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Characterization of semivolatile organic contaminants in the sediments of the Forge River – historical trends and potential toxicity

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Abstract of the Thesis

Characterization of semivolatile organic contaminants in the sediments of the Forge River – historical trends and potential toxicity

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This thesis study is one part of collaborative research project conducted by a team of faculty from the School of Marine and Atmospheric Sciences (SoMAS) investigating the causes of poor water quality issue in the Forge River. Other projects in this study examined nutrient budgets, water circulation, and trace metal contamination. The major objectives of this thesis study are characterization of semivolatile organic contaminants (SOCs) in the Forge River sediments, evaluation of their potential ecological risk, and reconstruction of their historical input to this area. Surface sediment samples and sediment cores were collected from the Forge River area in the late summer and early winter of 2006. SOCs analyzed in this thesis study included polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). Sediment properties (such as water content, grain size and total organic carbon) were also analyzed. SOCs analysis methods were modified from standard EPA methods to allow determination of multiple groups of contaminants on the same sample extract and to minimize sample size needed. PCBs and OCPs were detected by gas chromatography with electron capture detections and PAHs were measured by gas

chromatography - mass spectrometry. Compared to published data on SOCs in sediments from the New York - New Jersey Harbor Estuary, PCBs were generally low, while PAHs are relatively high, particularly when considering the rural nature of the Forge River estuary. Concentrations of most OCP were low to undetectable by our method except the DDTs, where appreciable concentrations, particularly near the head of the river were observed. PAHs were evenly distributed along the river except at Wills Creek, the most northern river flowing to the Forge River. Data on SOCs were interpreted as compared levels of particle reactive (lead - Pb, copper - Cu) and redox sensitive (molybdenum - Mo) trace metals measured by other investigators in the Forge River project to evaluate the anthropogenic sources for DDTs and PAHs. In addition to atmospheric input, local sources of DDTs from the upstream river, especially in the East Mill Pond where extremely high DDTs concentrations were detected were inferred. Run-off was identified as a probable local source of PAHs at Wills Creek. Comparison of measured SOC concentrations to numerical sediment quality guidelines indicated limited risk to biota from sediment contaminants.

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Introduction

The Forge River is a small estuary, only three miles in length, flowing into Moriches Bay located on the south shore of Long Island. The main connection to the Atlantic Ocean is through Moriches inlet. The tidal Forge used to be characterized by its natural beauty, attracting recreational boating, swimming and fishing activities in the summertime. Many houses were built along the river to take advantage of the location. However, the Forge River water quality has deteriorated over time due to both anthropogenic inputs of wastes from duck farms, and more recently from seepage from on-site disposal of sewage that occurs in high density housing areas, especially prevalent along the northwestern part of the watershed. Historically, water quality has also been affected by closures of Moriches Inlet, limiting flushing of more contaminated waters to the Atlantic Ocean. The effects of restricted flow were very pronounced during a complete closure of the inlet following a hurricane in 1950, but water quality improved markedly after the inlet was re-opened in 1954. Five decades later, the water in the Forge has become increasingly polluted, especially during summertime. The poor water quality was especially prominent during the summer of 2005, when dead fish and crabs were floating in milky yellow and foul smelling water. Based upon water quality monitoring by the Suffolk County Health Department and communications with local residents, highly polluted conditions continue to exist. This water pollution event led to an extensive scientific and engineering study on the Forge River attempting to determine the causes of degraded water quality (Swanson et al., 2008a).

The causes for the poor water quality has been studied by a team of scientists from the Stony Brook University's School of Marine and Atmospheric Sciences, (SoMAS), who found a complex situation with multiple contributing factors including: eutrophication, sluggish water circulation within the Forge and Moriches Inlet, and inputs of chemical pollutants. Eutrophication is largely responsible for many observed pollution effects in the river. Excessive nutrient input fuels an overproduction of phytoplankton and macroalgal biomass. As a result, decay of biomass by microbial respiration causes oxygen depletion in the water column and sediments, especially in summer. The depletion of dissolved oxygen in waters and sediments possibly contributed to the death

of fishes and crabs. The large amount of biomass production also contributes to the accumulated reservoir of labile organic matter in the sediments. The adjacent tributaries, notably the eutrophied East and West Mill Pond, supply a significant amount of suspended organic matter to the Forge River. West Mill Pond receives wastes from a major Duck Farm. However, it has been estimated that groundwater that is contaminated by local cesspools and septic tanks are likely the major source of nitrogen nutrients to the tidal Forge (Swanson et al., 2008a).

The organic matter levels in Forge River sediments greatly exceed levels measured in more moderately eutrophied estuaries (Mayer, 1994). For example, maximum total organic carbon (TOC) contents analyzed in our Forge River sediment samples range from 7.7 to 12.1% along the upper half of the tidal Forge River, decreasing towards the mouth. While in the highly urbanized NY/NJ/lower Hudson Basin Harbor complex, TOC contents measured in a system-wide surface sediment samples (113 in total) were typically between 2 and 4% with higher levels (7%) only found in highly sewage-impacted and eutrophied areas of Jamaica Bay (Adams et al., 2003). These very organic-rich sediments could be potential reservoirs for organic contaminants and some metals due to their sorptive capacity. The depletion of dissolved oxygen levels between water column and sediments also produces highly reducing and sulfidic sediments in the river, which could effectively scavenge selected metals (i.e molybdenum (Mo) and cadmium (Cd)) from seawater when it enters the Forge River (Brownawell et al., 2008).

The accumulation of nutrients and chemical pollutants is further enhanced by the sluggish water circulation within the Forge River and Moriches Bay due to the shallow water depths, increasing filling of the Moriches inlet mentioned above, and limited exchange of water between Moriches Bay and the ocean attributed to weak tidal circulation (Swanson et al., 2008a). The sluggish water circulation would maximize the impact of chemical contaminants and nutrients in the river and controls the extent of contaminants flushed out of the system via dilution and transport to Moriches Bay and finally the Atlantic Ocean. Weak circulation, especially in the summer, will strengthen the vertical stratification of water column and worsen the oxygen conditions in bottom

waters, with hypoxia or even anoxia being observed. Thus, the tidal Forge is naturally susceptible to accumulation of nutrients, eutrophication, and organic rich sediments.

Considering the unusually high organic carbon contents in the Forge River sediments, the possible accumulation of semivolatile organic contaminants (SOCs) in sediments is of concern due to their persistence, hydrophobicity and bioaccumulative potentials, which could directly or indirectly contribute to the health of fish and crabs in the overlying water. Characterization of sediment-associated SOCs is the focus of this thesis study. SOCs are mainly composed of nonpolar or slightly polar organic compounds with vapor pressure $<10^{-6}$ atm. These compounds include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides (Pirrone et al., 1995). SOCs are ubiquitous and widely detected in a variety of environmental media including air, water, sediments and biota. Considering their low vapor pressure, SOCs in the atmosphere mainly exist in the particle phase and can be transported globally. Under favorable meteorological conditions, SOCs in the atmosphere could be a significant source for local aquatic or terrestrial ecosystem contamination (Simcik et al., 1997). Due to their hydrophobicity, SOCs are known to accumulate in the aquatic and terrestrial food chains in all kinds of ecosystem such as Great Lakes of North America, the Arctic and high mountains (Burniston et al., 2007). In addition, these hydrophobic compounds are preferentially absorbed to sediments containing organic carbon (Lopes et al., 1998). The target SOCs analyzed in this thesis study included PAHs, PCBs and organochlorine pesticides. Those contaminants might have entered the Forge River from a number of sources, including: agricultural fertilizer use, illegal direct sewage input from homes, inputs from local businesses, past pesticide applications, duck farming activities, boating, stormwater run-off, and atmospheric deposition directly to water, or onto the watershed, from which it can then enter the Forge by run-off. The ground water could also be a great potential source due to the antiquated sewage treatment systems used in the local watershed (cesspools, septic tanks and small sewage treatment plants discharging to ground water) (Swanson et al., 2008b).

Background

PAHs

Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of anthropogenic organic contaminants. PAHs are hydrocarbons with two or more fused benzene rings. The names, abbreviations and structures of target PAH analytes in the Forge River sediments are listed in Table 1. PAHs can come from both natural and anthropogenic sources. There are some natural sources such as sediment weathering, forest fires, volcanoes and oil seeps. However, anthropogenic sources dominate in most areas affected by human activities. Two major types of anthropogenic sources release PAHs into the environment: petrogenic and pyrogenic sources. Petrogeninc sources such as crude oil and many fuel oils contain PAHs which can be discharged to aquatic environments through sewage effluent runoff, oil spill accidents, and small boat or tanker operations. The incomplete combustion of fossil fuels (i.e. coal and petroleum) and carbon-containing fuels such as diesel and biomass (i.e. wood, fat and tobacco) produce pyrogenic PAHs, which also end up into the aquatic environment (Zakaria et al., 2002). Most PAHs are lipophilic, and can be persistent depending on structure, the matrix they are associated with (e.g., strong binding to combustion derived soot particles), and environmental conditions, such as burial in suboxic sediments (Yan et al., 2006). The higher molecular weight PAHs are less water soluble and less volatile. Due to these properties, PAHs in aquatic environments are primarily found in sediments with high organic matter contents, and are better preserved under hypoxic and anoxic conditions such as those which exist in the Forge River sediments. The distribution of PAHs in sediments has been intensively studied since the mid 1970s. A wide range of concentrations of PAHs are found to be distributed globally from regional lakes and rivers to the open ocean (Zakaria et al., 2002). High concentrations of sediment PAHs with more than 10,0000 ng/g were reported in the highly urbanized and industrialized areas such as in lake and river sediments around New York City and Northeast New Jersey (Metre et al., 2000) and in surficial sediments of Sydney Harbor, Australia (McCready et al., 2000).

The toxicity of PAHs has been reviewed by Albers 1995. PAHs affect living organisms through their toxicity. In water the toxicity of PAHs increases with molecular weight (MW) up to MW 202 (fluoranthene, pyrene). The acute or chronic toxicity for

higher MW PAHs rapidly declines due to reduced solubility. However, sublethal effects can happen when aquatic organisms are exposed to very low concentrations of higher MW PAHs. The inhibited growth and cell division in aquatic bacteria and algae is observed at low concentrations (5-100 ppb) for individual lower MW PAHs, mostly two- and three-ring compounds. At high concentrations (0.2-10 ppm), the same PAHs can be detrimental to algae and macrophytes through interference with cell division or photosynthesis. The LC_{50} values from short-term exposures (24-96 h) for several aquatic invertebrates vary from 0.3 to 5.6 ppm for individual PAH compounds. The early developmental stages including eggs and larvae are more sensitive to dissolved PAHs than later stages including juveniles or adults. Individual PAH compounds with LC_{50} values ranging from < 1 to > 100 ppm are reported for selected fish species in the same exposure (24-96 h) test. Less is known about the toxicity of PAHs on reptiles and amphibians, but laboratory injection of perylene or benzo(a)pyrene and 3-methylcholanthrene are reported to produce cancerous and noncancerous tumors. Limited information is available on the effects of individual PAHs on birds. Petrogenic PAHs (from crude and refined oils) are reported to cause lethal and sublethal effects on bird embryos. As for mammals, acute oral LD_{50} values with the range of 50-2000 mg/kg are reported for selected PAHs on laboratory rodents. Thus, there are large differences in the sensitivity of aquatic species to individual PAHs. Although the dissolved PAH concentrations in water are several magnitudes of order lower than the acute toxicity levels to aquatic organisms, sediment-associated PAH concentrations are typically much higher than those encountered in water. The numerical sediment quality guidelines for individual PAHs discussed later in the thesis are derived from an assembly of a large dataset with a variety of laboratory model organism toxicity tests and field toxicity observations (Swartz, 1999; Toro et al., 2000).

Since there are both natural and anthropogenic sources of PAHs, it is important to risk management to differentiate the sources in the evaluation of the anthropogenic contribution of PAHs to the environment. This can be often be accomplished by careful examination of the distribution patterns of individual PAHs and isomers. For example, petrogenic sources (weathered gasoline, diesel and oil) produce an abundance of alkylated 2-3 ringed PAHs, diesel combustion releases 3-4 ringed PAHs, and gasoline

combustion mainly yields 4-5 ringed PAHs. Therefore, certain PAH compounds or ratios of compounds to total PAHs can be used as indicators for source apportionment of PAHs in the sediments. Six currently applied and sensitive ratios are used for PAH data interpretation in this thesis: 1). MePH/PHEN, the ratio of methylphenanthrene to phenanthrene; 2). FLA/ (FLA+PRY), the ratio of fluoranthene to fluoranthene plus pyrene, both have a mass of 202; 3). ANTH/ (PHEN+ANTH), the ratio of anthracene to the sum of mass 178 PAHs (phenanthrene+anthracene); 4). BAA/(BAA+CHRY), the ratio of benzo(a)anthracene to PAHs with mass 228 (BAA+Chrysene); 5). IND/(IND+BGHIP), the ratio of indeno[1,2,3-cd]pyrene to the sum of IP and benzo[g,h,i]perylene; and 6). the ratio of high molecular weight PAHs (the sum of 4-,5- and 6-ringed) to total PAHs (Yan et al., 2006). The relative discrimination ability of the six ratios is briefly summarized below:

1). MePH/PHEN

The ratio of methylphenanthrenes to phenanthrene in sediments is an indication of anthropogenic sources. This ratio is around 0.5 for atmospheric PAH deposition; 0.5-1 in sediments dominated by phenanthrenes derived from combustion processes; 2-6 in sediments dominated by fossil-fuel-derived phenanthrenes; and 4.0 for used crankcase oil (Pereira et al., 1999).

2). FLA/ (FLA+PRY)

Fluoranthene and pyrene are abundantly distributed in sediments. Based on Yunker et al.'s (2002) analysis on 345 suspended particle and sediment samples, the demarcation between petroleum/crude and combustion sources for the ratio of Fl/ (Fl+Py) is around 0.4; 0.4-0.5 for petroleum combustion products; >0.50 is typically observed for biomass burning products (Yan et al., 2006; Yunker et al., 2002).

3). ANTH/ (PHEN+ANTH)

The ratio of ANTH/(PHEN+ANTH) is generally <0.1 for petrogenic sources, while > 0.1 indicates combustion sources (Yan et al., 2006).

4). BAA/ (BAA+CHRY)

According to Yunker et al.'s (2002) results, the ratio of BAA/ (BAA+CHRY) <0.2 implies petrogenic products; the ratio greater than 0.35 represents combustion sources.

5). IND/ (IND+BGHIP)

Also from Yunker et al.'s (2002) study, the ratio of IND/(IND+BGHIP)<0.2 suggests petrogenic derivation; 0.20-0.50 implies liquid fossil fuel combustion; and >0.50 may indicate biomass combustion (Yan et al., 2006).

6). 4-6 Ring PAH/TPAH

Yan, et al. (2006) suggested the ratio of high molecular weight PAHs (sum of all 4-6 ring PAHs) to total PAHs was strongly correlated with the ratio of FLA/ (FLA+PRY) and could be used as a sensitive indicator for source apportionment, especially in most recent sediment deposits (i.e. post-1990s). The ratio of 4-6 Ring PAH/TPAH less than 0.3 represents petrogenic sources, while > 0.70 indicative of combustion sources.

Considering the many factors that can influence PAHs composition in the environment (such as metabolism, weathering and diagenesis), we choose to evaluate all six ratios of these ratios in an attempt to obtain a more accurate source apportionment of PAHs in the Forge River sediment.

PCBs

Polychlorinated biphenyls (PCBs) are the chlorinated derivatives of a class of aromatic organic compounds. The empirical chemical formula for PCBs is $C_{12}H_{10-x}Cl_x$, where x=1-10. A PCB congener is a single and unique chemical compound in the PCB category. For example, 2, 4'-dichlorobiphenyl is a congener consisting of the biphenyl structure with two chlorine substituents, one on the #2 and another on #4 carbon of the two rings. Based on the number of chlorine substituents, theoretically, there are 209 PCB congeners in total. Table 2 list the target PCBs analytes in the Forge River sediments. PCBs were commercially produced and widely used as coolant and insulating fluids for transformers and capacitors in electrical industries, stabilizing additives for PVC building materials, reactive flame retardants and other sources. In the US, commercial PCBs were

first produced in 1929 and used to be marketed under the trade name: Aroclor. Commercial PCBs usually contain 50 or more mixtures of multiple congeners with different degree of chlorination. These congeners vary in their degree of toxicity. It is more complex to evaluate the toxicity of mixtures than individual congener in the environment. Due to their persistence in the environment and bioaccumulation potentials through the food web, there is a risk of posing threat to the environment and human health. Their domestic manufacture was discontinued by the US in 1979 and worldwide production was prohibited by the Stockholm Convention on Persistent Organic Pollutants in 2001.

Even though their production has ceased, PCBs continue to be a great concern in the environment due to their wide distribution in the soils and sediments and extreme resistance to degradation (i.e. oxidation, reduction, addition, elimination and substitution). Of 1416 Superfund hazardous waste sites in the US, PCBs have been detected in more than 387 sites (Danse et al., 1997). In the aquatic system, due to their insolubility in water and high solubility in organic solvents, oils and fats, PCBs are mainly accumulated in tissue fats and enriched in the sediments through adsorption processes. PCBs are detected in nearly all marine animal species including fishes, mammals, birds, also in humans (Rice et al., 1995).

The adsorptive capability of sediments generally increases as organic matter, clay and mud particle contents in the sediment substrates increase. Thus Forge River sediments with high organic carbon content and fine-grain particles could be a significant sink for PCBs. Ingestion of sediment or redissolution of PCBs into the water column through bioturbation and/or changes in oxic environment may potentially threaten benthic organism and fish health (Faroon et al., 2003). The composition and consequent toxicity of PCBs mixtures in the sediments significantly differ from those original commercial mixtures (i.e. Aroclor 1254) due to thermodynamic stability and environmental degradation.

Rice et al, 1995 reviewed the toxicity data on PCBs. Early, laboratory animal toxicity tests were conducted on the commercial PCB mixtures (i.e. Aroclor 1260, Aroclor 1242, Aroclor 1254, Aroclor 1248 mixtures). More specific tests on effects of

individual congener are common in most recent studies with the help of improved analytical techniques. LD50 values to be between 6.1 and 12.5 ppm were reported for acute doses of PCB mixtures in marine invertebrates such as grass shrimp (*Paleomonentes pugio*), brown shrimp (*Penaeus axtecus*), and pink shrimp (*Penaeus duorarum*) reported the. Acute doses of PCB mixtures to fishes showed a range of LC_{50s} generally lying between 10 to 300 ppm depending on Aroclor type as well as organism types (i.e. marine or freshwater). In addition to the varied mixture toxicity, the effects of specific congeners differ with respect to their structure. The LD50s for PCB congeners 126, 77, 105 and 153 using chicken embryo injection tests were approximately 0.6 ppb, 4 ppb, 3000-9000 ppb, and higher than 14,000 ppb respectively. The developmental and reproductive toxicity of PCBs were observed in both fishes and other aquatic organisms in the lab-controlled toxicity tests. Rainbow trout treated with 0.4 mg/kg of Aroclor 1242 produced eggs with high mortality and deformed fry 0.1 μg/l of Aroclor 1254 inhibited the growth of diatoms and 10 μg/l of Arocolor 1016 affected the growth of oysters. The avian species are more resistant to PCB toxicity; however, trophic level accumulation of PCBs still poses a great threat to fish-consuming birds such as eagles and hawks.

Organochlorine Pesticides

Organochlorine pesticides (OCPs), including hexachlorocyclohexane (HCH) and 1, 1, 1-trichloro-2, 2-bis (4-chlorophenyl) ethane (DDT), had been widely used against a variety of insects in the United States and around the world. Some OCPs such as hexachlorobenze and pentachlorophenol have been used primarily as fungicides and antimicrobials. These chemicals were first introduced around 1940s and several commonly known OCPs including DDT, lindane, aldrin, dieldrin, toxaphene, chlordane and heptachlor, had been restricted by US EPA by the 1970s due to their persistence in the environment.

Similar to PCBs, most of OCPs degrade very slowly and can remain in the environment long after application and in the organism long after exposure. OCPs also tend to accumulate to the organic phase of sediments due to their high hydrophobicity. The distribution and toxicity of OCPs in the sediments vary with respect to the difference

in their physicochemical and biochemical characteristics, for example, HCHs are more water soluble, biodegradable, volatile and less sorptive than DDTs (Tang et al., 2007), thus DDTs persist in the sediments and are more likely to pose adverse effects. Table 3 lists the entire target OCPs analytes in the Forge River sediments. Base on our analyzed results, only DDTs are significantly detected in the sediments. DDT is one of the most well-known synthetic pesticides. Commercial DDT is a mixture of several closely related compounds including p,p'isomer (>75%), o,p' isomer (15%) and dichlorodiphenyldichloroethlene (DDE) and dichlorodiphenly dichloroethane (DDD) make up the rest. DDE and DDD are two major metabolites and breakdown products of DDT in the environment. Under aerobic conditions, DDTs are dehydrochlorinated to DDEs by microorganisms in the sediments. DDE is more recalcitrant and less biodegradable in the environment than DDT. Under anaerobic and reducing conditions, DDTs are degraded by microorganism or pigments containing iron to DDDs. DDD is also a relatively stable compound and undergoes little degradation in the environment (Pereira et al., 1996). The primary metabolic pathway of DDT in the Forge River sediments is supposed to be reductive dechlorination to DDD under anoxic conditions, which should be reflected in a higher ratio of DDD/DDE. While technical mixture of DDTs also contains DDDs and DDEs, the ratio of DDD/DDE will depend on the amount of input and stability of each metabolite in the sediments.

DDT and its metabolites are most toxic pesticides in the OCPs group. DDT, DDE, and DDD can be significantly bioaccumulated through the food chain, with higher trophic level animals, especially apex predators such as raptors having a far greater capacity to bioaccumulate DDTs than those that situated at lower trophic levels in the same environment (Shaw et al., 1998). DDTs are most famously known as reproductive toxicants for bird species and have been directly linked to the decline of brown pelicans, bald eagles, osprey, and peregrine falcons populations throughout the world. The reasons for these depressed avian populations or reproductive failure are attributed to the embryotoxicity and eggshell thinning effects induced by DDTs. The thinned eggshell can be easily crushed by adult birds. DDE turns out to be more potent than DDT. The brown pelican is most sensitive to the effects of DDE on reproduction, with 3μg/g in the egg leading to near complete reproductive failure. The peregrine falcon is moderately

sensitive to reproductive effects of DDE with lowest adverse level of DDE lying between 15 and 30 μg/g. The bald eagle is similar, with a complete reproductive failure when DDE higher than 16 μg /g in the eggs. The critical level of DDE in eggs of osprey resulting in deleterious reproductive effects is around 10 μg /g (Blus, 1995). In addition to the ecotoxicological effects of DDTs in birds, they also affect other biota including many species of fish such as lake trout (*Salvelinus namaycush*), sea shrimp, and daphnids.

