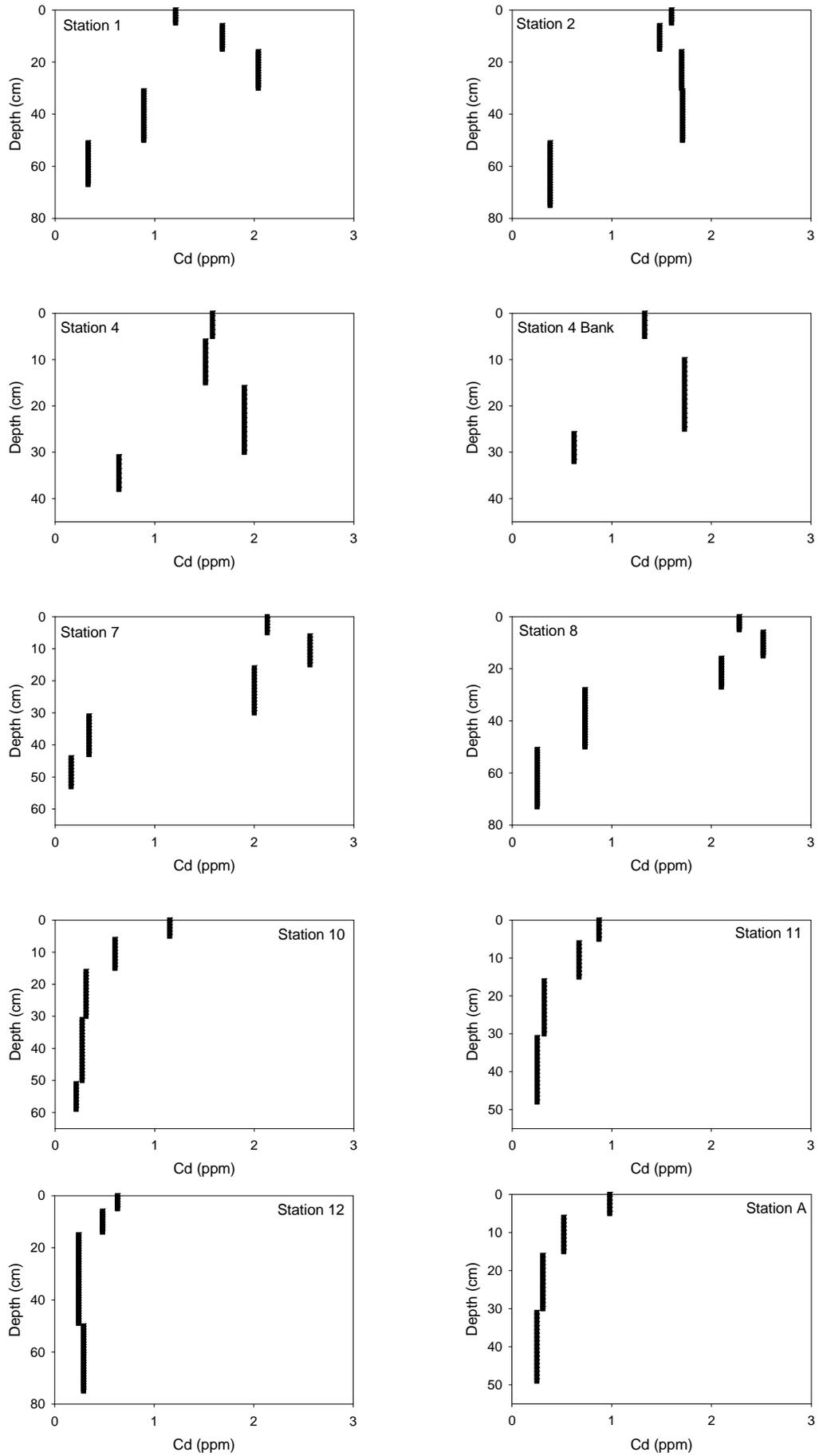


Figure 9. Co concentration profiles in 10 sediment cores

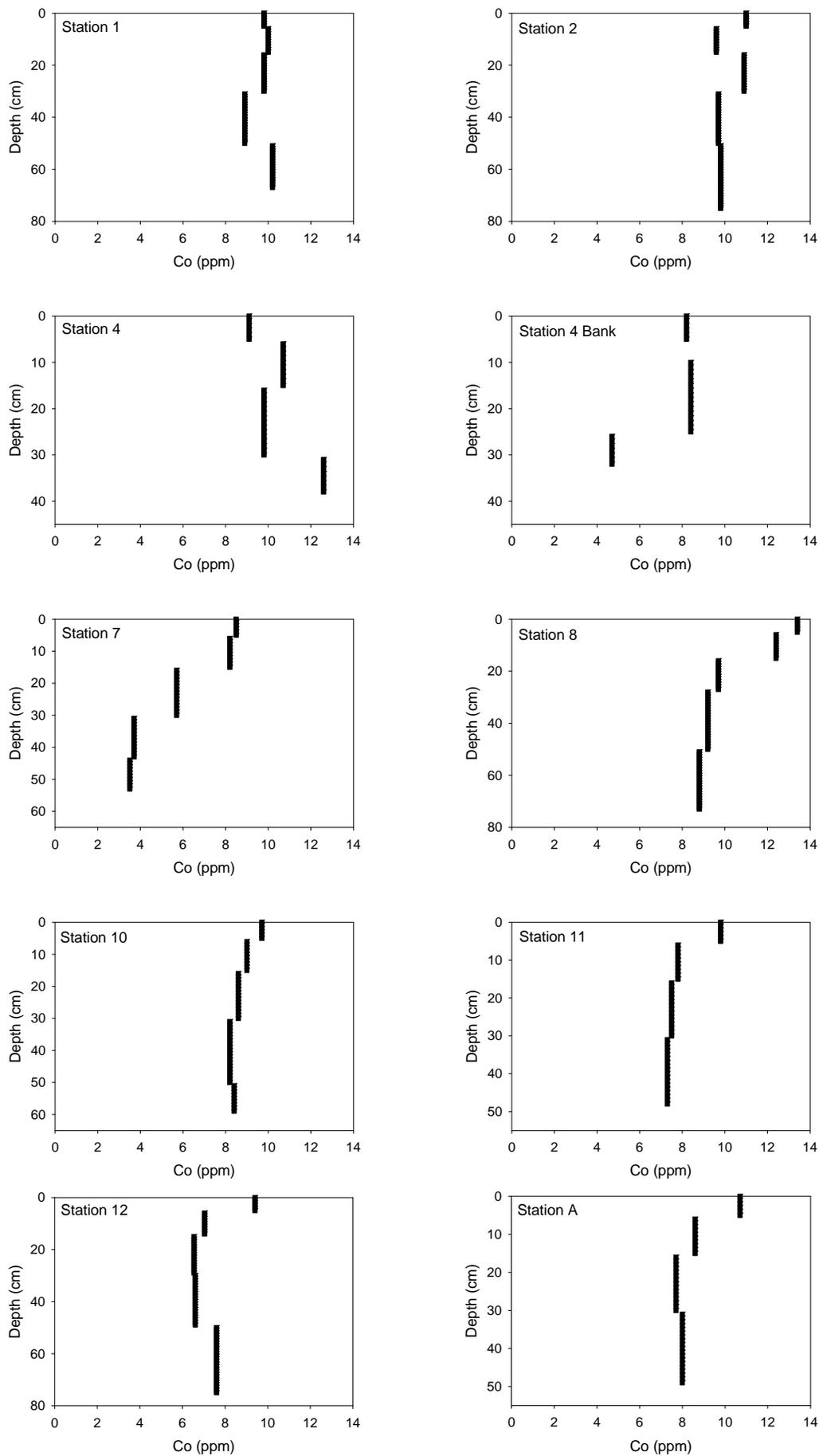


