

**The environmental implications of the UCM in
sediments of the New York Harbor complex**

**A Final Report to the Hudson River Foundation on Contract
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EXECUTIVE SUMMARY

In urban environments such as the New York-New Jersey Harbor Complex, contaminated sediments that fail toxicity tests lead to large increases in dredging costs threatening the viability of port operations. Knowledge of what classes of contaminants contribute most to toxicity would aid in management decisions on source reduction and dredging options. In many urban harbor sediment sites, the most dominant class of anthropogenic contaminants are complex mixtures of petroleum hydrocarbons whose compositions are not readily resolved by traditional gas chromatography that typically separated hydrocarbons according to vapor pressure alone. This unresolved complex mixture of petroleum hydrocarbons has been referred to as the UCM and can be due to either physical and biological weathering of crude or refined oil products, where initially more prominent peaks are preferentially lost by physical or biological processes. The UCM in urban harbor sediments may also be due to inputs of motor oils or lubricating oils. The median concentrations of UCM in 46 EPA REMAP Program collected sediments across the harbor complex was 980 ug/g, with selected samples exceeding or approaching 1% oil by weight. The concentrations of UCM were much higher than that of total PAHs in the same samples (averaging over 600 times higher), and as in other urban harbor studies, there was almost no correlation between total petroleum hydrocarbons (TPH) and PAHs, with the latter showing compositions characterized by variable and mixed sources.

We have found that in many areas of the NY/NJ Harbor complex, the UCM pattern and spatial distribution is consistent with a major source being used or leaking motor oil. For example the highest UCM concentrations (2.0 – 2.6% by weight from samples collected in close proximity to large CSO discharges, and the UCM compositions of those sediments (determined by GC and comprehensive two-dimensional GC at Woods Hole) are consistent with the pattern observed in much of the lower Hudson Basin.

Furthermore the patterns of UCM found in sediments is similar in many respects to the compositions determined also by 2-D comprehensive GC for a selection of new and used motor oils. We have also now detected synthetic motor oil ingredients polyalpha olefins in sediments proximate to CSOs that should be most impacted by urban run-off sources. The concentrations of all 13 sediment muddy sediment samples from the CSO impacted areas of Bowery Bay and Flushing Bay were all over 1% UCM by weight. Latimer and Quinn (1998) made similar arguments that urban run-off of motor oil was the primary source of petroleum hydrocarbon input into Narragansett Bay, where they also reviewed the literature supporting similar conclusions for other urban estuarine environments. The NAS (2003) report on Oil in the Sea also suggests urban run-off as a major source of oil to the world's oceans. However, In two regions of the study area the UCM distributions indicated that other sources of petroleum hydrocarbons were also important. The clearest examples are many of the sediments analyzed in Newark Bay and adjoining Arthur Kill and Kill van Kull waterways. In those sediments there was clear evidence of lighter but weathered hydrocarbon mixtures, most likely derived from fuel oil operations and leaks that have been reported to be most extensive in this region (Gunster et al., 1993) that constitutes the largest petroleum port on the East Coast of the U.S. 2-D-GC

chromatograms of these sediments are consistent with important contributions of lighter aliphatic and aromatic hydrocarbons found in No. 2 and even No. 6 fuel oils that are commonly spilled in that area. There is also some evidence from our work on UCM patterns in Jamaica Bay for a lighter fraction of petroleum hydrocarbons in some sediments. In earlier work from Richard Bopp's group, they had noted this as well and speculated that this was a result of jet fuel spillage associated with operations at local JFK airport. Our work on this is not definitive, and would require us to go back to these samples and focus more on ensuring that we efficiently recover the lightest hydrocarbons in our samples that may be lost during evaporation.

Analysis of our own and EPA's data on 1993 and 1998 REMAP collected sediment suggests that both PAHs and neutral nonylphenol ethoxylate metabolites may contribute significantly to predicted narcosis based critical body residues for the sediment test species **Ampelisca abdita**, but only in a couple of sediments can the combined concentrations measured contaminants approach 10% of CBRs measured in our labs for this species. There is much more than sufficient UCM in the preponderance of REMAP samples that were toxic to amphipods to cause membrane disruption/narcosis based toxicity if UCM hydrocarbons are bioaccumulated by the organism with even relatively low BSAFs (0.01 to 0.1 g OC/g lipid) and partition into cell membranes. However, it is quite likely that high molecular weight UCM compounds from motor oil sources are not partitioned into membranes because of their size or because benthic organisms either are able to avoid injecting them, they are poorly assimilated, or possibly metabolized by benthic invertebrates. We were able to show that there was a much greater

likelihood that high UCM concentration sediments were toxic to *Ampelisca*, if there was a higher proportion of the UCM that was lower molecular weight and more volatile. It would be expected that these likely fuel oil derived hydrocarbons are more bioavailable and more toxic to membranes given their smaller size. The experiments that we began to directly test the bioaccumulation and toxicity of lower molecular weight fractions of UCM extracted from sediments were not successfully completed but our hope it to try to finish this important work.

Both laboratory bioaccumulation experiments with several highly UCM impacted sediments (exceeding 2% oil by weight) exposed to *Nereis succinea* and field bioaccumulation experiments with a range of deposit feeding and filter feeding organisms was conducted. While *Nereis* was less active in highly oiled sediments and did not grow well, they not only survived 21 day tests for the most part, but exhibited relatively little bioaccumulation of TPH, especially UCM hydrocarbons. In field organism collected from urban run-off impacted sediments, an apparently higher concentration of what appears, on one dimensional GC, to be UCM hydrocarbons are in fact not the same hydrocarbons (as determined by 2-D GC analysis) as those measured in the sediments. The 2-dimensional chromatograms of the hydrocarbons isolated from depurated organism tissues supports that they are unlikely to be petroleum compounds. Our preliminary interpretation of these results (which is consistent with work conducted earlier by LeBlanc in our lab) is that many organism have complex mixtures of biogenic hydrocarbons (including *Ampelisca*) that vary from organism to organism, and it is likely then these compounds pose little toxicological risk to the organism. With a new and now

operational 2-D GC-time-of-flight-MS at WHOI we plan now to identify these hydrocarbons better and compare organisms from reference and oil contaminated site. It remains a mystery, why and how benthic deposit feeders are able to avoid either ingesting, assimilating, or accumulating (metabolism??) many higher molecular weight petroleum hydrocarbons, when they have been observed to accumulate (at least for limited times) in suspension feeding mussels following oil spills or in urban estuaries. In Chapter 3 of this report is a discussion of some of the ideas that have been proposed for benthic organisms to adapt and sometimes thrive in the presences of high levels of oil. Also of interest, is the observation the suspension feeding *Mulinia lateralis* does accumulate a significant amount of lower molecular with hydrocarbons. Further work is required to determine whether or not these hydrocarbons are related to the petroleum derived mono-aromatic hydrocarbons found at high and approaching toxicologically significant levels in mussels studied by English investigators working with Rowland (e.g., Rowland et al., 2001).

TPH, as largely characterized by UCM of variable compositions, comprise a substantial fraction of the organic carbon in sediments of the NY/NJ Harbor complex. For the 46 R-EMAP samples analyzed, the median ratio of TPH to Total organic carbon was 5.6%; thus if an average hydrocarbon is 90% carbon by weight, this corresponds to 5.0% of the organic carbon in harbor sediments is comprised of more residual petroleum hydrocarbons. However, in many areas the TPH fraction of organic carbon is much higher. From the oil sheen present when collected many sediments, it is clear that TPH is in many cases present as a non aqueous phase liquid rather than sorbed to sediment

surfaces as individual sorbates. For example the median TPH/TOC value for the 17 stations sampled in the East River, Bowery Bay and Flushing Bay was 35%. The implications of this degree of petroleum contamination in urban harbor sediments have not been addressed adequately in the literature. In addition to potential toxicological implications of hydrocarbons that might exert stress either through membrane narcosis, induction of organism mixed function oxidases, or potentially in the case of many PAHs, act as important mutagenic contaminants, the other possible effects of having so much hydrocarbon in sediments may be manifold. Some of the possible effects of high levels of petroleum hydrocarbons may include: 1) changes in cohesiveness, compaction, and erodability of surface sediment deposits; 2) their use as substrates for selecting for microbial communities adapted to utilizing oil and resulting changes in sediment redox chemistry (not included in this report is preliminary evidence that sediments impacted by higher amounts of more easily degraded lower molecular weight hydrocarbons are more reduced as possibly indicated by ratios of redox sensitive metals in the same samples); and 3) possible changes in chemotaxis for organisms that rely upon hydrocarbon signals either of mating or larval settlement. Clearly more work needs to be done on the bioavailability of UCM hydrocarbons, its potential toxicity, and some of these other physical, biological, and biogeochemical effects that high levels of oil may have on bottom sedimentary environments.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Sediment Contamination in the New York-New Jersey Harbor Complex

The Hudson River Estuary is the largest urbanized estuary located on the eastern coast of the United States. The New York-New Jersey Harbor Complex makes up the lower part of the estuary and its area supports a population of over 20 million people located in both New York and New Jersey (Wakeman and Themelis, 2001). Commercial vessels such as oil tankers, container ships and freighters use the harbor to transport manufactured goods and raw materials. Passenger ferry ships, recreational boats, government vessels, tugs and cruise ships are also major users of the harbor.

Over recent years, the New York-New Jersey harbor operations have been threatened as a result of the need to manage the dredging and disposal of dredged materials in order to maintain shipping lanes and port facilities. Many of the materials that need to be dredged are contaminated with combinations of chemical contaminants and many are deemed inappropriate for either dredging or the cheapest disposal options due to risk assessment based on sediment testing for possible toxicity. Understanding which of the contaminants in sediment are the major causes of toxicity could result in more cost effective management of contaminant sources and be of great benefit to the Port. Clearly understanding and controlling sediment toxicity should also improve the condition of the benthic habitat for ecosystems in the Harbor.

It is not clear which chemical contaminants are most responsible for observed toxicity that is seen in some standardized tests that are used in managing disposal options

for dredged material. In this thesis, we focus on probably the single most abundant class of sediment contaminants, petroleum hydrocarbons. The harbor is subjected to hydrocarbon contamination from a wide variety of sources including storm water and wastewater from- municipal wastewater treatment plants, municipalities and industrial discharges (Gunster et al., 1993). The harbor is also a major commercial and industrial site; it includes petroleum storage containers, chemical manufacturers and power plants, among other industries.

Sources of sediment toxicity

The spatial distribution in the harbor complex of acute sediment toxicity in standard amphipod tests is not random, but is rather more concentrated in areas of Newark Bay and its surrounding waterways; Jamaica Bay, and other areas of the upper New York Harbor (especially around the shipyards around Brooklyn), apparently more depositional areas of the East River and very far western Long Island Sound (in areas often referred to as the Narrows) that are characterized by high energy tidal currents and concentrated discharge of New York City's municipal wastewater (Long et al., 1995; Adams et al., 1998; Adams and Benyi, 2003). Although the data for the lower saline portion of the Hudson River is relatively limited, there is a lower frequency of sediment toxicity there, despite the known important upstream Hudson River sources of polychlorinated biphenyls (PCBs) and selected metals (especially cadmium). Perhaps not surprisingly, toxicity is rarely observed in more oceanographically open or better flushed areas of New York's outer harbor and the Raritan Bay estuary.

The different areas of the harbor complex are stressed by contaminant inputs from a combination of sources, but the importance of local sources likely varies dramatically. For example, Newark Bay receives no direct discharges from municipal sewage treatment plants, although treated sewage enters from one of the major tributaries (the Hackensack River) and also from estuarine transport of water from local treatment plants on the Arthur Kill and Kill van Kull. However, Newark Bay and the surrounding Kills represent a vibrant Port for both container and oil carrying ships and many oil terminals and refineries are located in this area; has storm water and combined sewer overflow (CSO) discharges that drain present and relict industrial properties, and receives tributary input from the Elizabeth, Hackensack, and Passaic Rivers, which serve as sources to Newark Bay of metal and organic contaminants reflective of a variety of inputs, including substantial present or past industrial activity, highly contaminated in-place sediments, and releases from operations at Newark Airport.

The watershed of Jamaica Bay is presently much more residential and the effluent of three large sewage treatment plants provides enough freshwater that salinity is a reliable marker of wastewater input (Ferguson et al., 2001; Swanson et al., 2004). Up to 15 % of the Bay's volume can sometimes be from water that has recently been through a treatment plant or entered from CSO sources. Even more treated municipal wastewater enters the Harbor complex in upper New York Harbor and the East River. Given the regional variation of the many contaminant inputs sources entering the harbor complex, and the high degree of tidal and wind-driven mixing in many areas, it may not be surprising that it is difficult to relate sediment chemistry to measurements of toxicity. Furthermore, despite the likely local variability in the loadings, the sediment

concentrations of several of the more particle reactive metals and even persistent hydrophobic contaminants are generally co-correlated remarkably on a system-wide analysis or when conducting within basin analysis of data, further complicating statistical correlation approaches for elucidating the sources of toxicity (Long et al., 1995; Adams et al., 1998).

There is clear evidence for regional variation and strong gradients in the distribution of sediment toxicity. This variability is seemingly not matched by clear and dramatic gradients in contaminant levels when contaminant concentrations are adjusted for sediment type (total organic carbon, iron, aluminum or grain size). It may be true that toxicity is related to intense local loadings of contaminants or the extent of organic enrichment in sediments and that causal effects of specific contaminant class are hidden by either the complexity of the system, the coarse diagnostic potential inherent in the amphipods test conducted (biological and experimental weaknesses combined with a toxicity scale that only varies between 20 -100% mortality in the absence of sediment dilution tests with highly toxic sediments). Among the scenarios that would be consistent with a control of local sources on toxicity include a situation in which the major source of toxicity has not been measured and that stress does not correlate with that of contaminants measured; one in which acute amphipod toxicity is due to a complex set of interactions between chemicals (e.g., synergistic or antagonistic effects); or one that is due a contaminant or a set of contaminants that has been measured but for which bioavailability is not strongly correlated with sediment concentration. It is possible that the simple approach of comparing spatial distributions of toxicity to estimates of local loadings of specific contaminants (alone or in combination) or to loadings of stressors

distinguished by source (e.g. quantitative fluxes of water coming from storm sewers, CSOs, and municipal sewage treatment plants) can still yield insight or test hypotheses concerning the causes of toxicity, but the level of data analysis to date has not been exhaustive.

Particle reactive trace metals, such as copper, lead, zinc, and mercury are significantly elevated in sediments of the Harbor complex, but levels have decreased (often dramatically) following application of source controls over the past 35 years of environmental regulation and management (illustrated in Steinberg et al. 2004 using dated core profile information from Richard Bopp (Rensselaer Polytechnic University)). While metal concentrations in some sediments exceed estimated ERM (Effects Range Medium; Long et al., 1995) values (e.g., notably but not limited to Mercury; Steinberg et al. 2004), a large number of toxic sediments have metal concentrations that are only modestly elevated above background sediments (determined by measuring basal levels down core or by crustal abundance ratios compared to aluminum or iron). The observed toxicity is not consistent with metal concentrations when the risk is assessed with the model of acid volatile sulfide (AVS) protection of metals where increased risk to some metals is predicted when simultaneously extracted metals (SEM)/AVS approaches or exceeds unity (DiToro et al. 1991); in fact, when the 1993 regional environmental monitoring and assessment program (R-EMAP) data is considered there is a tendency for the opposite to be true i.e., sediments with lower ratios of sulfide extractable metals to AVS are in fact often the most toxic.

Sediment toxicity evaluation

Toxicity tests with amphipods are often used to determine whether harbor dredge spoils should be disposed of as hazardous waste (Adams et al., 1998). Understanding what types of contaminants control or contribute to this observed toxicity could lead to improved management of contaminant sources and eventually to disposal options for harbor dredged material. The marine amphipod *Ampelisca abdita*, a tube dwelling benthic suspension and deposit feeder is a prominent member of the local benthic community (Ho et al., 2000) and is also the primary species used to determine sediment toxicity in estuarine waters.

A focus of several investigators in recent years has been to better understand and test the role of relatively nonpolar or hydrophobic chemicals in causing toxicity in animal tests as a result of the cumulative partitioning of such compounds into cellular membranes to levels that impair membrane function due to alterations of membrane permeability/viscosity or associated function of proteins. Such non-specific mechanisms are referred to narcosis or baseline narcosis and occur at very high sediment exposure concentrations of hydrophobic chemicals. It is well documented that the effects are approximately additive which provides a mechanistically based assessment approach if one knows the concentrations and biota sediment accumulation factors (BSAF) for all important narcotic chemicals. Good examples of this modeling framework are found in DiToro et al. (2000), and DiToro and McGrath (2000). In prior work in the McElroy and Brownawell labs at Stony Brook, the species-specific critical body residue (CBR) was found to be between 19 and 37 $\mu\text{mol/g}$ lipid for model PCBs, polycyclic aromatic hydrocarbons (PAHs), chlorobenzenes and nonylphenol accumulated by *A. abdita* (Faye

et al. 2000; Nannen, 2001; Du, 2004; McElroy et al. in prep.). Measured CBRs are somewhat lower than the best estimate range (40-160 $\mu\text{mol/g}$ lipid) predicted from a review of many vertebrates and invertebrates across a wide range of laboratory studies (DiToro et al., 2000; DiToro and McGrath 2000), but appear reasonable given the fact that amphipods, and crustacea in general, are thought to be more sensitive to many contaminants including those acting through narcosis. Analysis of organic contaminant data from the R-EMAP studies and have come to similar conclusions: the preponderance of the predicted body residues contributing to possible narcosis based toxicity derives from PAHs (the sum of predicted body residues from all other measured nonpolar contaminants are approximately 5% of that attributed to PAHs, but that there are not nearly enough PAHs in the sediments of the Harbor complex to account for observed toxicity. Among the uncertainties in the analysis include the estimation of total PAHs compared to the subset of most non-alkylated PAH from NOAA/NIST list analyzed by the REMAP program and the likely variation in PAH bioavailability between different sites. Figure 1.1 shows results of predicted body residues of PAHs calculated from 1998 REMAP data ($\text{BSAF} = 0.3 \text{ g Org C/g lipid}$ and without a conversion from measured PAH to total PAHs in the sediments). The observed toxicity of some of the samples tends to rise with increasing predicted body residues of PAHs in a predicted "sigmoidal" manner that would be expected from a dose response relationship. However, the concentrations of PAHs corresponding to this rise are much lower than measured CBR values (on the order of negligible up to 1 - 10% of predicted CBR for some sites) determined experimentally. The fact that several samples have high PAH levels and no mortality might be explained by poor bioavailability of PAHs in those samples; low PAH samples

exhibiting toxicity suggest alternative sources of toxicity at these sites. It is likely that PAHs are an often significant but unlikely sole or primary cause of observed toxicity.