Risk assessment of SOCs in the Forge River sediments

It is easier to determine the toxicity of individual SOCs using model organisms such as benthic vertebrates or fishes in the laboratory study. It becomes difficult to evaluate the toxicity of a mixture of SOCs even in the well-controlled laboratory bioassays as the interactive effects (i.e. additive, synergistic or antagonistic effects) among different compounds are less clear most of the time. The dimension of this "interactive effects among chemicals" problem quickly increases as more chemicals are involved. The situation turns out to be more complex when conducting the risk assessment of all kinds of SOCs in the sediments. In addition to the unknown mixture effects, sediment geochemical properties (i.e, water content, organic matter, pH, particle size and microorganisms) greatly affect the toxicity of organic chemicals. Many tools have been developed to address the risk of SOCs in sediments. Some of these tools are commonly applied: sediment quality TRIAD which combines sediment contaminant concentrations with an assessment of benthic community structure and some kind of standard sediment toxicity test (such as the acute *Ampelisca abdita*; (ASTM, 2008) (Pinkney et al., 2005), stand alone sediment toxicity testing, sediment bioaccumulation tests, and/or comparisons to sediment quality guidelines (numerical values derived some an assessment of available toxicity data on specific contaminants (Long et al., 1998).

Numerical sediment quality guidelines were adopted in this thesis for an informal, interpretive ecological risk analysis of the targeted organic contaminants. Further analysis of toxicity or even bioavailability of in place contaminants was beyond the scope and budget of the project. When measured sediment contaminant concentrations are directly compared to numerical sediment quality guidelines, caution is advised due to the complexity of the underlying science and factors affecting bioavailability of sediment

bound contaminants may vary with sediment type. Almost all the sediment quality guidelines are established largely based on statistical analyses of a combination of laboratory dose-response data from literature studies, which utilize a wide range of model organisms, different sediment types and also a number of biological endpoints. This statistical approach for sediment quality guidelines was first suggested by Long et al. 1990. The most commonly used sediment quality guidelines generally include two guidance values: effects range low (ERL) and effects range median (ERM) defined by Long et al. 1995. ERL is a lower concentration threshold that borders on a no or low probability of adverse biological effects. ERM is a higher concentration threshold with a greater probability of adverse biological effects associated with the contaminants. These numerical values are derived for individual contaminants. Approaches taking in account the potential additive effects of co-occurring contaminants were not considered in this thesis study.

Methods

Sediment Collection

It is challenging to do sediment sampling in the Forge River due to the shallow water depth. We first conducted a tidal river-wide sediment grab reconnaissance study on June 30, 2006 using a vessel operated by the Suffolk County Department of Health Services (SCDHS), and we collected 11 grab samples near to SCDHS water monitoring sites. That trip provided us information on the sediment types and the best way of sampling sediment approaches appropriate for the shallow river. Based on this information, we conducted the primary sediment grab and core sampling on August 8-9, 2006. Grab sampling at 13 sites was completed on August 8 using a modified Eckman grab sampler with the aid of SCDHS. Sampling locations are shown in Figure 1 and Table 4. The grab sampler was operated following the same methods used for the U.S.EPA Coastal 2000/National Coastal Assessment Program. The grab samples were split on board for later analyses of various physical and chemical properties. The fractions of samples taken for analysis of total organic carbon (TOC), nitrogen and

semivolatile organic contaminants were kept chilled on board and stored in a freezer upon return to the laboratory.

Ten sediment cores were collected on August 9 using a standard Benthos gravity corer with acrylic core tubes (2 5/8" ID x 1.3 m) attached (core sample locations Figure 2 and Table 4). The methods for collecting sediment cores were modified based on the distance between the water's surface and the winch on the ship as well as water depth, which was minimal at some locations. We first tested the coring methods by collecting several test cores at Station 2, off the Town dock (Figures1 & 2, Table 5) on August 8. One of those cores was kept and transported to the lab and sectioned to separate depth intervals (5-15, 15-30 and 30-40 cm) by extrusion that evening. The physical and chemical property data obtained from this test core were not used for the discussion of our findings, but are included for reference, labeled as Stn 2 in the tables. The results presented in this thesis were obtained from ten cores collected on August 9. All the cores were sectioned into discreet depth intervals (typically 0-5, 5-15, 15-30, 30-50, and 50 cm to near the bottom, for cores longer than 50 cm) on the evening of collection. We chose these rough depth intervals to get the penetration information of target organic contaminants into the sediments, rather than to recreate the history of deposition. In most of the cores, a transition layer (based on sediment color and texture) was observed and typically occurred between 15.2 and 60 cm below the sediment water interface. This depth of sediments was referred to as a transition zone and hypothesized to represent a surface to which sediments were dredged in Forge River channels in years around 1970 (Swanson et al., 2008b). Above the transition zone, the sediments were generally dark brown to nearly black, and easily disintegrated; below the transition zone, the sediments appeared either gray or light brown transitioning to gray.

Surface sediments were also collected at a site in the upper tidal Forge along the east bank (one sample each in East and West Mill Ponds, Figure 1 and Table 5) on December 21, 2006. Since the boats that accommodated the grab sampler couldn't access the sampling sites, a kayak was used and the samples were collected by inserting a Benthos tube core into the sediment and securing the sediment from below with a plastic cap. These cores were between 6.35 and 11.43 cm in length. The sediment from these

samples were split for different property analyses back in the laboratory, but were otherwise processed the same way as other grab samples discussed previously.

A 38 cm iron bar with a removal T-handle on one end was used to measure the mud thickness at each of the sediment grab sample sites on our August 8 sampling. The iron bar was inserted into the sediment and the depth below the sediment-water interface where penetration was impeded recorded if a sand-layer was reached. The mud thickness was obtained after correcting the water depth from the recorded iron bar depth. In many locations no sand was encountered and a minimum thickness of fine grain sediment was recorded. Mud thickness data are shown in Tables 4 and 5.

Measurements of Sediment Properties

Water Content

Water content was measured only in sediment core sections. The water content was obtained by drying fractions of newly collected wet sediment directly from the core at 110 ^{o}C to a constant weight in a drying oven.

Grain Size

We sent aliquots of wet sediment samples to Professor Richard Styles' laboratory at the University of South Carolina for grain size analysis. Three separate aliquots of each sample were analyzed on a Beckman-Coulter LS100 particle size analyzer in triplicate. When our samples were introduced to the circulating sample well in the analyzer, large clumps of organic rich sediment that broke up were noted. They did not use sonication to further disaggregate the clumps of sediment particles. Rather, they conducted multiple replications to ensure the clumps of particles were broken up into visibly "individual particles". In the cases where grain size distribution varied significantly, an additional three runs were made to provide consistent results.

C-N-S (organic carbon, nitrogen and sulfur) analysis

Samples for C-N-S analysis were pretreated with 0.01 M HCl to remove inorganic carbon. Then the total organic carbon (TOC) and nitrogen were measured on those sediments by combustion and analysis with a thermal conductivity detector (CHNS analyzer). The total sulfur in our sediment samples turned out to be quite high. The

CHNS analyzer was then calibrated to also measure the total sulfur on a second batch of sediments following acidification. To determine the amount of sulfur existing in the form of iron pyrites relative to "acid volatile sulfur (AVS)" mineral phases, we measured additional sediments without acidification for CNS analysis. There was no appreciable difference between the two treatments, indicating that the sulfur was mainly in the form of pyrite, and that sulfate reducing conditions predominated in the anoxic sediments.

Analytical Methods

Both the grab and sediment core samples were analyzed for organic contaminants using analytical methods developed for this project. The methods were modifications of those previously used in the Brownawell laboratory for analysis of PCBs, PAHs and chlorinated pesticides (Achman et al., 1996; Lamoureux et al., 1999; LeBlanc et al., 2006a; Rust et al., 2004). The rationale for these modifications is outlined below. 1) We wanted to use methods that follow as closely as possible standard EPA methods or methods used in EPA funded monitoring studies such as the study by Mayura et al. (1997), which simultaneously determine the three classes of target organic contaminants, and use standard component mixtures used in EPA methods. 2) We wanted to use a single solvent extract of sediment samples for subsequent purification and analyses of different compound classes. Although a common practice, this makes it difficult to optimize conditions for all analytes.

3) We scaled up the sample size to approximately 20 g dry weight, to maximize our chances of detecting anticipated low concentrations of PCBs and many pesticides in the Forge River. Unfortunately, this created additional problems, as high levels of sulfur weaken the capability of the electron capture detector used for PCBs and chlorinated pesticides analysis. Our prior methods of using activated copper to remove elemental sulfur were insufficient to remove the sulfur in these organic rich samples requiring us to purify samples with silica gel chromatography. This added step not only required time-consuming methods development, but resulted in significantly increased sample analysis time.

The sample preparation scheme is briefly described below. 20-30 g per sample of freeze-dried sediment was extracted by Soxhlet continuous extractors. More specifics on

the analytical approach is provided in the Appendix below. After volume reduction using Kuderna Danish evaporative concentrators, the extract was loaded onto the silica column and eluted into three fractions using different organic solvents. After testing a number of solvent mixtures and volumes, we settled on the following protocol to optimize separation of the analytes of interest. All PCBs, some PAHs (low MW) and non-polar pesticides were eluted in the first fraction (F1) using 70 ml hexane, and the remaining PAHs and some pesticides were eluted in the second fraction (F2) using 30 ml of 1:1 mixture of hexane and dichloromethane (DCM), and finally the rest of pesticides were eluted into the third fraction (F3) by adding 20 ml DCM to column. Following extract cleanup, each fraction was blown down under N_2 until only 1.0 ml of hexane was left. Half of this volume was further removed from the F1 and F2 fractions and combined into a separate vial for PAH analysis. Prior to injection of each fraction onto instruments (Hewlett-Packard 5890 GC-ECD or GC-MS) for analysis, standards were added. Tables 2, 3 and 12 list the surrogate/recovery standards and the internal standards used. The internal standards included the same components as used in EPA studies and methods: PCB (20 component NIST standard mix from Crescent); PAHs (18 component NIST standard mix from Crescent) and Pesticides (34 components in three separate mixtures for Method 1618 from Absolute Standards).

The concentrations of internal standards were same as those used in the six point calibration curves run with each batch of samples; an intermediate concentration standard was run at least once within or at the end of each batch of samples to check on the stability of instrument detector response and chromatographic retention times. Quantification was performed with normalization to internal standard and comparison of that response to the calibration curve; the concentrations extrapolated below the response of the lowest standards were not reported. A blank sample (combusted sand) was also included in each batch of four to five sediment samples and processed in the same way as done for sediments to determine background contamination levels.

It was quite straightforward to quantify the targeted PAHs in our samples as PAH signals were almost always undetectable in blanks and even trace signals were always far below the lowest signals for each analyte in our samples. The recovery of two

isotopically labeled standards, d12-pyrene and d10-phenathrene were 92 ± 16 % and 86 ±22%, respectively (Table 12).

However, it was quite difficult to quantify PCBs and chlorinated pesticides due to low signal strength and high interference of the rich organic matrix in Forge River sediment samples. The peak signals of all PCBs and most pesticides (except p,p'-DDE, p,p'-DDD, and sometimes p,p'-DDT) turned out to be either very low (below the lowest or second point in the calibration curves in most cases) or difficult to be differentiated from matrix with near the identical retention times that might lead to false identification of peaks. We could neither identify nor quantify the o,p'-isomers of DDT residues, which may represent 10-15% of the total DDT used.

Considering this high signal to noise ratio, we determined a way to maximize the chances of identifying targeted analytes in our samples. Briefly, the PDF files of both sample and standard chromatograms were generated from our instrument software. The two PDF files could be overlayed precisely and scaled appropriately for careful examination at each analyte retention window in each fraction of each sample. We set the following criteria for determining whether to report detectable concentrations of PCB congeners and pesticides.

- the peak height above that of the lowest standard;
- the peak height was at least 3x greater than that of the blank; this was applied only for certain PCB congeners in several samples;
- the peak shape matched that of the standard; we took into account the minor differences in the retention times of two or three standards in each sample;
- the peak should be found in the expected or correct fraction;
- the pattern of PCB congeners was similar to that in nearby sediment samples.

All the concentrations of PCB congeners present in this thesis barely met all the above criteria. The low values of total PCBs are uncertain. The recoveries of surrogate PCB standards 29 and 143 (Table 2) were 81 ± 28% and 79 ± 34%, respectively. The recoveries of pesticide surrogate standards DBPFB (F1) and epsilon BHC (F2) (Table 3)

were 84 ± 27% and 103.9 ± 30%, respectively. Neither surrogate standard nor pesticide analytes were detected in fraction 3.

Results and Discussion

General sediment properties

General observations from sediment grabs and cores

We encountered muddy, organic rich surface sediments in each of the over 40 samples collected on different dates. This was probably due in part to our sampling strategy. As we sampled primarily in deeper or formally dredged channels by boat, mud may have preferentially accumulate in deeper areas, especially under the sluggish water circulation in the Forge River. However, it is noted that much of the intertidal portion of the Forge River is also characterized by "soupy" unsolidated sulfidic muds. We also observed black suboxic or anoxic mud in almost all of our samples from the dredged areas of the Forge. Only at sites closest to the mouth of the Forge River (Station 12 & 13) and outside the mouth of the Forge in Moriches Bay (Station M), less dark (more oxidized) surface sediments were observed. The oxidized interface at those three sites was only visible in the near surface (around 1mm in depth). These observations along with the presence of black sulfide minerals and the smell of sulfide indicated high levels of remineralization of organic matter and sulfate reduction. The suboxic or anoxic conditions in the sediments might result in part from the low oxygen levels in the overlying water. We saw a clear spatial gradient trend in the darkness of mud from north to south along the axis of the Forge, which reflected pollution sources and increased exchange of cleaner water toward the mouth of the Forge. In addition, sediment samples collected from Wills Creek (north end of the River) were noticeably enriched with high levels of organic matter.

No clear evidence of benthic activities was observed upon visual inspection of the entire grab sample and the transparent core tubes in most of our sampling sites. While we did find polychaete worms at Station M in Moriches Bay and at the Upper Forge East Bank (UFEB) site located above Montauk Highway. The later site was sampled in December when oxygen conditions in sediment and water column could have been better

than in summer when we collected the other samples. A large amount of grass shrimp were also evident in UFEB. There were also rotting amphipod tubes appearing at Station 13, near the mouth of the Forge, where opportunistic, but oxygen sensitive amphipods might colonize under more favorable oxygen conditions earlier in the year.

No detritus was visible in any of our samples except EMP, where there was abundant rotted leaf and twig detritus lying around 30 m of the sampling site. In the shallow depths in West Mill Pond, the sediments were covered by algal mats and we sampled sediments just below the surface of the algae. The sediments from WMP and UFEB were sandier than those collected in the tidal Forge. Thus, the very high organic matter contained in the tidal Forge sediments was interpreted to be not associated with detritus or recent animal excrement but organic mineral particles coated with organic matter.

All our observations above are in very good agreement with sediment sampling of the Forge River and other tidal tributaries of Moriches Bay conducted 50 years ago by Nichols (Nichols, 1964). The Forge River and other tributaries along Moriches Bay were characterized by Nichols 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…" As further illustrated below, it seems that there has been little change of the sediments of the Forge River over the past five decades.

It was difficult for us to collect sediment cores deeper than 75 cm due to the stiffness of sediments (brown transitioning to gray) sitting below the much darker sediments with higher water contents (Tables 4 and 6, Figure 3). The approximate depths of the transition zones between those two layers are listed in Table 4. The transition zone appeared to be pronounced in many cases when we extruded cores that were not as deep as we wanted. Considering the stiffness of the underlying sediments, it was hypothesized that the transition zone might be the old surface sediment layer associated with dredging in the Forge around 1970s (Swanson et al., 2008b). As shown later in this thesis, based on the known contaminant deposition history, the deeper, stiffer parts of the cores are older than those just above the transition zone.

Estimates of the distance between finer grain sediment and its underlying sand layer varied between 70.1 cm and > 2.8 m (Table 5). Only at four sampling sites located in the most northerly direction of the Forge (core/grab at Stations 1 and 7, a grab at Station 3 in Wills Creek and a grab at Station A) was the depth of fine grain sediment < 2.44 m. More precise methods such as radiochemical dating would be more useful in understanding the sedimentation of the tidal Forge and how sedimentation has been affected by natural and artificial changes in the hydro-geological regime.

Water Content

Water contents were not surprisingly high in the darker upper sediment layers (Table 6; Figure 3). The average water content for all ten cores measured in sediments below the transition zone was 56.3%, compared to 86.4%, the average water content measured in the upper 15 cm of four cores (Stations 1, 2, 4, 4B and 7), the most northern and most affected by pollution. It is hard to analyze the changes in water content below the hypothesized transition zone due to the small number of sediment sections collected, however, it was noted that water content decreased further with depth at Station 10, possibly by additional compaction or level off (e.g. Station 12).

Organic carbon and nitrogen content

The TOC and nitrogen content of the sediments are extremely high (Table 7 and 8; Figure 4), especially at Stations 1, 2, 3, 4, 4B, 7, 8 and 10, with maximum TOC contents ranging from 7.7 to 12.1%. These levels are very much higher than those normally found in moderately eutrophied estuaries (Mayer, 1994). For example, in the highly urbanized NY/NJ/lower Hudson Basin Harbor complex, TOC contents measured in a system-wide analysis of surface sediments (113 stations in total) were typically between 2 and 4% with higher levels (7%) only found in highly sewage-impacted and eutrophied areas of Jamaica Bay (Adams et al., 2003). The very high TOC levels in the tidal Forge probably result from “hyper-eutrophication”, which combined with the poor water exchange between the Forge with the Moriches Bay, produces, retards, and then delivers immense amount of organic matter to the sediments from algae and phytoplankton production. The abundant organic matter depletes oxygen in the overlying water and the sediments, which further limits the metabolic rate of bacteria oxidizing the organic matter loadings. This positive feedback coupled with enhanced sediment burial leads to tremendous

preservation of organic matter. In addition, it is likely that the Mill Ponds input some amount of suspended organic matter into the River, especially algal biomass during summer months. Although this was not measured directly in this study, an upper limit on the magnitude of these inputs could be estimated from the extensive monitoring of chlorophyll and TOC around the East and West Mill sites conducted by other investigators on the Forge River Team (unpublished data from the Suffolk County Department of Health Services). Wills (Stations 3, 4, 4B) and Poospatuck (Station 10) Creeks are less affected by the Mill Ponds than are upstream sites (1 and 7). The high and deeply buried TOC contents at Stations 3, 4, 4B, 7 and 10 prove that local plankton and algal production are the major source of organic matter enrichment in the Forge River. The highest TOC levels encountered in East Mill Pond are attributed to leaf detritus, which is consistent with the higher TOC to organic nitrogen ratio at that site. While the lower TOC levels measured at sites WMP and UFEB might have been due to the coarser sand substrate.

Similar to TOC, organic nitrogen levels are greatly elevated all over the Forge River. The well-preserved organic nitrogen could serve as a potential reservoir of nutrients that can be released back into the overlying water when sediment organic matter is degraded by bacteria. The rate of microbially-mediated remineralization of organic matter and release of nutrients back to the water column is highest during warmer summertime and thus will further promote eutrophication in the Forge and exacerbate degraded water quality.

Compared to the aforementioned profiles of water content, there appears to be a good correspondence between TOC and organic nitrogen and water content in both spatial (site to site) and depth distribution (Table 6, 7 and 8; Figure 3 and 4). This might reflect the result of water contents being regulated by recent deposition of more organic rich sediment and also the same processes affecting deposition of organic matter and sediments.

Although the TOC and organic nitrogen levels decrease from the surface to deeper sections of the cores (Table 8; Figure 4), interestingly even in the deeper sections, they are still much higher than those typically encountered in fine grain estuarine

sediments less affected by eutrophication (normally around 1-2%); (Mayer, 1994). This provides evidence that the Forge River is naturally susceptible to nutrient enrichment, eutrophication, and accumulation of organic rich sediments due to its sluggish water circulation and weak tidal flushing with the Moriches Bay. Unfortunately, we cannot tell whether the organic enrichment was present before human activities on the Forge, such as duck farming, due to unknown ages of deeper sediment cores. Sediment contaminant measurement indicates no evidence of DDT residues, PCBs, or excess trace metals being present below the transition zone in the cores (Figure 5 and 6). The absence of DDTs indirectly suggests that the deeper core sections of sediments predate the 1950's (when DDT started to be used in large amounts) and that the horizon represented by the transition zone might have been removed by dredging between 1965 and 1972. To better understand whether organic enrichments in sediments took place before man's activities influence the Forge, additional high resolution sediment cores with radiochemical dating methods need to be conducted. This would be useful as it could provide information about whether the Forge was highly eutrophied before duck farming commenced near the turn of the 20th century.

It is seen in the depth profiles of TOC and several contaminants that sediments with excessive organic matter were deposited before the most recent deterioration of water quality in the Forge River. Subsurface maxima of contaminants like DDE and lead (Brownawell et al., 2008) are noticed in the sediment cores (Figure 5; Table 9) resulting from maximum inputs of those contaminants in the 1960s/early 1970s. The same sediment sections also have high TOC contents. The high total organic matter contents were even reported earlier by Nichols (1964) in the Forge River sediment collected in 1959. Nichols estimated total organic matter to be up to 21% in the Forge by loss of weight following peroxide treatment. Using a factor of two to convert between TOC and the total organic matter, the agreement between the data collected nearly 47 years ago and ours is compellingly consistent. Nichols also showed that total organic matter in muddier Moriches Bay sediments were around one fourth of that in the upper tidal Forge, which is in good agreement with our measurements.

Sediment Sulfur Contents

There is no appreciable difference in concentrations of sulfur determined by the CHNS analyzer whether or not sediments were pretreated with acid. As sulfur was not dissolved during the acid treatment, the dominant form of sulfur in our samples it likely to be pyrite. The pyrite levels indicate consistently high rates of sulfate reduction under the conditions of almost no oxygen and plenty of labile organic matter available for microbial oxidization. The measured sulfur/pyrite levels are highly elevated and consistent with excessive enrichment of labile organic matter in the Forge.