Figure 10. Cu concentration profiles in 10 sediment cores

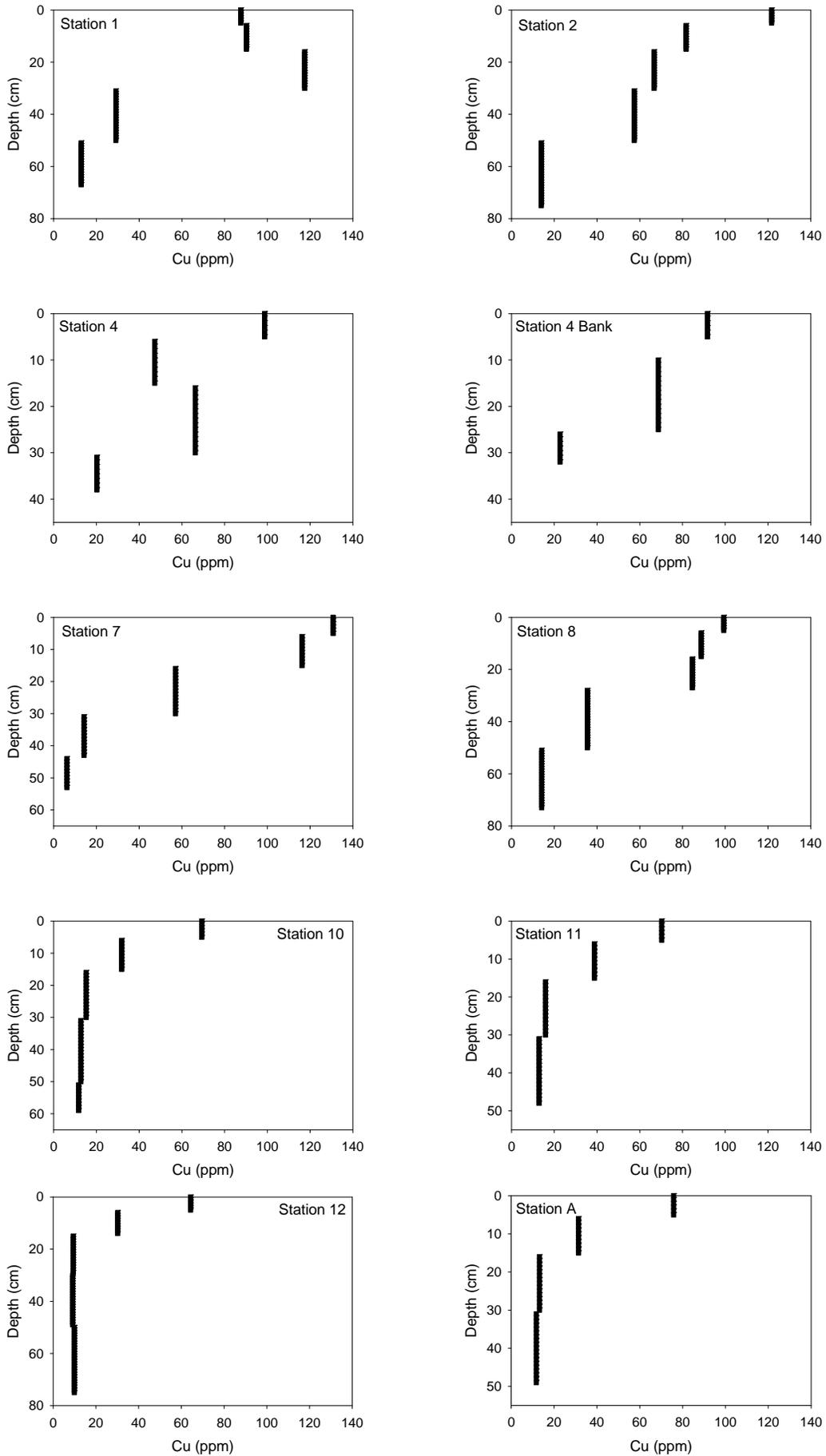


Figure 11. Fe concentration profiles in 10 sediment cores