Alkylphenol ethoxylate (APEO) metabolites (derived primarily from nonylphenol polyethoxylate transformations) in 49 of the 112 1998 collected REMAP samples were previously analyzed (Yin, 2006) and have found that nearly a quarter of the samples are contaminated with these compounds at levels approaching or exceeding 10 µg/g in sediment. Comparison of the predicted nonylphenol body residues (using BSAF results from Fay et al., 2000) suggests that the exposure to these contaminants may lead to non-negligible contributions to cumulative narcotic stress, but that concentrations measured in only 3 out of 50 1998 R-EMAP sites resulted in predicted body residues exceeding 1-3 % of the CBR that was typical of many of the more contaminated samples. Two major sources of alkylphenol ethoxylate metabolites into Harbor system are treated municipal sewage effluents and CSO discharges. These metabolites have been shown to persist in some highly depositional sedimentary regimes (Ferguson et al., 2003) but likely degrade more readily in more disturbed environments.

Results from manipulative toxicity identification evaluation (TIE) experiments conducted with Harbor complex sediments by Ho and collaborators at the EPA also did not implicate cationic metals as likely causative agents. The same TIE studies that did not implicate a role of metals in toxicity and complementary "reverse-TIE" studies (McElroy et al., 2000) have suggested the possible causative role of nonpolar and semivolatile organic contaminants in the toxicity of selected Harbor sediments. It has also been observed that organic contaminants in general, and more specifically PAHs

(Long et al., 1995) and PCBs (Steinberg et al., 2004) provided the best correlations with amphipod toxicity.

Petroleum Hydrocarbons

Petroleum contamination of urban estuarine sediments is usually associated with large oil spills and chronic inputs which include surface runoff, sewage effluents and operational losses from refinery and shipping operations. In Newark Bay for example, between 1982 and 1991 more than 18 million US gallons of hazardous materials and petroleum products, specifically No. 6 Fuel oil (103 spills, 12,829,272 US gal) and gasoline (207 spills, 48,816 US gal), was accidentally released into the bay (Gunster et al., 1993). In the most recent edition of the National Academy of Sciences (NAS) sponsored study "Oil in the Sea" (NRC, 2003), best estimates of inputs of total petroleum hydrocarbons (TPHs) into the marine environment indicate that most likely the largest source (excluding natural seeps) is from land in estuaries and that most of that is estimated to be the result of urban run-off that includes TPH from automobile derived motor oil, residues from incomplete automobile combustions; and atmospherically deposited hydrocarbons. The NRC report concluded that the error in these estimates is enormous. They also decided to use oil and grease measurements to estimate TPH loading in order to utilize data from a larger number of rivers. The NRC report cites over 70 papers that bear on this analysis, and there are many more studies that have used widely different and complementary approaches for identifying or quantifying oil inputs to waters receiving storm water inputs from urban watersheds. In one report, Latimer and Quinn (1998) synthesize several studies of TPH loadings and mass balances in

Narragansett Bay, and concluded that approximately half of the loadings to the Bay occur under wet weather conditions, with much of the remainder coming from sewage treatment plants and in-place sediment sources. We hypothesize that urban runoff is a major source of TPH entering the Harbor complex from storm sewers/drains, CSO discharges, as well as municipal sewage plant effluents. It is likely that whether storm water inputs of TPH are a locally dominant source will depend upon the intensity of other sources that include legal (e.g., inefficient two stroke marine engines) and illegal (e.g., discharges of bilge oil and residual fuel oil sludge) marine transportation related releases, accidental spills from tankers and other ships, and inputs from shore facilities involved in the storage, shipment, or refining of petroleum products. Because the relative intensity of suspected or potential sources of TPH varies greatly in the Harbor complex, it will not be surprising that urban runoff is the dominant source of TPH in areas that receive selected areas that are susceptible to intense storm water and sewage (e.g., upper NY Harbor, the East River and Jamaica Bay), whereas other inputs may dominate in regions where there are more frequent oil spills, and more concentrated marine transportation or petroleum industry activities (e.g., Newark Bay and the adjacent Kills).

The most abundant class of anthropogenically mobilized chemicals in urban harbor sediments is undoubtedly the residual TPH. In the absence of a recent local oil spill, the preponderance of the TPHs found in urban harbor sediments is characterized analytically as an unresolved "hump" that elutes from capillary gas chromatographic analysis and has long been referred to as the unresolved complex mixture (UCM).

The UCM is a complex mixture of petroleum derived hydrocarbons that are widely detected in urban harbor sediments. Due to the hydrophobicity of most UCM

constituent properties, the UCM tends to sorb to the surfaces of particulate matter and has been detected at high concentrations (100 to greater than 1000 µg/g) in aquatic environments that are highly impacted by industrial and port activity (Farrington and Tripp, 1977; Hong et al., 1995; Readman et al., 2002). Thus the UCM is often the most abundant class of chemical contaminants in urban harbor sediments and possibly the only class of non-polar organic contaminant in high enough abundance to lead to narcotic stress in exposed organisms. The components of the UCM include alkanes, branched alkanes, cycloalkanes, monoaromatics, multi-ring aromatics, heteroatomic aromatics, steranes and cyclic triterpenoids (Frysiner et al., 2003). When crude oil or refined fuels enter the marine environment evaporation removes the most volatile compounds; dissolution removes the more polar and water-soluble compounds; and biodegradation generally attacks the linear alkanes, branched alkanes, and then the cycloalkanes and aromatic compounds (Volkman, 1984; Frysiner et al., 2003). The weathering processes produce the UCM which persists in sediments and has often been used as a marker for petroleum contaminated sediments (Boehm et al., 1982).

The UCM was previously thought to be relatively un-reactive and non-toxic, and therefore not an environmental hazard (Connell and Miller, 1984), though sediment concentrations are usually present at much higher levels than other traditional organic contaminants such as PAHs, polychlorinated biphenyls (PCBs) and phenols. Recently research has shown that components of the UCM may be the cause of toxicity caused by weathered oils when the toxic effects are based upon a mass of known toxic components in oil (e.g. PAHs and phenols) (Neff et al., 2000). Studies performed have also shown that the monoaromatic components of the UCM (Rowland et al., 2001), and synthesized

cyclohexyltetralin compounds which are structurally similar to the aromatic UCM components (Smith et al., 2001), produce a toxic response in *Mytilus edulis* in aqueous exposures. The concentrations of the monoaromatic UCM components (100-500 µg/g tissue dry wt) that produced a toxic response (reduced scope for growth) in the *Mytilus edulis* were within the range of aromatic UCM concentrations detected in mussels from polluted environments (Rowland et al., 2001). The UCM is lipophilic and therefore can accumulate in the fatty tissues of benthic organisms like *Mytilus edulis* which are continuously exposed to it in the environment. Rowland et al (2001) measured nonaromatic UCM concentrations of up to 3610 µg/g dry wt in mussels collected from the east coast of the United Kingdom.

UCM composition

Different sources and types of petroleum give rise to different elution and carbon number ranges in one dimensional GC chromatograms, therefore the UCM shape is different (Frysinger et al., 2003). In order to identify contaminant sources, chromatograms of all our sediment extracts were compared to chromatograms of a diesel standard and motor oil standard (synthetic Mobil 5W-30, Valvoline 10W-30 and synthetic Q 5W-30). The *n*-alkane ranges were as follows for the various standards and oils: diesel standard ranged from nC_{11} to nC_{24} and lubricating/motor oil ranged from nC_{16} to nC_{40} . This identification method is known as “hump-fitting” and has been used for over 30 years to distinguish different sources of the UCM, but it is limited because it provides little information about the chemical composition of complex organic mixtures like the UCM (Reddy et al., 2002; Frysinger et al., 2003).

To address this gap in information the relatively new analytical method called comprehensive two-dimensional gas chromatography (GC×GC) was applied in order to identify the different chemical components of the UCM. The GC×GC is much more advanced than traditional gas chromatography because it is able to separate an order of magnitude more components than traditional gas chromatography, which is limited to fewer than a hundred components (Reddy et al., 2002). Using this method allowed us to resolve and identify the chemical groups of the UCM. Chromatograms produced by the GC×GC are presented as a two dimensional retention plane which leads to better identification of the individual components, unlike the traditional GC chromatograms which show only one retention plane (Gaines et al., 1999). Components of the UCM in this study were separated based upon a compound's polarity and volatility.

Research goals of this project and organization of this report

Among the goals of this project were to provide an assessment of the likely sources and distribution and fate of the UCM preserved in sediments of the New York-New Jersey Harbor complex. We also wanted to assess the possible extent to which the sediment UCM contributes to the toxicity observed in the *A. abdita* sediment toxicity tests. To achieve this goal the concentrations and composition of the UCM in sediments was related to observe *A. abdita* mortality determined separately in sediment samples characterized by the Region 2 USEPA sponsored R-EMAP program conducted in 1998. We have also measured bioaccumulation of UCM and UCM components in deposit-feeding polychaetes in laboratory and field experiments and in a filter feeding bivalve in petroleum contaminated Flushing Bay. The report shows mixed evidence for a

toxicological roles of UCM and petroleum hydrocarbons in affecting benthic deposit feeding organism, but places the issues of UCM bioaccumulation and toxicity into a better context. The report also provides important information about the likely sources this important class of anthropogenic contaminants in the metropolitan NY/NJ Harbor complex, and discusses other effects that high concentrations of UCM may have on sedimentary environments in the system.

Chapter 2 of the report describes the analysis of total petroleum hydrocarbons in a subset of samples (n=46) of the 1998 R-EMAP sediment samples that have been characterized by U.S. EPA for sediment chemistry and toxicity. In this work, we are interested in relating the occurrence of UCM throughout the metropolitan NY/NJ harbor complex, relating the concentrations and of compositions of UCM to both possible sources and to observed amphipod toxicity to test whether the concentration or compositions of UCM might help to understand the likelihood or conditions under which residual oil might be toxic in such tests. Two-dimensional GC was used to characterize the patterns in a significant number of these samples to help guide our interpretation.

Chapter 3 provides the results of some more targeted studies of petroleum hydrocarbons in surficial sediments and selected benthic organisms collected on a cruise conducted in August 2004, that was focused on sediment collections along the East River, and in the areas of Bowery Bay and Flushing Bay, which surround LaGuardia Airport in the very far western area of Long Island Sound. Several of the sites studied were next to or very affected by large local CSO discharges and sediments from those areas were very enriched in organic matter and no visible macrofauna (nor oxic layer of surface sediment) was found in those samples. From this work, we have gained more

confidence in the pattern of hydrocarbons coming from urban run-off sources (CSOs) and have examined the accumulation of UCM compounds in some polychaete and bivalve sediments exposed to high UCM levels.

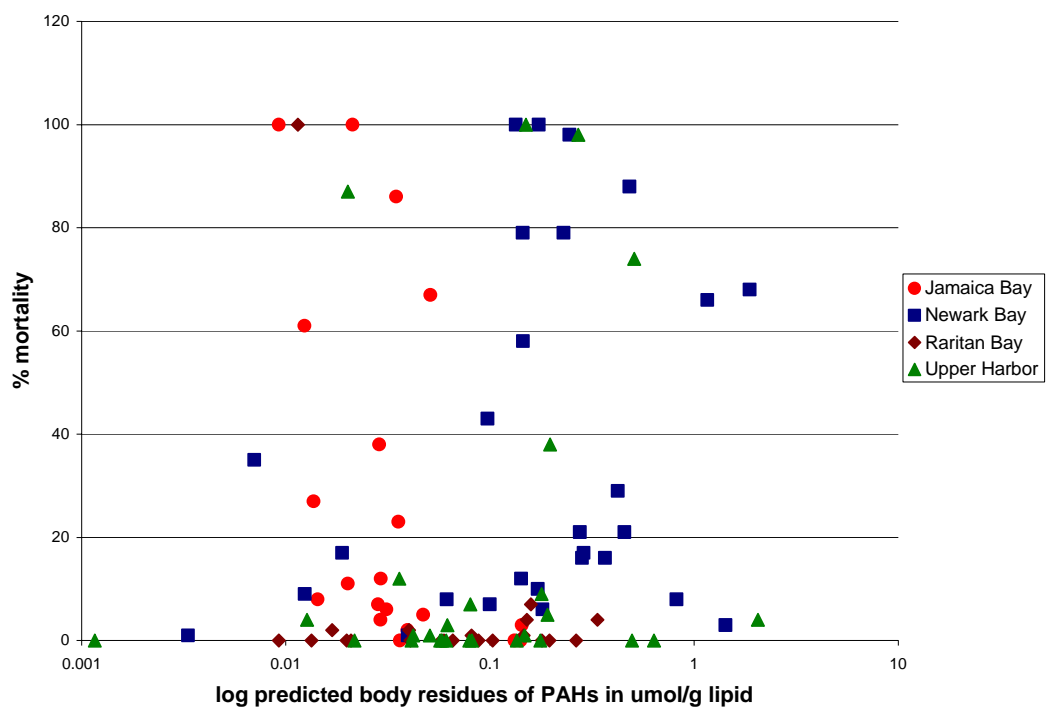


Figure 1.1. % *Ampelisca abdita* mortality plotted against predicted PAH body residue for sediments collected during the 1998 R-EMAP survey.

CHAPTER 2

The distribution of the Unresolved Complex Mixture in the New York/New Jersey Harbor Sediments

Introduction

The major sources of petroleum hydrocarbons to the New York-New Jersey Harbor Complex sediments include combined sewer overflows (CSOs), discharges of treated sewage, storm water runoff, riverine discharges, industrial effluents, land-based runoff, aeolian input resulting from partial combustion processes, shipping and terminal operations and accidental spills that are prevalent within the lower Hudson Estuary (Wakeman and Themelis, 2001). Once in marine surface waters, petroleum hydrocarbons may be lost by evaporation or volatilization; microbial transformations; photodegradation; loss to sediments by impaction, sinking of denser liquids (after volatilization of lighter materials) or sorption to sinking particles (NAS report, Oil in the Sea). Due to low aqueous solubility, relative stability and hydrophobic properties, petroleum hydrocarbons tend to have strong partitioning with associated particulate surfaces which eventually leads to accumulation and persistence in harbor sediments (Means et al., 1980).

Traditional gas chromatographs of typical petroleum contaminated urban harbor sediments produced by capillary GC analysis with FID or MS detection are often characterized as being dominated by a largely unresolved “hump” which is made up many unidentified aliphatic and aromatic components which is known as the unresolved complex mixture (UCM). The UCM was previously believed to be non-toxic but recent studies have shown that some components cause toxicity to the bivalve *Mytilus edulis*

(Neff et al, 2000; Smith et al, 2001). Other studies have shown that UCM exposure will be detrimental to organisms that live in, ingest or come into contact with contaminated sediment through narcotic toxicity (Donkin et al, 2003).

In this study, the sources, distribution, composition and concentration of the UCM was measured in surface sediments collected from sites within the New York-New Jersey Harbor Complex to test whether the presence of UCM components can be related to the incidence of amphipod toxicity observed. The GC-FID (gas chromatograph-flame ionization detector) was used to quantify (using a carbon-based response factor) the total petroleum hydrocarbons (TPH) present in the sediment samples. The TPH value was used in this study as a proxy for the sediment UCM concentration. Recent advances in chromatographic analysis have led to a new technique that facilitates in-depth analysis of complex hydrocarbon mixtures like the UCM. This new technique, called comprehensive two-dimensional gas chromatography (GC×GC), is well suited for petroleum analysis because it is capable of separating one order magnitude more components from complex mixtures than traditional gas chromatography which is often limited to separating mixtures containing fewer than one hundred compounds (Gaines et al, 1999; Reddy et al, 2002). Use of the GC×GC allowed us to resolve the components of the UCM and may provide us with more insight with respect to sources of UCM and components that are more strongly associated with samples that are toxic in amphipod tests. One class of petroleum hydrocarbons, which has received much more attention are the polycyclic aromatic hydrocarbons. Here we have interpreted the concentrations and compositions of the PAHs reported on the same samples to assist in understanding the likely sources of

these more toxic hydrocarbons in the R-EMAP sediments that have been analyzed (Adams et al., 1998).

Materials and methods

Sediment collection

Indicators of benthic quality (sediment chemistry, toxicity, and benthic structure) were estimated with known confidence by an EPA Regional Environmental Monitoring and Assessment Program (R-EMAP). Of the 112 sediment samples collected by R-EMAP, 46 were selected for analysis in this study, and those sample locations are illustrated in Figure 2.1. Ten-day acute, static, non-renewal sediment toxicity tests with *Ampelisca abdita* were conducted according to ASTM (American Society for Testing Materials) standards, and whether the sediments were assessed to be toxic in that test is also noted in Figure 2.1. Details of REMAP field sampling and data analyses, including alternative thresholds of sediment quality (TOC and PAH concentration) and site coordinates, are described by Adams et al. (1998).