Grain Size

The grain size data for surface grab and sediment cores are listed in Table 10 and 11, respectively. Unexpectedly, the average and median grain size indicated sandier sediments. These results were not anticipated based on water contents and TOC contents as discussed above. We re-analyzed the grain size of the frozen sediments under the supervision of Sedimentary Geologist David Black (SUNY-Stony Brook). The results suggested a mixture of mud (silt and clay less than 63 μm in diameter) and sand size mineral particles, which agree with the results obtained at the University of South Carolina. However, the same sediments disaggregated and passed the 63 μm after sonication and extensive water washing under pressure of the sediments. Therefore, the presented grain size values are believed to be reflective of aggregated assemblages of sediment particles rather than of individual mineral particles.

Organic Contaminants

PAHs

The concentration of targeted individual and summed total PAHs in surface grab samples and sediment cores are presented in Tables 13 and 14, respectively. The depth profiles of total PAHs in sediment cores are illustrated in Figure 7. There is no consistent variation in the composition of PAHs both among sites and between depths, at least above the depths where PAH levels drop to much lower values, as is seen with other anthropogenic ally derived contaminants such as DDTs and lead in the same cores. The concentrations of PAHs in deeper core sections are still detectable. However it is not possible to determine whether these contaminants result from natural sources or human

development of the area due to missing dates on the deep layers of the cores. There are always backgrounds levels of PAHs in sediments produced from natural processes such as erosion of sedimentary rocks like shales that contain PAHs, and burning of organic material such as occurs in forest fires. In Tables 13 and 14, the individual PAHs are ordered by retention time which is correlated with increasing molecular weight. The reported values in the tables show that high molecular weight (HMW, those with four to five rings) PAHs as well as appreciable levels of the three-ring PAH phenanthrene dominated in the PAH composition in sediments. Total PAHs levels are well correlated with TOC levels mentioned above (data not shown).This finding along with the absence of variation in PAHs composition indicates that there is probably a single, dominant source of PAHs in this area. The speciation of PAHs being dominated by HMW PAHs indicates combustion-derived PAHs sources rather than petrogenic sources such as would result from spilled oil (Pereira et al., 1999; Yan et al., 2006).

Six PAH ratios including MePH/PHEN, FLA/(FLA+PRY), ANTH/(PHEN+ANTH), BAA/(BAA+CHRY), IND/(IND+BGHIP) and 4-6 Ring/TPAH were calculated and are are shown in Table 15. Regardless of which ratio is calculated, the numerical values are surprisingly consistent, providing information on the sources of PAHs to these sediments. Comparison of the ratios calculated here to the source apportionments provided in the literature (Yan et al., 2006; Yunker et al., 2002), indicates that the source of PAHs to the Forge is dominated by incomplete combustion processes. Two of the ratios indicate that the combustion source is most likely associated with lower temperature combustion of biomass. Such sources could include historic forest fires or wood burning stoves. Isotopic analysis (e.g. $\delta^{13}C$) of individual PAHs would give more detailed sources apportionment. In addition, there is no significant difference in the speciation of PAHs between those from the tidal Forge and those from the freshwater Mill Ponds, which is consistent with the conclusion of a single dominant combustion-derived source of PAHs from the atmosphere, and not sources that discharge directly into the tidal Forge River. The deposition characteristics of the Forge, especially the sluggish estuarine circulation, also contribute to the preservation of PAHs in the Forge River sediments.

Total PAH concentrations in surface grab samples vary between 302 and 3330 ng/g, with the mean levels being approximately 1200 ng/g. These levels are higher than background coastal sediments, while well within the reported values measured in other estuaries in the coastal watersheds in the New York region. For example, the total PAHs ranged between 30 and 91,000 ng/g in 113 samples collected around the NY/NJ Harbor area (Adams et al., 2003). Several factors might contribute to the elevated levels of PAHs in the Forge. Extremely high levels of sediment TOC indicate great sorptive capacity for hydrophobic contaminants such as PAHs, and also indicated very efficient estuarine sediment trapping. Low oxygen conditions also greatly favor the preservation and retention of PAHs, as bacteria could rapidly degrade them under oxic conditions (LeBlanc et al., 2006b).

The potential of elevated PAHs to pose an ecotoxicological risk will be discussed later in the thesis. However, it should be noted that PAHs may be bound to the soot particles generated from the combustion processes which renderes them less bioavailable (Quensen et al., 1999). In addition, the PAHs measured in this and most other studies do not represent the full range of PAHs likely found in sediments, particularly the aklylated homologues found in petrogenic sources. Thus a multiplication factor is usually applied to the total PAHs to account for the additional PAHs. That factor is typically < 2 (Yan et al., 2006). In this thesis, that factor will be lower than typical value considering some aklylated PAHs such as the methylphenanthrenes were actually measured, and the fact that our analyte list included most PAHs from combustion sources.

DDT residues and other chlorinated pesticides

DDT had been widely used for agricultural and mosquito control applications prior to early 1970s (Quensen et al., 1999). DDD and DDE, two of the most stable metabolites of DDT dominated in our measured levels of chlorinated pesticides. There are great variations among the concentrations and depth distributions (Tables 16 and 17; Figure 5) and ratios of DDE to DDD seen among the sampling sites. Total parent DDT concentrations are low in almost all the surface sediment samples except East Mill Pond site, where very high levels were detected (Table 16). East Mill Pond is located at the most northern part and near the head of the tidal Forge. Local sources from agricultural or

mosquito control uses might contribute to the higher levels of total DDT at this site. The total DDT levels in West Mill Pond are appreciably lower than those in East Mill Pond, but still higher than most of those measured in the tidal Forge. However, caution is advised when comparing total DDT concentrations in West Mill Pond and the tidal Forge due to different sampling methods used and possible differences in burial rates.

In several sediment cores, there appeared to be subsurface maxima of DDT residues, which is consistent with historical use of DDT in this area, as its use was banned in the late 1960s to early 1970s on Long Island. It appears that DDT had been rapidly buried at these sites, which is well exemplified in Station 7 (Figure 5), as well as at Stations 1, 2, and 8. At these stations, the historical records are seemingly well preserved, likely due to minimal bioturbation in anoxic sediments and hypoxic waters, or perhaps lack of mixing due to powerboats. The depth profiles of DDT in each sediment core agree in some respects with the PAHs (further discussed below), and also sediment properties like TOC and water content. The penetration of DDT in sediment is also consistent with the observed transition zone mentioned above.

The primary sources of DDT in the tidal Forge are difficult to determine based on our data. The DDTs in the tidal Forge could result from local DDT application or atmospheric transport of DDT uses outside the watershed of the Forge. In contrast, in East Mill Pond, localized use or direct inputs at some time in history is certainly the major source for the high levels of DDTs detected. However, only one sample was collected from East Mill Pond, and thus might not be representative of conditions in the Pond in general.

The ratio of DDD to DDE can tell us something about conditions at the time of metabolism of DDT. Under low oxygen sediment conditions, DDT is mainly metabolized to DDD by microorganisms. While at higher oxygen levels, DDE is the major metabolite of DDT. The DDD to DDE ratio varies greatly over all our sampling sites in the tidal Forge. The ratio could also be influenced by the amount of parent DDT that directly entered anoxic sediment in the tidal Forge, relative inputs of DDE that does not convert to DDD. The ratio of DDD to DDE is much higher in the upper reaches of the tidal Forge

as the sediments tend to be anoxic over a longer time period than those close to mouth of the Forge River.

Although initial examination indicated a broad suite of pesticides in the Forge River sediment samples, most of the concentrations were just above detection. After applying the entire criteria discussed in the methods section, almost all of the possible detections were discarded. The exceptions were the detection of lindane at or near 1 ppb in a few samples (e.g. Station 1, 0-5cm) and of the two chlordane isomers in our targeted analytes, γ- and α- chlordane, also referred to as trans- and cis-chlordane, respectively. The possible detections of lindane are not reported in this thesis for two reasons. The levels were close to the detection limit and signals were observed in samples at sediment core depth just below or at a site near to it. The possible detections of chlordane are not reported in the thesis for the following reasons. The peak shape of trans-chlordane tails off with a longer retention time, and the cis-chlordane was detected at a retention time almost the same as PCB100. Since there are a lower percentage of many similarly structured compounds in the technical chlordane mixture in addition to the cis and trans-isomers, the presence of other chlordane compounds might explain the tailing observed for trans-chlordane. A more sensitive GC-MS system with greater selectivity would be needed to confirm whether low levels of other chlordane compounds are present in these sediment samples.

PCBs

The PCBs concentrations in surface and sediment cores are listed in Tables16 and 18respectively. The depth profiles are illustrated in Figure 6. These data should be viewed as containing significant uncertainty due to the following reasons. Most PCBs levels were very low, falling between the lowest and second lowest standard. Sometimes blank levels approached the peak height of a specific congener. PCB congeners 66, 101, 77 (co-elutes with 110), 118, 153+105, and 138 were detected in over half of the surface sediment samples; followed by frequent detections of congeners 28 and 52. Other congeners were rarely detected. There were no detections for congeners 8, 206 and 209. There is a general agreement in the depth profiles between PCBs and DDTs and also in the absence of detection in the deeper sections of the sediment cores. The consistency

provides some measure of confidence in the presence of PCBs in the samples and the relative magnitude of the concentrations. The total PCB concentrations in the tidal Forge are appreciably close to or lower than those reported in the EPA 1993 survey of 146 samples collected from the NY/NJ Harbor complex and adjacent waters (Adams et al., 2003). In addition, the PCB levels in surface sediments of the Forge are much lower than those measured in the lower Hudson River Estuary, where average levels were 150 ng/g and maximum levels were 2500 ng/g of total PCBs (Adams et al., 2003). The most commonly detected congeners are those with 5 or 6 chlorines, typically associated with atmospheric sources (Gambaro et al., 2005), which is in good agreement with the low concentrations of total PCBs detected in Forge River sediments.

Additional information of the sources and histories of SOC inputs to the tidal Forge

Contaminants such as SOCs and trace metals (i.e. lead and copper) are particle reactive and tend to sorb to suspended particles in the water column and eventually settle to the bottom as sediments. This sorption process could efficiently remove the contaminants from water column and the resulting deposition of contaminants may be well preserved in the sediment layers. Thus, the depth distribution profiles of SOCs in the undisturbed sediment cores can allow for the reconstruction of the extent and history of pollution in the watersheds (Santschi et al., 2001). The reconstruction of pollution history using sediment cores can provide information useful to develop effective management strategies (i.e. remediation by dredging) and can be useful in monitoring the success of pollution control effects. However, most of the time, the original sediment layers may have been greatly reworked by human activities (i.e. dredging) and multiple postdepositional mixing mechanisms including physical (i.e. tides), chemical (i.e. redox cycling), and biological (i.e. bioturbation) mechanisms. The transition zones observed in ten Forge river sediment cores are one example of reworked sediments. As mentioned above, these transition layers are hypothesized to be the old surface sediments associated with past dredging in the tidal Forge conducted between 1965 and 1972. The dredging activities and possibly other postdepostional processes have potentially altered the original history of pollution trends in the Forge sediments. In addition, contaminants such

as SOCs and trace metals come from both natural and anthropogenic sources. The anthropogenic component needs to be identified to evaluate the extent of pollution.

In this thesis, the anthropogenic input of trace metals is calculated as the excesses of observed concentrations minus background values which are taken from the core bottoms where contaminants went to background levels and high iron levels were consistent with fine grain sediments existing at almost all the collected sites and different depth (Daskalakis et al., 1995); the anthropogenic input of SOCs in the sediment cores is computed as the measured concentration normalized to the concentration at the depth where maximum lead were observed. In areas where postdepositional mixing is negligible to the accumulation of sediments, the anthropogenic imprint may be well preserved (Stations 1, 2, 7, and 8). While at other sites where postdepositional mixing is comparable to (perhaps Stations 4 and 4B, where the record appears to be smeared over the depth interval of these short cores) or faster than the sedimentation rate (Stations 10, 11, 12, and A'), where the maximum levels of organic contaminants are highest at the surface, despite known anthropogenic source inputs of DDTs, PCBs, and Pb having decreased markedly over time. Three trace metals (Pb, Cu, and Mo (in the case of surface sediment distributions)) are used to sort out the anthropogenic imprint from postdepostional processes.

Lead is a very good proxy for the postdepostional processes because most likely comes from atmospheric sources to the watershed and its concentrations in surface sediments are relatively even distributed in the Forge, and well correlated with sediment properties such as organic matter content (data not shown). Atmospheric sources of Cu are also known to be important in the region (Brownawell et al., 2008) and like Pb and the SOCs studied, is very particle reactive and transported along with those contaminants when fine grain sediments are redistributed by wind or tidal currents. However, Mo and Cu behaved differently than Pb in the Forge River. The concentrations of Mo decreased from the Upper Forge River to the lower reaches of the river to a greater extent than did Pb and Cu. Mo concentrations in the lower part were nearly an order of magnitude lower than those encountered in the upper sites (2-3 μg/g v.s. 10-25 μg/g) (Brownawell et al., 2008) with the highest concentration or accumulation near to entrance of the river

(Station 1). Mo is a redox-senstive metal and is generally scavenged from the dissolved phase under the low oxygen and high sulfur content. Mo enrichment is highly correlated with the degree of reducing and sulfidic conditions in the sediments and has been proposed as an indicator of bottom sediment redox status in coastal or estuarine watersheds (Adelson et al., 2001). Cu is a modest particle-reactive metal and has also been found to be enriched in sulfide-rich sediments (Adelson et al., 2001). Cu concentrations tended to increase by a factor of 2 going up the Forge River. It is uncertain whether the accumulation of Cu in the upper part of the Forge River came from local sources or from redox processes (scavenging from water column to bottom). As postdepositional processes (i.e. mixing) affect both Pb and other trace contaminants, normalizing the excess of trace contaminants to excess of Pb may be useful for eliminatating much of the effects of postdepositional redistribution processes and be useful to understand if there are spatially variable sources of other trace contaminants (Cochran et al., 1998).

To understand the possible sources of Cu in the surface sediments, the excess of Cu (Cu_{xs}) against the excess of Pb (Pb_{xs}) and the ratios of Cu_{xs}/Pb_{xs} relative to Mo are plotted in Figure 8. It is evident that Cu_{xs} is well correlated with Pb_{xs} in most of the surface stations except in five stations (Stn 2, 3, 7, 4bank and B), where Cu_{xs} is enriched relative to Pb_{xs}. All the five stations except StnB are located in the upper reaches of the Forge River. This would be consistent with Cu and Pb sharing a common source in the main stem and lower part of the Forge River, hypothesized here to mainly come from atmospheric source and that there may be local sources for Cu that exist in the upper part of the river. Alternatively, Cu may be scavenged by the more sulfidic sediments in the upper Forge River. Interestingly, the normalized ratios of Cu_{xs}/Pb_{xs} at the same five stations except StnB are associated with higher surface Mo concentrations than those measured at all other stations, which suggest that redox processes (scavenging) play important roles in the enrichment of Cu in the upper reach of the river. The elevated Cu in Station B, proximate to the dock, might be associated with the use of Cu-containing boat bottom paints, but additional studies would be needed to test the latter possibility.

The total PAHs and DDTs relative to Pb_{xs} and Cu_{xs} are illustrated in the Figure 9 and 10 respectively. As seen in Figure 9, the total PAHs in the surface Forge sediments generally increase with both Pb_{xs} and Cu_{xs}. However, the concentrations of PAHs are consistently higher in samples from Stn 3, 4 and 4bank collected from the Wills Creek River, a tributary flowing into the upper part of the Forge River. It is hypothesized that the sources of these contaminants all primarily come from the atmosphere. The high accumulation of total PAHs in Wills Creek, may be due contribution of local run-off sources known to exist at the head and mouth of the Creek; evidence from PAH compositions suggests that the elevated levels of PAHs in Wills Creek are not due to local petroleum derived sources. Similarly, sum DDTs at two Stns (4 and 7) stand out to be highly enriched with respect to both Pb_{xs} and Cu_{xs}. The elevated levels of sum DDTs at Stn 7 may be attributed to East Mill Pond sources as very high levels are measured in a signle sediment sample from EMP, the most northern station in the tidal Forge. The high levels of sum DDTs at Stn 4 may be due to the local application of pesticides. The likelihood of major DDT inputs coming from the freshwater portion of the Forge River is better seen when comparing the distributions of maximum DDT levels that are buried in cores at stations. Maximum concentrations are at the northern most Stn 1 (270 ng/g). Proceeding southward, levels are 45 ng/g at Station 7; 15-53 ng/g at Stns 2, 3, 4, 4bank, and 8; and then drop markedly to levels of 1.0 – 5.4 ng/g at more southern stations. These levels can be compared to the surface sediment concentration at the East Mill Pond site of 2340 ng/g. Thus, it is very likely that the sources of DDT to the tidal Forge were upriver, either from the Mill Ponds, or to local spraying of marshlands north of Station 7.

The depth profiles of C/Cmax for SOCs and two trace metals (Pb and Cu) in ten sediment cores collected along the axis of Forge River are plotted in Figure 11. The C/Cmax for Pb is calculated as the ratios of the excess of Pb concentration at different depth to the maximum excess of Pb in the same core. The C/Cmax for other analytes including Cu, sum DDTs and total PAHs are computed as the excess of each analyte relative to the excess of same analyte at depth of maximum Pb. The depth of transition layer at each core is also marked in the Figure 11. Four cores (1, 2, 7 & 8) in the upper part of Forge River appear to have well preserved historical pollution input in the Forge suggesting the sediment accumulation faster than postdepositional mixing in these areas;

Four cores (10, 11, 12 & A') in the middle or lower part of the Forge River, on the contrary, unanimously display that postdepositional mixing faster and deeper than accumulation. This might be due to the effects of increased water exchange between Forge River and Moriches Bay close to the mouth of the Forge. The other two cores (4, 4bank) most likely display pollutant distribution profiles controlled by both accumulation and mixing processes. The reconstruction of historical input is mainly based on the interpretation of four well-preserved cores. The subsurface maxima of Pb, DDTs and PAHs are all observed in the same cores (1, 2, 7, and 8) which are consistent with their historical inputs. Pb input peaked around 1970 and was banned as a gasoline additive in 1972; DDT use peaked around 1955-1965 and was restricted then banned between 1966 and 1972 on Long Island. This is corroborated by the depth of subsurface maxima of Pb higher than that of DDTs in the cores, which is well exemplified at Station 7. PAHs peaked later than Pb, which might be explained by increased use of diesel combustion automobiles, wood or coal burning activities from 1970s to 1990s. The major input for Cu is likely from the atmosphere; there is no consistent subsurface maximum of Cu, which would be consistent with the absence of great restrictions or bans on its ues (DDT. PCBs, Pb). The reason for subsurface maximum and apparent reduction in the source of PAHs is not known, but could be related to less wood burning for heat or even restrictions on brush fires.

Comparison of semivolatile organic contaminants with sediment quality guidelines

A fundamental problem with establishing simple numerical concentration values based guideline are high uncertainties in correlating and extrapolating the laboratory measure of biological response to individual contaminant levels in the field. Contaminant bioavailability and even sediment properties (e.g. grain size/surface area, TOC, or sulfur) could significantly affect concentrations and falsify the bioavailability predictions. Some sediment guidelines used for management purposes do try to consider this problem in their approaches; e.g. the State of Washington use the organic carbon normalized concentrations of nonpolar organic contaminants such as PAHs, PCB and chlorinated pesticides (WSDE, 2009). Considering the Forge River sediments with 8-10% range of

TOC levels, simply using organic contaminant concentrations normalized to dry weight would produce risk estimation 4 to 10-fold greater than organic carbon normalized values estimated for sediments with an average TOC of 1-2%.

Therefore, the organic carbon normalized semivolatile organic contaminants concentrations (range of values) in surface sediments of the tidal Forge are used and compared to three sets of sediment guidelines: the ERL and ERM from Long et al. (1995), Sediment Quality Standards from the State of Washington and some of the "Sediment Criteria" values recommended in a "Technical Guidance for Screening Contaminated Sediments" (NYDEC, 1999). The data comparison is listed in Table 19. As seen from Table 19, none of the organic contaminant concentrations detected in the Forge (even deeper cores) reach the Washington State no effect level. On the other hand, there are a couple of surface sediments of the Forge River, where the sum of PAHs approach the ERL. All but one value of total PCBs did not exceed the ERL, the exception being the subsurface maximum at Station 7. Total DDTs in the surficial sediment of the tidal Forge generally lie between the ERL and ERM, with none exceeding ERM. The subsurface total DDT maximum is higher than ERM at Station 7.

Based on the above data comparison, levels of semi volatile organic contaminants in the Forge do not appear to present a serious ecotoxicological risk. None of the measured organic contaminant concentrations in the Forge exceeds the NY DEC chronic benthic value.

Summary

The water quality problem in the Forge River had been studied by a team of SOMAS scientists from different perspectives including eutrophication, nutrients (nitrogen) benthic fluxes, and sediment contamination. This thesis study was based on the hypothesis that semivolatile organic contaminants (SOCs) in the sediments could directly or indirectly contribute to death of aquatic organisms (fishes and crabs) in the Forge River water considering SOCs' lipophilicity, persistence and bioaccumulative potentials. Coupling with the sediment properties (organic carbon, fine grain size), redox conditions (hypoxia or even anoxia in summer) and hydraulic characteristics (sluggish water

circulation in a lagoonal system), SOCs could be greatly enriched in the Forge River sediments. Under favorable conditions (i.e. strong currents), these chemicals could be mobilized to the water column and pose great risks to aquatic organisms.

The main results in this thesis study are summarized as:

1. Compared to EPA survey reports in NY/NJ complex and lower Hudson River regions, ∑PCBs and sum DDTs in Forge River sediments are generally low, while total PAHs are relatively high.

2. The low ∑PCBs levels were consistent with atmospheric sources.

3. The spatial distribution pattern of sum DDTs in the surface sediments is different from that of total PAHs. Sum DDTs concentrations decreased from the head of the Forge River to the mouth of the river along the northern-southern axis. PAH concentrations were more evenly distributed along the river except at Wills Creek where much higher PAH concentrations were measured.

4. The spatial pattern of sum DDTs suggests that DDTs might come mainly from upstream sources (possibly East Mill Pond where much higher DDTs were measured relative to those in other sites). PAHs spatial distribution was consistently associated with atmospheric input in the Forge River. The high PAH concentration at Wills Creek were attribute to multiple local run-off.
5. Although PAHs were clearly elevated in the Forge River sediments, their concentrations were well within the range at larger NY/NJ complex region reported by EPA. PAHs in the Forge appear to come mainly from combustion sources.

