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Organic Geochemical Investigations of Urban Sediments by Pyrolysis-Gas Chromatography / Mass Spectroscopy

Kevin Olsen
Montclair State University

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ORGANIC GEOCHEMICAL INVESTIGATIONS OF URBAN SEDIMENTS BY PYROLYSIS-GAS CHROMATOGRAPHY / MASS SPECTROSCOPY

A DISSERTATION

Submitted to the Faculty of
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of the requirements
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by
KEVIN OLSEN
Montclair State University
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Dissertation Chair: Dr. Michael Kruge

MONTCLAIR STATE UNIVERSITY

THE GRADUATE SCHOOL

DISSERTATION APPROVAL

We hereby approve the Dissertation

ORGANIC GEOCHEMICAL INVESTIGATIONS OF URBAN SEDIMENTS BY PYROLYSIS-GAS CHROMATOGRAPHY / MASS SPECTROSCOPY

of

Kevin Olsen

Candidate for the Degree:

Doctor of Philosophy

Department of Earth and
Environmental Studies

Certified by:

[redacted]

Dr. Joan C. Ficke
Dean of The Graduate School

4/21/14
Date

Dissertation Committee:

[redacted]

Dr. Michael Kruge
Dissertation Chair

[redacted]

Dr. Mahmood Barbooti

[redacted]

Dr. Sandra Passchier

[redacted]

Dr. Johannes Schelvis

[redacted]

Dr. Tamara Sorell

[redacted]

Professor Eric Stern

ABSTRACT

ORGANIC GEOCHEMICAL INVESTIGATIONS OF URBAN SEDIMENTS BY PYROLYSIS-GAS CHROMATOGRAPHY / MASS SPECTROSCOPY

by Kevin Olsen

Pyrolysis-Gas Chromatography / Mass Spectrometry (Py-GC/MS) can be used to study the organic matter in sedimentary environments.

An urban sediment is not simply defined by proximity to a city. Because cities have anthropogenic contamination, one important urban sediment characteristic is ongoing recontamination. Another is legacy contamination from industrial activity and a third is the alteration of natural bio-geochemical systems.

Two case studies are presented. The surface sediments of the Gateway National Recreation Area were sampled during the summer of 2007. The ratio of two pyrolysis products, Vinylguiacol, from terrestrial plant lignins, and Indole, from proteins, (VGI Index) is moderately well correlated with the sediment C/N ratios. A low VGII (0.33) suggests that the primary input of organic matter along the shores of the National Park's Jamaica Bay is terrestrial while the inputs are primarily marine in areas where there has been a dramatic loss of salt marshes. In contrast, healthy marshes on the park's nearby Sandy Hook unit had a VGII of 0.82. The VGII could also be correlated with the Carbon Preference Index (CPI) ($r = 0.54$) and the Syringol / Vanillyl (S/V) ratio ($r = 0.87$). Increased values of the CPI often indicate an organic input from terrestrial plants while

increasing S/V values are often associated with grasses. A Principle Component Analysis (PCA) grouped the sample points associated with either water pollution control plants or combined sewer overflows into one component. This serves to reinforce the observation that most of the current freshwater inputs to Jamaica Bay have been from sewer discharges.

The suitability of Py-GC/MS to study conditions in a sediment core is the focus of the second case study. A 2-meter sediment core was obtained from the Passaic River's Dundee Lake. The core was taken from a highly disturbed part of the river and clear temporal trends were not discernible. Compounds of the same chemical class showed clear patterns of co-occurrence and correlations were frequently 0.9 or higher among petrogenic compounds. These results suggest related co-deposited compounds tend to remain together despite disturbance.

Because the majority of human populations now live near the coastlines a more sustainable sediment management policy needs to replace the current system of "dredge and dump." One challenge in the future will be to have an adequate supply of sediment to protect the coasts against rising sea levels. Characterizing the organic matter in those sediments is another potentially useful application of py-GC/MS.

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Dr. Jason Curtis, the manager of the Stable Isotope Mass Spectrometry Laboratory at the University of Florida, Gainesville, Florida, provided the carbon/nitrogen analysis. The staff of the Gateway National Recreation Area, and especially Dr. George Frame, were instrumental in providing support for this project. Dr. Paul Bologna and the members of my PhD dissertation committee provided valuable feedback and helpful discussions. Mr. Joseph Liscandrello, our local Thermo Electron Service Engineer, kept our GC/MS running at peak efficiency.

Dedication

To friends and colleagues at Montclair State who over the long course of this project gave me support and encouragement, and to my two children Christian and Emily.