Sediment Extraction

Splits of collected sediment were frozen and sent to MSRC for organic contaminant analysis. Aliquots of the sediments were freeze dried, homogenized and ground into a powder using a mortar and pestle. The extraction of sediment was done utilizing a flow through sonication extraction method developed by Ferguson et al. (2001). 2 g of freeze dried sediment was packed in a 150-mm stainless steel column (4.6-

mm i.d.) fitted with 0.5- μ m stainless steel frits (Alltech Chromatography, Deerfield, IL) and spiked with surrogate standard dodecahydratriphenylene (DDTP). The empty volume in the column was then filled with sea sand which had been baked in a muffle furnace at 450 °C overnight. The packed column was then immersed in a heated ultrasonic bath (30 °C), and dichloromethane (DCM) was pumped through the extraction cell at 0.5 mL/min for 14 minutes to collect a total sample extract of 7 mL. Additional extractions yield no significant increase in total petroleum hydrocarbon concentrations. Blank sediment extractions, consisting of baked sea sand spiked with surrogate standard and packed into extraction columns, were performed alongside actual samples to maintain quality control. The collected extract was then reduced under a gentle stream of nitrogen, solvent exchanged to hexane and concentrated to 1 mL.

Purification of sample extract

Column chromatography was used to clean-up and fractionate the sediment extracts by passing the extract through a silica column. Silica (100-200 mesh) was activated at 450 °C for at least 4 hours and then partially deactivated the day before use with 5% water. The chromatography column (1-cm i.d.) was prepared by slurry packing in hexane 0.5 g sodium sulfate, followed by 4 g of silica and finally another 0.5 g of sodium sulfate in hexane. The sample was eluted using 12 mL of hexane/dichloromethane (50:50) to yield a relatively non-polar fraction consisting of a combination of aliphatic and aromatic hydrocarbons. The eluent was concentrated under a gentle stream of nitrogen and solvent exchanged to hexane and the sediment extracts were reduced to 1.5mL. These samples were stored in 2mL amber vials with Teflon lined

screw caps and spiked with internal standard (stearyl palmitate, SP) just prior to injection on the GC.

Total petroleum hydrocarbon analysis

GC-FID

Hydrocarbon concentrations in the sediment samples were quantified using a Hewlett-Packard 5890 Series II gas chromatograph coupled with a flame ionization detector (GC-FID). A 1 µL sample was manually injected into the instrument, the compounds were separated on a 95% dimethylsiloxane capillary column (Zebron ZB-5, 30m, 0.32-mm i.d., 6.25 µm film), with a helium carrier gas. The GC oven was temperature programmed from 50 °C to 290 °C for total run-time of 60 minutes. The range of n-alkanes in the UCM was determined using hydrocarbon standards and the UCM was quantified by integrating the total area and using response factors determined for the internal and surrogate standards.

GC×GC

Selected sediment samples were analyzed using a GC×GC by the Reddy laboratory at Woods Hole Oceanographic Institution. The analytical technique used here followed a method described in Reddy et al (2002).

Results and discussion

Occurrence and distribution of UCM and relationship to sediment properties

Sediment physio-chemical characteristics such as organic content, texture and geochemistry have an effect on the accumulation and distribution of the hydrocarbon

contaminants in the estuary (Means et al., 1980). For nonpolar hydrocarbons sorption and bioavailability in sediments are known to often correlate in a predictable way with total organic carbon content (Means et al., 1980; Wang et al., 2001; Schwarzenbach et al., 2003). Here hydrocarbon concentrations are reported both on a dry weight basis and also normalized with respect to sediment organic matter (TOC) content in order to standardize the concentrations between sites. The sediments that were characterized (by the EPA) as having high fine grain silt and clay content had higher organic matter content, and often also contained higher hydrocarbon concentrations (Table 2.1). The sites that were characterized by lower organic content and coarser grained sediments had relatively low hydrocarbon concentrations. The concentrations decreased towards the seaward part of the estuary and this could be related to proximity to oil pollution sources, but also to the change in sediment character and in particular to the decrease in fine particles and organic matter which are sources of sorption sites for the hydrocarbons.

The majority of Hudson River estuarine sediments have high oil loading with several samples approaching (one exceeding) 1% oil in sediment by dry weight. The concentrations of petroleum hydrocarbons measured were relatively high and much higher than a previous study done in the study area (35-2,900 µg/g) (Farrington and Tripp, 1977) and another done in the Arabian Gulf (11-6,900 µg/g) (Readman et al., 1996). The total petroleum hydrocarbons (TPHs) represented in the chromatograms was dominated by the presence of the UCM and not resolved peaks. This is evidence that the harbor sediment is widely contaminated by weathered petroleum (Farrington and Quinn, 1973). The mean and median concentration of the TPH was 2224 µg/g and 1360 µg/g sediment dry weight, respectively. The UCM contributed a significant fraction of the

FOC as the mean and median ratio of the TPH to total organic carbon content was 0.026 and 0.056. Because petroleum hydrocarbons are high percentage carbon by weight (approximately 90%, depending on the ratio of aliphatic and aromatic hydrocarbons), this means that a sizable fraction of organic matter in these urban harbor sediments is comprised of residual petroleum hydrocarbons. This relationship is further discussed in Chapter 3, when we compare the TPH/TOC in the R-EMAP sediments to those in samples collected in more oil-rich sediments in the East River, Bowery and Flushing Bays. The large amount of oil in sediments compared to organic matter is consistent with the common observation of an oil sheen when sediment samples are brought to the surface, as well as the occasional smell of “diesel” from sediments collected in the Arthur Kill, Kill van Kull and Newark Bay. Thus, at some sites TPH exists probably both sorbed to sediment surfaces and also as a non-aqueous phase liquid which coats some of the particles.

The concentrations of TPH were much greater than any of the other typically studied sediment contaminants (polychlorinated biphenyls, polycyclic aromatic hydrocarbons and metals). Importantly for risk assessment purposes, the levels of TPH do not correlate with that of total PAHs (Figure 2.2), which has been corrected by a factor of two which is a common approximation factor for converting more conventionally measured PAHs (25 in this analysis) to the sum of total PAHs in a sediment samples from urban harbors. The average ratio of TPH to the sum of PAHs is 2100. However, the range of TPH/PAH was quite variable, ranging from 10 to 22,000, with a median value of 580. This analysis means that TPH or UCM hydrocarbons have much more potential than PAHs to act as narcotic compounds if they are bioavailable and partition into biological

membranes, and further that any risks associated with UCM can not be estimated based upon more commonly measured PAHs. A lack of correlation between UCM and PAHs in other marine coastal and estuarine environments has also been found in other studies (Macias-Zamora, 1996; Tolosa et al., 1996; Readman et al., 2002). The fact that UCM and PAHs are so poorly correlated should not be surprising given that PAHs can be derived from sources other than petroleum product sources, that PAHs have highly variable concentrations and compositions in petroleum products and crude oils (NRC, 1985) and that it is likely that the fates of PAHs and residual UCM compounds are sometimes decoupled after they enter marine ecosystems..

*Association between UCM concentrations and *Ampelisca abdita* toxicity*

The relationship between the TPH (predominantly UCM and not resolved peaks) and amphipod toxicity is first illustrated in Figures 2.3 and 2.4. Figure 2.3 displays the TPH normalized to sediment fraction organic carbon (foc) content, which would be the normal way to conduct first order assessment of risk of hydrophobic contaminants given the demonstrated ability of sediment organic matter to predict the sorption and bioavailability of hydrophobic contaminant (DiToro et al., 1991). It is seen (Figure 2.3) that for the few (5) low TOC/foc (<12,000 g/g OC), amphipod toxicity is not observed. When TPH/foc approaches and exceeds approximately 30,000 g/g OC there is a steep increase in the tendency for sediments to be toxic to *Ampelisca* (defined as mortality > 20% compared to controls). However, as TPH/foc increases further there is a bimodal split between samples in the upper left portion of Fig 2.3 where several samples are highly toxic (mostly from the area in and around Newark Bay), and samples that are not

toxic (in the bottom right portion of Fig 2.3. Figure 2.4 illustrates that using three simplifying assumptions it is predicted in Figure 2.3 that most of the R-EMAP sediments measured in this study possess narcosis based risk to exposed *Ampelisca abdita*: 1) a lipid and carbon normalized BSAF of 0.3 g OC/g lipid, used to estimate lipid normalized tissue concentrations; 2) that UCM hydrocarbons permeate membranes and can cause narcosis-based toxicity; i.e., that BSAF predicts both total tissue and membrane lipid burdens of UCM; and 3) that the average molecular weight of UCM-derived hydrocarbons is 250 Da.

The reason why many high TPH/foc sediments are not as toxic as predicted is not understood but may either be related to the possible inappropriateness of using foc normalization of the data when so many of the sediment samples are so highly enriched with oil; i.e., the median percentage of organic carbon (TOC) in the sediments that can be accounted for as TPH-derived carbon (assuming 90% of hydrocarbon mass is C; see Chapter 3 for more discussion) is 5.0% and much higher for samples in Figure 2.3 and 2.4 found to the right side of the graph. Thus, partitioning sorption theory, which implicitly assumes dilute solution behavior of hydrocarbons in sediment organic matter, is not a valid assumption in this assessment. Other explanations of the bifurcated toxicity data at high TPH/foc include the possibility that something other than hydrocarbons is driving the toxicity, or that most of the TPH hydrocarbons that persist in many urban harbor sediments are too big to permeate into biological membranes. Very little is known about the size constraints of solutes with respect to their ability to affect membrane narcosis, especially for less rigid elongated hydrocarbons that comprise a high fraction of the UCM.

Another way to examine the relationship between TPH levels and amphipod mortality is to simply plot mortality vs. total concentration of TPH/UCM (Figure 2.5). While there is a high degree of variability in the relationship seen in this figure, there is a tendency for more oiled sediments to be more toxic. In the most heavily oiled sediments (TPH > 980 µg/g), there is significant toxicity reported in 59% (n=27) of the sediments; and toxicity was less frequently observed (26%; n=19) in samples that had TPH levels less than 980 µg/g. The increase in toxicity that is generally found with increasing TPH is consistent with a hypothesized narcosis based effect of some components of TPH. However, the lack of toxicity found in some of the highest TPH concentration sediments is contrary to initial expectations. In addition to possible explanations for these results provided above, it is also possible that in these high UCM sediments that amphipods are able to avoid exposure to the hydrocarbon contaminated sediments if it is patchy (e.g., small tar balls or even asphalt particles (however, it should be mentioned that three sediments in this study were sieved to see whether extracted oil was more associated with large particles, and in those cases there was no evidence for such an effect), either due to localization/patchiness of oil contamination, or that amphipods are able to survive for 10 days with little ingestion of sediment

*UCM composition and relationship to *Ampelisca abdita* toxicity*

The composition of the UCM in high TPH samples (> 980 µg/g) samples that were toxic was compared to the UCM composition of non-toxic samples of the same concentrations. We found that the UCM composition from each group (toxic and non-toxic) was quite variable but qualitative differences between the toxic and non-toxic

sediments were noted. The non-toxic samples appeared to generally be characterized as often having much lower abundances of lower molecular weight (LMW), early eluting, more volatile, and more soluble hydrocarbon components. This is shown in the GC/FID chromatograms where the portion of the chromatograms (retention time < 20 mins) that contains these LMW compounds in the toxic samples is much more pronounced. To investigate this hypothesis, we divided the area of UCM chromatogram which is spread over a 60 min chromatogram in four sections, a 10-20 min, 20-30 min, 30-40 min and 40-50 min (Figure 2.6). With increasing GC retention time there is a tendency for hydrocarbon solubility, volatility, and probably bioavailability and toxicity to decrease with a corresponding increase in molecular weight or average carbon. As predicted by Raoult's Law calculations (for which aqueous solubility is a function of mole fraction when a hydrocarbon phase is present), high UCM samples which possessed a greater proportion (not concentration) of earlier eluting more soluble hydrocarbons were more than twice as likely to toxic in the amphipod test as is shown in Figure 2.6. Using a histogram which compared the four sections mentioned previously to the proportion of the total UCM area (calculated as a fraction) between toxic and non-toxic sites. Only the 10-20 min section was significantly different between toxic and non-toxic sites ($p = 0.04$, student's t-test) (Figures 2.7b and 2.7c), further evidence that the LMW section lends more to toxicity. While these differences in average composition are clearly not pronounced, the results presented in Figures 2.6 and 2.7 would be consistent with lower boiling hydrocarbons being some combination of more bioavailable or better able to partition into and disrupt cell membranes and that the presence of these hydrocarbons can determine whether the sediment UCM will cause toxicity in the amphipod toxicity tests.

Previous research has demonstrated that the LMW UCM compounds desorb much more readily than the bulk of the UCM that elutes at later retention times on gas chromatographs (LeBlanc, 2001).

Composition of UCM in GC-FID chromatographs and implications for likely sources of hydrocarbons

GC- FID traces of the TPHs show that the UCM distribution is typical of petroleum contaminated sediments. The shape of the UCM was generally similar depending on the basin that they were sampled from (Jamaica Bay (JB), Newark Bay (NB), Raritan Bay (RB) or Upper harbor (UH)) (Figure 2.8). Comparisons were made between the UCM patterns in the analyzed sediments to a diesel oil and lubricating motor oil chromatograms (Figure 2.9) for comparison. Some of the Jamaica Bay samples exhibited a bimodal UCM distribution which was attributed to pollution by light and heavy petroleum fractions (weathered diesel oil or potential jet fuel from airport operations at nearby JFK International Airport, as indicated by a UCM range of n -C₁₁ to n -C₂₄ and motor oil indicated by a UCM range of n -C₁₆ to n -C₄₀ (Frysinger et al., 2002). Many Newark Bay chromatograms displayed a raised hump in the 10- 20 minute area (Figure 2.8c) with a peak mode in the chromatograms around 34 minutes on the 60 minute long chromatogram. The UCM humps in Newark Bay sample chromatograms was generally not bimodal as was sometimes exhibited by the Jamaica Bay extracts (Figures 2.8a and 2.8b), but they too had similar carbon ranges indicative of light and heavy oil contamination (Colombo et al, 1989). This result is expected because these lower eluting compounds were found in the Newark Bay tributaries, Arthur Kill and Kill

Van Kull, where the lighter #2 and #6 fuel oil spills have been documented (Gunster et al., 1993). The Upper Harbor samples did not exhibit nearly as much early eluting material as in Jamaica Bay and Newark Bay. The chromatograms from this basin (Upper Harbor) were generally void of the early eluting material and also had a maximum height at approximately 34 minutes and a carbon range $n\text{-C}_{16}$ to $n\text{-C}_{40}$. This was very similar to the UCM from used motor oil which also had a maxima around 34 minutes and did not have a broad UCM, but did have a similar carbon range (e.g., compare Figure 2.9b to 2.9c and even the synthetic oil in 2.9d). The RB samples had generally low concentrations except for one sample (RB211) which may be affected by a point source, or perhaps have a small amount of asphalt or a tar ball that was over sampled in that project; these latter hypotheses are based upon the fact that our aliquot of sample of RB211 yield higher levels of TPH than the value of TOC reported by EPA (Adams, et al., 1998). The chromatograms of other RB samples were barely above the baseline and were similar to those of blank extracts.

Composition of UCM in GC×GC chromatographs and implication for likely sources of hydrocarbons

Two-dimensional GC×GC chromatograms for a selected Newark Bay sediment extract from the harbor and a diesel fuel sample are presented in Figure 2.10, showing many hundreds to thousands more resolved peaks over the two dimensional plane are displayed. The concentration patterns of alkanes, isoprenoids and petroleum biomarker peaks in the sediment were identified by comparing them to chemical standards and potential source materials including no. 2 fuel oil and diesel oil that were previously run

on the instrument. Some of the peaks were also identified depending on the elution pattern that homologous groups of compounds display. Figures 2.10a and 2.10b show a GC-FID and GC×GC-FID chromatograms respectively for a representative Newark Bay UCM extract (NB211). The comparison of the two GC×GC chromatograms in figure 2.10, indicate that the sediments in Newark Bay were widely contaminated by lighter fuel oils (note diesel fuel and number 2 Fuel Oil are essentially the same range of products with different tax structures). UCM extracts from the Upper Harbor basin were also compared to standard diesel oil and motor oil two dimensional chromatograms and they further reinforce the findings done by “hump-fitting” that suggests that for most of the Harbor Complex outside of the area around Newark Bay, and selected samples in Jamaica Bay, that the composition of TPH or UCM in sediment extracts are generally consistent with that of motor oil derived contaminants. The GC×GC was able to show that the motor oil contaminated sediment was comprised of more saturated alkanes and were depauperate in aromatic components (chromatograms analyzed at Woods Hole but not presented in this thesis). It is known that used motor oil does accumulate low amounts of PAHs through a combination of vapor transport from the fuel and from high temperature combustion.

*Composition of UCM in GC×GC chromatographs and implication for cause of
Ampelisca abdita toxicity*

GC×GC chromatograms of UCM extracts from representative samples were also qualitatively related to the amphipod toxicity data. The chromatograms in Figure 2.11 are displayed as peaks instead of color intensity as is shown in the previous GC×GC

chromatograms. The Newark Bay sediment that was highly toxic (>60% mortality) had much less molecular weight (LMW), more volatile compounds and more soluble compounds. These compounds should be more bioavailable to benthic organisms through sediment ingestion and/or contact, and therefore would contribute to high body burdens and consequently narcotic toxicity. Some samples were highly contaminated with UCM hydrocarbons did not cause any significant toxicity. This group of non-toxic sediments had a UCM composition that was different from the highly toxic samples containing more saturated compounds, less aromatics and less LMW compounds than more toxic sediments. The GC×GC was also used to identify crude oil biomarker compounds (hopanes and steranes) and PAHs in the sediment extracts.

Composition of PAHs and their implications for sources of hydrocarbons

PAH distribution can give a general understanding of hydrocarbon sources (petrogenic or pyrogenic) and their degree of weathering. Petrogenic PAHs (containing three or less aromatic rings with a high proportion of alkylated homologues) and pyrogenic PAHs (parental compounds with four or more aromatic rings) were both detected in the sediments.