6. When compared to available sediment quality guidelines, none of the SOCs in the surface sediments exceed ERL, only at one station 7, the subsurface maxima of PCBs and DDTs are higher than ERM.

7. Historical pollutant input in this area, as well exemplified in the station 7 core, DDTs peaked first and then lead followed and finally PAHs increased possibly due to increased number of local residents with increased use of automobiles and wood burning activities.

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Appendix

– Standard Operating Procedure for Analysis of Semivolatile Organic Compounds

Purpose

To determine the quantity of PAHs, chlorinated pesticides, and PCB congeners in environmental sediment samples.

1.0 Summary
Sediment samples are extracted by Soxhlet, cleaned by silica column and analyzed by GC-ECD.

2.0 Procedure

2.1 Sample Collection and Preparation
Samples are collected and stored in a freezer at temperature -4 ºC. Before extraction, sediment samples are freeze-dried for three days.

2.2 Material Preparation

- Glassware should be washed with acetone, DCM and hexane.
- Glass thimber, glass pipette, sand, silica gel, injection vial and sodium sulfate should be muffled before use
- Injection vials should be weighed before and after loading the extracts. Record the weight in the black notebook.
- Copper powder is soaked with 10 % HCl in a beaker for 5-10 minutes, then rinse with MilliQ water, acetone, hexane and acetone. Dry the copper powder in the oven at 60 ºC. Copper powder should be prepared freshly before packing the silica column.
- Silica Column Preparation
  1) Before use, muffle the silica gel (100/200 mesh) at 450 ºC for at least 16 hours. Then deactivate it to 3.3% with MilliQ water in a glass jar. Shake the jar for a few minutes to mix the contents thoroughly and allow it to equilibrate for 6 hours. Store the deactivated silica gel in a sealed glass jar. Prepare the new silica gel every 2-4 weeks.
  2) Pack the chromatographic column with glass wool, anhydrous sodium sulfate (2-3 cm), copper power (1 cm), 7 gram deactivated silica gel (3.3%), and anhydrous sodium sulfate (2-3 cm). Tap the column gently every time when packing the material. Make sure there is no gap between the layers. Then add hexane to rinse the silica column. Never let the silica column go dryness! Cover the top of the silica column with alumina foil all the time.

2.3 Extraction

- Weigh 20-30 gram dried sediment in a glass thimber. Use glass syringe to spike 25 µl surrogate mixture onto the sediment.
- Put the thimber into the middle piece of Soxhlet glassware.

- Add 300 ml DCM into the Soxhlet flask.
- Add 2-3 piece boiling stone into the flask.
- Set up the Soxhlet system; make sure the glassware is held firmly.
- Turn on the cooling water, and heater.
- Set the temperature at 60 ºC to make the hexane drops continuously.
- Cover the top of Soxhlet with alumina foil.
- Extract the sediment for 16 hours.
- Turn off the heater first, and then turn off the cooling water.

2.4 Concentration of Extract

- Pour the extracts into the K-D flask.
- Add 2-3 pieces boiling stone into K-D flask.
- Concentrate the extracts with K-D concentrator.
- Add 10 ml hexane into the K-D flask when most of DCM has evaporated.
- Take out the K-D when the volume of extract is around 5-6 ml.
- Tilt the K-D, and rotate the K-D to rinse the wall of K-D glassware with hexane, which comes from the top part of K-D.
- Use N_2 blowdown to further concentrate the extract until the volume of extract is around 2-3 ml.

2.5 Cleanup of Extract

Fraction 1

- Load the extract onto the silica column;
- Put a solvent-cleaned K-D flask at the bottom of the silica column;
- Let the extract pass through the column without going dryness;
- Add 70 ml hexane to elute PCBs.
- Collect the fraction (F1), and concentrate it through K-D to 1 ml;
- Use glass pipette to transfer the extract to preweighed injection vials, weigh the vials and record its weight in the notebook.

Fraction 2

- Add 30 ml hexane: DCM (1:1) to elute pesticides.
- Use a solvent-cleaned 50 ml test tube to collection this fraction (F2);
- Use N_2 blowdown to concentrate the extracts to 1 ml.
- Use glass pipette to transfer the extract to preweighed injection vials, weigh the vials and record its weight in the notebook.

Fraction 3

- Add 20 ml DCM to elute the rest of pesticides.
- Use a solvent-cleaned 30 ml test tube to collection this fraction (F3);
- Use N_2 blowdown to concentrate the extracts to 1 ml.

- Use glass pipette to transfer the extract to preweighed injection vials, weigh the vials and record its weight in the notebook.

2.6 Sample Analysis

- Add the amount of 250 ng internal standard is to 1.0 ml extracts prior to injection;
- 1 µl out of 1.0 ml extracts are injected onto GC-ECD;
- The operation method of GC is listed below,

  Injection temperature: 275 ºC;

  Detector temperature: 275 ºC;

  Oven temperature program:

  $$40\ ^{\circ}C\ (2\ min) \xrightarrow{30\ ^{\circ}C/min} 120\ ^{\circ}C \xrightarrow{2\ ^{\circ}C/min} 240\ ^{\circ}C\ (10\ min)$$

- After injection, replace the caps of injection vials as soon as possible to avoid the evaporation of the hexane.

2.7 Sulfuric Acid Treatment

To clean the interference in the PCB congeners' chromatogram, extracts of fraction 1 (only) should be treated with sulfuric acid after the injection. Then inject the extracts again by GC-ECD; this method was tested to remove sulfur from extracts prior to instrumental analysis, in the end, we increased the amount of activated copper in the silica gel columns, which greatly decreased the achievable flows of solvent through the columns.

- Transfer 50 % of extract (by weight) in a 2ml injection vial;
- Add 3-4 drops of concentrated sulfuric acid into the vial;
- Cover the vial with alumina foil, and screw it tightly;
- Vortex the vial for one minute;
- Let the vial sitting for 4 hour;
- Take accurate amount of hexane in the upper layer to injection vial
- Avoid to take the liquid from bottom layer;
- Add the internal standard, and inject it on the GC-ECD.

2.8 Quality Control

- A lab blank sample should be extracted and analyzed in each batch to monitor the background;
- A GC blank should be analyzed prior to any other injections to clean the GC system.
- A daily check standard should be analyzed every 20 samples;
- A calibration curve should be updated every 2 weeks.

3.0 Reference

1. EPA SW846 method 3630C(EPA)

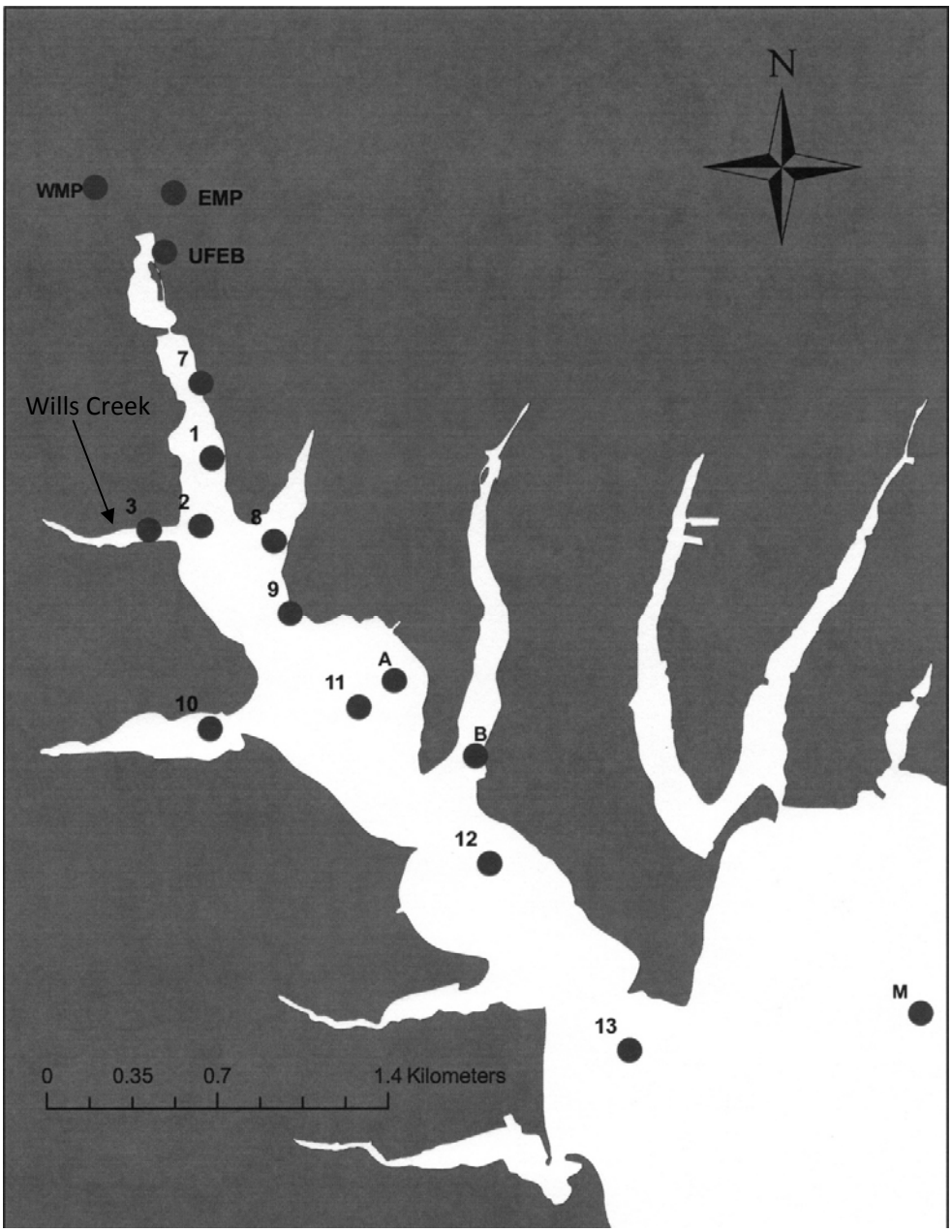


Figure 1. Surface sediment (0-5cm sediment grab samples) sampling locations (detailed coordinates and sampling dates listed in Table 4).

Note: The Upper Forge East Bank, West and East Mill Pond (WMP and EMP) samples were collected by hand-held benthos tubes from a Kayak.

Figure 2. Sediment Cores sampling locations (detailed coordinates and sampling dates listed in Table 3).

Note: Sampling stations 4 and 4B were nearby each other.