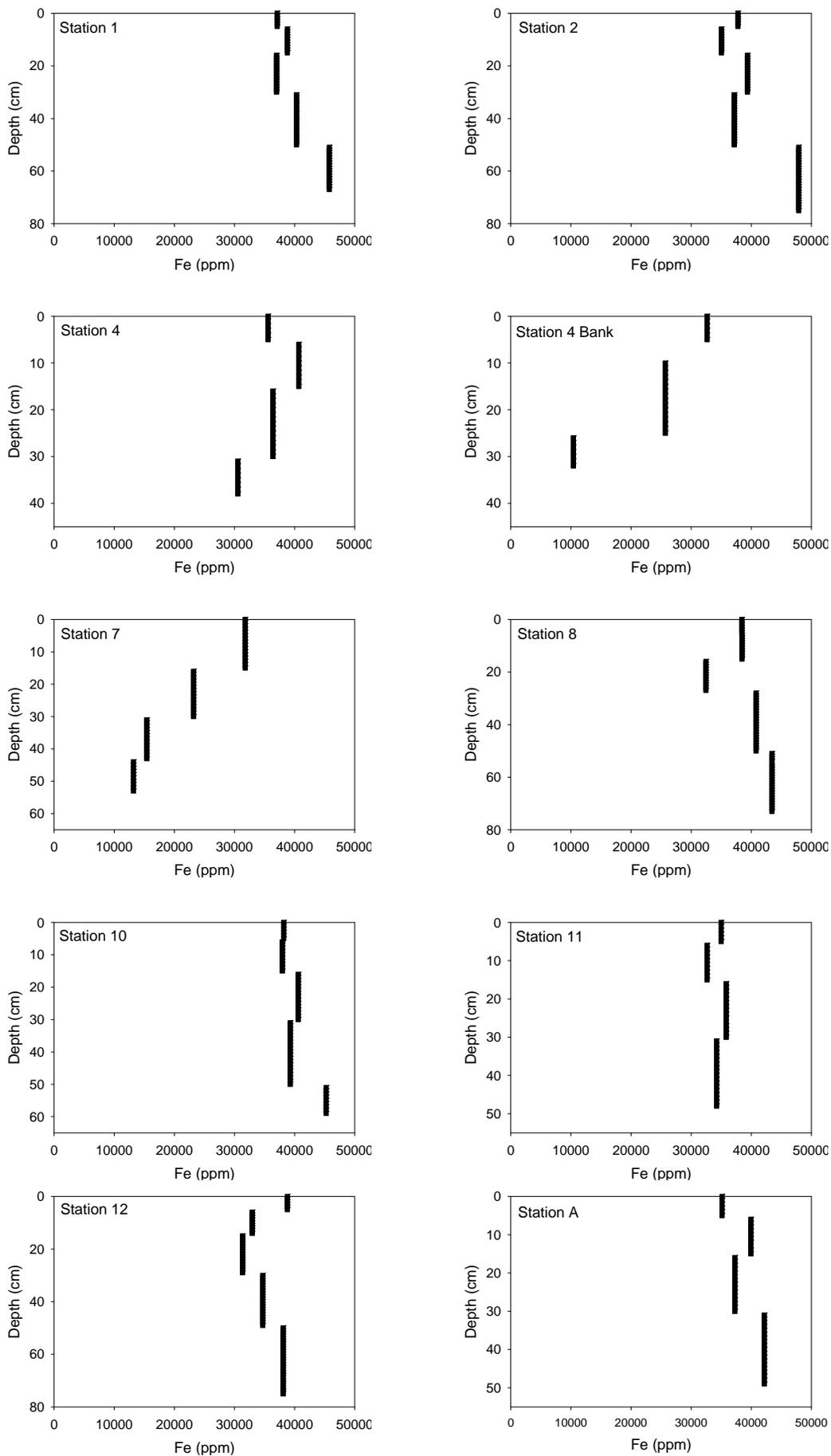


Figure 12. Ni concentration profiles in 10 sediment cores

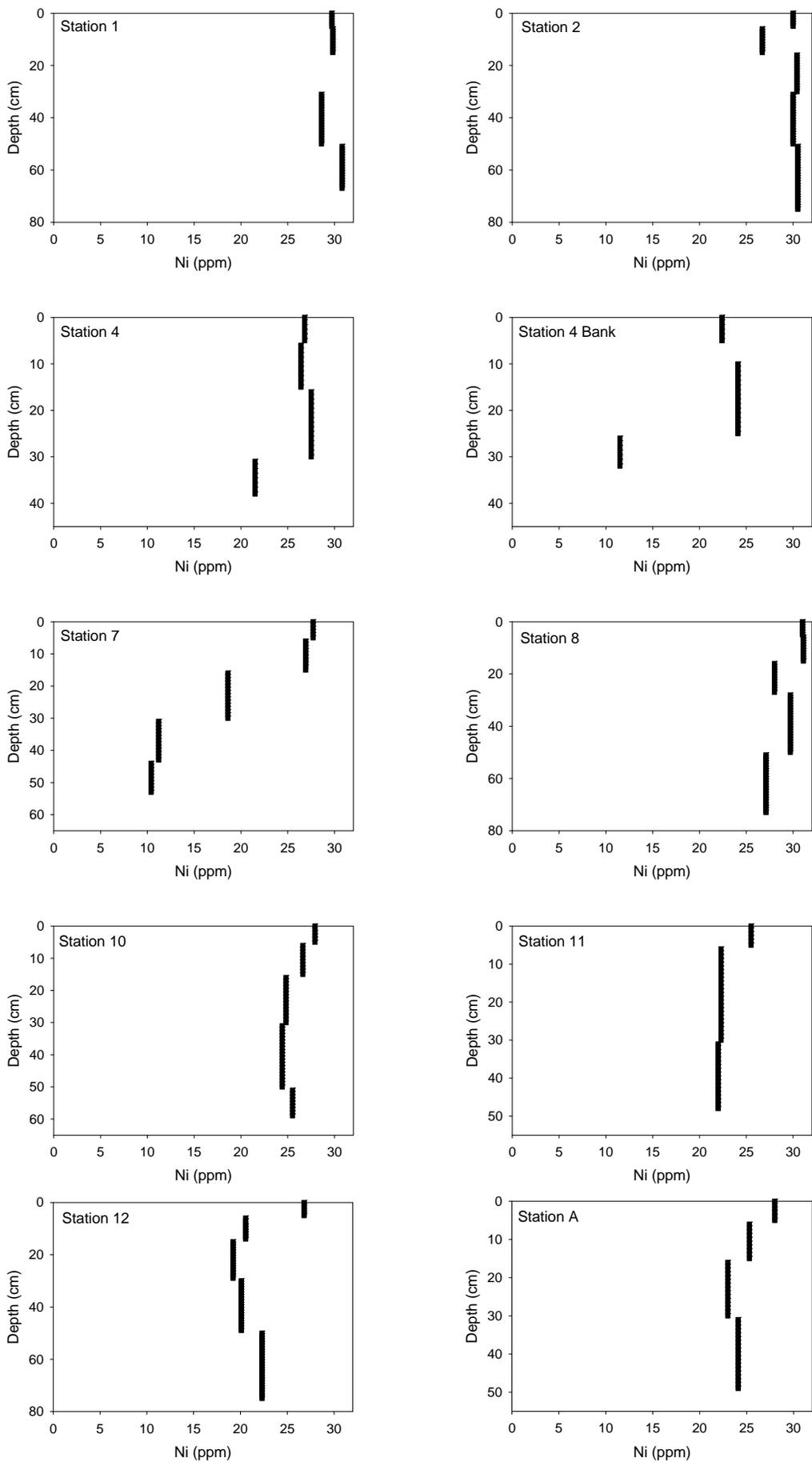