The samples analyzed had varying concentrations of total PAHs (sum of 25 PAHs in table 2.2), ranging from undetectable to 19.5 µg/g dry wt. These concentrations were generally high compared to concentrations observed in other studies (Readman et al. 2002 and references cited therein). The highest PAH concentrations were analyzed from sites in the New York/New Jersey Harbor that are most heavily industrialized and urbanized. Figure 2.12 shows the distribution of PAHs in the sediment extracts from each

of the 46 sites sampled. PAHs range from left to right, progressing from the lightest aromatics (naphthalenes and the substituted naphthalenes) to the heaviest ((dibenzo (A, H) anthracene). Clearly, the most abundant PAHs in most samples are 4-ring PAHs that include pyrene, benzanthracene and chrysene.

To further assess the sources of hydrocarbons to the sediments, two hydrocarbon distribution indexes that have been used to identify likely sources of PAHs in marine sediments (LeBlanc, 2001; Boehm et al., 1982) were calculated: (1) the sum of all methyl phenanthrenes: phenanthrene ($\Sigma\text{MPHE}/\text{PHE}$) ratio and (2) the phenanthrene: anthracene (PHE/ANTHRA) ratio. A ($\Sigma\text{MPHE}/\text{PHE}$ ratio <2 and a PHE/ANTHRA ratio <10) was calculated for the almost all of the sites where PAH data was available and this is usually indicative of PAHs that are of pyrogenic origin. This pattern, in addition to the tPAH concentrations for all the sites (Table 1) is typical of what is observed in coastal sediments in urbanized areas as the result of chronic, low level input of PAHs (Readman et al., 2002). Some sites in Newark Bay and Jamaica Bay were dominated by the presence of naphthalenes and some of the LMW PAHs further reinforcing the argument that these sites were likely impacted by fresh inputs of fuel oil range petroleum hydrocarbons. The composition of the PAH in the majority of the samples was dominated by the pyrogenic compound pyrene and other 4-ring PAHs in a pattern that is indicative of combustion or creosote contamination (Peven et al., 1996).

The data obtained suggests that total petroleum hydrocarbons in the harbor were derived from mixed sources. This finding is further reinforced by the lack of correlation between the TPHs and the PAHs ($r^2 = 0.0825$) (Figure 2.2). The petrogenic contamination of the harbor complex is most likely a result from oil and petroleum

contamination from ships, direct sewage, CSOs and industrial inputs. The extensive burning of fossil fuels associated with urban areas is also a potential hydrocarbon source, especially PAHs (Choiseul *et al.*, 1998). The pyrogenic signature results from sources like automobile soot from industrial processes entering the marine environment as a result of aeolian influence. A previous study by Lake *et al.* (1979), mentioned in Choiseul *et al.* (1998) calculated estuarine hydrocarbon sources as 80% from combustion and 20% from used motor oil. However, outside of Newark Bay samples, and a few samples in Jamaica Bay, our results are in agreement with several other studies showing that urbanized coastal sediment hydrocarbons look a lot like used motor oil (Hoffman *et al.*, 1984; Hoffman and Quinn, 1979).

Table 2.1. Site locations, sedimentary TOC,TPH, PAH concentrations and % mortalities.

STATION	TOC (%)	Σ TPH (µg/g)	Σ PAH (µg/g)	% mortality
1. JB008	6.35	3250	1.56	38
2. JB033	4.52	672	0.601	100
3. JB042	0.22	393	0.202	0
4. JB043	0.19	354	0.0290	11
5. JB203	7.05	3290	0.800	8
6. JB204	4.90	1510	1.24	23
7. JB206	3.18	1340	3.25	3
8. JB210	0.47	463	0.0794	12
9. JB211	0.57	320	0.0495	27
10. JB215	1.86	1280	0.130	61
11. JB216	0.34	90	0.000	57
12. JB223	3.53	1370	0.950	86
13. NB203	2.55	1420	2.44	100
14. NB204	2.00	825	4.52	16
15. NB207	0.76	2240	8.81	68
16. NB210	0.59	333	1.91	88
17. NB211	2.52	5120	4.83	98
18. NB212	2.38	2890	6.58	21
19. NB216	3.54	289	0.0776	1
20. NB217	1.15	1630	6.24	8
21. NB218	1.52	2270	1.76	10
22. NB222	3.03	1550	7.47	29
23. NB223	3.83	7400	6.15	79
24. NB224	2.18	1370	2.01	79
25. NB227	1.74	678	14.6	66
26. NB231	2.43	5840	0.131	35
27. RB007	0.53	290	0.193	0
28. RB019	3.29	360	5.88	0
29. RB202	0.82	690	0.347	0
30. RB211	0.34	6550	1.24	0
31. RB213	0.56	180	0.0934	0
32. RB216	2.29	25	1.20	0
33. UH003	3.29	1810	1.19	1
34. UH010	3.89	2760	13.5	74
35. UH011	5.98	750	8.08	5
36. UH014	1.45	1240	0.0314	0
37. UH018	5.25	2820	1.97	0
38. UH020	5.66	12600	0.833	87
39. UH023	2.61	7360	11.8	0
40. UH029	2.27	103	0.710	0
41. UH030	0.65	251	0.392	0
42. UH204	1.79	236	0.477	1
43. UH206	10.30	7080	19.5	98

STATION	TOC (%)	Σ TPH (µg/g)	Σ PAH (µg/g)	% mortality
44. UH211	3.02	3470	0.242	4
45. UH213	1.83	4530	1.61	1
46. UH214	2.08	1040	2.77	38

Table 2.2. List of 25 Polycyclic Aromatic Hydrocarbon compounds measured by the REMAP sampling regime.

COMPOUND	SYMBOL	# OF RINGS	MOLECULAR WEIGHT
1. NAPHTHALENE	NAPH	2	128.2
2. 1-METHYLNAPHTHALENE	MENAP1	2	142.2
3. 2-METHYLNAPHTHALENE	MENAP2	2	142.2
4. ACENAPHTHYLENE	ACENTHY	3	152.2
5. ACENAPHTHENE	ACENTHE	3	154.2
6. BIPHENYL	BIPHENYL	2	154.2
7. 2,6-DIMETHYLNAPHTHALENE	DIMETH	2	156.2
8. FLUORENE	FLUORENE	3	166.2
9. 1-METHYLPHENANTHRENE	MEPHEN	3	170.3
10. 2,3,5-TRIMETHYLNAPHTHALENE	TRIMETH	2	170.3
11. ANTHRACENE	ANTHRA	3	178.2
12. PHENANTHRENE	PHENANTH	3	178.2
13. FLUORANTHENE	FLUORANTH	4	202.3
14. PYRENE	PYRENE	4	202.3
15. BENZ(A)ANTHRACENE	BENANTH	4	228.3
16. CHRYSENE	CHRYSENE	4	228.3
17. BENZO(A)PYRENE	BENAPY	5	252.3
18. BENZO(E)PYRENE	BENEPY	5	252.3
19. BENZO(B)FLUORANTHENE	BENZOBFL	5	252.3
20. BENZO(K)FLUORANTHENE	BENZOKFL	5	252.3
21. PERYLENE	PERYLENE	5	252.3
22. BENZO(G,H,I)PERYLENE	BENZOP	6	276.3
23. INDENO(1,2,3-C,D)PYRENE	INDENO	6	276.3
24. DIBENZO(A,H)ANTHRACENE	DIBENZ	5	278.3
25. HEXACHLOROBENZENE	CL6BNZ	1	284.8



Figure 2.1. Map of sediment sampling sites in the New York-New Jersey Harbor Complex. JB = Jamaica Bay, NB = Newark Bay, RB = Raritan Bay and UH = Upper Harbor.

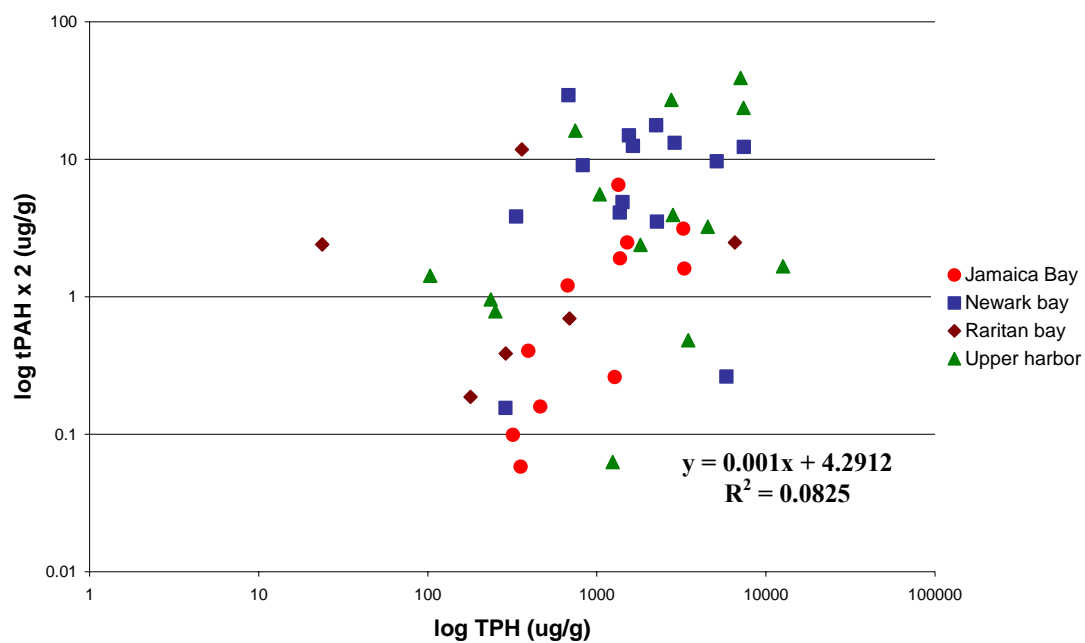


Figure 2.2. Total PAHx2 against TPH concentration.

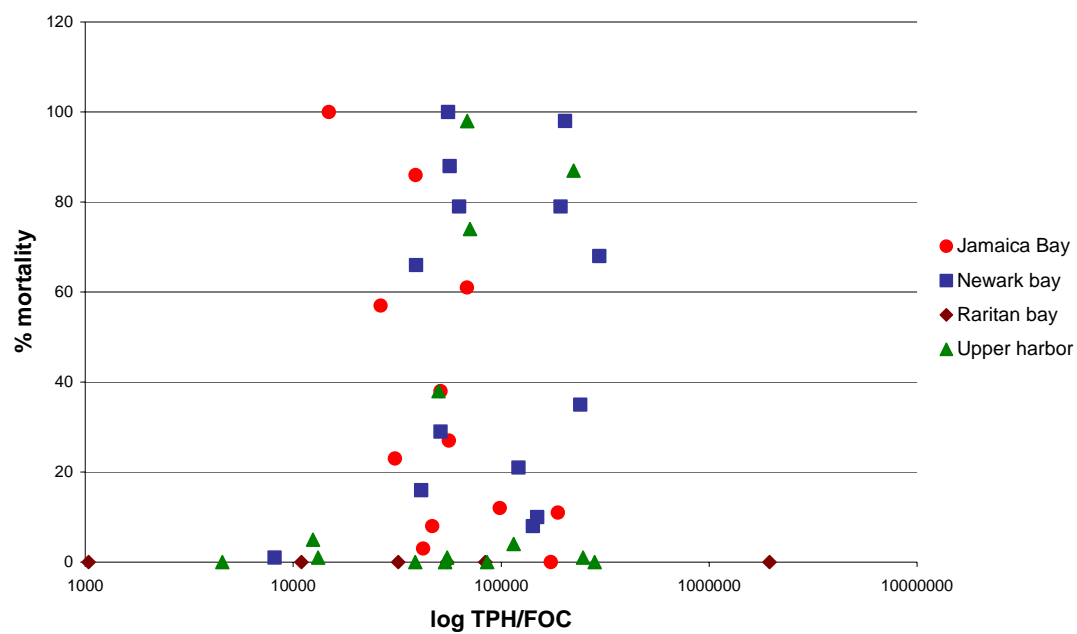
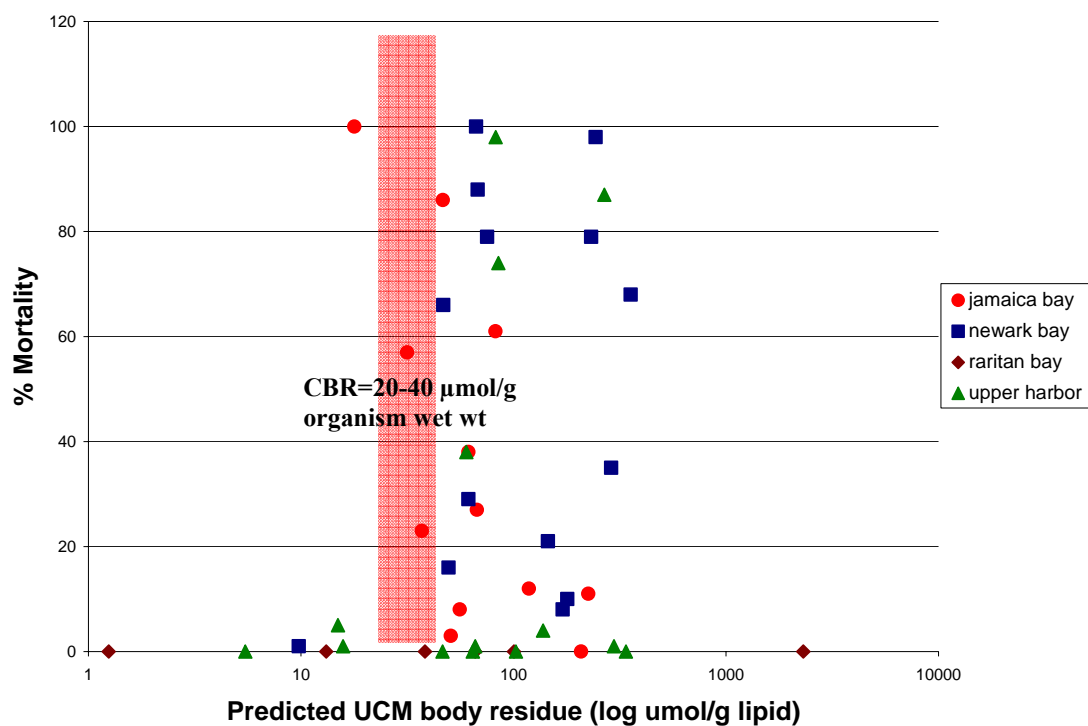


Figure 2.3. % *Ampelisca abdita* mortality against TPH normalized to FOC.



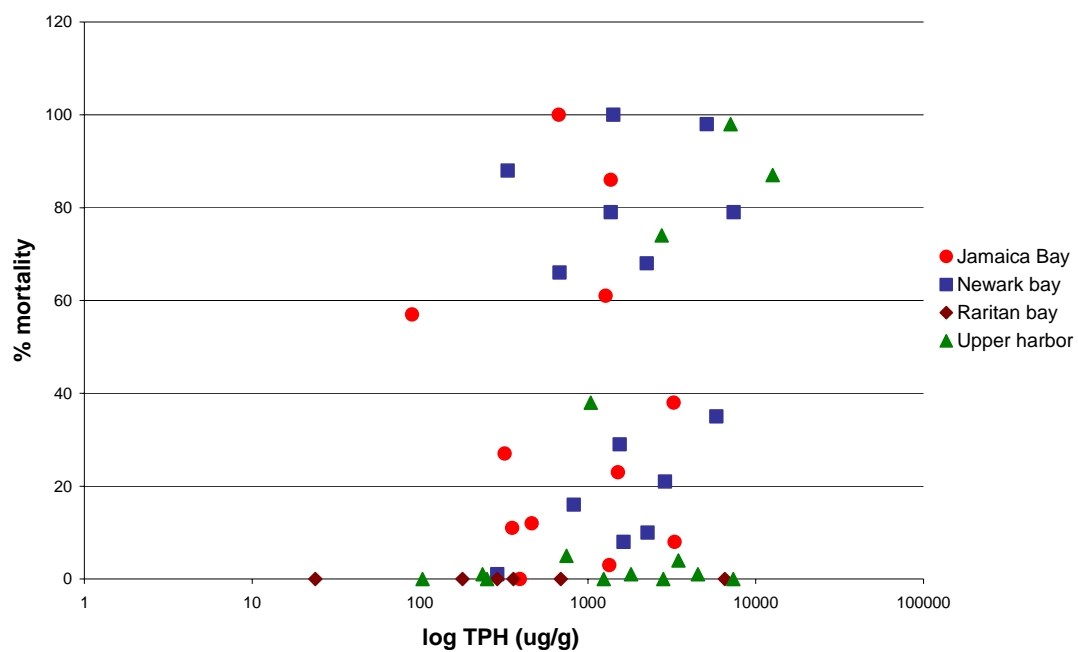


Figure 2.5. % *Ampelisca abdita* mortality against TPH concentration.