Figure 3. Profiles of Water Contents in Sediment Cores

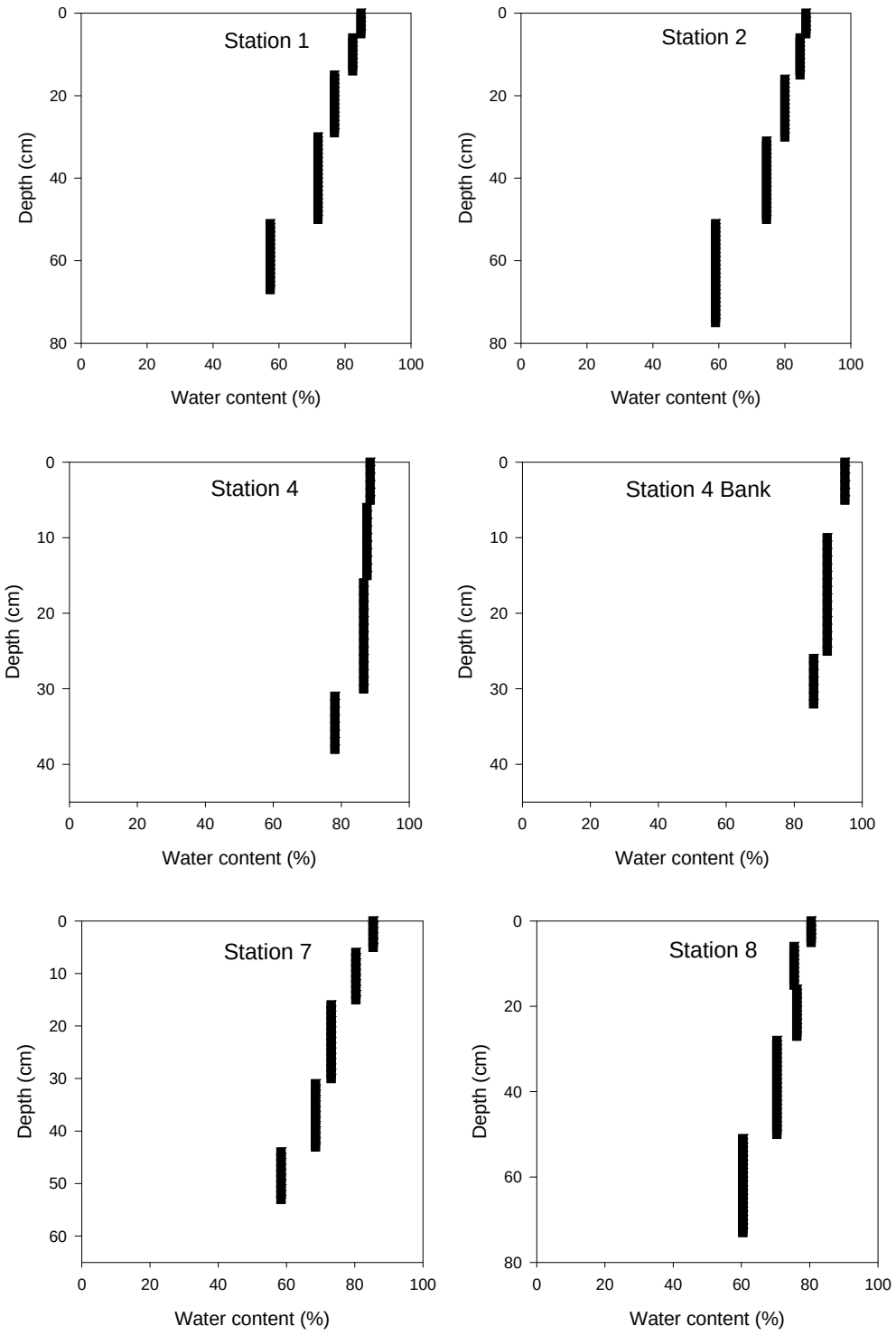


Figure 3. Cont…

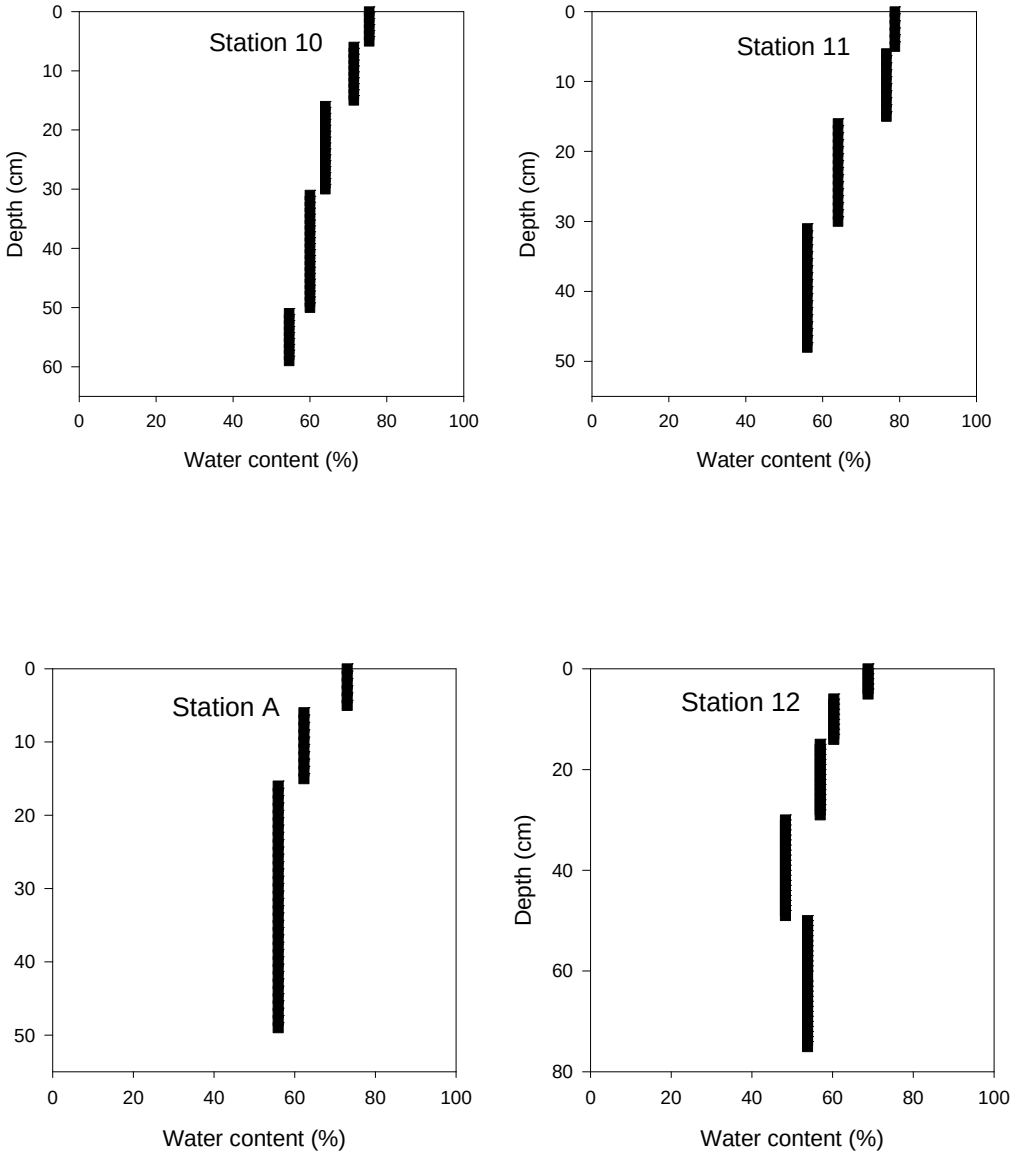


Figure 4. Profiles of Total Organic Carbon (TOC) contents in sediment cores

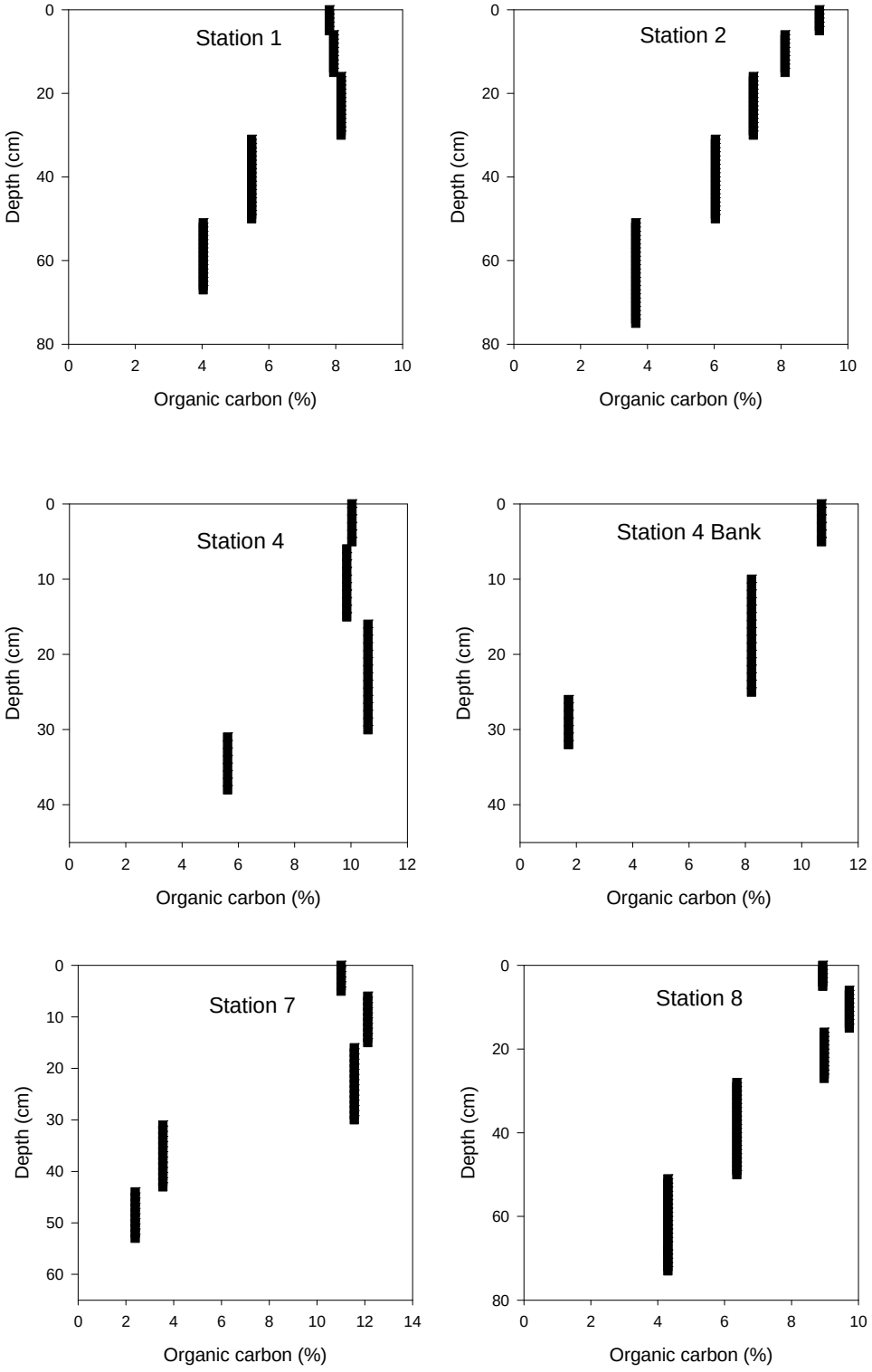


Figure 4. Cont…

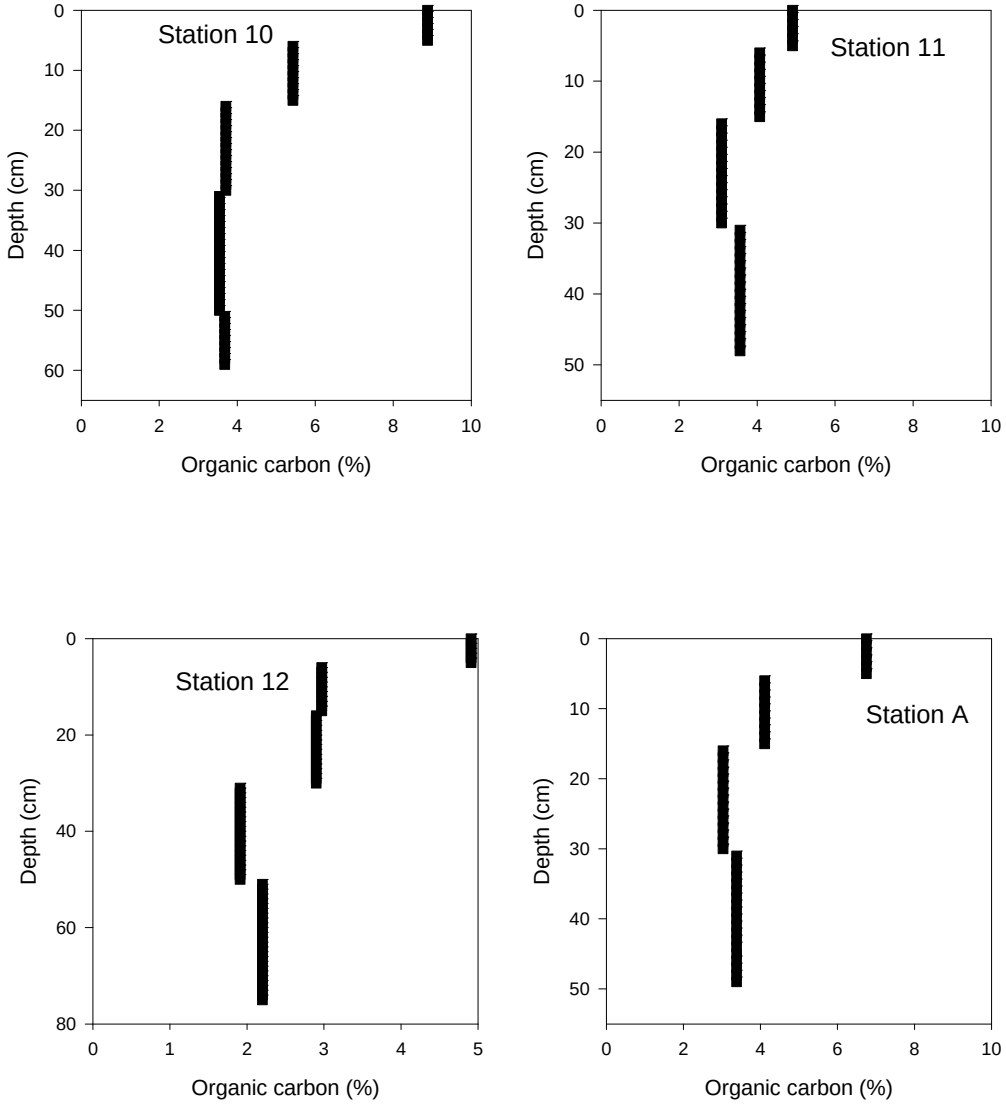


Figure 5. Profiles of total DDT residues in ten sediment cores

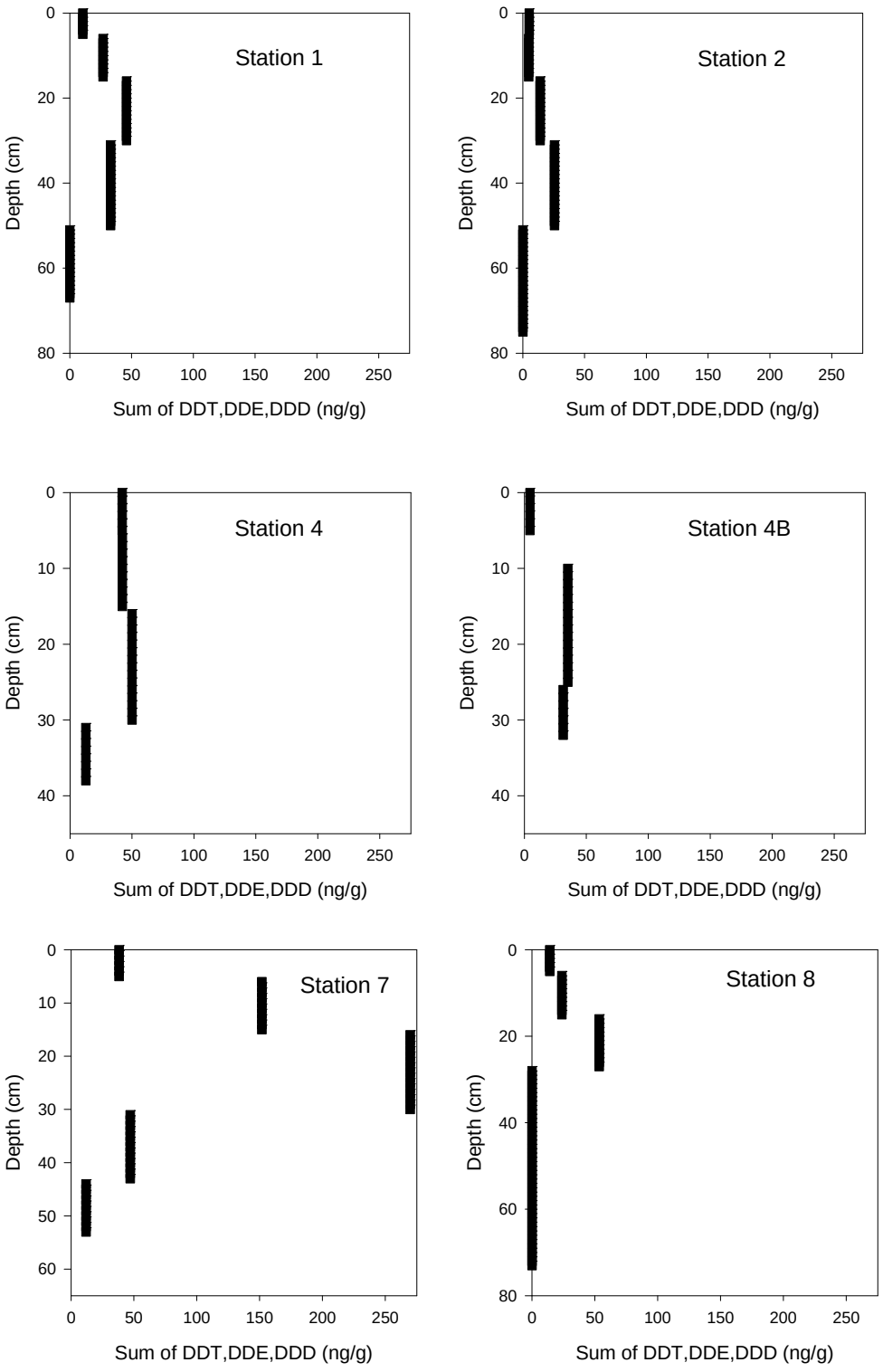


Figure 5. Cont…

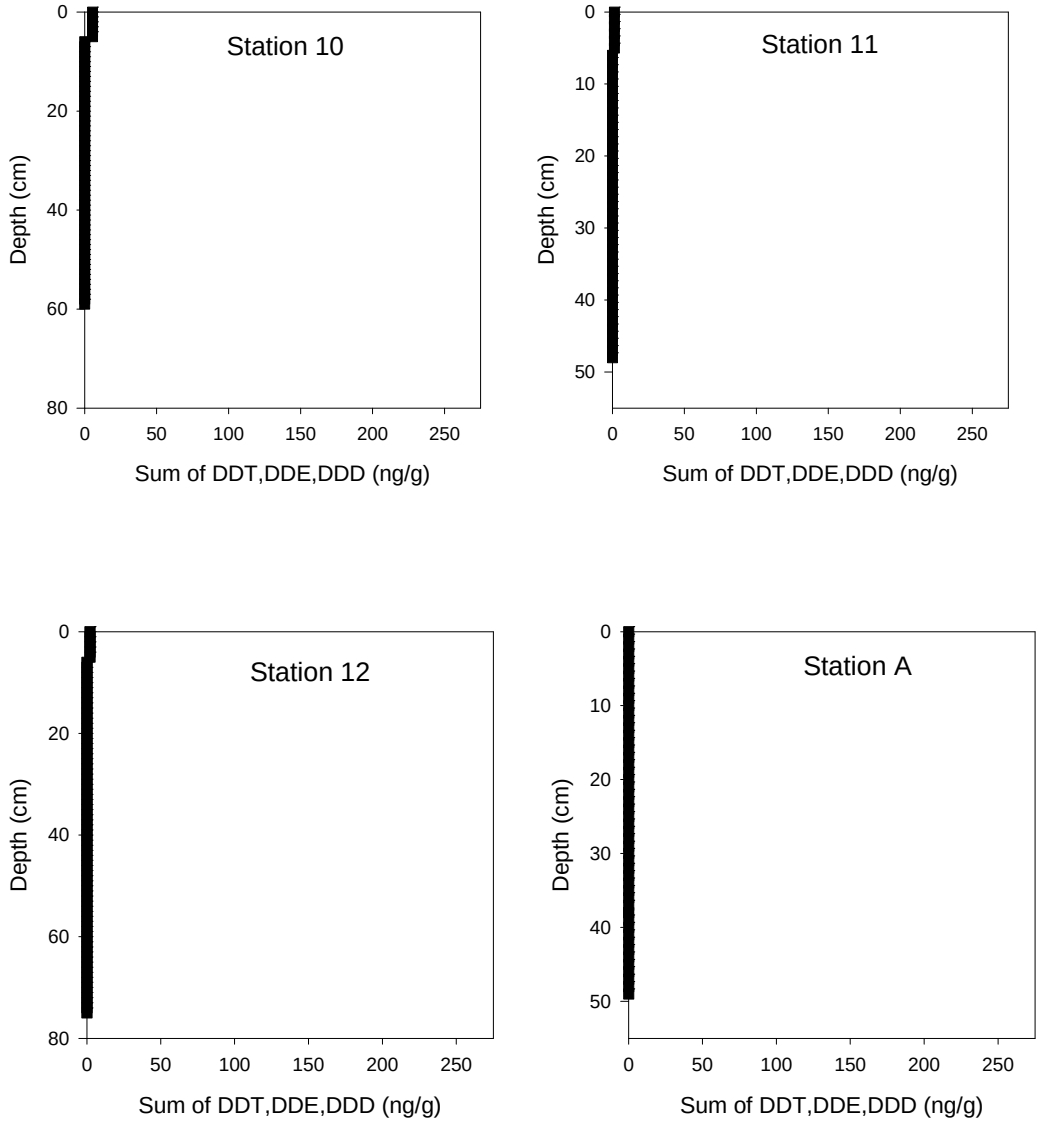


Figure 6. Total PCB core profiles (ng/g)