Figure 13. V concentration profiles in 10 sediment cores

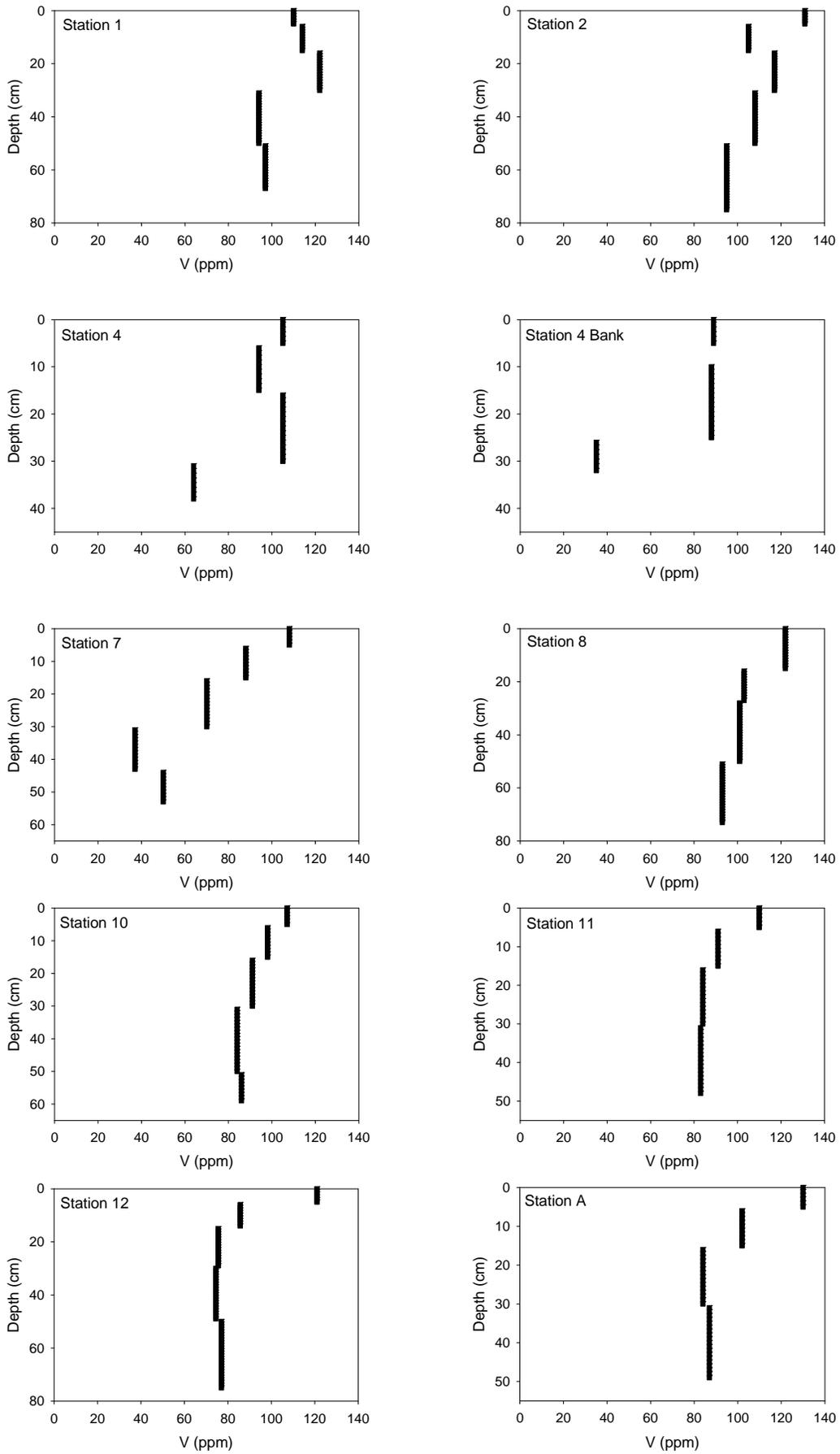


Figure 14. Zn concentration profiles in 10 sediment cores