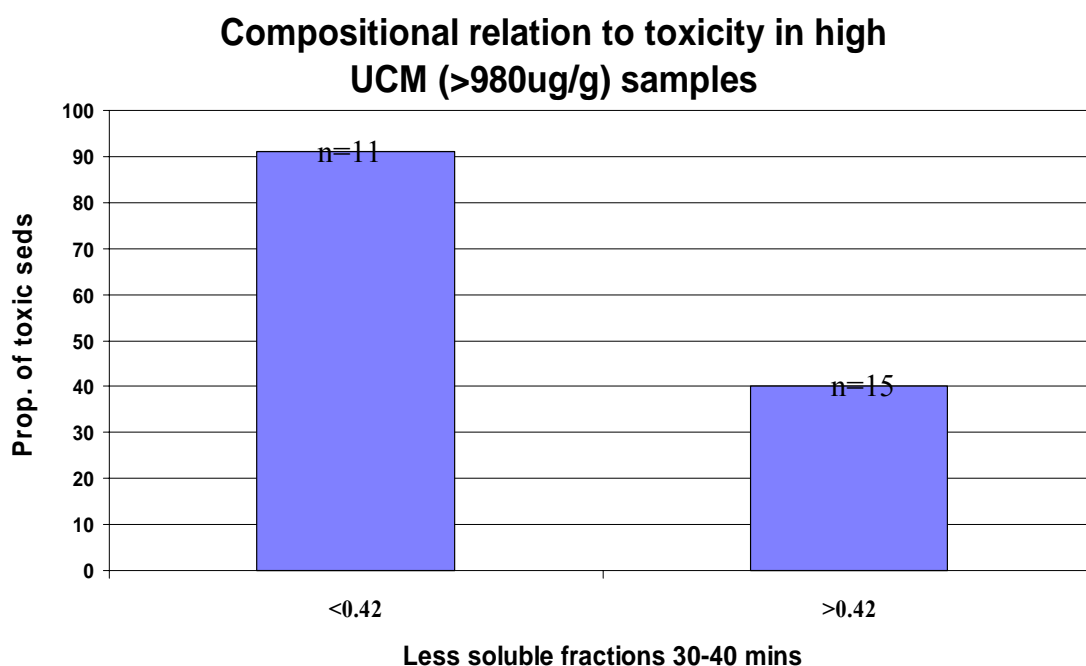
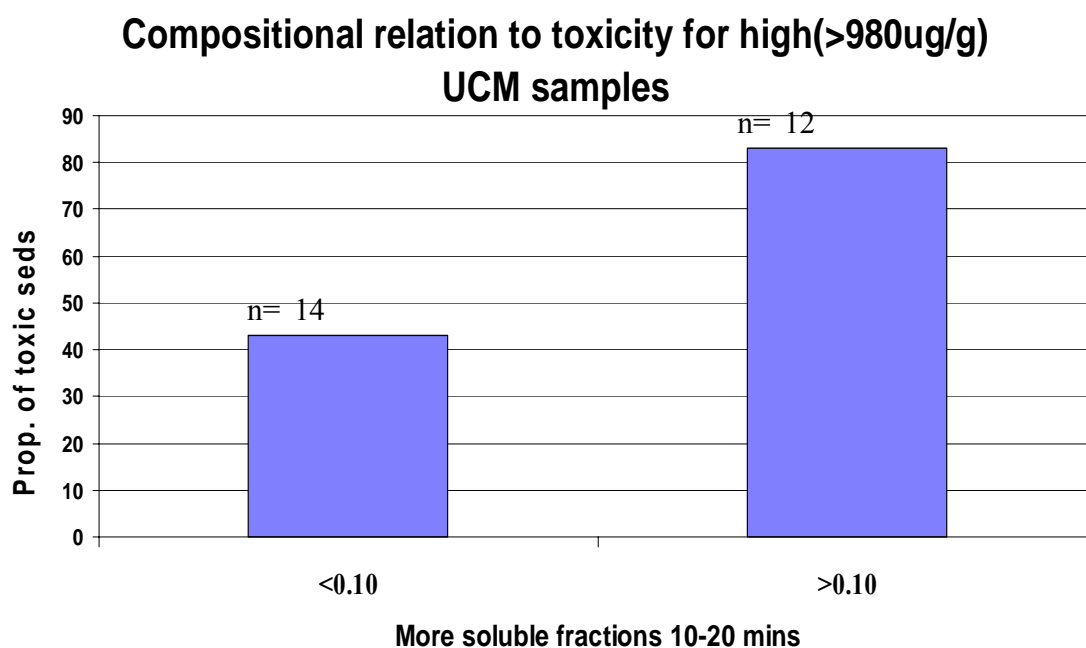
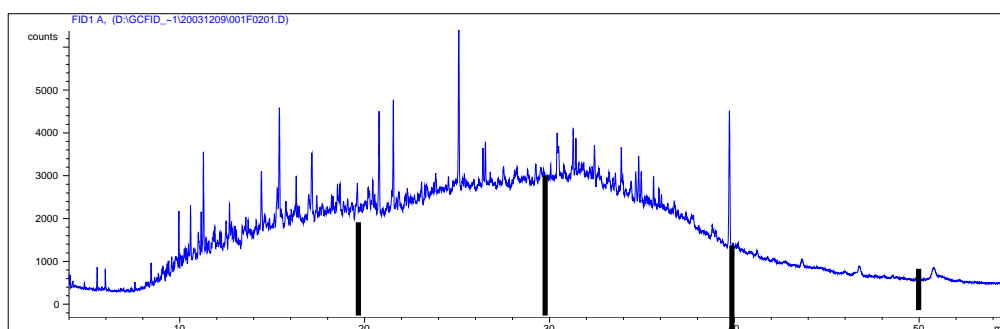


Figure 2.6. The frequency of early eluting (10-20 min) UCM fractions being associated with amphipod mortality for high TPH samples >980 (a); and similarly, the frequency of less soluble and bioavailable UCM fractions (30-40 min) being associated with amphipod toxicity (b).

(a)



(b)

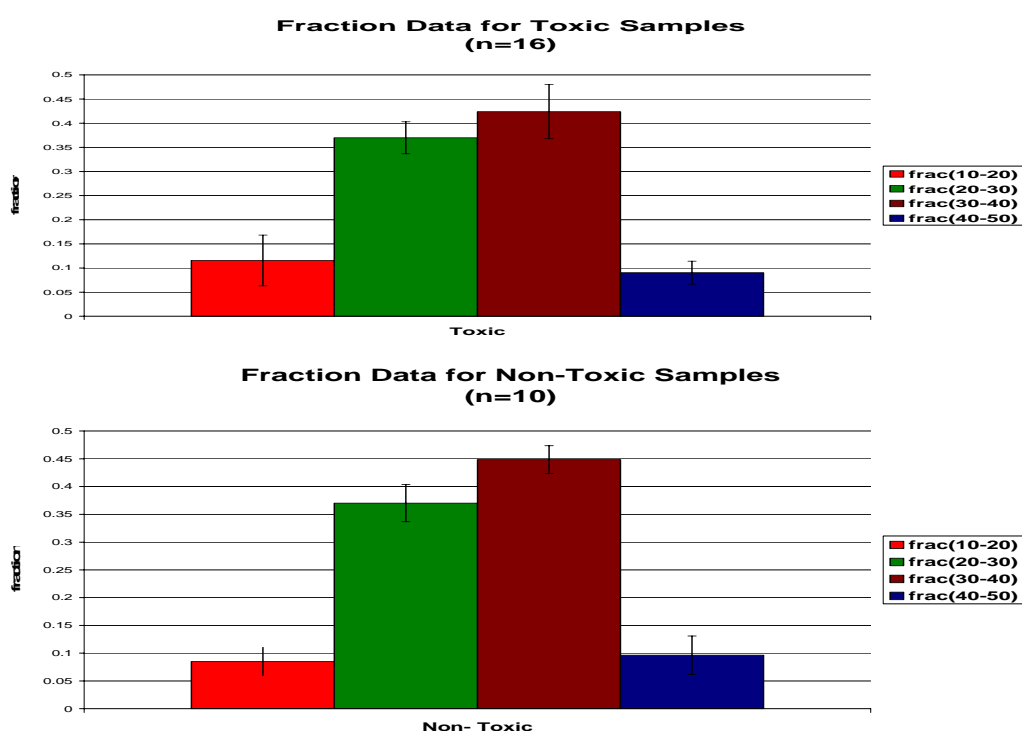
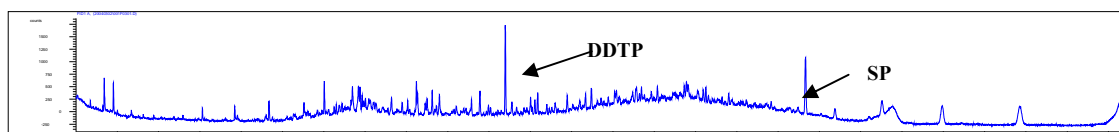
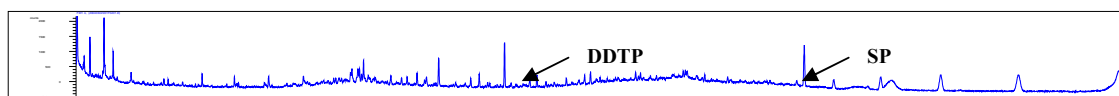


Figure 2.7. (b) Histograms comparing the contribution to toxicity of four different fractions of the GC/FID chromatograms (a) in samples containing TPH >980 µg/g. The figures show that the 10-20 minute fraction containing the LMW compounds was the only fraction significantly different between toxic and non-toxic samples ($p=0.0490$).

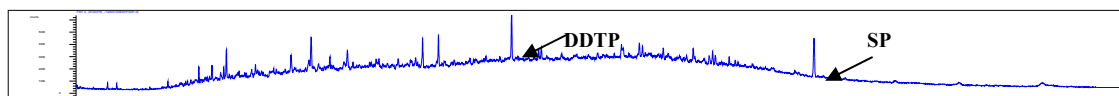
a) JB043



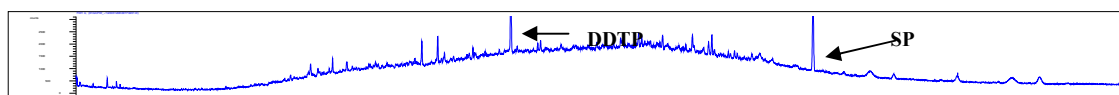
b) JB210



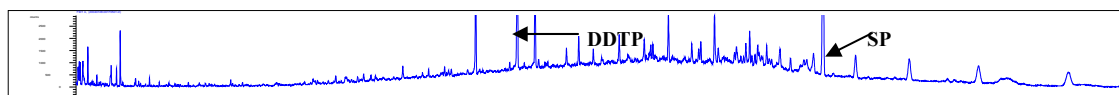
c) NB211



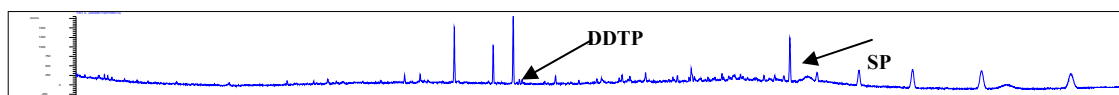
d) NB207



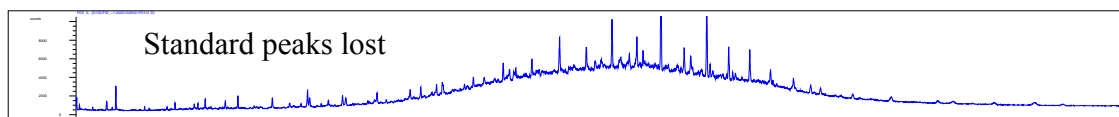
e) RB213



f) RB007



g) UH020



h) UH206

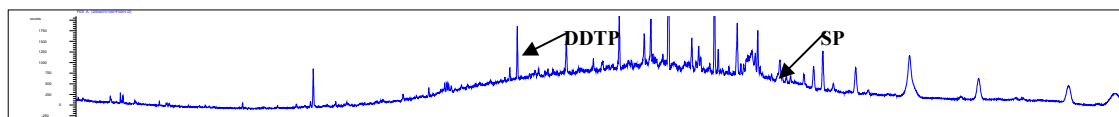
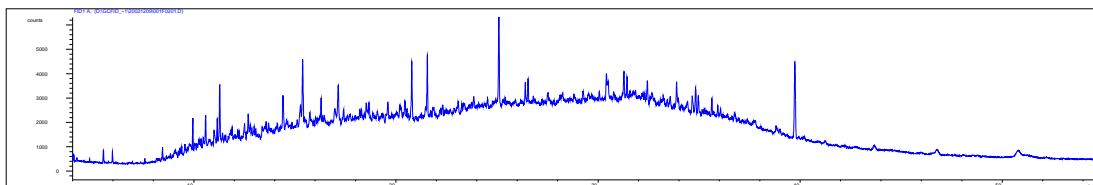
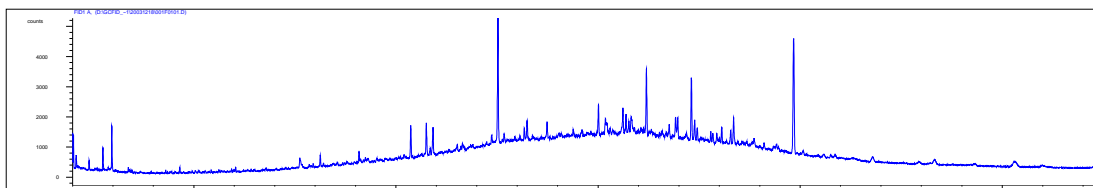


Figure 2.8. Characteristic GC/FID traces of extracts from the four sampling basins. Arrows indicate standard peaks (a) and (b) Jamaica Bay, (c) and (d) Newark Bay, (e) and (f) Raritan Bay, and (g) and (h) Upper Harbor.

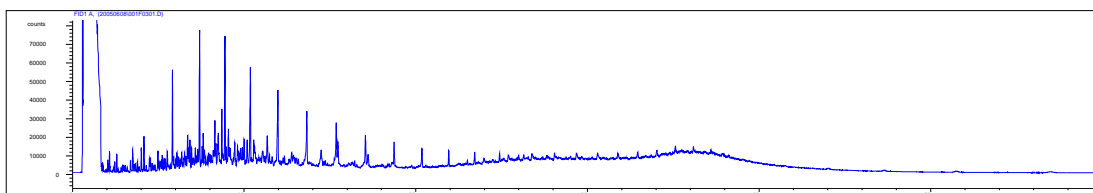
a) Newark Bay Sediment



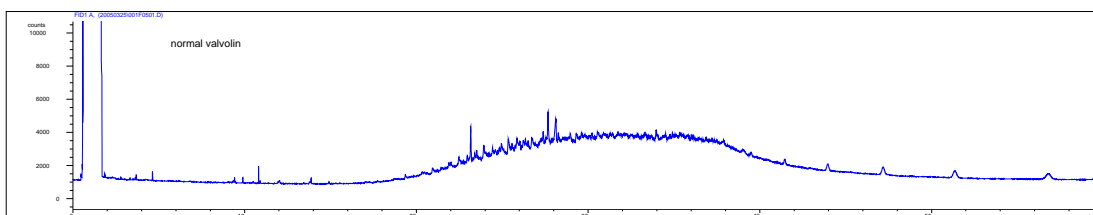
b) Upper Harbor sediment



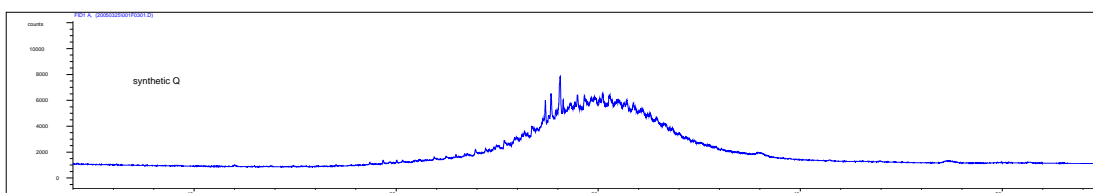
c) Diesel Standard



d) Valvoline 10W-30



e) Synthetic Q 5W-30



f) Synthetic Mobil 5W-30

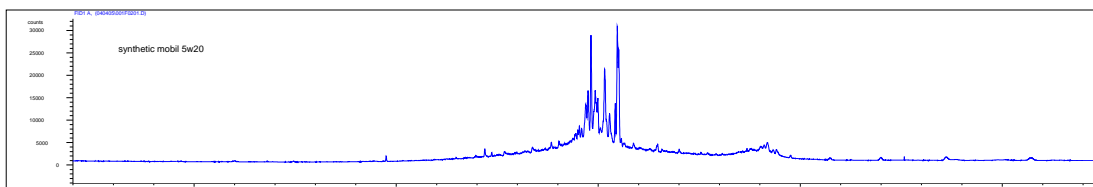


Figure 2.9. Comparison of UCM in selected sediments to petroleum standards and motor oils