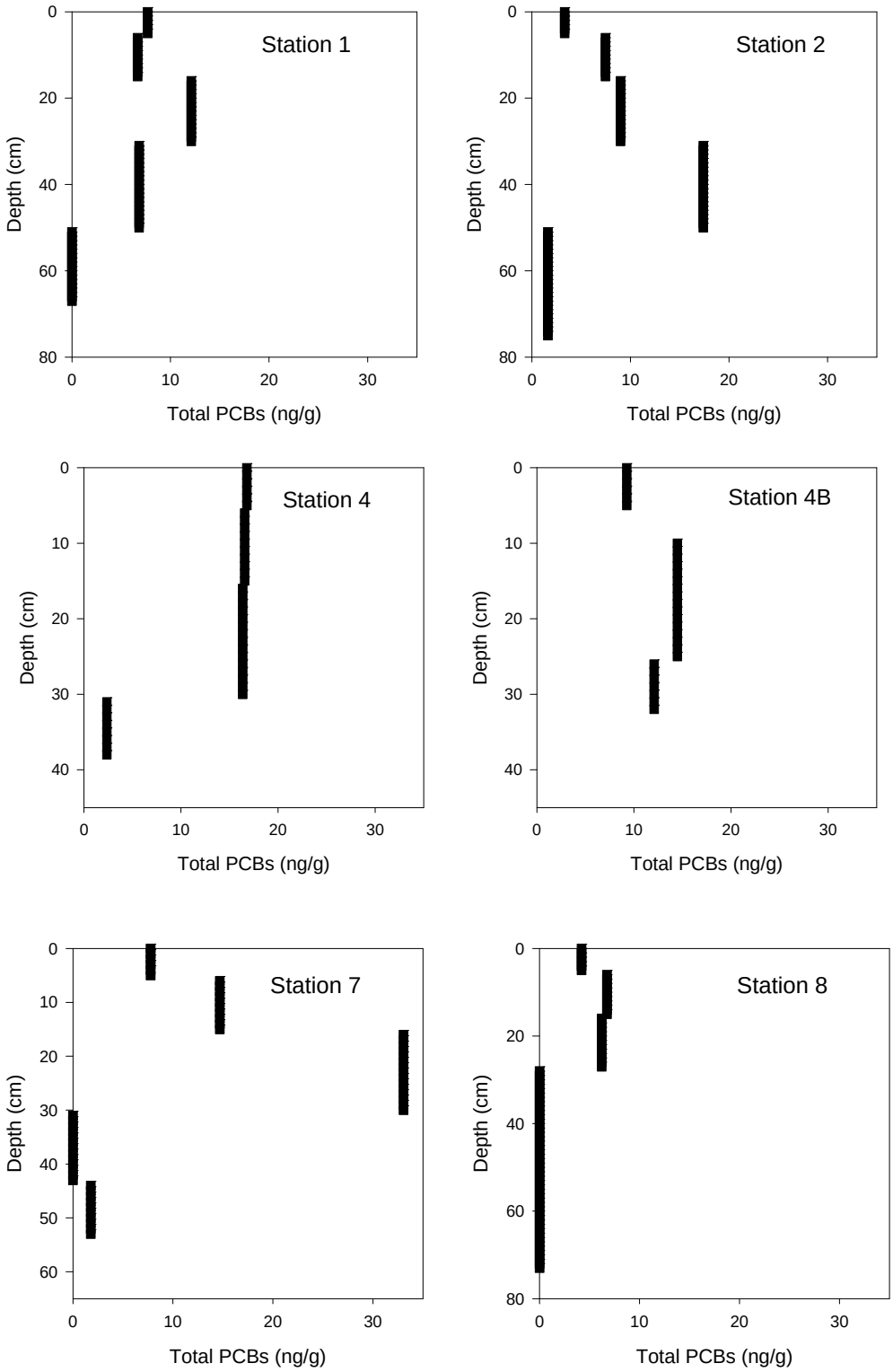


Figure 6. Cont…

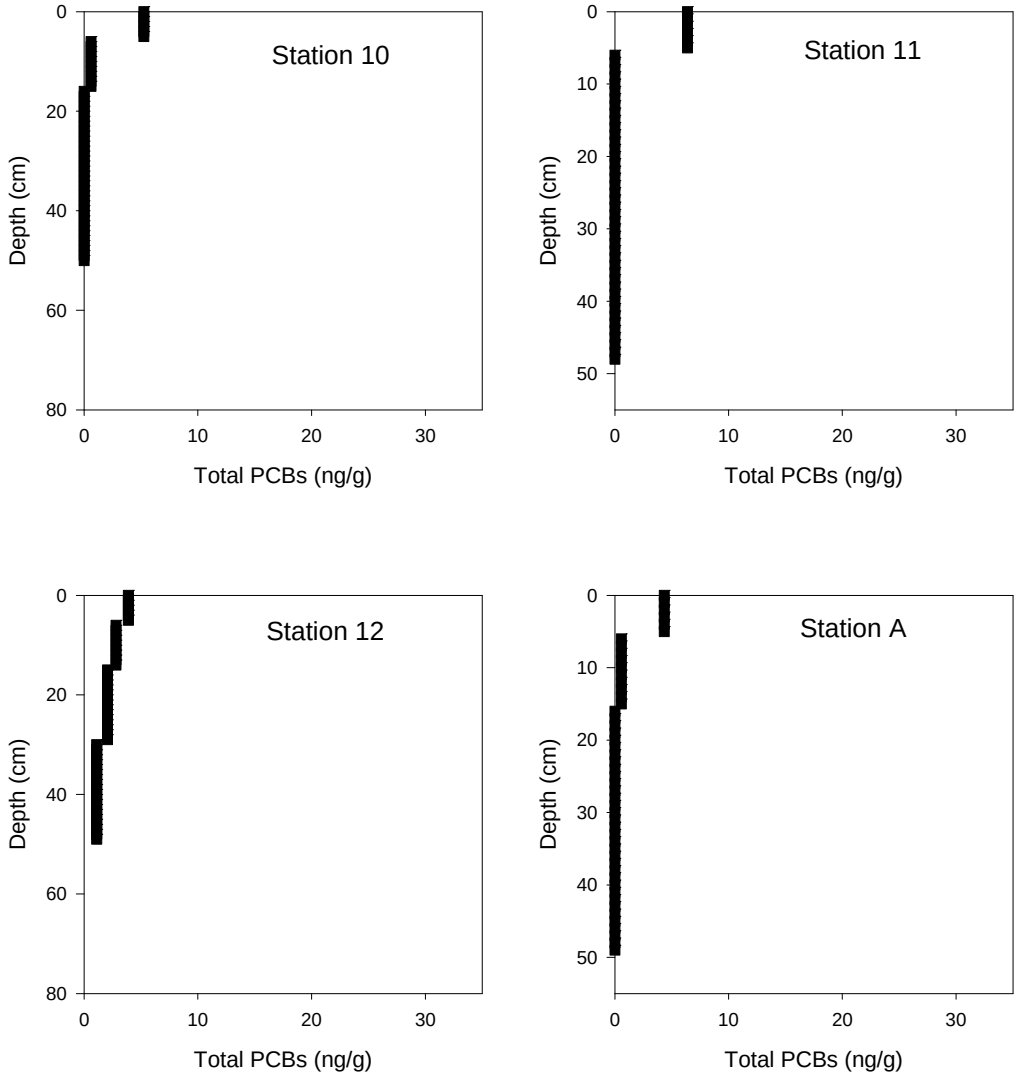


Figure 7. Profiles of total PAHs in the ten sediment cores

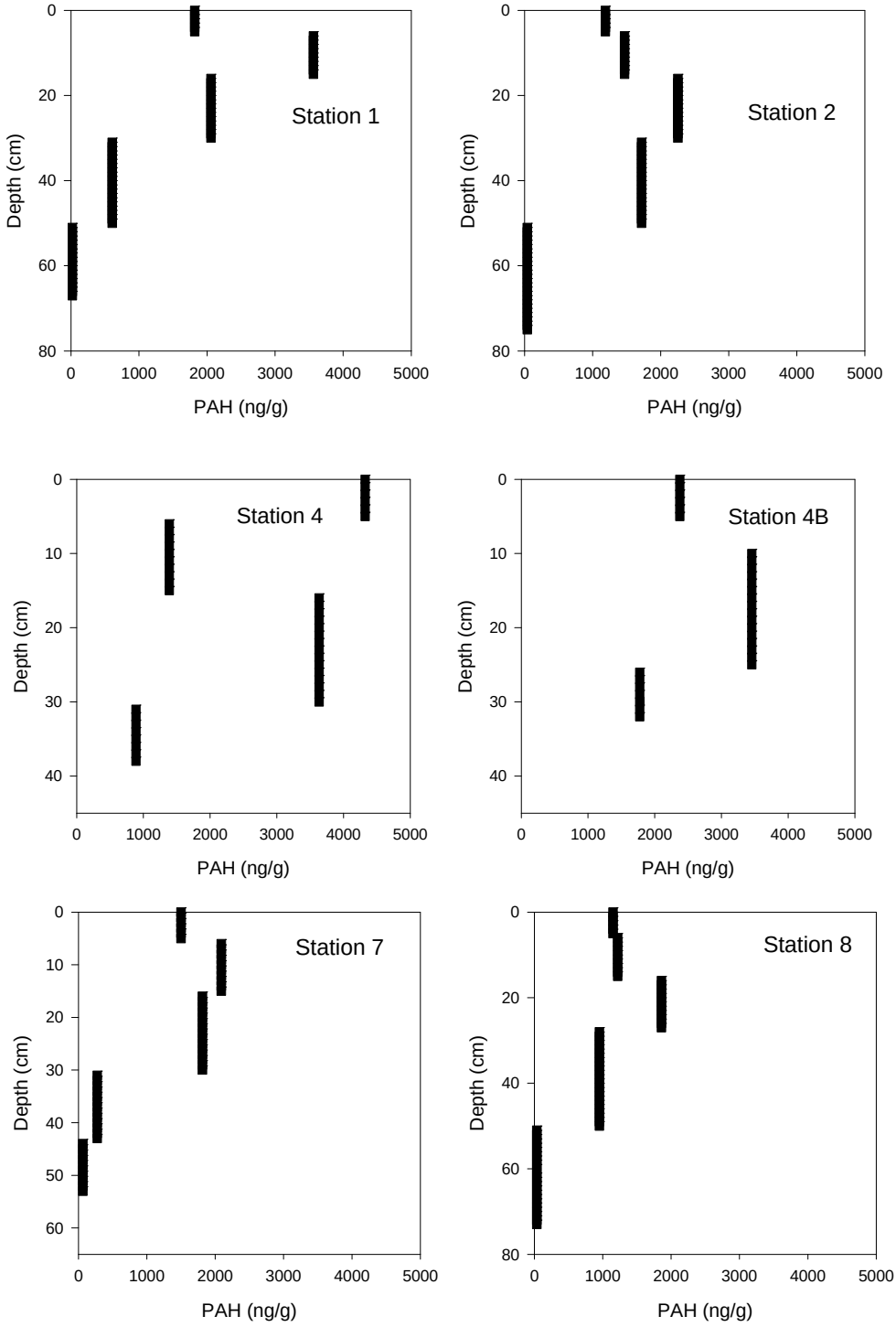


Figure 7. Cont…

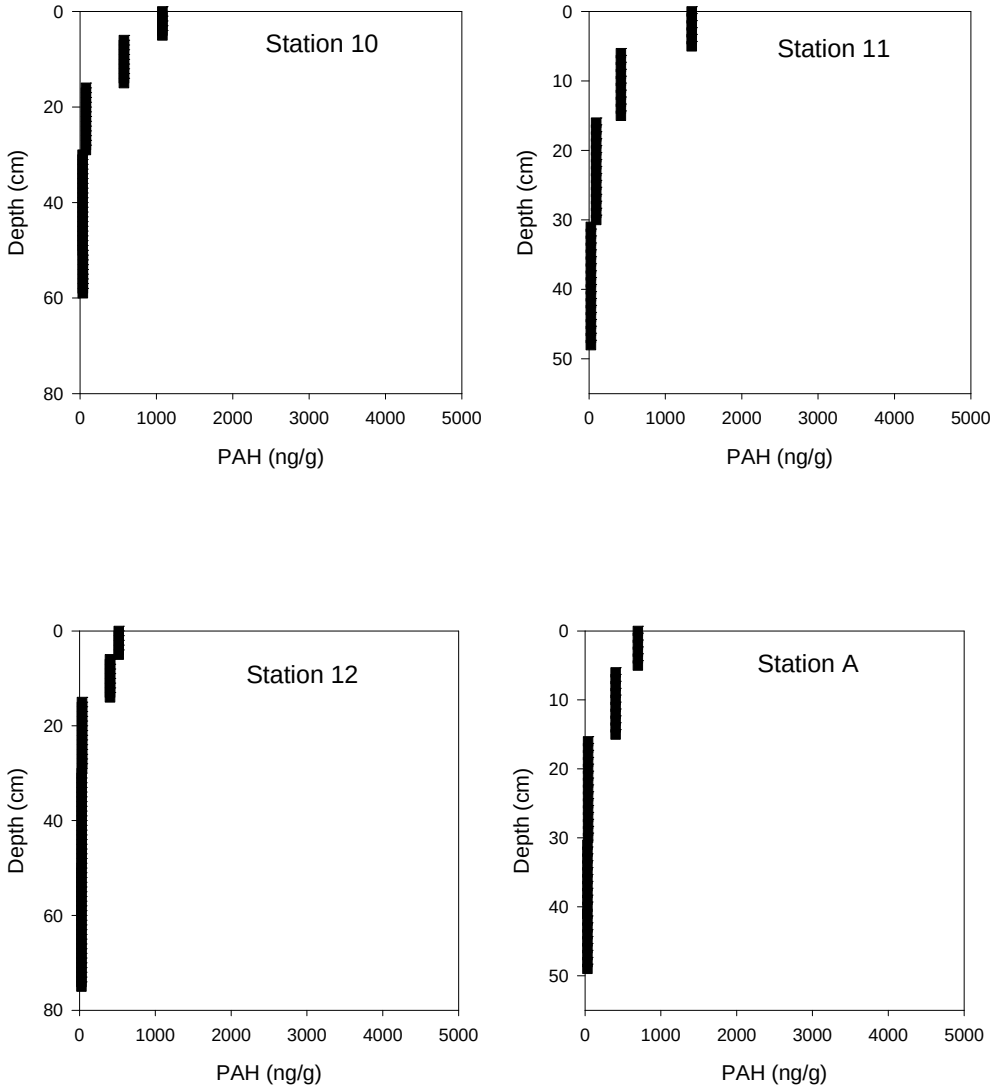
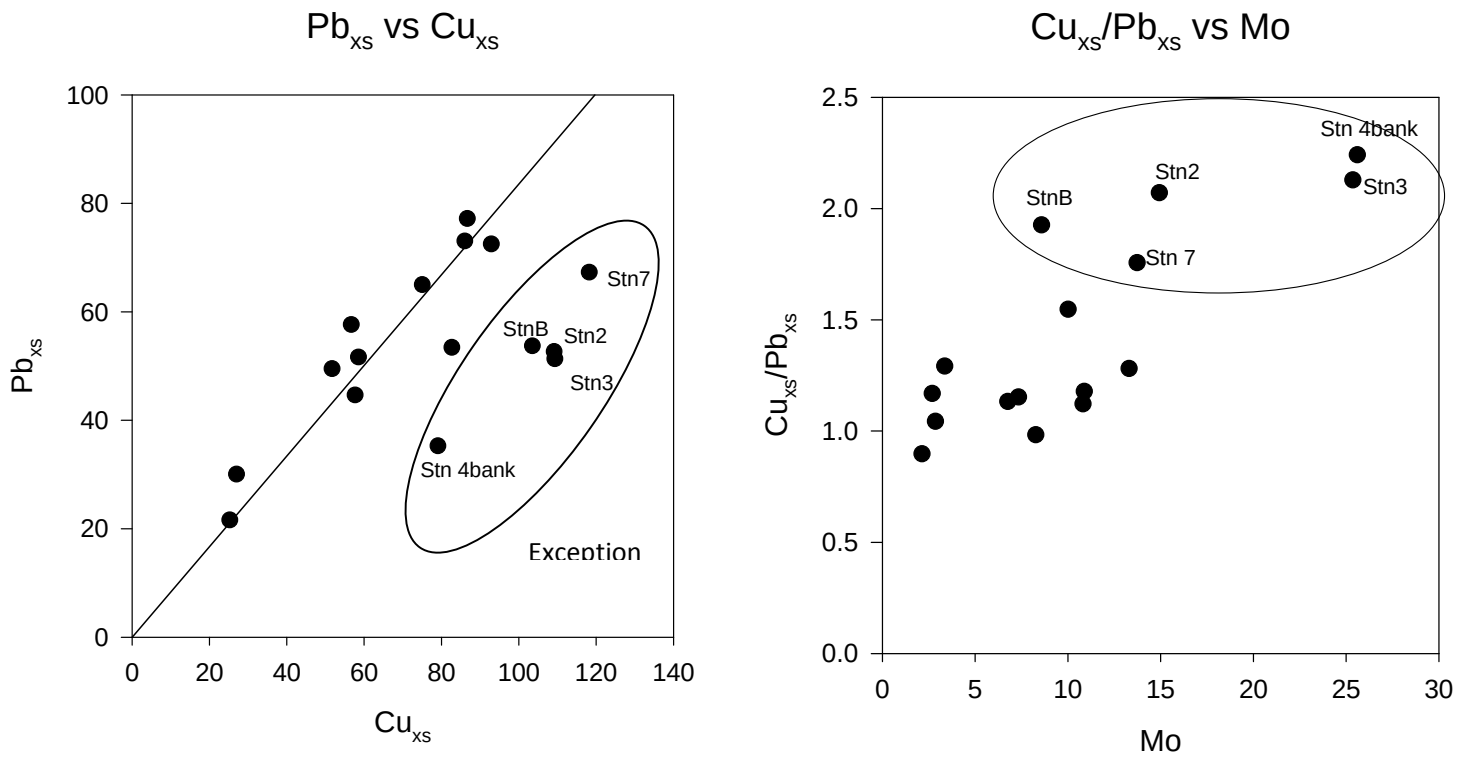


Figure 8. The Pb-excess relative to Cu-excess, and the ratio of Cu_{xs}/ Pb_{xs} relative to Mo in the surface sediments



Note: The Pb_{xs} and Cu_{xs} were calculated as the measured value minus background levels. The background levels were taken from the core bottom data where contaminants went to background levels and high iron levels were consistent with fine grain sediments existing at almost all the collected sites and different depth. The background levels for Pb and Cu were 13.6 and 12.6 (ng/g) respectively.

Figure 9. Total surface PAHs relative to the excess of Pb and Cu in the surface sediments

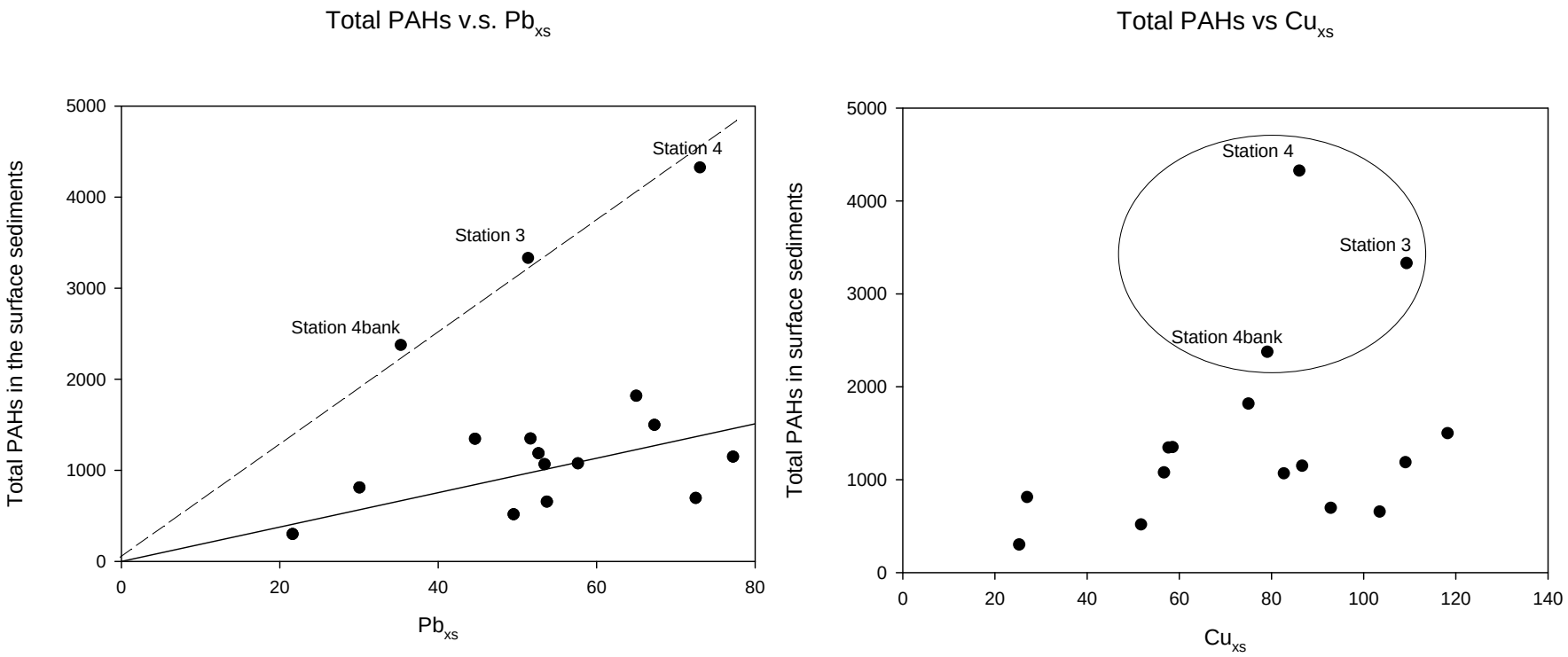


Figure 10. Total surface DDTs relative to the excess of Pb and Cu in the surface sediments

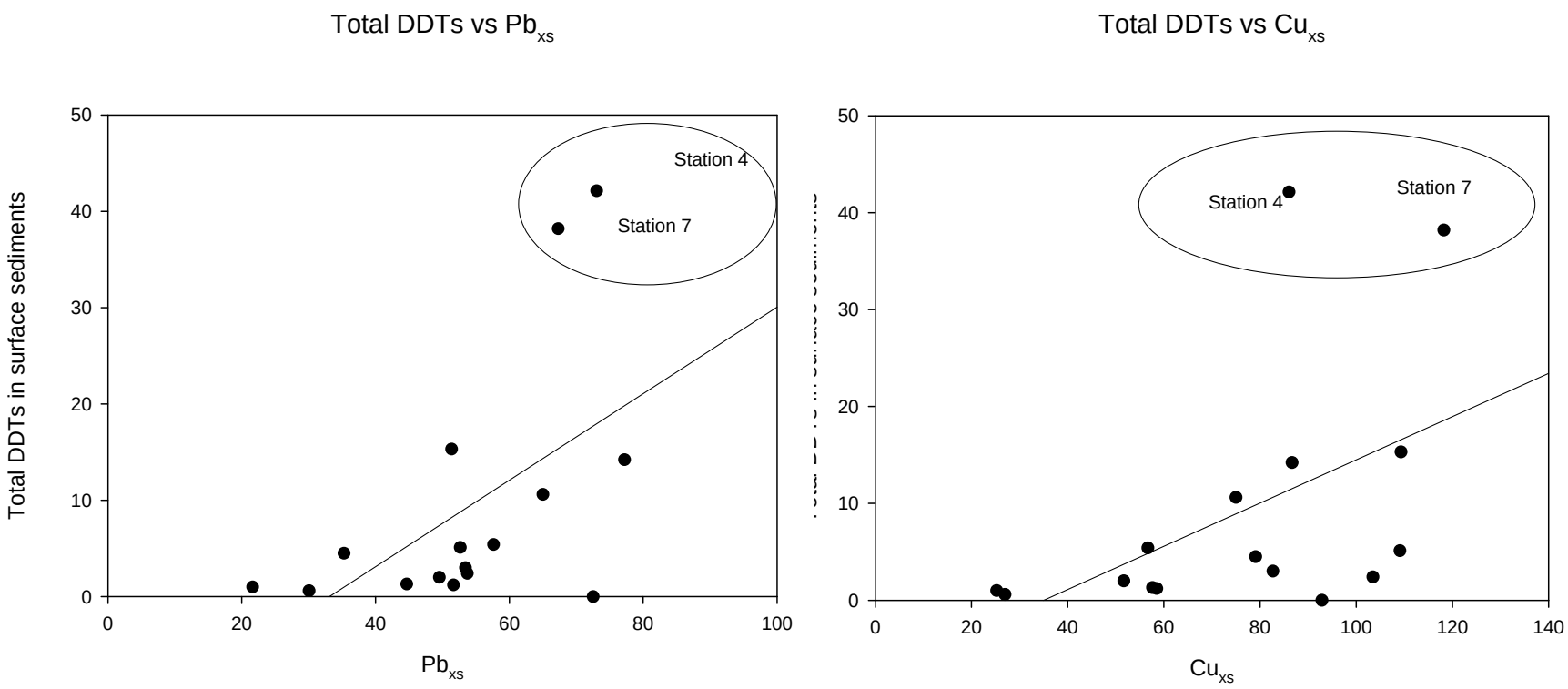


Figure 11. C/Cmax core profiles for excess Pb and excess Cu; Sum DDT and Total PAHs

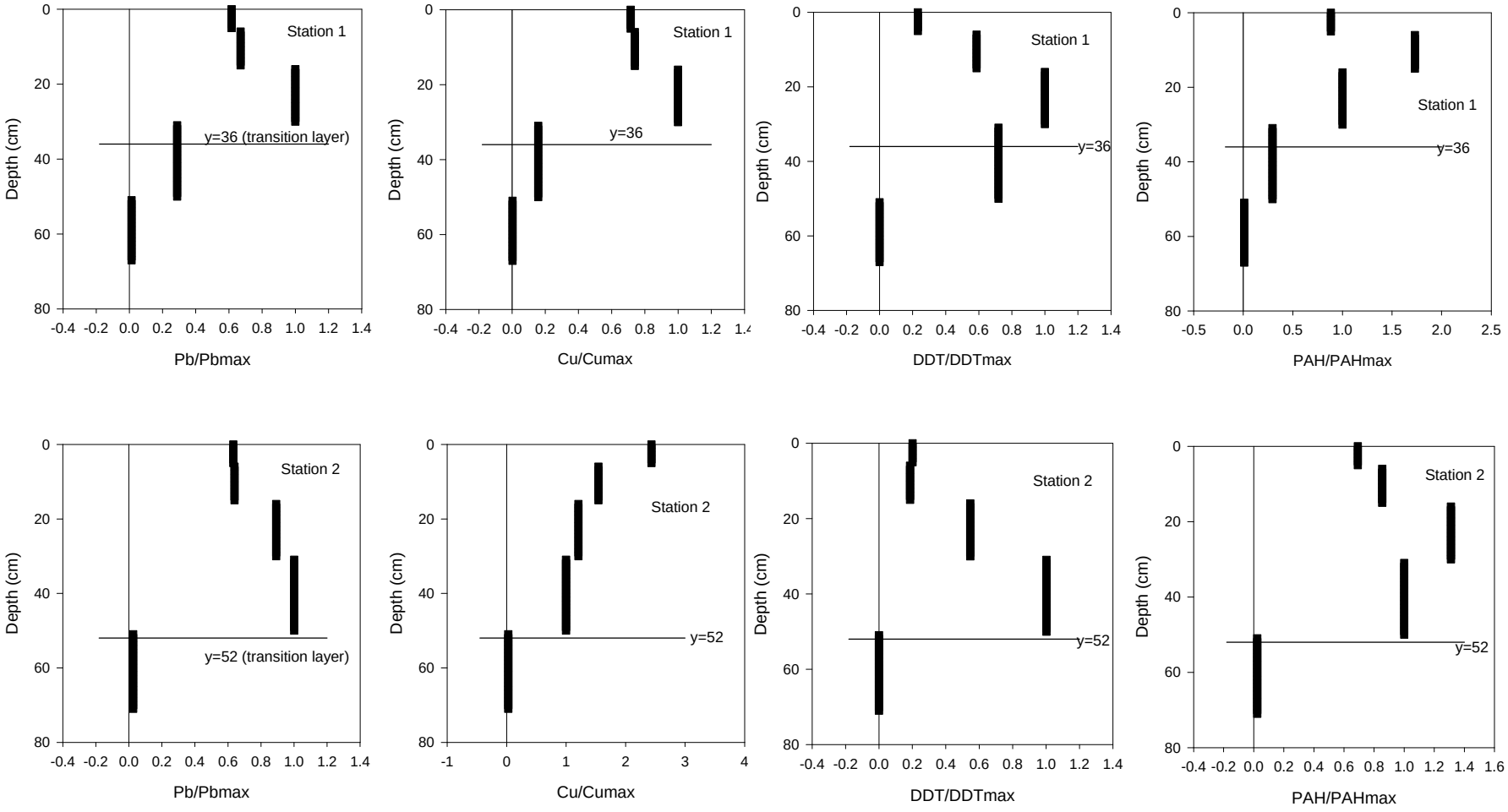


Figure 11. cont….

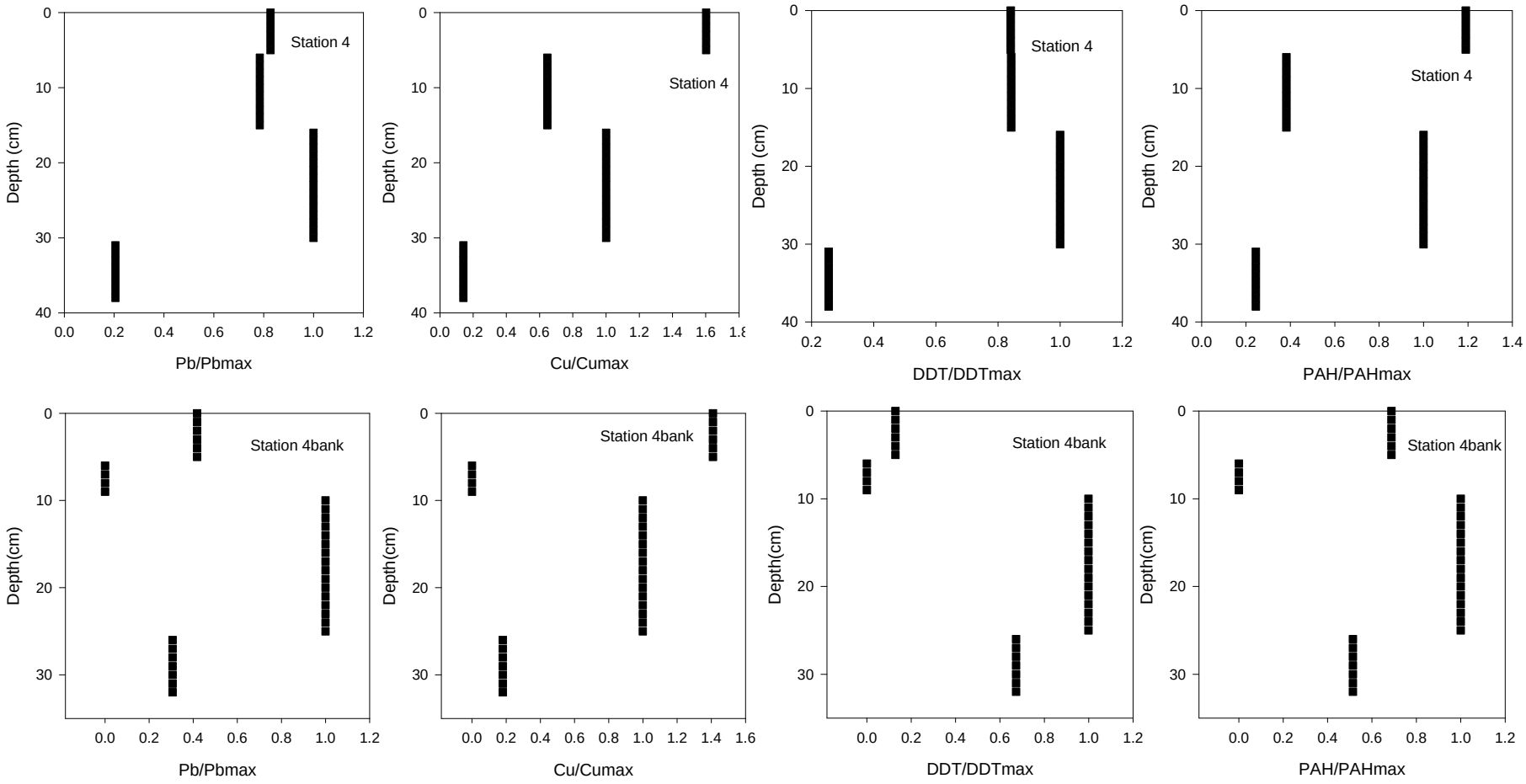


Figure 11. cont….