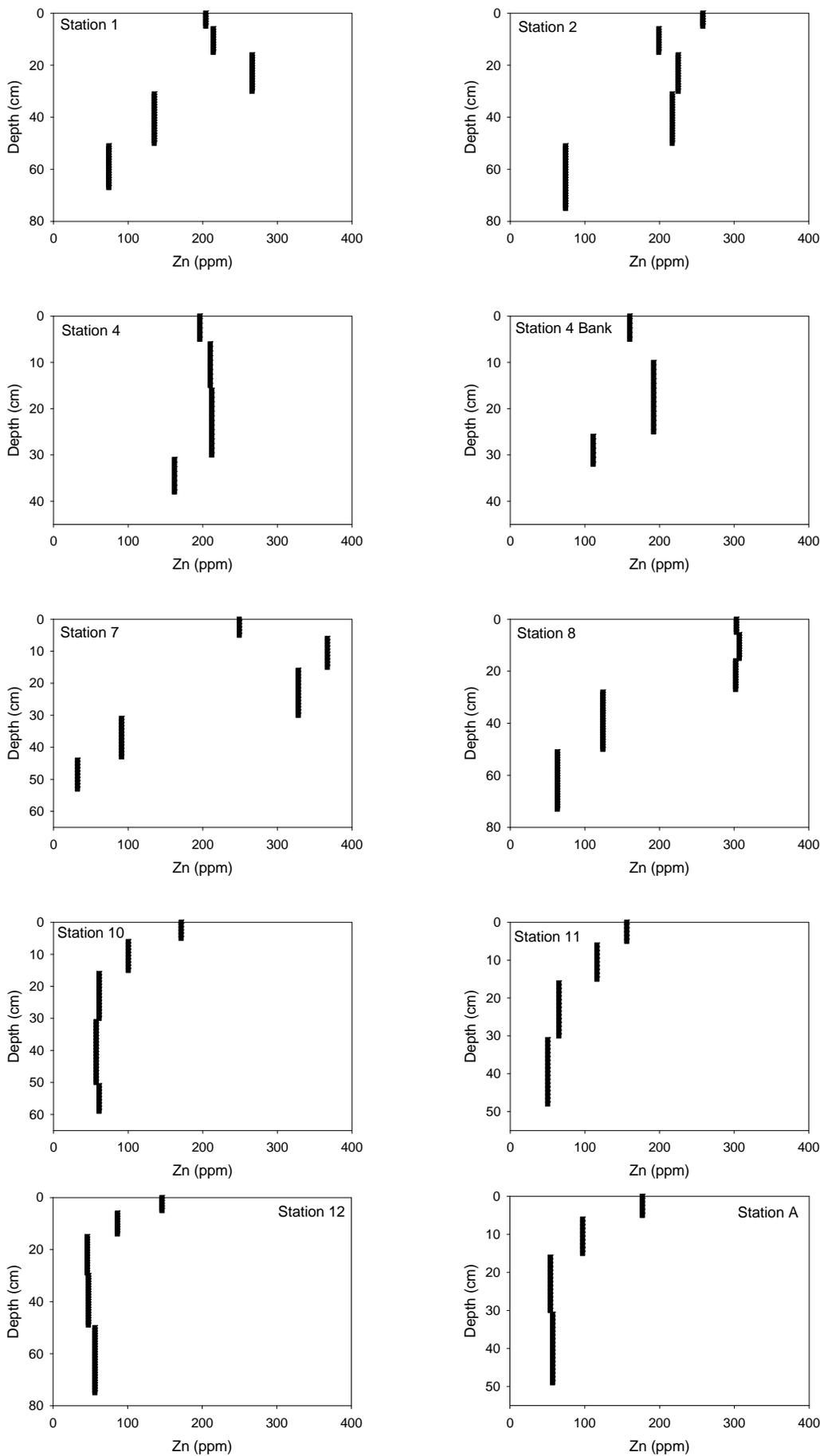


Figure 15. Ti concentration profiles in 10 sediment cores

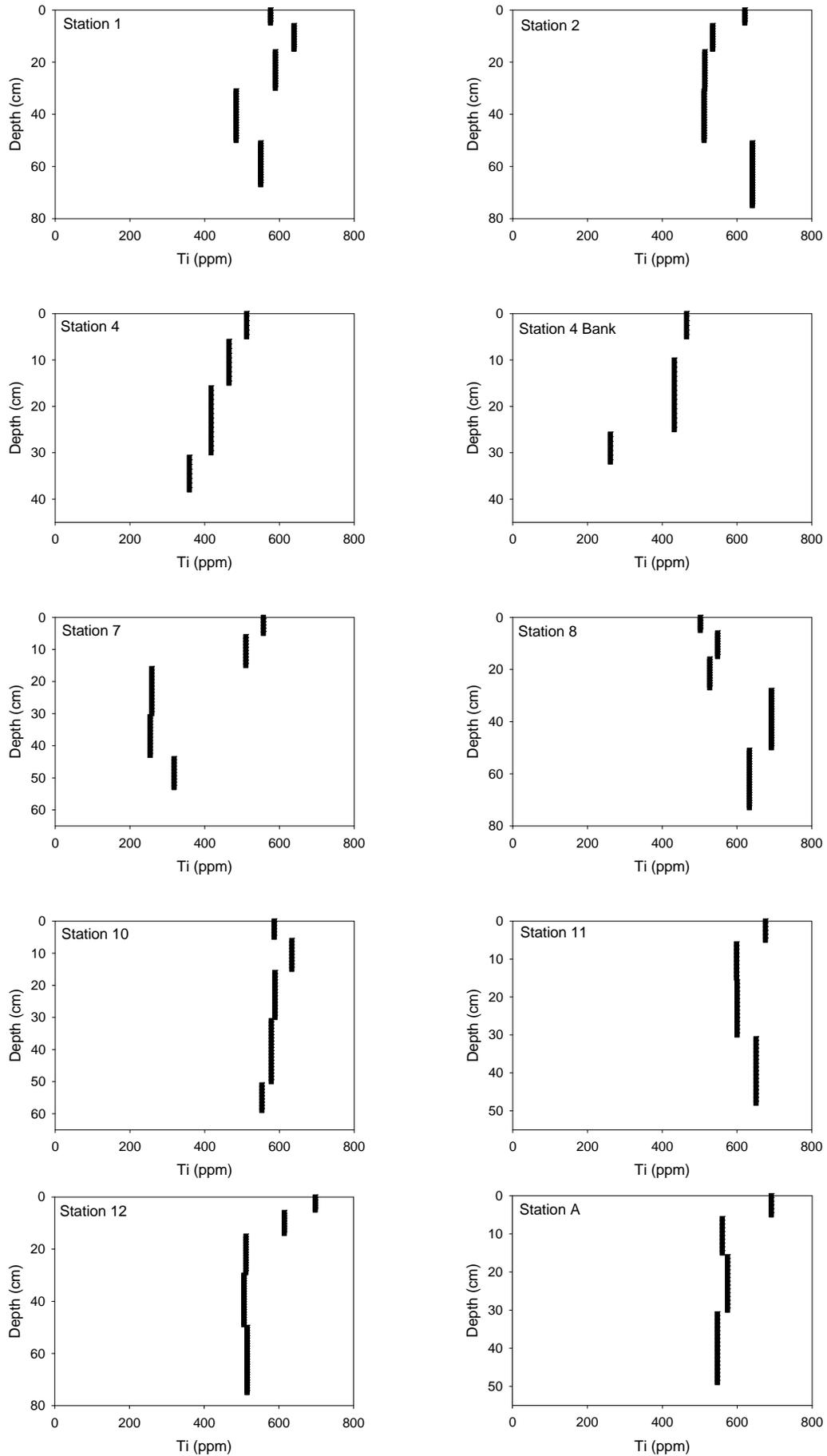