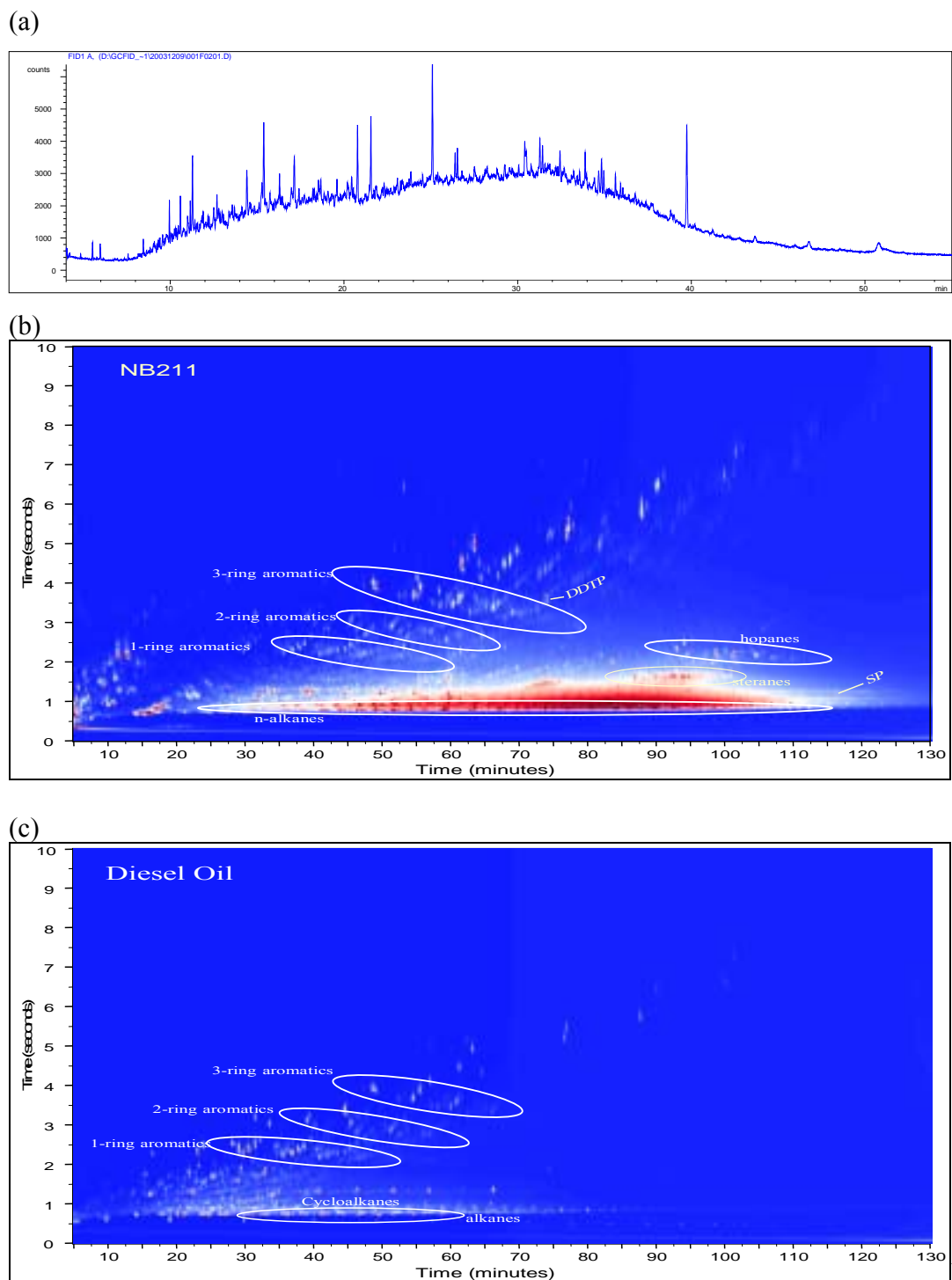
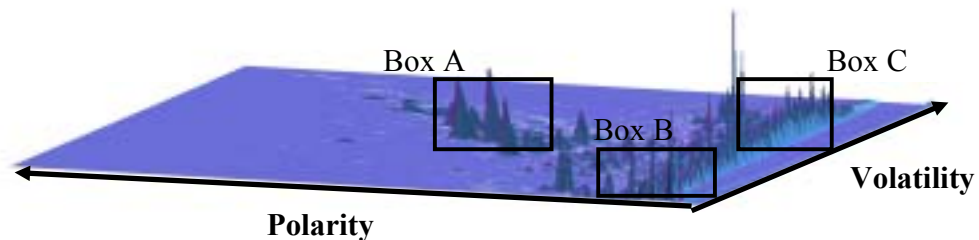
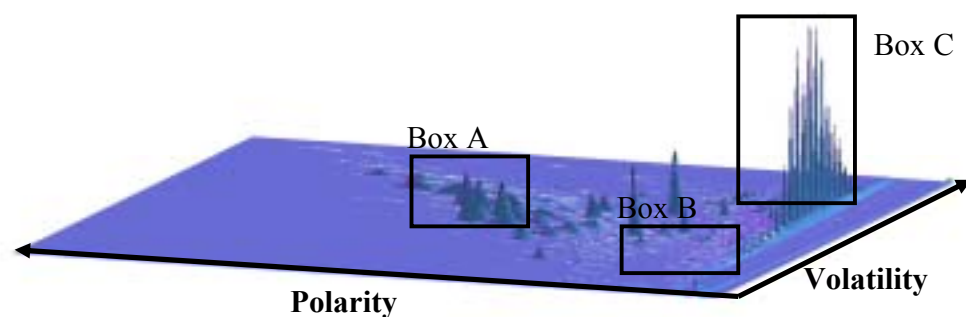


Figure 2.10. Gas Chromatogram (a) and GC×GC chromatogram (b) of a Newark Bay sediment extract. The GC×GC of diesel fuel (c) is shown for comparison. In the GC×GC chromatogram, the x-axis is the first dimension volatility-based separation. The y-axis is the second dimension polarity-based separation. The z-axis is FID response. Background color is blue, minor peaks are white, and larger peaks range from red to black.

(a) NB211- toxic



(b) UH213- non-toxic



(c) UH023-non-toxic

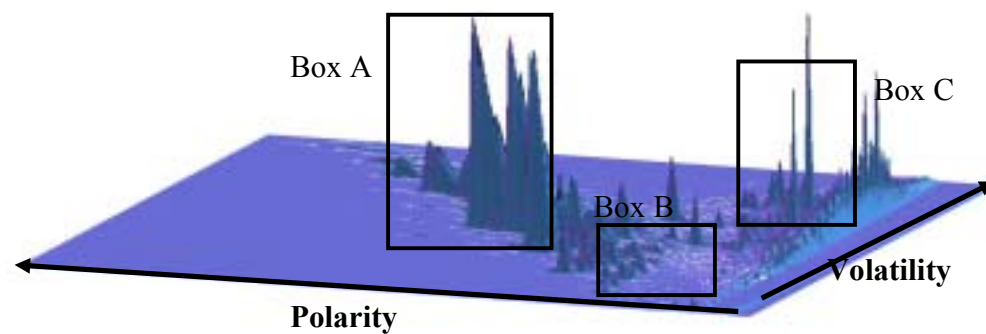


Figure 2.11. GC×GC chromatograms of three harbor sediment extracts. Each sample represents a typical UCM distribution for the sediments. (a) This is characteristic toxic sediment. (b) and (c) are two characteristic chromatograms of non-toxic sediments. Box A represents the area where PAHs elute, Box B displays LMW hydrocarbons and Box C displays the HMW hydrocarbon fraction. The x-axis separates based on volatility and the y-axis separates on polarity. The FID response is shown as peaks.

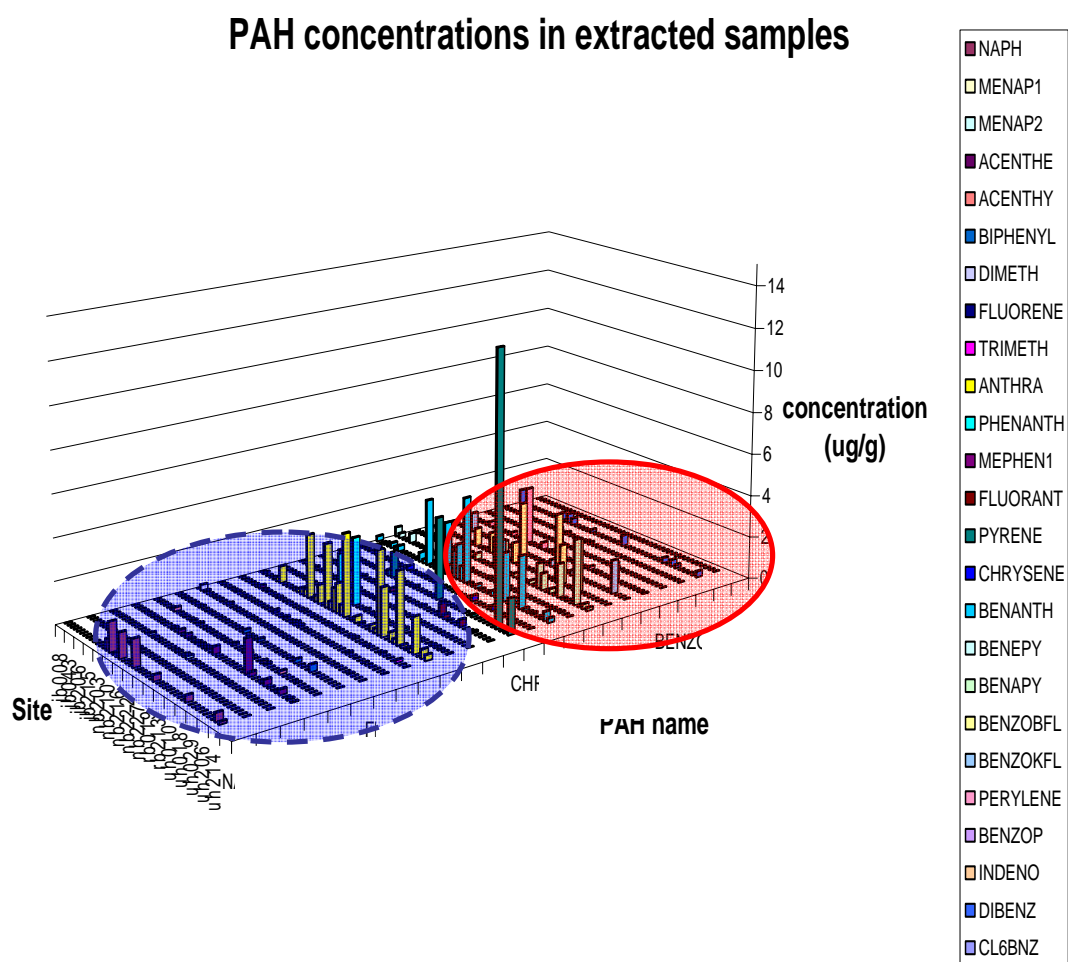


Figure 2.12. PAH signature of the extracted samples. The area encircled with dashes represents petrogenic PAHs while the area encircled by a solid line is pyrogenic. This figure shows that the NY/NJ harbor is impacted by mainly prolific PAHs.

CHAPTER 3

Bioaccumulation of the Unresolved Complex Mixture in New York-New Jersey

Harbor sediments

Introduction

The unresolved complex mixture (UCM) of petroleum derived hydrocarbons, found in extremely high concentrations in urban harbor sediments and in benthic organisms, have recently been shown to be toxic to *Mytilus edulis* in some urban coastal settings (Rowland et al., 2001), but until recently the UCM has been neglected in the assessment of sediment toxicity and bioaccumulation. It is hypothesized that a portion of the UCM is bioaccumulated by benthic organisms and could contribute significantly to the overall body burden of narcotic chemicals (Chapter 2).

The hydrocarbons making up the UCM have been generally considered to be unreactive and not of environmental concern, except as a marker for weathered oil, which may contain toxic compounds such as polycyclic aromatic hydrocarbons (PAHs). However, this view of the UCM is changing. A recent study by Neff et al., (2000) on the toxicity of weathered crude oils could not account for all of the toxicity based upon the mass of known toxic components in the oil (such as PAH compounds and phenols). These authors suggested that compounds associated with the UCM might account for the extra toxicity. GoldBouchot et al. (1995) found a strong correlation between body residues of UCM and histopathological lesions found in the oyster *Crassostrea virginica* collected from three Mexican coastal lagoons. More direct evidence of UCM toxicity comes from the work of Rowland and coworkers. They have shown that monoaromatic

UCM components (Rowland et al., 2001) and a series of synthesized cyclohexyltetralin compounds (Smith et al., 2001) that are structurally related to monoaromatic UCMs, cause a toxic response in *Mytilus edulis* in aqueous exposures. The concentrations of the monoaromatic UCM (100-500 µg/g dry wt) that caused a reduction in *Mytilus* filtration rates in the laboratory were very similar to concentrations found in field collected mussels that had a reduced scope for growth (Rowland et al., 2001).

Most of the UCM in sediments consists of saturated hydrocarbons that are less soluble than aromatic fractions. Saturated UCM components were not toxic to *M. edulis* in aqueous exposures (Thomas et al., 1995), although chemical oxidation of the UCM enhanced hydrocarbon solubility and these products did elicit a reduction in filtration rate in *M. edulis*. It was argued that such oxidized UCM products might be important from an ecotoxicological perspective due to UCM oxidation in the environment as well as by oxidation in engines prior to release in the environment. It is known, however, that the saturated fraction can be accumulated by animals from environmental exposures. In mussels collected from the east coast of the United Kingdom, nonaromatic UCM was significantly accumulated (up to 3610 µg/g dry wt), to levels much higher than the monoaromatic UCM fraction (Rowland et al., 2001). It has also been hypothesized that deposit feeding invertebrates that possess high levels of gut surfactancy are at greatest risk to accumulate hydrocarbons that are otherwise difficult to desorb from sediments, because their gut fluids contain surfactants known to be effective at solubilizing sparingly soluble hydrophobic contaminants (Ahrens et al., 2000; Mayer et al., 2001), such that high molecular weight petroleum hydrocarbons may be bioaccumulated even if not very soluble in sediment pore water.

Even if these poorly soluble UCM compounds are only slightly available for uptake by organisms, they can be important contributors to the hydrocarbon body burden and narcotic-based toxicity. Narcotic toxicity is nonspecific and additive for mixtures of accumulated hydrocarbons. Narcosis is caused by the disruption of cell membrane function due to the fluidization of membranes from hydrocarbons partitioning into the lipid bilayer (McCarty et al., 1992). Narcosis based critical body residues (CBR) are reported to generally fall in a range of 2-8 $\mu\text{moles/g}$ organism wet weight, although CBR estimates lower than this range were measured in the amphipod *Ampelisca abdita* (0.5 - 1.1 $\mu\text{mol/g}$ wet wt; Fay et al., 2000; Nannen, 2001; Du, 2004).

In a review of published data on the UCM bioaccumulation, LeBlanc (2001) found many reports (mostly in bivalves) of bioaccumulated UCM in the range of 0.02 - 7.2 $\mu\text{mol/g}$ wet tissue. Organisms and sediments have been analyzed for total UCM at five sites in the NY Harbor complex (LeBlanc, 2001); significant UCM bioaccumulation (0.1-1.0 $\mu\text{mol/g}$ wet wt, assuming a average molecular weight of 250 for UCM compounds) was measured in the filter feeder *Mulinia lateralis* and in several deposit feeders, *Yoldia limatula*, *Pectinaria gouldii*, and *Cirratulus sp.*

In this study we attempt to relate the concentrations and compositions of the UCM accumulated in tissues of *Nereis succinea* that have been exposed to sediments collected near known point sources (CSOs) in the Harbor Complex. Field collected organisms were also analyzed in order to see if accumulation in the field was similar to what was observed in the laboratory exposed organisms. This field study was conducted to better determine the sources and distributions of UCM hydrocarbons in sediments in areas receiving extensive inputs from combined sewer overflows (one site next to a big

outfall in an inlet in the East River, and in Bowery and Flushing Bays) as well as possible inputs from the vicinity of LaGuardia Airport bounded by Bowery Bay, Flushing Bay and the western head of Long Island Sound that connects to the East River, an area often referred to as the Narrows. As part of this work, we examined the accumulation of hydrocarbons in benthic polychaetes and filter feeding mollusks collected in oil contaminated sediment, and also in polychaetes (*Nereis succinea*) collected from a reference site relatively free of hydrocarbons and exposed to some of these sediments, to test for bioaccumulation and effects on organism growth and acute mortality in ten-day lab exposures.

Material and Methods

Sediment Collection

Surface sediments (0-2) were collected using a modified Van Veen grab sampler (0.04 m²) from sites within the New York Harbor complex. Multiple grab samples were collected at each site, pooled, and sediment not used for sediment chemistry analysis was sieved through 250 µm stainless steel sieves, the animals sorted by approximate species, rinsed with clean seawater, and left to depurate in glass jars containing a large excess of seawater and placed in a cooler for approximately 8- 14 hours. In the laboratory, species were then identified and separated under a dissecting microscope and further cleaned to remove small amounts of sediment and feces. Samples for chemistry were sieved to 1 mm, placed into solvent rinsed jars and transported on ice back to the Marine Science Research Center (MSRC) and stored in the laboratory at + 1°C until analysis.

The field stations included seven sites in Bowery Bay (BB), seven sites in Flushing Bay and one site each near the Williamsburg Bridge (WB), off Rikers Island (RI) and in the East River (Table 3.1 and Figure 3.1). All of these sites were chosen either because of their proximity to large CSOs, or proximity to the hydraulically pumped storm drains that remove precipitation from the runways at LaGuardia. The station sampled closest to a large CSO discharge was WB1 located in an inlet off the East River and tens of feet from a very large CSO outlet. However, the entire area of Flushing Bay is known to be affected by many CSOs and Bowery Bay and the East River sediments identified as being highly affected by direct discharges from municipal wastewater treatment plants as well. It was clear from inspection of sediments that BB2 was very affected by the local CSO (the only site with leaf debris) and that BB1, BB2 and BB3 were influenced more by the CSO than other sites sampled because they were the only sites in Bowery Bay not to have vibrant communities of benthic macrofauna and have a thin oxidized surface layer at the sediment water interface. Also of interest to this study is that station FB6 was taken within a mooring field proximate to large marina. The control sediment used for the laboratory exposure/bioaccumulation tests was collected from a relatively unpolluted site in Flax Pond, in Old Field, NY, a protected on the north shore of Long Island area with very low density housing.

The Williamsburg Bridge (WB) sediment sample was previously determined to have an extremely high UCM concentration (unpublished data). A 25% dilution of this sediment was done in order to represent a less toxic sediment sample than the 100% WB sample. To remove the ammonia and sulfides from pore water, the sediments were rinsed in one or more volumes of clean sea water and allowed to settle by gravity between

washes. The sediments were thoroughly mixed with the seawater and left to settle overnight, and the water was poured off the next day and replaced. 40 grams of each treatment was placed into solvent rinsed 80 mL glass jars and again thoroughly mixed with 50 mL of seawater. The seawater was again poured off, and another 50 mL of clean seawater was added

Organism collection and exposure

The field collected animals analyzed in this study were also obtained in August 2004 from Bowery Bay and Flushing Bay. The polychaetes from BB5 and BB6 stations extracted and analyzed included *Capitella sp.*, *Glycera alba.*, and *Nephtys incisa.*. The filter feeding bivalve *Mulinia lateralis* was collected from several sites in Flushing Bay and analyzed as two samples. Another deposit feeding polychaete, *Nereis succinea* was collected from Flax Pond. Polychaetes from Flax Pond were also used in the bioaccumulation/toxicity experiment. Five worms were exposed to each of six sediments that were selected: Flax Pond, Rikers Island 3, BB 5, BB 6, WB 100% and WB 25%. The jars containing the sediment and 5 worms each had perforated teflon caps and were aerated with an airstone. The worms in each jar were fed 25 mg of ground Purina® cat food on days three and seven of the exposure regime. The sediment ammonia concentration was tested and the water changed before the worms were added to the sediment as well as on days three and seven.