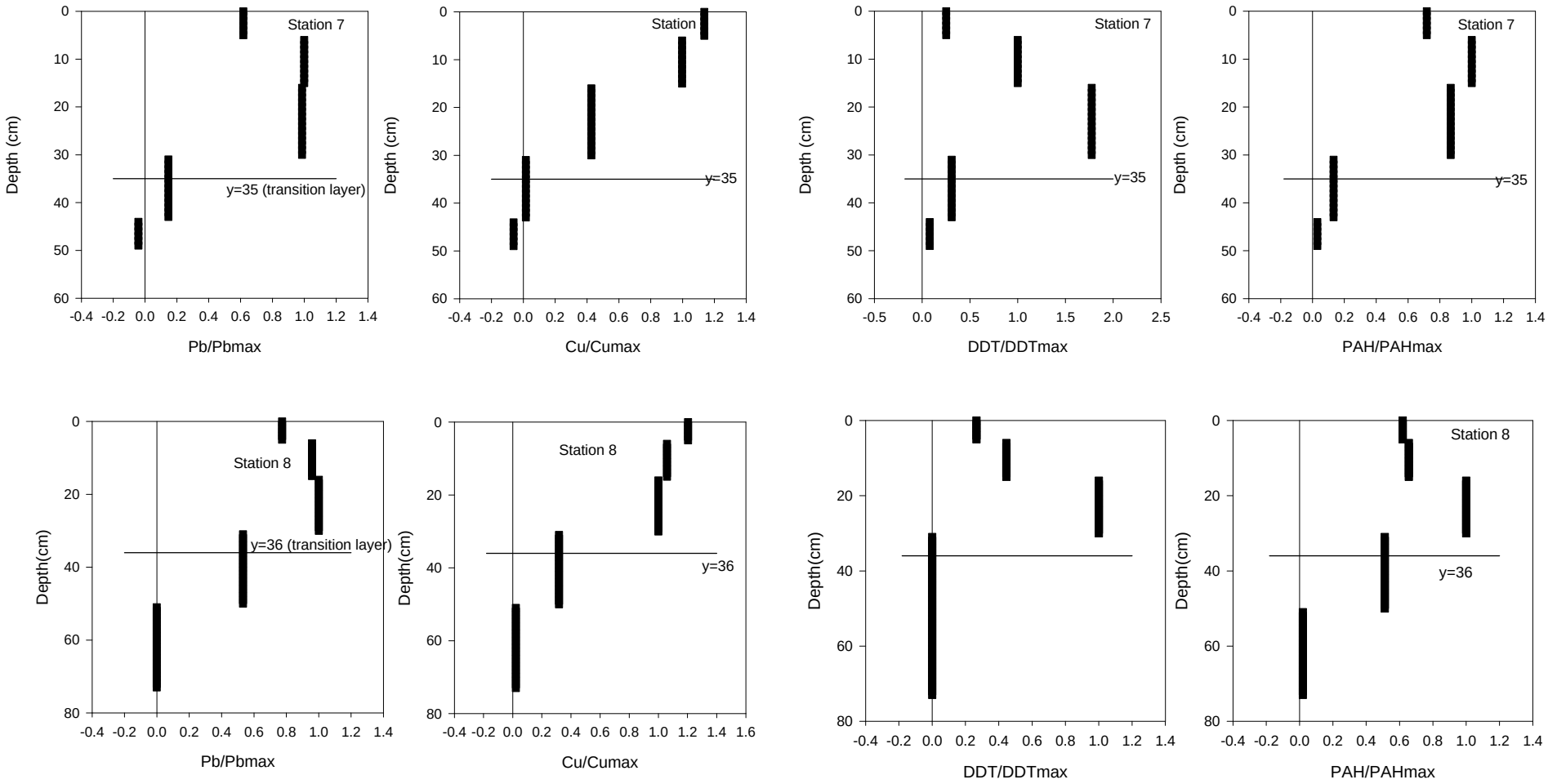


Figure 11. cont….

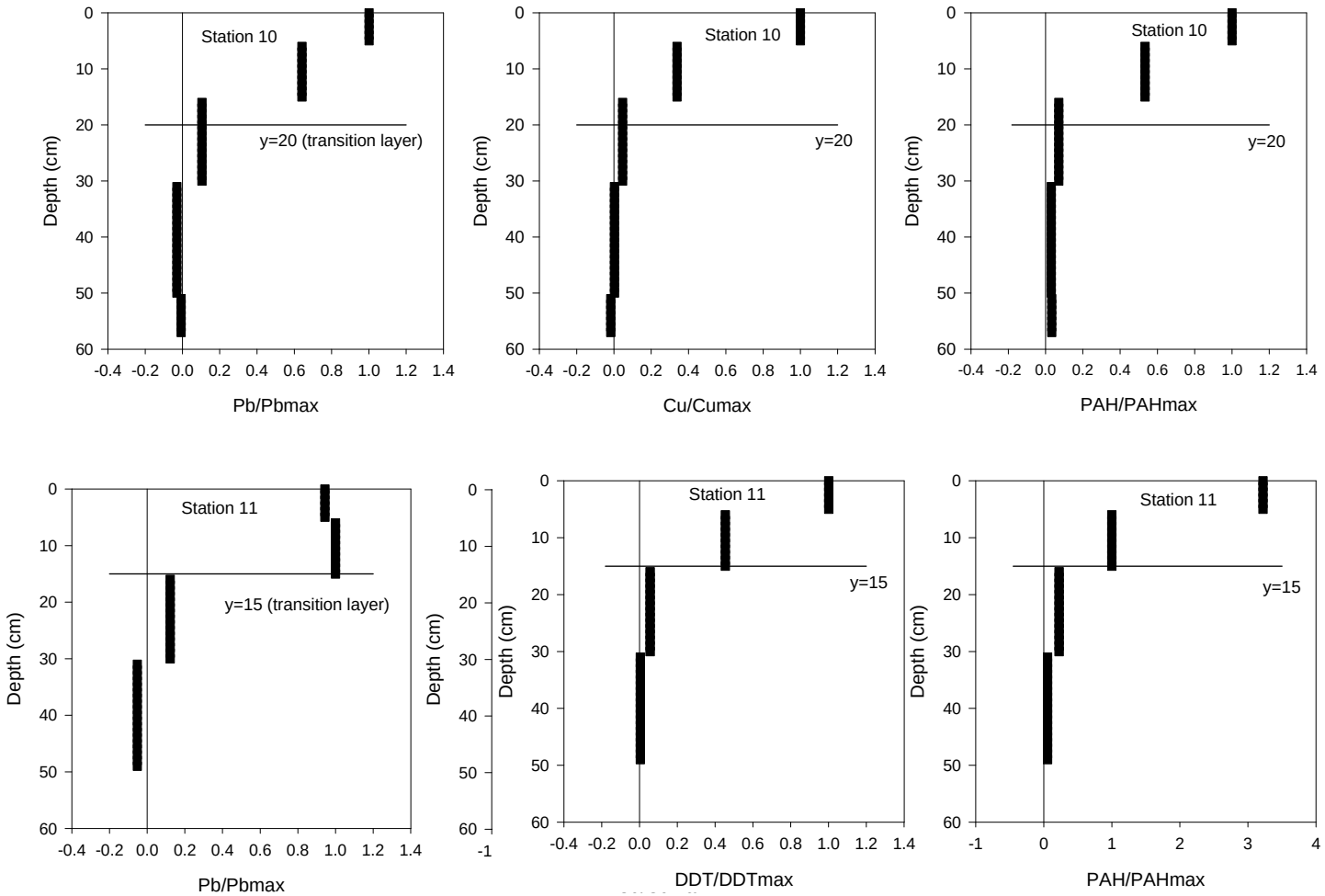


Figure 11. cont….

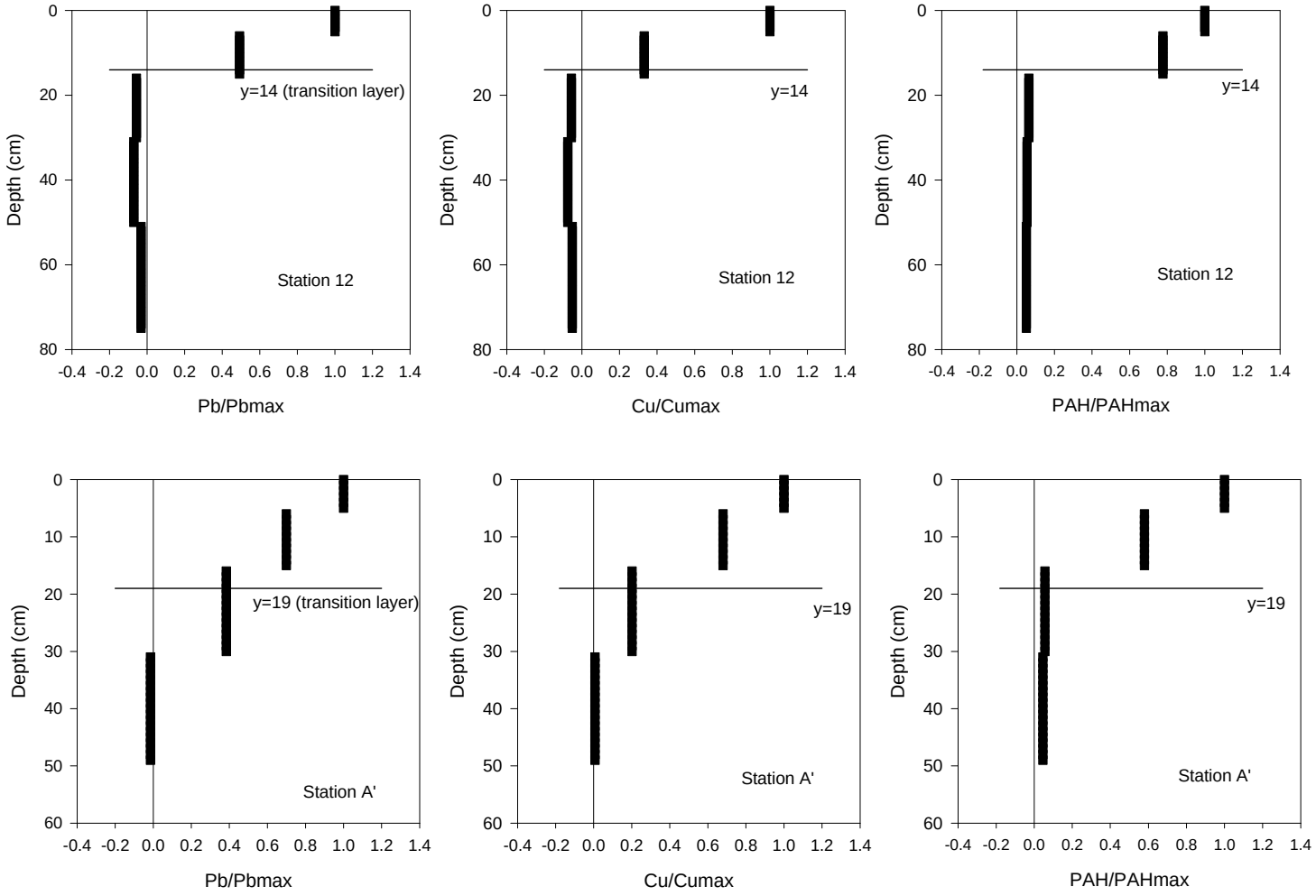


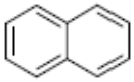
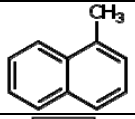
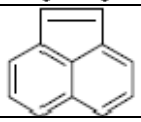
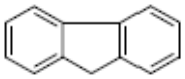
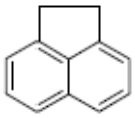
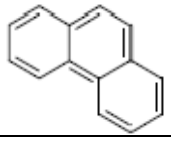
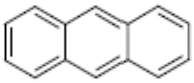
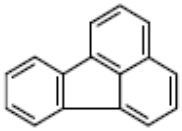
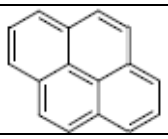
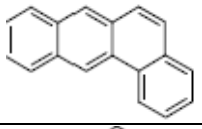
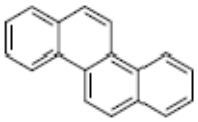
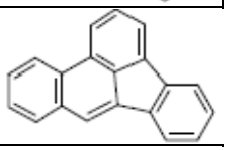
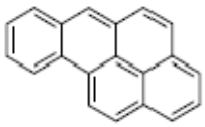
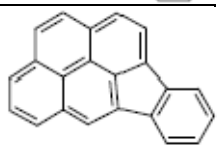
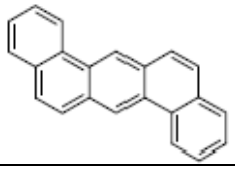
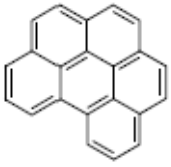
Table 1. Names, abbreviations and structures of PAHs measured in the Forge River Sediments					
Common Name	**Abbrevi--ations**	**Structure**	**Common Name**	**Abbrevi--ations**	**Structure**
Naphthalene	NAP		1-methylnaphthalene	1-MeN	
2-methylnaphthalene	2-MeN		Acenaphthylene	ACEY	
Fluorene	FLU		Acenapthene	ACE	
Phenanthrene	PHEN		Anthracene	ANTH	
Methylphenanthrene	MePH		Fluoranthene	FLA	
Pyrene	PYR		Benz(α)anthracene	BAA	
Chrysene	CHRY		Benzo(β)fluoranthene	BBKF	
Benzo(α)pyrene	BAP		Indeno(1,2,3-cd)pyrene	IND	
Dibenz(a,h)anthracene	DBA		Benzo(g,h,i)perylene	BGHIP	

Table 2. PCB congener standards (IUPAC numbers); see text for MDL		
PCB Congeners:		**MDL (ng/g)**
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
Surrogates:		
2,4,5-Trichlorobiphenyl	PCB 29	
2,2',3,4,5,6'-Hexachlorobiphenyl	PCB 143	
Internal Standard:		
Octachloronaphthalene	OCN	

Table 3. Chlorinated pesticide analyte list; see text for definition of MDL.	
Pesticide Analytes:	**MDL (ng/g)**
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
Surrogates:	
DBOFB	
e-BHC	
Internal Standard:	
Octachloronaphthalene	

Table 4. Sediment Core Samples (collected 8/9/2006)				
Station No.	**Time**	**Upper Layer Thickness (cm)**	**Latitude**	**Longitude**
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 5. Sediment Grab Samples (0-5cm) + Sediments Collected above the Railroad Track						
Station No.	**Date**	**Time**	**Water Depth (ft)**	**Mud Thickness (ft)**	**Latitude**	**Longitude**
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 6. Water Content measured in Sediment Cores		
Station No.	**Depth (cm)**	**H_2O (%)**
1	0-5	84.80
	5-15	82.30
	15-30	76.80
	30-50	71.80
	50-67	57.30
2	0-5	86.40
	5-15	84.60
	15-30	80.00
	30-50	74.40
	50-71	59.00
4	0-5	88.50
	5-15	87.60
	15-30	86.60
	30-38	78.10
4B	0-5	94.90
	10-25	89.70
	25-32	85.70
7	0-5	85.40
	5-15	80.30
	15-30	73.10
	35-43	68.50
	43-49	58.40
8	0-5	80.40
	5-15	75.40
	15-30	76.20
	30-50	70.40
	50-73	60.40

Table 6. Cont…		
Station No.	**Depth (cm)**	**H_2O (%)**
10	0-5	75.40
	5-15	71.40
	15-30	64.00
	30-50	60.00
	50-57	54.60
11	0-5	78.80
	5-15	76.60
	15-30	64.00
	30-49	56.00
12	0-5	68.80
	5-15	60.30
	15-30	56.90
	30-50	48.30
	50-75	53.80
A'	0-5	73.00
	5-15	62.30
	15-30	55.90
	30-49	55.90

Table 7. C-N-S Analysis on Forge River Grab Samples			
Station No.	**C (%)**	**N (%)**	**S(%)**
1	7.81	0.90	
2	8.58	1.10	
3	9.61	0.17	
7	11.01	1.25	
8	8.93	1.12	
9	7.67	1.15	
10	8.88	0.72	
11	4.91	0.69	
12	4.91	0.63	
3	2.93	0.38	
A	5.90	0.79	
B	6.57	0.86	
M	2.29	0.29	
Upper Forge	2.47	0.23	
E Mill Pond	24.30	1.65	1.25
W Mill Pond	2.82	0.23	0.26

Table 8. C-N-S Analysis on Sediment Cores				
Station No.	**Depth**	**C (%)**	**N (%)**	**S(%)**
1	0-5	7.81	0.900	
	5-15	7.945	0.850	2.309
	15-30	8.161	0.789	2.439
	30-50	5.54, 5.476, 5.227	0.515, 0.503, 0.508	2.04, 1.908, 1.839
	50-67	4.030	0.390	
2	0-5	9.147	1.155	2.215
	5-15	7.87, 8.369	0.94, 0.929	2.310
	15-30	7.07, 7.279	0.84, 0.803	2.502
	30-50	6.2, 5.875	0.67, 0.578	2.281
	50-71	3.650	0.350	
4	0-5	10.030	1.010	
	5-15	9.850	0.830	
	15-30	10.600	0.950	
	30-38	5.620	0.450	
4B	0-5	10.700	1.330	
	10-25	8.220	0.710	
	25-32	1.720	0.120	
7	0-5	11.010	1.250	
	5-15	12.124	1.113	2.533
	15-30	11.563	0.884	2.330
	35-43	3.550	0.290	
	43-49	2.385	0.160	0.705
8	0-5	8.930	1.120	
	5-15	9.726	1.010	2.664
	15-30	8.974	0.882	2.790
	30-50	6.364	0.627	2.600
	50-73	4.302	0.404	2.573

Table 8. Cont…				
Station No.	**Depth**	**C (%)**	**N (%)**	**S(%)**
10	0-5	8.880	0.720	
	5-15	5.428	0.585	2.344
	15-30	3.705	0.388	2.486
	30-50	3.543	0.337	2.511
	50-57	3.681	0.352	2.532
11	0-5	4.910	0.690	
	5-15	4.064	0.436	1.836
	15-30	3.091	0.325	2.113
	30-49	3.560	0.370	
12	0-5	4.910	0.630	
	5-15	2.970	0.330	
	15-30	2.900	0.300	
	30-50	1.910	0.190	
	50-75	2.200	0.230	
A'	0-5	6.750	0.866	1.539
	5-15	4.110	0.431	2.505
	15-30	3.027	0.308	2.471
	30-49	3.380	0.350	
2'-08	5-15	7.660	0.830	
	15-30	6.840	0.680	
	30-40	4.310	0.410	

Table 9. Sediment Core Data for DDT Residues						
Sample Locations	**core depth**	**grams sed. extracted**	**4,4' DDE (ng/g)**	**4,4' DDD (ng/g)**	**4,4' DDT (ng/g)**	**sum (ng/g)**
site 1	0-5	21.53	6.92	3.69	0	**10.62**
	5-15	22.30	9.96	16.96	0	**26.92**
	15-30	20.33	30.01	15.89	0	**45.90**
	30-50	22.92	19.31	13.71	0	**33.01**
	50-67		0.00	0.00	0	**0**
site 2	0-5	21.48	1.52	3.63	0	**5.15**
	5-15	21.77	4.36	0.41	0	**4.77**
	15-30	20.25	10.45	3.55	0	**14.00**
	30-50	21.00	16.13	9.52	0	**25.65**
	50-71	20.52	0.00	0.00	0	**0**
station 2	5-15	17.67	10.53	7.60	0	**18.13**
	15-30	18.72	32.22	11.13	0	**43.35**
site 3	surface	15.35	6.81	8.48	0	**15.30**
site 4	0-5	10.93	14.41	27.72	0	**42.13**
	5-15	20.57	20.31	21.89	0	**42.20**
	15-30	12.03	24.93	25.17	0	**50.10**
	30-38	20.50	5.25	6.93	0.58351426	**12.77**
site 4 bank	0-5	3.98	0.00	4.51	0	**4.51**
	10-25	20.37	13.32	21.08	0.67146707	**35.07**
	25-32	9.13	19.78	19.29	0	**39.06**
	25-32	12.47	10.55	11.25	1.80136124	**23.60**
site 7	0-5	20.69	12.26	24.94	1.014	**38.21**
	5-15	20.59	55.57	95.74	0.52114701	**151.84**
	15-30	19.08	103.90	165.86	0	**269.76**
	35-43	26.45	13.20	33.83	0	**47.03**
	43-49	15.85	3.59	8.40	0	**11.99**
site 8	0-5	21.18	6.78	7.40	0	**14.18**
	5-15	21.79	15.06	8.73	0	**23.79**
	15-30	16.91	39.15	14.29	0	**53.44**
	30-50	14.96	0.00	0.00	0	**0**
	50-73	21.54	0.00	0.00	0	**0**
site 10	5-15	22.80	0.00	0.00	0	**0**
	15-30	22.32	0.00	0.00	0	**0.00**
	30-50	25.58	0.00	0.00	0	**0**
	50-57	16.35	0.00	0.00	0	**0**
site 11	0-5	21.89	1.34	0.00	0	**1.34**

Table 9. Cont…						
Sample	**core depth**	**grams sed.**	**4,4' DDE**	**4,4' DDD**	**4,4' DDT**	**sum**
Site11	5-15	28.76	0.00	0.00	0	**0**
	15-30	22.39	0.00	0.00	0	**0**
	30-49	16.13	0.00	0.00	0	**0**
	30-49	22.78	0.00	0.00	0	**0**
site 12	0-5	27.69	1.05	1.03	0	**2.07**
	5-15	28.91	0.00	0.00	0	**0**
	15-30	24.63	0.00	0.00	0	**0**
	30-50	19.78	0.00	0.00	0	**0**
	50-67	17.28	0.00	0.00	0	**0**
	50-75	18.35	0.00	0.00	0	**0**
site A'	0-5	21.48	0.00	0.00	0	**0**
	5-15	23.39	0.00	0.00	0	**0**
	15-30	22.78	0.00	0.00	0	**0**
	30-49	15.97	0.00	0.00	0	**0**

Table 10. Grain Size Analysis on Forge River Grab Samples								
Station No.	**Mean Diameter (µ)**	**Average Mean/Med**	**Average Mode**	**Average Skewness**	**Average Kurtosis**	**Average d10**	**Average d50**	**Average d90**
1	161.70	1.44	245.20	1.70	4.12	11.71	113.62	353.47
2	224.93	1.27	237.93	1.42	1.70	19.98	177.57	516.70
3	195.03	1.62	269.97	1.52	1.98	13.54	122.65	481.73
7	225.40	1.24	269.20	1.33	1.51	20.37	182.10	506.00
8	192.10	1.08	223.40	1.64	4.19	18.39	177.57	364.20
9	291.97	1.42	305.10	0.89	-0.49	16.91	205.23	773.03
10	128.27	2.22	216.77	2.33	6.30	7.26	57.97	321.53
11	229.07	2.35	251.37	1.25	0.18	10.41	97.39	733.70
12	177.83	1.69	169.37	1.76	2.85	11.08	106.11	459.53
13	141.50	1.75	116.60	2.42	6.12	11.25	81.15	347.30
A	174.03	1.34	223.40	1.82	3.84	11.21	129.87	380.43
B	NA	NA	NA	NA	NA	NA	NA	NA
M	121.00	1.79	105.90	2.74	8.41	8.21	67.48	284.83
Upper Forge	106.00	1.92	53.49	3.12	10.85	13.38	55.33	236.30
E Mill Pond	135.87	2.31	28.70	2.16	4.71	11.10	58.71	370.03
W Mill Pond	353.53	1.15	751.10	0.39	-1.21	19.38	307.53	790.60