Figure 16. Mn concentration profiles in 10 sediment cores

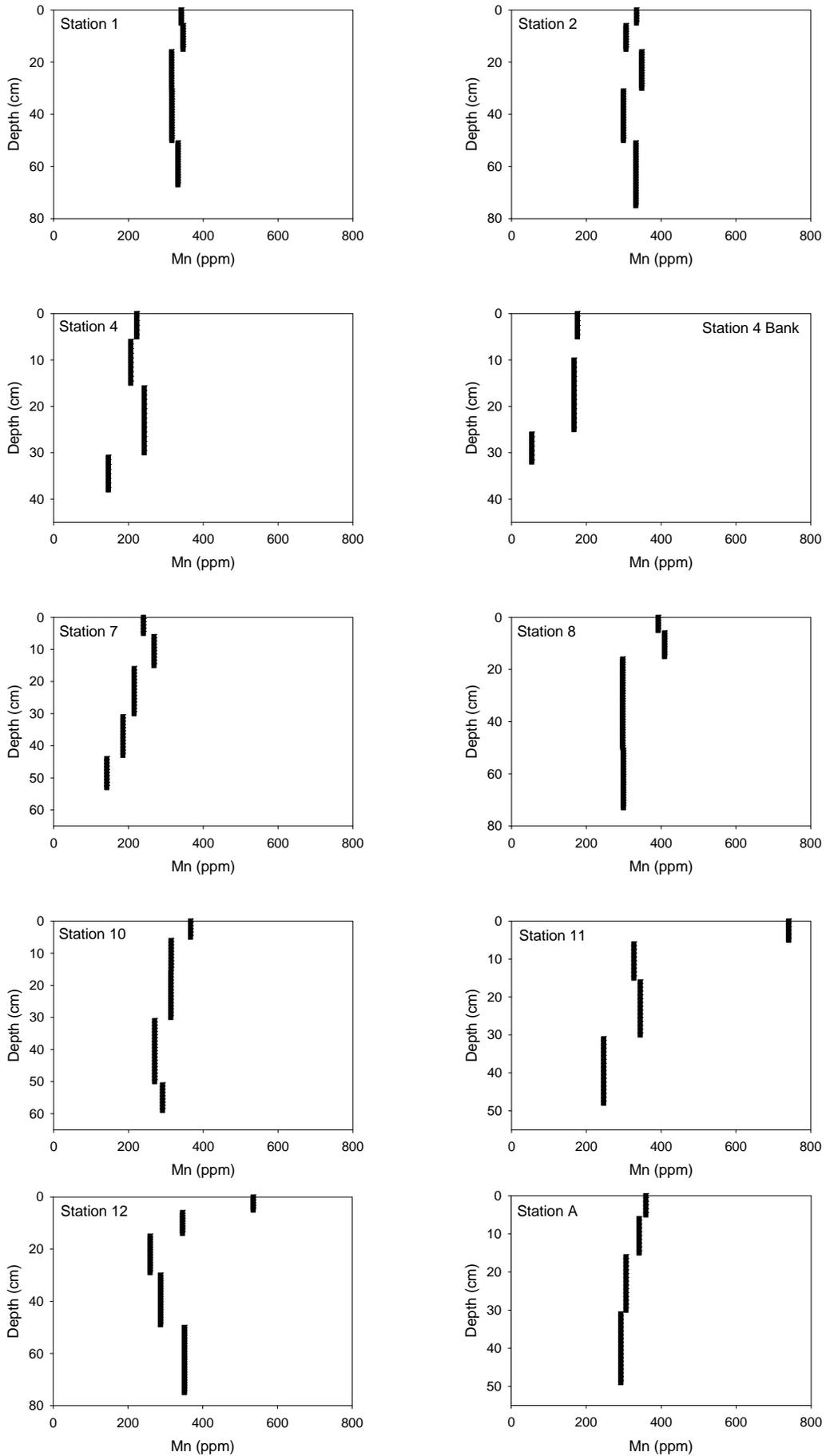


Figure 17. Al concentration profiles in 10 sediment cores