Sediment chemistry analysis

The extraction of sediment was done following a protocol developed by Ferguson et al. (2001). 1-2 g of freeze dried sediment was packed in a 150-mm stainless steel column (4.6-mm i.d.) fitted with 0.5- μ m stainless steel frits (Alltech Chromatography, Deerfield, IL) and spiked with surrogate standard (DDTP). The empty volume in the column was then filled with sea sand that had been baked in a muffle furnace at 450 °C overnight. The packed column was then immersed in a heated ultrasonic bath (30 °C), and dichloromethane (DCM) was pumped through the extraction cell at 0.5-mL/min for 14 min to collect a total sample extract of 7-mL. Blank sediment extractions, consisting of baked sea sand spiked with surrogate standard and packed into extraction columns, were performed alongside actual samples to determine extraction efficiencies. The collected extract was then blown down under a gentle stream of nitrogen, solvent exchanged to hexane and concentrated to 1mL.

Tissue chemistry analysis

All organisms were depurated for at least two hours prior to analysis, rinsed with filtered seawater and stored in solvent rinsed glass vials at -20 °C until analysis. The organisms were stored, extracted and analyzed in pools of 2-10 individuals depending on sites they were sampled from, and species. Tissues were thawed, rinsed with milli-Q water, blotted dry, ground with a mortar and pestle, and a sufficient amount of sodium sulfate (Na_2SO_4) was added to dry the sample. The amount of Na_2SO_4 necessary to dry

the sample depended upon the amount of sample and the amount of moisture in the sample but generally ranged from 1 to 2 g. The tissues were then loaded in Teflon centrifuge tubes, 15 mL of extraction solvent (25% DCM in hexane) was added and spiked with the surrogate standard (DDTP), (bivalve organisms were freeze dried, ground into a fine powder and then loaded into the Teflon tubes. The sample was then homogenized using an Ultrasonic Homogenizer 410 series for 120 seconds at 50% duty cycle. It was then transferred to a GS-GR centrifuge at 15°C and at a speed of 3000 RPM for 10 minutes. After centrifugation the DCM/hexane layer was removed, concentrated to 1 mL under a gentle stream of nitrogen

Purification of sample extracts

Column chromatography was used to clean-up and fractionate both sediment and tissue extracts by passing the extract through a silica column. Silica (100-200 mesh) was activated at 150 °C for at least 4 hrs and then partially deactivated the previous day with 5% water. The chromatography column (1-cm i.d.) was prepared by packing slurry packing 0.5 g sodium sulfate, followed by 4 g of silica and finally another 0.5 g of sodium sulfate in hexane. Elution was performed using 12 mL of hexane/dichloromethane (50:50) to yield a mostly non-polar fraction of aliphatic hydrocarbons and some polycyclic aromatic hydrocarbons (PAHs). The eluent was collected then again transferred to only hexane by concentration of the eluate to approximately 0.5 mL, addition of 2 mL hexane, and concentration to approximately 1.5 mL for sediment extracts, while the tissue extracts were concentrated to 0.25 mL. The

samples were stored in 2mL amber vials with Teflon lined screw caps and spiked with internal standard just prior to injection on the GC.

Calculation of accumulation factors

Biota sediment accumulation factors (BASFs) were calculated using the body burdens of the survivors measured at the end of 10-day exposures for the laboratory organisms exposed to sediments. For comparison, bioaccumulation factors were also calculated for the organisms that were collected from the polluted sites within the harbor. The total petroleum hydrocarbon (TPH) concentration was used as a proxy for UCM concentration in the calculations.

$$\text{BASF} = \frac{(\mu\text{g TPH in organism/g wet tissue}) / (\text{g lipid/g wet tissue})}{(\mu\text{g TPH in sediment/g dry sediment}) / (\text{g organic carbon/ g dry sediment})}$$

$$\text{BAF} = (\mu\text{g TPH in organism/g wet tissue}) / (\mu\text{g TPH in sediment/dry sediment})$$

Results and Discussion

Sediment appearance

When first collected, all the sediments in Bowery Bay and Flushing Bay appeared to be fine-grained muddy sediments. They were very black and silty, producing an oil sheen on the water and having an extremely strong smell similar to diesel fuel. At the

Rikers Island, the sediment was coarser grained and not as dark, but also produced an oily sheen. At this site, relatively fine grained sediment was distributed in patches between areas of cobble and sand. Sediment from the East River near the Williamsburg Bridge was black and also produced an oil sheen on the water. It is of interest to note that the four sites most affected by proximity to large CSOs (BB1, BB2, BB3, and WB1) had extremely elevated levels of both TPH and of TOC in sediments. As mentioned above, not only were sediment grab samples at these sites devoid of visible benthic macrofauna, but they appeared to be anoxic to the sediment-water interface.

Sediment characteristics and UCM distributions

The summary of TPHs in the sediments analyzed is presented in Table 3.1. The extent of TPH contamination found in this study in areas of the East River, and Bowery and Flushing Bays that encompass LaGuardia Airport, was impressive. In the 13 muddy samples analyzed, TPH concentrations varied between 0.9 and 2.6 % by weight, with the very highest levels found in samples nearest to a large CSO discharge point at the head of Bowery Bay. Total petroleum hydrocarbon levels were also greater than 2.5% by weight in sediments collected proximate to another CSO discharge point off of the main stem of the East River (site WB, Table 3.1).

The chromatograms of these extracted sediments, except one in Flushing Bay (FB 3) and the East River were dominated by the UCM which indicates the presence of weathered petroleum (Farrington and Quinn, 1973; NRC, 1985) or used motor oil. The

Williamsburg bridge sediment was particularly noteworthy because of its exceptionally high TPH concentration (26,600 µg/g). The UCM pattern in the almost all of the sediment extracts was similar and resembled that of used motor oil indicating the presence of significant oil pollution in this area as a result of run-off from road surfaces, combined sewer overflows and motor oil spills directly into the marine environment. Figure 3.2a illustrates a chromatogram that is typical of what was extracted from almost all the sites; Figure 3.3 compares the comprehensive 2-dimensional gas chromatogram of the extract from the CSO site WB1 to used motor oil (Kendall 10W-30) collected from a 1993 Volvo 240 station wagon after a few thousand miles of driving, showing a compelling similarity in the composition of oil in these sediment to that of used motor oil.

The gas chromatographic traces of UCM patterns in the Bowery Bay samples did not vary appreciably between different sites and looked much like those in Figures 3.2 and 3.3. The chromatograms from Flushing Bay sites also appeared similar but qualitatively had somewhat greater abundances of earlier eluting, lower boiling hydrocarbons.

Bioaccumulation of and toxicity of hydrocarbon contaminated sediment in Nereis succinea

As part of this work the bioaccumulation potential of the TPH (dominated by the UCM) and the effects of the TPH on growth rates of laboratory exposed *Nereis succinea* was investigated. Over the ten-day experiment, 31 out of 40 worms survived, yielding a

77.5% overall survival rate. The TPH concentration in the sediments did not seem to affect the *N. succinea*. This was observed by the fact that the worms survived and grew in the most highly contaminated sediments (Rikers Island and Williamsburg Bridge). Mortality in the control (Flax Pond) may have resulted from improper handling, individual animal fitness, or potential ammonia build-up in aged control sediment.

There did not appear to be strong evidence of bioaccumulation in the exposed worms. The TPH extracted from the polychaete tissues was variable and generally low (114 to 1279 µg/g) (Table 3.2). Tissue TPH concentrations measured were higher than what was measured in another polychaete, *Pectenaria gouldii*, which was collected in the New York Harbor (0.42 and 0.48 µg/g; LeBlanc, 2001). Sediment TPH concentrations ranged from 9090 to 26600 µg/g, with the control sediment concentration 1440 µg/g (Table 3.2). Further, the hump of hydrocarbons that characterized the UCM in GC chromatograms of analyzed sediments was not observed in the chromatograms of worm extracts. The chromatograms seemed to reflect the presence of non-polar lipids or biogenic hydrocarbons that were not totally removed by the silica gel clean-up (Farrington and Tripp, 1977)

Bioaccumulation of TPHs from the sediment includes various stages: desorption of TPHs from the sediment into interstitial water, uptake of TPHs from interstitial water into the tissues of organisms, and also the direct ingestion of sediment particles by organisms (Landrum et al, 1991). The occurrence of TPHs in the interstitial water and exchange of TPHs between overlying water and air are related to Henry's law constants of the compounds. The importance of uptake from ingesting the compounds or

accumulation from the aqueous phase is regulated by desorption (Du, 2003). When the desorption rate from particles is rapid in comparison to ingestion rate, uptake from the overlying and interstitial water would be most important; when desorption rate is slower compared to ingestion rate, then ingestion becomes most important (Landrum et al, 1989). In this study, accumulation of TPHs most likely occurs through the particle ingestion route.

Though the polychaetes were ingesting food (as evidenced by their growth during the experiment), it may be possible that the worms were able to avoid ingesting oil contaminated muds during the 10-day exposure period (behavioral avoidance /selective ingestion) (Hoke et al., 1995; Kihlslinger and Woodlin, 2000). Another possible reason for this apparent absence of significant bioaccumulation is that the worms are capable of metabolizing the ingested hydrocarbons to a greater extent than was expected. Prior research has examined hydrocarbon metabolism benthic organisms (Hoke et al., 1995; McElroy, 1990; Driscoll and McElroy 1997; McElroy et al., 2000; and review by Livingstone 1998) but outside of some work on PAHs, hydrocarbon (especially UCM component) metabolism in marine polychaetes has not been well studied to date.

Bioaccumulation of hydrocarbons in field collected organisms

Body burdens of the UCM in polychaetes collected from site BB5 within Bowery Bay are shown in Figure 3.2b. These organisms were present in relatively high densities and the fact that they were able to live in such highly contaminated sediment is of interest. Two of the polychaetes collected, *Nephtys sp.* and *Glycera sp.*, showed no significant UCM bioaccumulation (Fig. 3.2b compared to 3.2a). *Nephtys* is known to be

omnivorous, while *Glycera* is a carnivore (Faulchald & Jumars, 1979). The third species *Capitella* sp., did show significant UCM upon tissue analysis (Figures 3.2b), however *Capitella* ingests sediment more directly). *Capitella*, is a well-known opportunistic species that settles quickly in disturbed areas and survives toxic environments where other species are excluded, has also been previously associated in areas of high oil pollution (probably because those areas are organically enriched (Spies et al., 1980). The UCM body burden in polychaetes ranged from 461 to 2040 µg/g and the bioaccumulation factors were relatively low (Table 3.3). Despite finding measurable hydrocarbon levels, the pattern of hydrocarbons measured in polychaetes (even in *Capitella* where the GC-FID generated UCM chromatogram (Figure 3.2 a and b) is not dramatically different from the corresponding sediment).

Higher levels of UCM and as well as a different composition of hydrocarbons was noted for the two samples of *Mulinia lateralis* sampled from Flushing Bay (Fig. 3.4. *M. lateralis* is a filter feeder and some of the earlier eluting UCM compounds found in this species may be accumulated from more soluble compounds that may be enriched in the water column of this Bay from extensive CSO discharges and significant summer boat traffic. More analytical work is required to determine the structures of the hydrocarbons in *Mulinia* and whether they are in fact petroleum derived. Of interest however, are the measured body residues of UCM in *Mulinia* (2.5 – 3.7 mol/g wet tissue). These levels of hydrocarbons within the range normally thought to cause narcosis based toxicity in aquatic vertebrates and invertebrates (Fay et al., 2000; Nannen, 2001; Du, 2004).

There are dramatic differences in the actual composition of hydrocarbons determined by comprehensive two-dimensional GC (see Figure 3.5) comparing the composition of hydrocarbons between the polychaetes and the sediment extracts. We interpret the chromatograms in the polychaete samples to reflect biogenic hydrocarbons that either represents endogenous hydrocarbons or hydrocarbon degradation products from the diet of the worms. Further GC-GC-MS work is required to determine the structures of the hydrocarbons found in the polychaetes sampled.

Survival of benthic organisms in highly contaminated sediments

The ability of organisms to survive in such high oiled environments (> 1% oil by weight) could be explained by three hypotheses developed by Spies et al., (1980). A natural petroleum seep off the Californian coast was used to simulate the chronic contamination in estuarine areas and the probable biological effects. Two hypotheses are discussed here: (1) the organic enrichment hypothesis; and (2) the adaptation hypothesis. In the organic enrichment hypothesis, the oil in the sediment acts as a source of carbon and energy to the benthos. This was demonstrated by an increase in microbes associated with fresh seep oil; this phenomenon can occur in chronically oil polluted marine areas such as the New York Harbor. This increase in microbial biomass acts as a major source of food for the deposit feeders in the harbor, thus allowing the organisms present in the sediment to thrive. The adaptation of organisms to oil polluted environments is another possible reason why the organisms are able to survive. Adaptation to pollutants may increase an organism's tolerance to contaminants in their environment (Elskus et al., 1999). Several possible mechanisms may cause resistance in organisms to contaminants

(Elskus et al., 1999): Tolerance may be achieved by (1) decreasing contaminant uptake, (2) altering detoxification rates, (3) increasing release, or (4) by sequestration.

Another possible reason for high benthic survival especially in deposit feeding organisms may be the presence of combustion based (soot) particles in the sediment. Previous studies have observed pyrogenic vs. petrogenic hydrocarbon signatures in organism tissues suggesting that the pyrogenic hydrocarbons are less bioavailable (Farrington et al. 1983). This conclusion was based on the observation that mussel and polychaete tissues from New York Bight appeared to contain PAH signatures that were indicative of petroleum uptake while the sediments contained a mixture of petroleum and pyrogenic source PAH. Farrington (1985) hypothesized that pyrogenic PAHs are much more tightly bound to or incorporated into particulate matter, while the petrogenic PAHs are in a more soluble, colloidal, or more loosely bound particulate form and thus are more available for biological uptake. Other research has shown that a high proportion of PAHs in sediment is associated with soot particles (pyrogenic in nature) and that partitioning to the soot-carbon fraction of the sedimentary organic carbon can dominate equilibrium partitioning processes (Rust 2003; and references cited therein). Sediments that contain a large proportion of condensed organic carbon are expected to have substantially lower PAH/ hydrocarbon bioavailability than what is predicted (Ahrens and Hickey, 2003). The bioavailability of the hydrocarbon contaminants depends on the amount of organic carbon in the sediment; this inverse relationship forms the basis of the equilibrium partitioning coefficient (K_{oc}). K_{oc} values for soot was determined to be one order of magnitude higher than for uncondensed, amorphous organic carbon (Ahrens and Hickey, 2003). Soot is widely present in marine sediments in the USA, with coastal waters

containing from 0.11-6.6 mg/g dry sediment of black carbon (3-14% of the total organic carbon).

TPH as a significant fraction of sediment organic carbon: implications for benthic habitats and properties

Figure 3.6 shows that TPHs are largely characterized by UCMs of variable compositions comprise a substantial fraction of the organic carbon in sediments of the NY/NJ Harbor complex. For the 46 R-EMAP samples analyzed, the median ratio of TPH to Total organic carbon was 5.6%; thus if an average hydrocarbon is 90% carbon by weight, this corresponds to 5.0% of the organic carbon in harbor sediments is comprised of more residual petroleum hydrocarbons. However, in many areas the TPH fraction of organic carbon is much higher. For example the median TPH/TOC value for the 17 stations sampled in the East River, Bowery Bay and Flushing Bay was 35%. Figure 3.6 shows illustrative lines corresponding to 2, 5 and 30 percent of the TOC being represented by petroleum hydrocarbons.

The implications of this degree of petroleum contamination in urban harbor sediments have not been addressed adequately in the literature. In addition to potential toxicological implications of hydrocarbons that might exert stress either through membrane narcosis, induction of organism mixed function oxidases, or potentially in the case of many PAHs, act as important mutagenic contaminants, the other possible effects of having so much hydrocarbon in sediments may be manifold.

Some of the possible effects of high levels of petroleum hydrocarbons may include: 1) changes in cohesiveness, compaction, and erodability of surface sediment

deposits; 2) their use as substrates for selecting for microbial communities adapted to utilizing oil and resulting changes in sediment redox chemistry; and 3) possible changes in chemotaxis for organisms that rely upon hydrocarbon signals either of mating or larval settlement. Clearly more work needs to be done on the bioavailability of UCM hydrocarbons, its potential toxicity, and some of these other physical, biological, and biogeochemical effects that high levels of oil may have on bottom sedimentary environments.

Table 3.1. Sample sites, coordinates, FOC and TPH concentrations for sediments collected in and around Bowery Bay and Flushing Bay.

Site	Latitude	Longitude	FOC	TPH (µg/g)
BB 1	40° 56.550' N	73° 53.228' W	0.0674	20000
BB 2	40° 56.515' N	73° 53.305' W	0.122	18440
BB 3	40° 56.566' N	73° 53.304' W	0.0991	24470
BB 4	40° 56.644' N	73° 53.250' W	0.0569	10950
BB 5	40° 56.747' N	73° 53.269' W	0.0333	9090
BB 6	40° 56.843' N	73° 53.211' W	0.0417	10700
BB 7	40° 56.458' N	73° 53.808' W	0.0208	11400
FB 1	40° 47.083' N	73° 51.810' W	0.0382	12520
FB 2	40° 46.911' N	73° 51.879' W	0.0475	7760
FB 3	40° 46.850' N	73° 52.094' W	0.0114	1130
FB 4	40° 46.764' N	73° 51.863' W	0.0399	13250
FB 5	40° 46.813' N	73° 51.641' W	0.0366	23540
FB 6	40° 46.718' N	73° 51.204' W	0.0364	12450
FB 7	40° 46.385' N	73° 51.086' W	0.0362	10160
WB 1	40° 42.409' N	73° 58.197' W	0.0592	26600
RI 3	40° 47.724' N	73° 52.579' W	0.0169	20500
ER	40° 47.624' N	73° 55.807' W	0.0138	1700

BB = Bowery Bay
 FB = Flushing Bay
 WB = Williamsburg Bridge
 RI = Rikers Island
 ER = East River

Table 3.2. TPH concentrations in *N. succinea* tissues and in sediments that they were exposed to. FOC, % lipid (estimated to be 0.53 % from Rust, 2003), bioaccumulation factors after 10 days of exposure and % mortality of the laboratory-exposed animals are also provided.