Table 11. Grain Size Analysis on Sediment Cores									
Station No.	**Depth**	**Mean Diameter (μ)**	**Average Mean/Med**	**Average Mode**	**Average Skewness**	**Average Kurtosis**	**Average d10**	**Average d50**	**Average d90**
1	0-5	161.7	1.435	245.2	1.701	4.116	11.706	113.616	353.466
	5-15	176.966	2.048	263.183	1.723	2.948	11.035	89.94	44.319
	15-30	122.856	2.037	51.856	2.561	8.309	9.425	59.94	320.533
	30-50	102.713	2.2	53.493	3.085	11.368	6.393	46.393	260.966
	50-67	74.78	3.037	23.81	2.394	6.039	3.676	24.393	224.066
2	0-5	224.933	1.268	237.933	1.417	1.701	19.976	177.566	516.7
	5-15	194.566	1.58	254.7	1.586	2.33	14.593	125.966	471.566
	15-30	173.2	1.949	218.81	1.851	3.471	10.917	91.943	452.366
	30-50	125.686	1.874	94.85	2.752	9.558	9.733	66.426	318.4
	50-71	81.3	2.607	26.14	2.624	8.758	4.213	30.756	223.933
4	0-5	179.466	1.552	204.1	1.868	3.51	17.58	116.32	422.666
	5-15	301.766	1.352	800.03	0.826	-0.433	25.946	225.666	736.933
	15-30	195.666	1.791	204.1	1.606	1.879	12.73	109.816	544.866
	30-38	202.733	1.861	169.366	1.54	1.445	11.613	109.746	607.033
4B	0-5	203.266	1.97	350.326	1.677	1.763	21.3	103.363	631.633
	10-25	189.933	1.894	179.9	1.7	2.076	13.32	100.393	559.433
	25-32	353.933	1.109	728.8	0.414	-1.051	24.256	319.066	773.9
7	0-5	225.4	1.239	269.2	1.331	1.506	20.373	182.1	506
	5-15	206.3	1.445	232.033	1.56	2.25	20.72	144.7	485.966
	15-30	188.533	1.767	191.433	1.661	2.203	12.493	107.09	506.866
	35-43	217.73	1.69	254.966	1.32	0.943	11.184	131.133	587.933
	43-49	266.633	1.307	390.9	0.795	-0.442	7.174	204.033	674.566
8	0-5	192.100	1.082	223.400	1.642	4.186	18.386	177.566	364.2
	5-15	189.066	1.282	230.666	1.716	3.42	16.28	148.066	399.866

Table 11. Cont…									
Station No.	**Depth**	**Mean Diameter (μ)**	**Average Mean/Med**	**Average Mode**	**Average Skewness**	**Average Kurtosis**	**Average d10**	**Average d50**	**Average d90**
8	15-30	136.266	2.415	204.100	2.242	5.155	6.69	56.49	353.866
	30-50	145.300	1.728	192.566	2.195	5.699	8.754	85.086	344
	50-73	70.703	2.293	26.140	2.601	8.202	4.573	30.39	192.333
10	0-5	128.266	2.221	216.766	2.33	6.296	7.255	57.966	321.533
	5-15	126.966	1.589	169.366	2.72	9.354	9.722	80.456	275.733
	15-30	76.566	2.039	31.500	2.694	9.711	5.454	36.53	197.166
	30-50	83.466	2.681	26.140	2.987	11.645	4.559	30.93	234.1
	50-57	74.563	2.149	26.140	2.561	8.216	5.017	34.426	193.733
11	0-5	229.066	2.353	251.366	1.254	0.182	10.406	97.39	733.7
	5-15	149.100	1.848	277.966	1.946	4.303	9.341	80.92	370.866
	15-30	107.776	1.904	58.723	3.042	11.143	7.649	56.593	250.633
	30-49	94.183	2.161	88.833	3.123	13.1	5.571	43.553	237.333
12	0-5	177.833	1.694	169.366	1.757	2.846	11.084	106.113	459.533
	5-15	143.933	1.896	94.756	2.153	4.899	9.271	76.220	372.133
	15-30	97.556	1.811	56.926	3.316	14.316	7.278	53.87	226.766
	30-50	79.740	1.759	47.240	4.227	24.62	6.802	45.283	183.333
	50-75	55.110	2.082	28.700	2.638	8.937	3.929	26.463	0.657
A'	0-5	204.000	1.246	223.400	1.651	2.833	17.943	163.733	435.333
	5-15	134.800	1.702	149.833	2.247	6.204	10.065	79.83	326.333
	15-30	100.846	2.056	48.730	3.146	11.998	6.52	49.09	240.933
	30-49	89.336	2.250	28.700	3.529	15.758	5.369	39.576	216.533
2'-08	5-15	140.200	2.160	245.933	2.064	4.962	8.421	65.56	358.266
	15-30	96.080	2.304	44.393	3.255	11.783	7.283	41.713	240.133
	30-40	86.026	2.619	27.846	3.388	13.826	5.133	32.493	224.433

Table 12. List of PAH analytes and standards; see text for definition of MDL.	
PAH Analytes:	**MDL (ng/g)**
naphthalene	0.40
1-methylnaphthalene	0.40
2-methylnaphthalene	0.40
acenaphthylene	0.40
fluorene	0.40
acenapthene	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
Surrogates:	
d12 chrysene	
d10 phenanthrene	
Internal Standard:	
p-terphenyl	

Table 13. Concentrations of PAHs in surface sediments (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	196.7	49.18	89.42	190.10	67.78	87.45	11.00	69.75	1350
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 14. Concentrations of PAHs in sediment core samples (ng/g)																				
Station	**Depth**	**NAP**	**1MeN**	**2MeN**	**ACEY**	**ACE**	**FLU**	**PHEN**	**ANTH**	**ΣMePH**	**FLA**	**PYR**	**BAA**	**CHRY**	**BBKF**	**BAP**	**IND**	**DBA**	**BGHP**	**Total PAH**
1	**0 - 5 cm**	13.85	11.72	5.87	8.76	2.90	8.23	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**
	5 - 15 cm	25.60	22.26	10.20	13.69	7.59	14.30	121.84	32.79	117.00	504.47	392.13	332.21	327.71	733.59	337.64	275.72	52.75	241.84	**3563**
	15 - 30 cm	19.90	17.85	7.50	9.36	5.65	15.64	93.12	28.38	119.55	362.18	322.85	139.76	157.23	348.37	161.91	127.69	18.11	102.80	**2058**
	30 - 50 cm	5.97	5.17	3.35	3.03	3.23	7.18	38.61	11.14	43.60	85.78	73.32	37.39	40.70	114.57	53.39	40.05	7.49	32.84	**607**
	50 - 67 cm	1.23	< RL	< RL	< RL	< RL	1.22	2.89	1.95	5.41	2.26	1.05	1.86	2.79	0.53	< RL	< RL	< RL	0.20	**21**
2	**0 - 5 cm**	6.32	7.46	3.93	6.12	2.84	6.54	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**
	5 - 15 cm	8.77	9.10	4.82	4.32	4.04	6.53	56.20	16.19	62.13	229.12	181.07	92.54	120.69	293.36	139.38	122.84	19.16	97.38	**1468**
	15 - 30 cm	11.54	9.93	4.51	5.64	3.99	12.96	78.16	32.13	91.71	377.94	310.39	140.58	189.40	433.43	207.16	170.28	32.49	140.11	**2252**
	30 - 50 cm	19.06	14.88	7.87	9.46	7.27	15.08	81.94	27.83	97.49	267.50	214.85	131.40	156.40	299.04	151.01	123.17	16.23	77.24	**1718**
	50 - 71 cm	4.73	1.74	1.65	< RL	< RL	2.01	4.02	1.64	7.06	3.06	1.69	2.18	3.69	3.19	0.12	1.46	< RL	0.92	**39**
4	**0-5 cm**	13.29	8.95	7.07	13.57	8.72	15.79	241.28	45.84	243.32	730.66	603.37	399.18	396.50	710.03	368.54	246.21	49.56	223.94	**4326**
	5 - 15 cm	18.76	17.50	13.68	23.24	15.18	29.88	417.46	54.21	302.75	79.41	71.34	42.17	50.52	99.19	49.56	36.38	41.47	27.72	**1390**
	15 - 30 cm	15.13	11.62	9.57	15.96	10.26	26.31	351.66	53.37	297.04	631.67	576.37	197.44	285.22	527.18	268.42	176.30	34.93	145.57	**3634**
	30 - 38 cm	4.38	4.10	3.42	3.53	2.89	5.16	57.67	11.08	80.69	148.30	130.20	64.18	74.87	133.81	68.80	49.26	9.07	36.98	**888**
4B	**0-5 cm**	< RL	< RL	3.46	20.98	< RL	8.75	67.40	21.47	111.25	322.01	189.39	233.14	277.69	502.80	254.73	164.30	41.19	157.93	**2376**
	10 - 25 cm	15.59	14.67	10.51	16.19	9.92	16.61	246.39	40.97	233.22	579.19	522.43	218.98	268.58	526.82	282.48	229.34	31.81	192.79	**3456**
	25 - 32 cm	10.05	11.67	7.90	9.64	3.30	11.43	134.83	23.31	115.45	241.73	226.22	111.45	144.34	297.07	144.90	134.91	28.22	119.86	**1776**
7	**0-5 cm**	9.49	9.96	5.05	7.91	4.38	8.68	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**
	5 - 15 cm	15.48	13.30	7.11	10.09	6.84	14.89	79.12	31.56	118.26	345.49	278.44	128.71	159.53	371.61	182.62	158.90	35.97	130.04	**2088**
	15 - 30 cm	15.70	12.30	6.04	7.59	6.22	20.58	108.60	33.06	164.82	317.08	261.60	119.38	111.16	289.09	131.20	99.25	19.21	89.35	**1812**
	35 - 43 cm	3.31	2.98	2.30	1.13	1.16	2.91	21.54	4.98	27.81	44.52	38.64	15.28	20.05	39.17	18.11	15.88	3.28	12.39	**275**
	43 - 49 cm	0.82	< RL	< RL	< RL	< RL	1.78	5.14	1.98	10.52	8.04	6.92	4.35	5.54	6.90	2.62	4.20	< RL	4.48	**63**

Table 14. continued																				
Station	Depth	NAP	1MeN	2MeN	ACEY	ACE	FLU	PHEN	ANTH	ΣMePH	FLA	PYR	BAA	CHRY	BBKF	BAP	IND	DBA	BGHP	Total PAH
8	0-5 cm	10.37	8.61	4.25	6.14	1.09	5.06	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
	5 - 15 cm	9.05	9.25	5.09	4.20	3.85	6.46	52.18	12.17	67.40	196.59	160.20	88.81	108.10	237.62	95.34	80.52	14.85	67.63	1219
	15 - 30 cm	17.48	16.03	7.80	8.74	4.45	12.17	87.34	26.90	122.61	312.29	267.29	131.98	142.11	307.31	145.70	128.38	19.20	101.16	1859
	30 - 50 cm	8.65	5.27	2.95	5.47	1.10	8.11	45.07	15.44	60.28	155.37	128.54	61.27	65.74	155.99	82.05	72.92	13.43	63.72	951
	50 - 73 cm	1.04	1.03	< RL	< RL	< RL	1.95	3.29	2.14	6.64	4.37	2.55	0.46	2.62	5.00	0.41	2.88	< RL	1.47	36
10	0-5 cm	8.74	8.35	4.33	5.62	3.53	6.71	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
	5 - 15 cm	3.76	3.06	1.56	2.56	1.97	4.57	31.12	7.35	30.43	80.66	64.12	34.98	43.80	110.99	53.37	52.12	9.56	39.18	575
	15 - 30 cm	2.11	1.65	4.08	1.54	1.38	2.02	4.44	2.50	6.15	10.16	6.46	2.87	4.28	11.14	3.85	5.93	1.68	4.74	77
	30 - 50 cm	1.50	1.46	< RL	< RL	< RL	1.97	3.22	2.33	5.40	2.91	1.38	1.90	2.76	4.28	1.00	2.08	< RL	1.01	33
	50 - 57 cm	1.45	< RL	< RL	< RL	< RL	2.02	3.44	2.80	6.39	3.65	1.99	< RL	3.68	6.14	< RL	2.43	< RL	2.02	36
11	0-5 cm	11.57	16.54	7.45	8.03	5.39	8.66	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
	5 - 15 cm	0.86	1.01	0.44	3.48	0.30	1.08	5.27	3.05	8.78	29.57	14.70	26.57	33.66	119.00	46.53	64.08	12.97	46.70	418
	15 - 30 cm	2.03	1.67	1.36	1.59	1.35	1.83	5.09	2.54	6.25	14.89	9.91	3.92	4.99	13.70	5.81	8.02	1.88	6.95	94
	30 - 49 cm	1.45	< RL	< RL	< RL	< RL	1.60	2.81	1.88	6.15	2.92	3.48	< RL	2.79	0.94	< RL	< RL	< RL	< RL	24
12	0-5 cm	9.25	7.70	3.14	3.10	0.55	3.64	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
	5 - 15 cm	3.33	3.31	1.54	2.25	0.93	2.86	17.48	6.34	20.04	51.71	45.77	23.85	29.52	80.23	36.57	39.40	7.35	29.77	402
	15 - 30 cm	1.58	1.29	< RL	< RL	< RL	1.64	2.89	2.24	3.77	3.55	1.87	0.64	1.76	5.30	1.37	2.27	0.93	1.65	33
	30 - 50 cm	3.37	1.52	1.25	< RL	< RL	1.10	3.42	1.43	7.65	2.29	1.29	1.69	2.37	0.34	< RL	< RL	< RL	< RL	28
	50 - 75 cm	1.20	< RL	< RL	< RL	< RL	1.37	2.52	1.95	4.36	2.89	1.43	0.10	2.99	5.05	< RL	2.11	< RL	< RL	26
A'	0-5 cm	8.45	6.01	2.74	4.40	2.06	2.95	18.65	6.31	21.63	81.29	61.66	55.36	67.90	162.94	70.28	61.29	11.40	51.50	697
	5 - 15 cm	3.65	2.89	1.38	1.84	0.83	2.67	16.51	5.63	18.66	54.13	44.67	29.23	29.76	80.42	36.46	39.12	6.76	29.53	404
	15 - 30 cm	1.70	1.45	< RL	< RL	1.32	1.62	3.17	2.26	4.56	4.51	2.77	0.81	1.98	6.10	1.84	2.24	0.91	1.91	39
	30 - 49 cm	< RL	< RL	< RL	< RL	< RL	1.93	4.64	2.32	7.05	4.03	3.92	2.61	3.24	2.03	< RL	< RL	< RL	< RL	32

Station No.	Table 15. Six PAHs source indicators					
	MePH/PHEN	FLA/ (FLA+PRY)	ANTH/(PHEN+ANTH)	BAA/(BAA+CHRY)	IND/ (IND+BGHIP)	Ring456/TPAH
1	1.36	0.59	0.19	0.45	0.53	0.80
2	0.95	0.58	0.22	0.47	0.53	0.81
3	0.98	0.59	0.18	0.43	0.53	0.82
4	1.01	0.55	0.16	0.48	0.52	0.81
4 bank	1.65	0.63	0.24	0.48	0.51	0.84
7	1.14	0.55	0.21	0.45	0.52	0.81
8	1.09	0.58	0.23	0.56	0.54	0.80
9	1.21	0.62	0.19	0.46	0.54	0.78
10	0.86	0.58	0.18	0.56	0.55	0.78
11	1.06	0.52	0.22	0.48	0.54	0.78
12	1.16	0.57	0.27	0.55	0.54	0.77
13	1.24	0.54	0.25	0.45	0.53	0.76
A	***0.64***	***0.94***	***0.07***	0.43	0.56	0.70
A'	1.16	0.57	0.25	0.51	0.54	0.82
B	1.02	0.57	0.31	0.53	0.56	0.80
M	0.97	0.57	0.22	0.46	0.56	0.75
Upper Forge	0.86	0.53	0.15	0.39	0.51	0.82
E Mill Pond	1.21	0.56	0.16	0.42	0.57	0.74
W Mill Pond	0.92	0.57	0.11	0.43	0.49	0.81
Mean	1.08	0.59	0.20	0.47	0.54	0.79
Standard Deviation	0.217	0.089	0.057	0.048	0.020	0.034
Reported value	0.5~1 (combustion)	>0.50 (biomass burning products)	>0.10 (combustion)	>0.35 (combustion)	>0.50 (biomass combustion)	>0.70 (combustion)

Table 16. DDT residue and ∑PCB concentrations (ng/g) in sediment Grab Samples (0-5cm) all DDT residues are the p,p' isomers						
Station No.	**DDT**	**DDE**	**DDD**	**∑DDT**		**∑PCB**
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	7.4	6.8	14.2		
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 17. Sediment Core Data for DDT Residues						
Sample Locations	**core depth**	**grams sed. extracted**	**4,4' DDE (ng/g)**	**4,4' DDD (ng/g)**	**4,4' DDT (ng/g)**	**sum (ng/g)**
site 1	0-5	21.53	6.92	3.69	0	**10.62**
	5-15	22.30	9.96	16.96	0	**26.92**
	15-30	20.33	30.01	15.89	0	**45.90**
	30-50	22.92	19.31	13.71	0	**33.01**
	50-67		0.00	0.00	0	**0**
site 2	0-5	21.48	1.52	3.63	0	**5.15**
	5-15	21.77	4.36	0.41	0	**4.77**
	15-30	20.25	10.45	3.55	0	**14.00**
	30-50	21.00	16.13	9.52	0	**25.65**
	50-71	20.52	0.00	0.00	0	**0**
station 2	5-15	17.67	10.53	7.60	0	**18.13**
	15-30	18.72	32.22	11.13	0	**43.35**
site 3	surface	15.35	6.81	8.48	0	**15.30**
site 4	0-5	10.93	14.41	27.72	0	**42.13**
	5-15	20.57	20.31	21.89	0	**42.20**
	15-30	12.03	24.93	25.17	0	**50.10**
	30-38	20.50	5.25	6.93	0.58351426	**12.77**
site 4 bank	0-5	3.98	0.00	4.51	0	**4.51**
	10-25	20.37	13.32	21.08	0.67146707	**35.07**
	25-32	9.13	19.78	19.29	0	**39.06**
	25-32	12.47	10.55	11.25	1.80136124	**23.60**
Site 7	0-5	20.69	12.26	24.94	1.014	**38.21**
	5-15	20.59	55.57	95.74	0.52114701	**151.84**
	15-30	19.08	103.90	165.86	0	**269.76**
	35-43	26.45	13.20	33.83	0	**47.03**
	43-49	15.85	3.59	8.40	0	**11.99**
site 8	0-5	21.18	6.78	7.40	0	**14.18**
	5-15	21.79	15.06	8.73	0	**23.79**
	15-30	16.91	39.15	14.29	0	**53.44**
	30-50	14.96	0.00	0.00	0	**0**
	50-73	21.54	0.00	0.00	0	**0**
site 10	5-15	22.80	0.00	0.00	0	**0**
	15-30	22.32	0.00	0.00	0	**0.00**
	30-50	25.58	0.00	0.00	0	**0**
	50-57	16.35	0.00	0.00	0	**0**
site 11	0-5	21.89	1.34	0.00	0	**1.34**
	5-15	28.76	0.00	0.00	0	**0**
	15-30	22.39	0.00	0.00	0	**0**
	30-49	16.13	0.00	0.00	0	**0**

Table 17. Cont…						
Sample	**core depth**	**grams sed.**	**4,4' DDE**	**4,4' DDD**	**4,4' DDT**	**sum**
Site 11	30-49	22.78	0.00	0.00	0	**0**
site 12	0-5	27.69	1.05	1.03	0	**2.07**
	5-15	28.91	0.00	0.00	0	**0**
	15-30	24.63	0.00	0.00	0	**0**
	30-50	19.78	0.00	0.00	0	**0**
	50-67	17.28	0.00	0.00	0	**0**
	50-75	18.35	0.00	0.00	0	**0**
site A'	0-5	21.48	0.00	0.00	0	**0**
	5-15	23.39	0.00	0.00	0	**0**
	15-30	22.78	0.00	0.00	0	**0**
	30-49	15.97	0.00	0.00	0	**0**

Table 18. Sediment core data for ∑PCBs		
Site Locations	**Depth (cm)**	**∑ PCBs (ng/g)**
Site 1	0--5	7.690
	5--15	6.668
	15--30	12.106
	30--50	6.825
	50--67	0.000
Site 2	0-5	3.330
	5--15	7.459
	15--30	9.000
	30--50	17.396
	50--71	1.629
Site 4	0--5	16.790
	5--15	16.565
	15--30	16.361
	30--38	2.362
Site 4 Bank	0--5	9.260
	10--25	14.476
	25--32	19.589
	25--32	4.580
Site 7	0-5	7.766
	5--15	14.692
	15--30	33.068
	35--43	0.000
	43--49	1.782
Site 8	0-5	4.207
	5--15	6.752
	15--30	6.220
	30--50	0.000
	50--73	0.000
Site 10	0-5	5.259
	5--15	0.609
	15--30	0.000
	30--50	0.000
	50--57	0.000
Site 11	0-5	6.387
	5--15	0.000
	15--30	0.000
	30--49	0.000
Site 12	0-5	3.890
	5--15	2.803
	15--30	2.051
	30--50	1.111

Table 18 Cont…		
Site Locations	**Depth (cm)**	**∑ PCBs (ng/g)**
Site 12	50--75	0.000
Site A'	0--5	4.346
	5--15	0.573
	15--30	0.000
	30--49	0.000

Table 19. 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.

	Pb	Cu	Fe		Fluorene	Pyrene	LPAH	HPAH	DDTs	PCBs
Forge River										
surface	35-91	38-122	25000-39000		0.003-0.013	0.020-0.56	12.5-66.8	83.9-391	0-38	2.3-16
Long et al. 1995										
ERL	47	34			0.019	0.665			1.6	23
ERM	218	270			0.54	2.6			46	180
NY DEC, 1999										
lowest effect	31	16	20000							
severe effect	110	110	40000							
Chronic benthic					1.9-3.8	17-35			50-100	2100-
Wash. State, 2009										
no effect	450	390			8-16	50-100	370	960		600
adverse effects	530	390			60-120	70-140				1200

Note: The **LPAH** criterion represents the sum of the following "low molecular weight polynuclear aromatic hydrocarbon" compounds: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, and Anthracene.

The **HPAH** criterion represents the sum of the following "high molecular weight polynuclear aromatic hydrocarbon" compounds: Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Total Benzofluoranthenes, Benzo(a)pyrene, Indeno(1,2,3,-c,d)pyrene, Dibenzo(a,h)anthracene, and Benzo(g,h,i)perylene (WSDE, 2009).