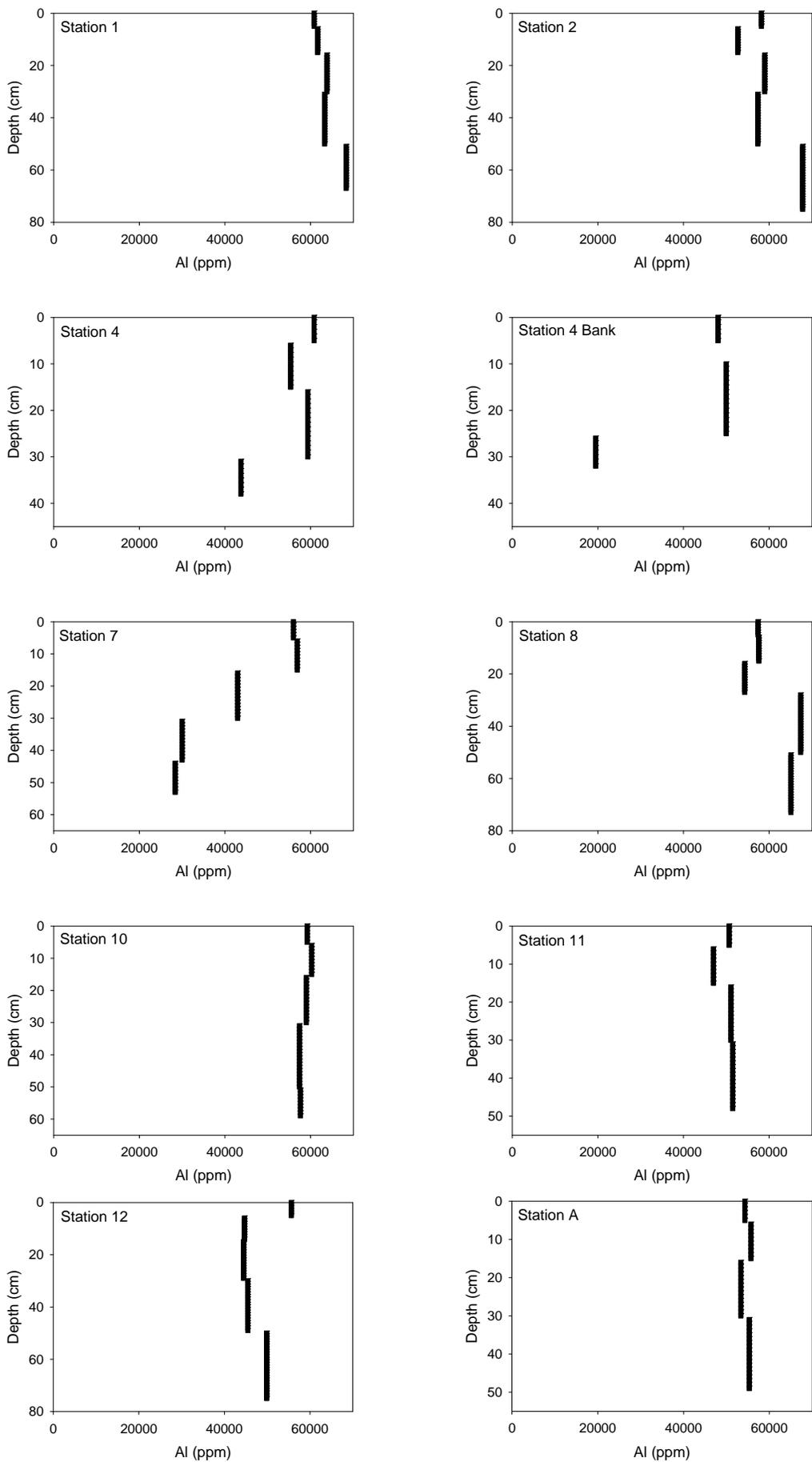


Figure 18. Profiles of total PAHs in the ten sediment cores

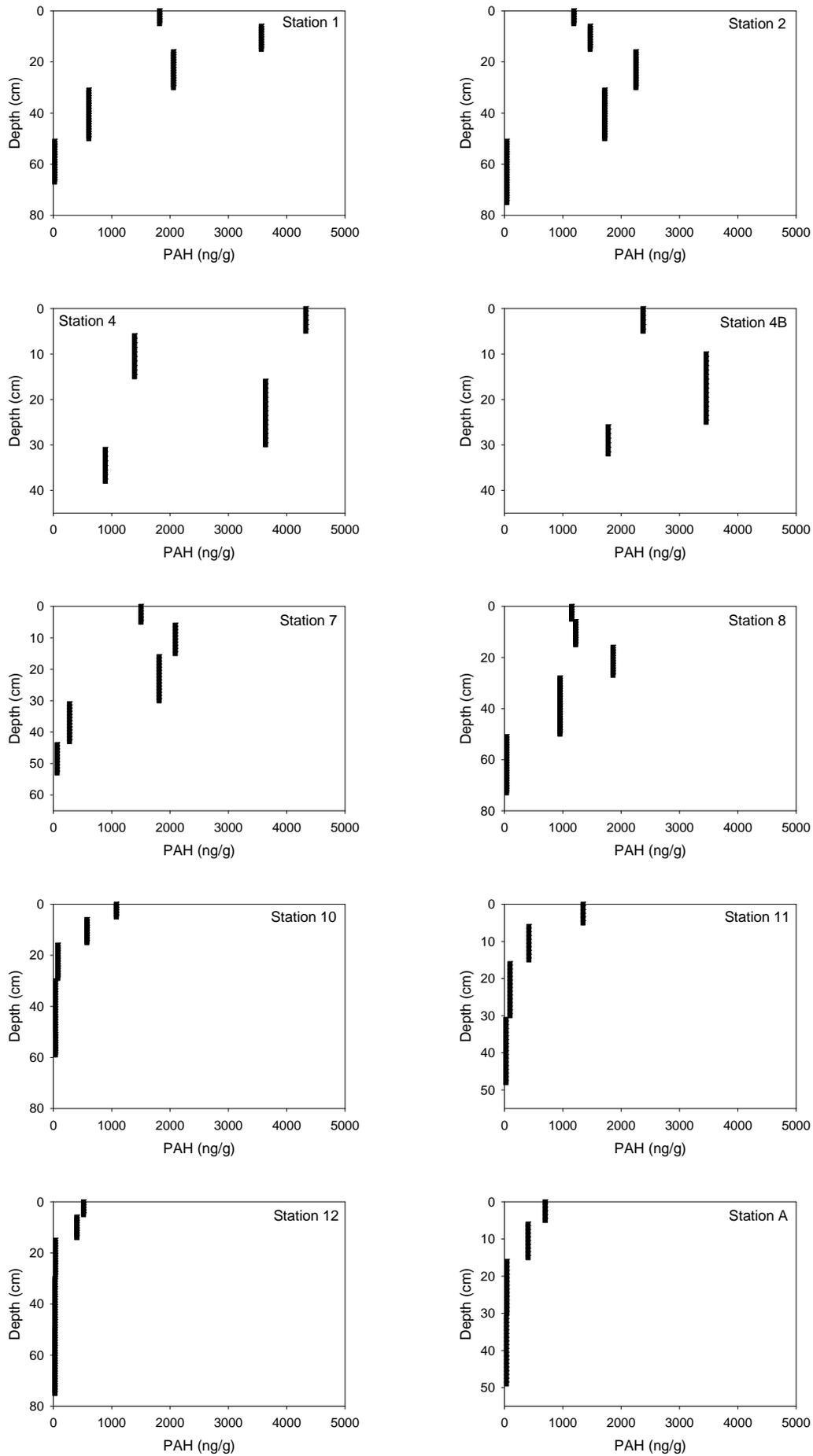