Sample	TPH (µg/g dry sediment)	FOC	TPH (µg/g wet tissue)	% Lipid	BASF	% mortality
Flax A	1440	0.0178	562	0.53	1.311	60
Rikers 3	20500	0.0169	1279	0.53	0.199	20
BB 5	9090	0.0333	999	0.53	0.691	0
BB 6	10700	0.0417	1100	0.53	0.806	40
WB 1	26600	5.92	114	0.53	0.0479	0
WB 1 ¼	6650	0.0148	417	0.53	0.175	20

Table 3.3. TPH concentrations in sediments and tissues of three field collected organisms.

Sample	TPH ($\mu\text{g/g}$ tissue)	TPH ($\mu\text{g/g}$ sediment)	BAF
Capitella (BB 5)	205	9100	0.0225
Nephtys (BB 6)	50	10700	0.00465
Glycera (BB 6)	45	10700	0.00419
Mulinia (FB 1)	925	12500	0.0739
Mulinia (FB 2)	625	7760	0.0805

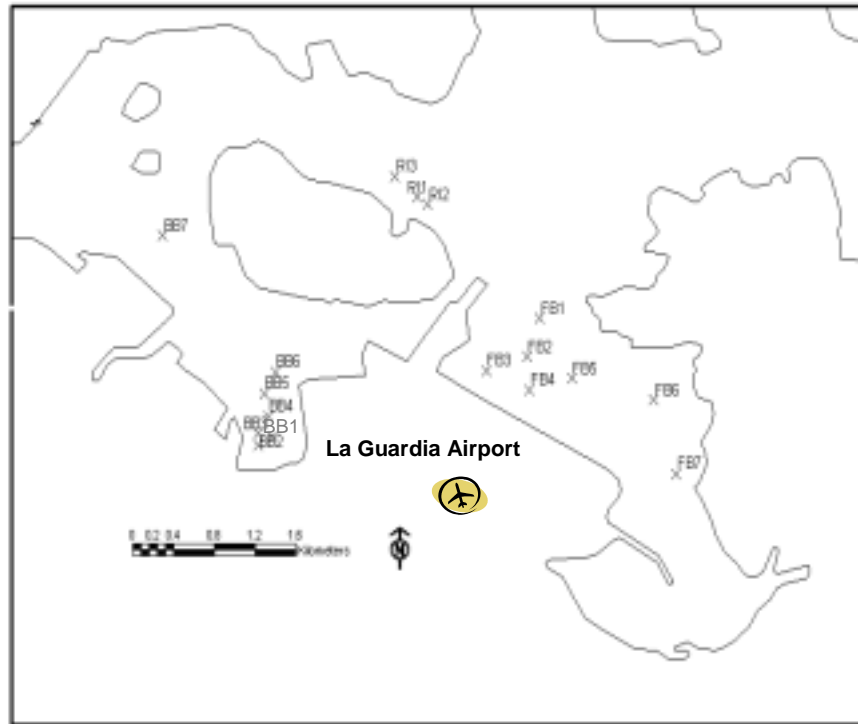
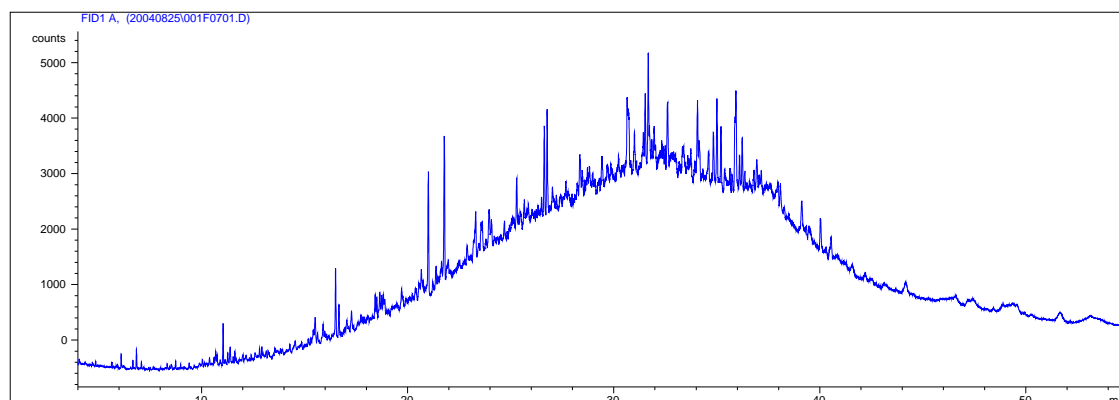


Figure 3.1. Map of sediment and tissue collection sites in Bowery Bay, Flushing Bay and one site analyzed off Riker's Island in the Narrows of the East River. Coordinates for the sites are in Table 3.1.

(a)



(b)

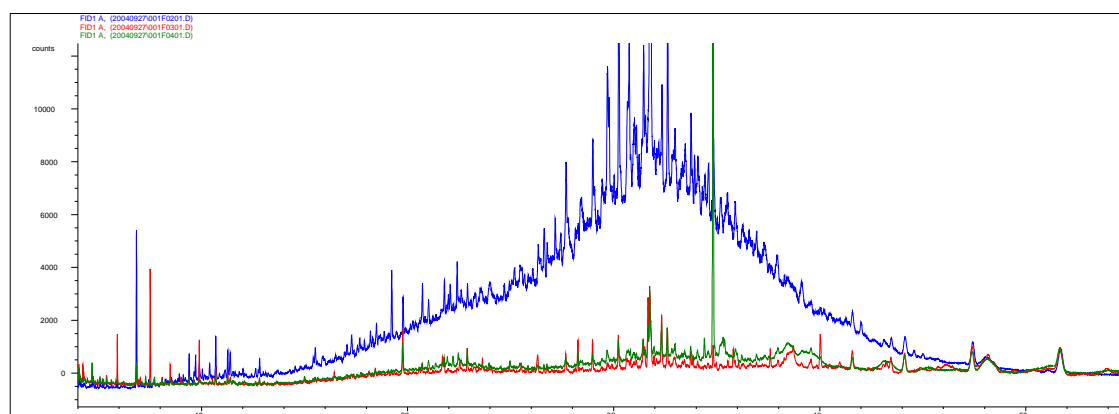
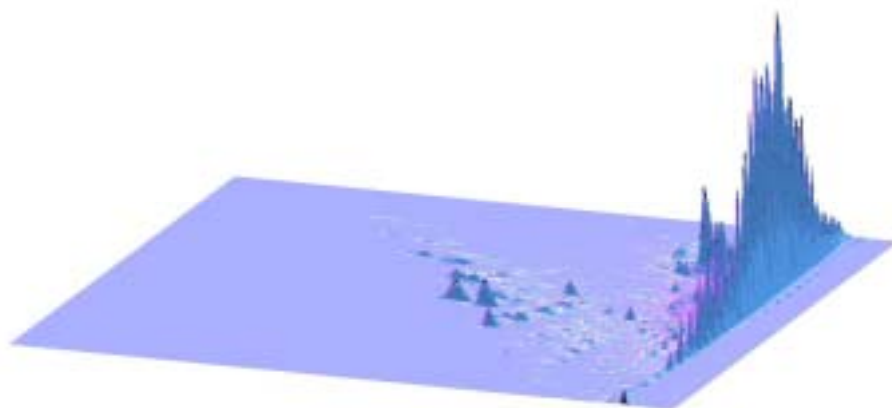


Figure 3.2. Gas chromatography- Flame Ionization Detector chromatograms. (a) A sediment extract collected from Bowery Bay in August 2004 and (b) Tissue extracts of three field collected polychaetes. In 3.2b the blue trace is the *capitella* sp., the red is the *glycera* sp. and the green is the *nephthys incisa*.

(a)



(b)

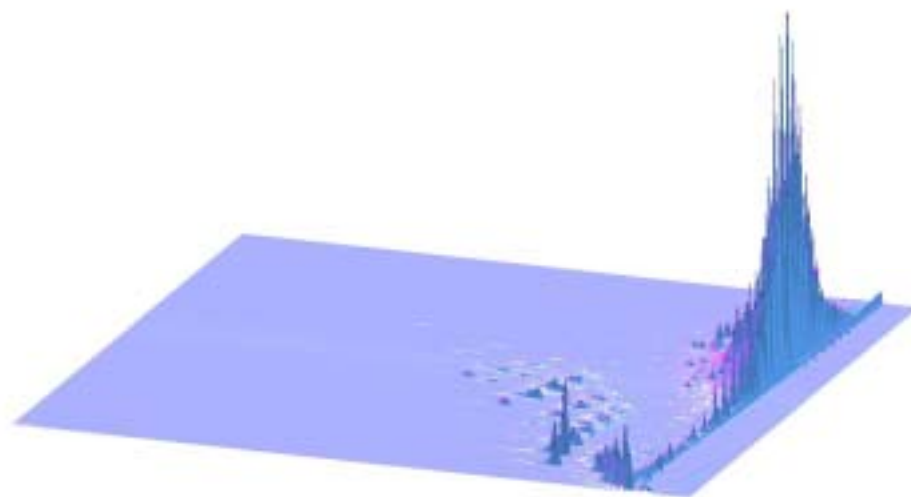


Figure 3.3. GC×GC chromatograms of (a) Williamsburg Bridge sediment extract and (b) a motor oil (used Kendall 10W-30).

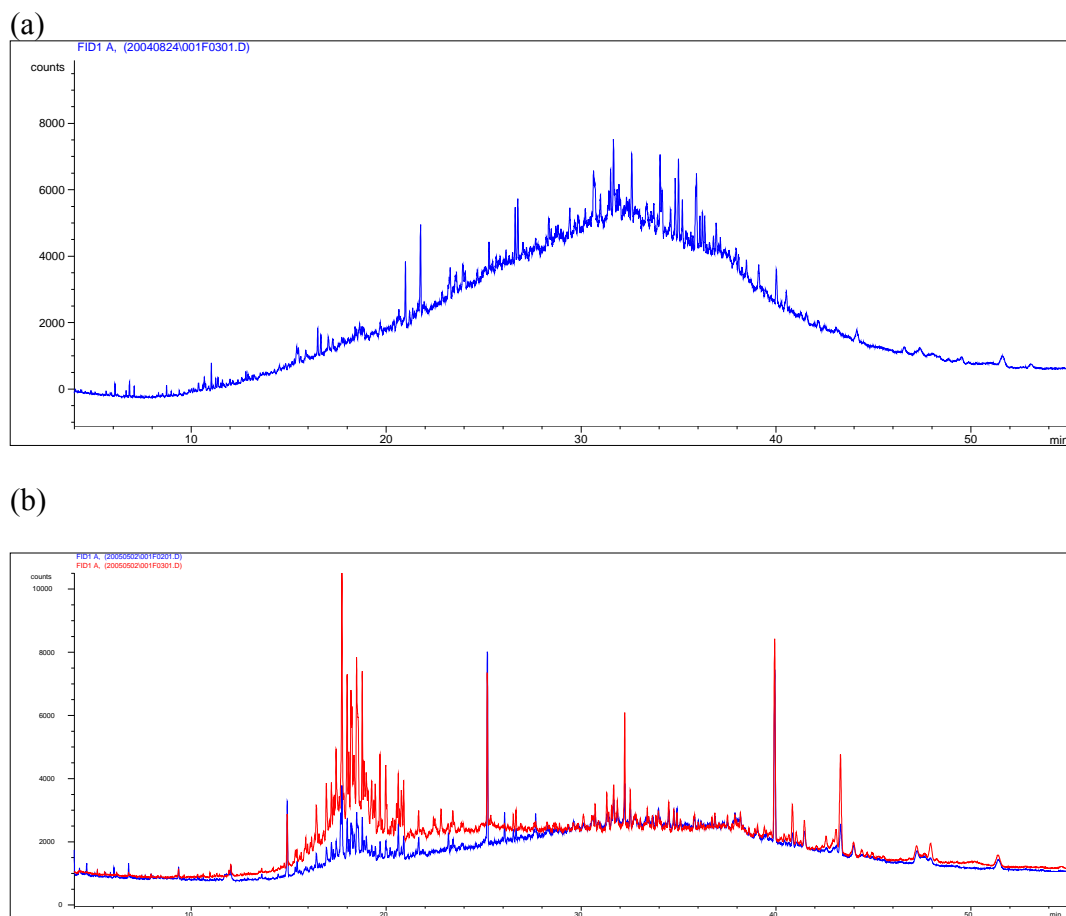
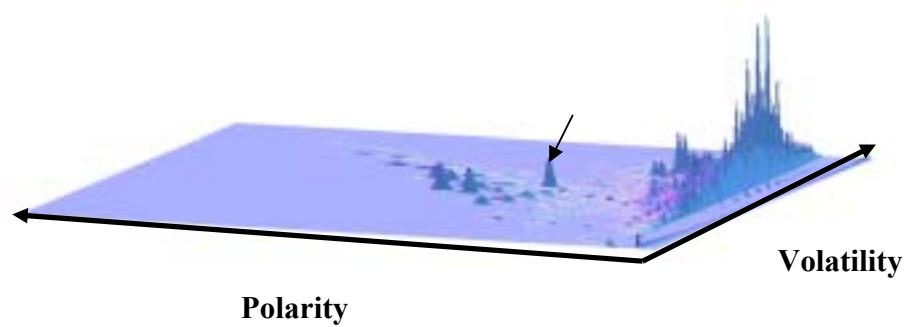


Figure 3.4. Chromatograms of (a) Flushing Bay sediment (FB6), which had a similar UCM pattern to all Flushing Bay sites and (b) two chromatograms of extracts from *Mulinia lateral* collected at Stations FB1 (blue trace) and FB2 (red trace).



(d)

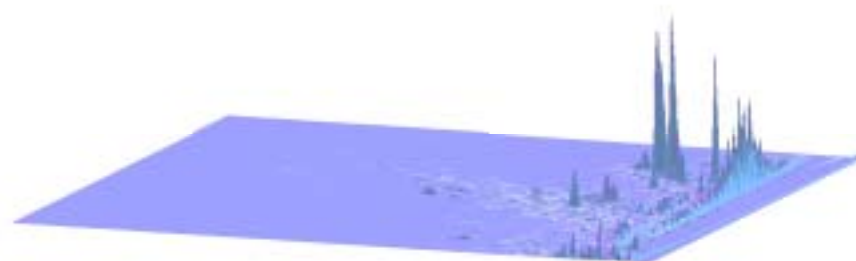


Figure 3.5. GC×GC chromatograms of (a) BB 6 sediment extract, (b) *Capitella* sp., (c) *Glycera* sp. and (d) *Nephtys Incisa*.

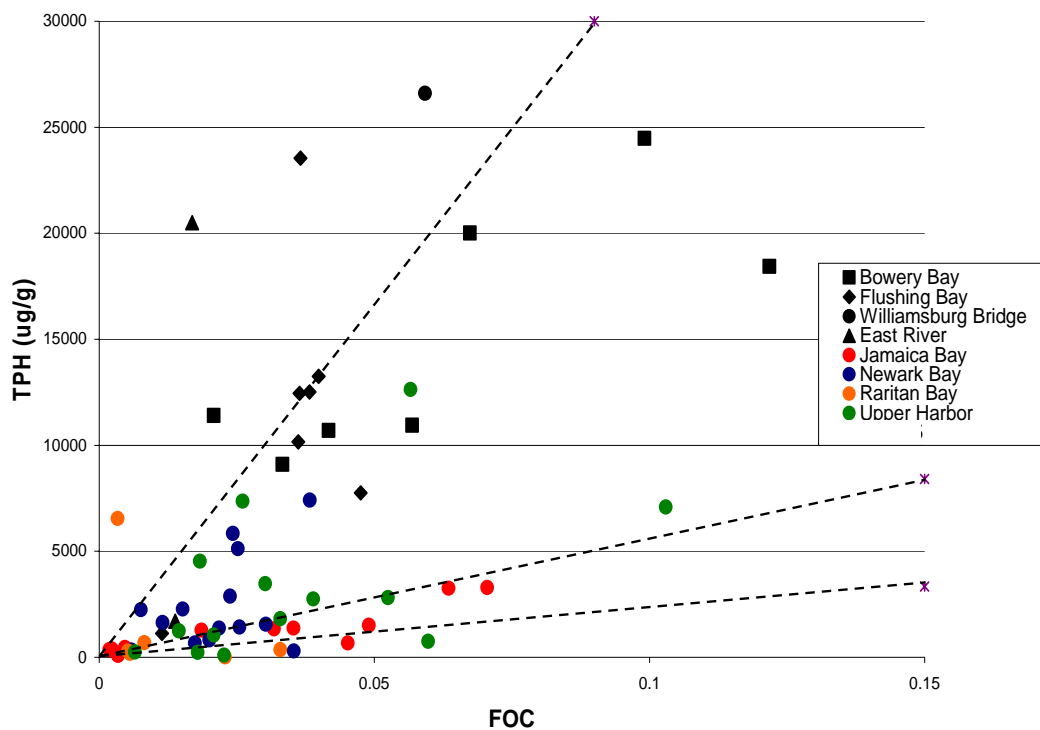


Figure 3.6. Plot of TPH against FOC in all the sediments extracted for this study.

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