Figure 19. Profiles of total DDT residues in ten sediment cores

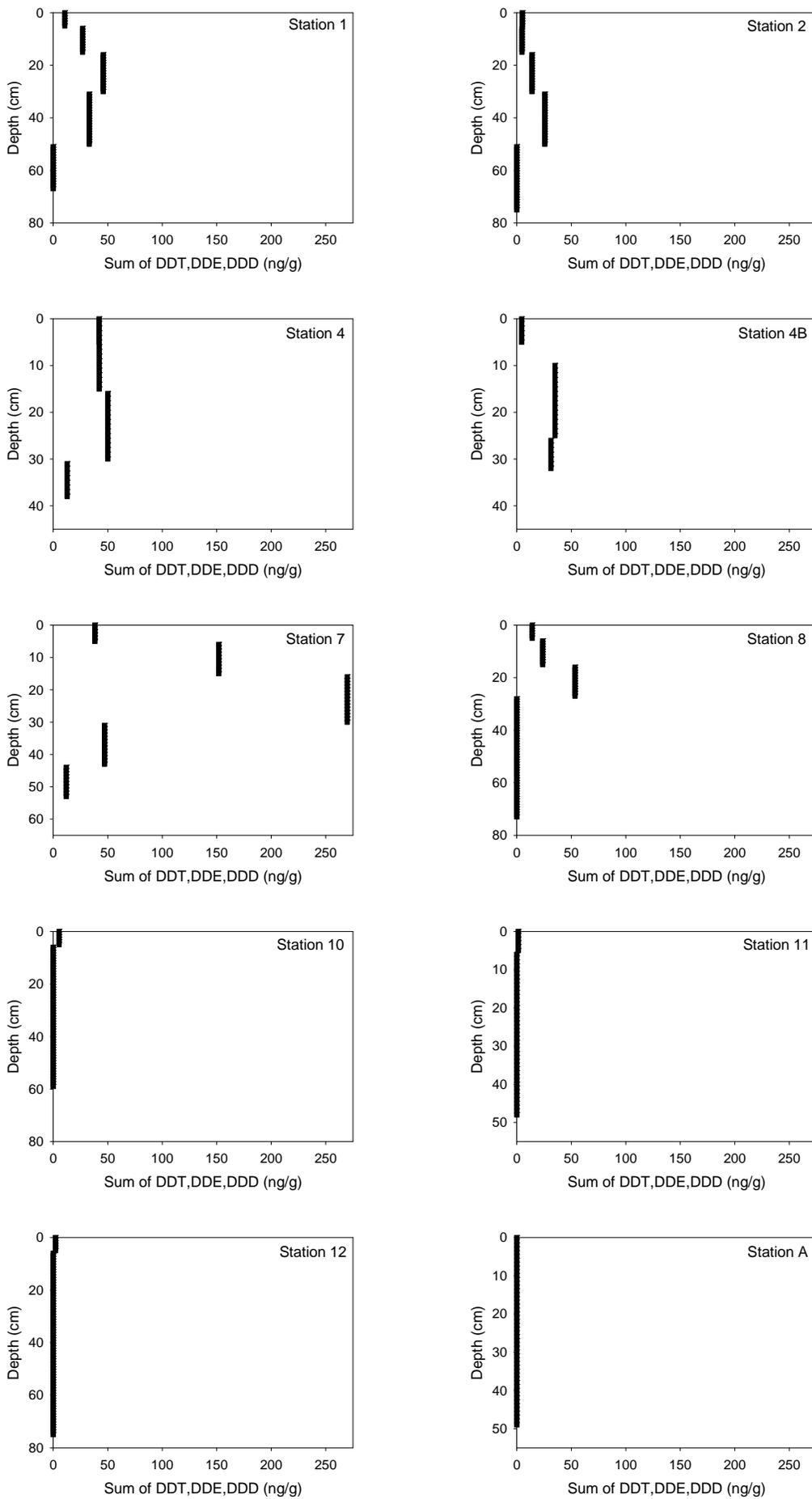


Figure 20. Total PCB core profiles (ng/g)