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Chapter One

Introduction to Research

Introduction

The goal of this project has been to demonstrate the applicability of Pyrolysis-Gas Chromatography / Mass Spectrometry (Py-GC/MS) to the study of the organic matter found in the sediments from urban environments. After considering two sediment case studies and exploring some future management challenges for urban sediements, two historical case studies of environmental management in an urban estuary are presented Urban sediments present unusual environmental challenges. In the perceptions of most people, the most pressing of these challenges is legacy contamination. Beginning with the industrial revolution and continuing to the introduction of the clean water act, huge amounts of pollutants were discharged into urban rivers and harbors. In additon to industrial wastes, sewers, combined sewer overflows (CSOs), discharges from shipping, and street runoff also contributed significant amounts of pollution. In many instances these remain problematic sources of contamination. Although highly modified, urban environments are still subject to natural influences. The typical urban sediment is therefore a mix of both legacy and ongoing contamination overlaying and interspersed with natural inputs of organic matter. A detailed exploration of these issues is presented in appendix one, *What Defines An Urban Sediment?*

To study such complex systems pyrolysis-gas chromatography / mass spectrometry is a very effective tool. In a conventional GC/MS analysis of sediments the materials are first dried and then spiked with appropriate quality control standards. If necessary, a preliminary grinding may also be employed. The sediment is then extracted with an organic solvents suited to the specific analytes of interest. Commonly used solvents include hexane and methylene chloride. Extraction processes include refluxing in a Soxhlet Extractor, and agitation by sonication. The majority of the solvent is then evaporated off, thereby concentrating the sample to the point where it can be injected into a GC/MS system.

In a Py-GC/MS sediment analysis the first step is to dry the sample. As with conventional analysis, if necessary, a preliminary grinding may also be employed. At this point the material is spiked with internal standards and loaded into the pyrolysis tube. No additional preparation is required. The savings on solvent make the technique attractive from both a cost and an environmental point of view. The time saved makes it well suited to studies where large numbers of samples must be analylzed or where fast turn-around times are desired.

Py-GC/MS allows the study of two types of materials. The first are intact molecules that are desorbed from the sediment particles simply by heating. These intact molecules are mobile and bio-available and thus represent the greatest risk to the environment. This category of molecules can include biological molecules in sewage, petroleum contaminants, and polycyclic aromatic hydrocarbons. In some instances recovery of low molecular weight substances are improved with Py-GC/MS over conventional extraction because the sediment samples are only heated during the drying step. Unlike solvent extraction, there is also no discrimination of recovered materials based on their solubilities. A second category of materials recovered in pyrolysis include the thermal breakdown products of larger organic molecules. These smaller breakdown products are often more suited to GC/MS analysis than the original molecules. The abbreviations used to identify compounds in the chromatograms and tables are listed in table 1-1. Quantitation of pyrolysis products has often been achieved by spiking the samples with known amounts of perdeuterated PAHs. The area of the analyte peaks are compared to the areas of the internal standard peaks. Because there is only one characteristic peak in the mass spectrum for the internal standard and the majority of chemical substances have multiple peaks in the mass spectrum, a simple one to one correspondence for peak areas will not provide accurate quantitation. Therefore a correction factor is often applied to the quantitation results.(Baumard, et. al., 1998)

A more detailed explanation of this analytical technique can be found in appendix two, *Detailed Examination of Materials and Methods*. Appendix three contains the chemical structures of important biomarkers.

The two case studies using Py-GC/MS are presented, one studying conditions over space and the other over time. The first is a study of the Gateway National Recreation Area, an urban national park in New York Harbor. During the summer of 2007, a large number of surfacial sediment samples are studied that span a large geographic area. The second case study uses a sediment core taken from the freshwater section of the Passaic River. If undisturbed, a sediment core allows the study of how conditions change over time at a single geographic location.

Significance of the Gateway National Recreation Area

The Gateway National Recreation Area (NRA) deserves study because it is one of the country's most-visited urban national parks, provides critical habitat for many species, is located on the Atlantic Flyway, and in the case of the Jamaica Bay unit, the islands in the park are disappearing. A map of the neighborhoods and important geographical features in Jamaica Bay is provided in figure 1-1.

Tidal salt marshes such as the ones in this study, cover approximately 1.7 million hectares on the coastline of the continental United States and the state of Alaska. Salt marshes commonly occur in high latitude and temperate estuaries of open coasts. They are typically protected from extreme wave action by wide intertidal flats or barrier islands. Marshes in the southern coastal plain of North America can annually produce up to 80 metric tons of plant material per hectare. The typical salt marsh is characterized by fine sediments and halophytic vegetation. (Leonard et al. 2000)

Tidal marsh losses associated with urban estuaries have typically been the result of landfilling while additional damage has been caused by mosquito control ditching and surface water impoundments. (Chaffee et al. 2012) Numerous factors currently contribute to salt marsh loss in urban estuaries including sea level rise, eutrophication, and sediment starvation. Much of the present work will focus on analyzing the biogeochemical signatures of various types of organic matter (OM) because in natural systems, geomorphological, ecological, and botanical processes all work in combination to maintain salt marshes. One example of this interaction is when the presence of emergent macrophytes reduces wave and tidal shear stresses thereby increasing sediment deposition. Healthy root systems protect marsh edges from erosion. (Fagherazzi et al. 2013)

Alterations in plant productivity, plant communities, and microbial fauna resulting from nutrient enrichment can create negative feedbacks leading to adverse effects on marsh stability and biogeochemical cycling. (Fagherazzi et al. 2013) Laboratory studies have shown that a combination of rising salinity and eutrophication can result in decreased marsh plant biodiversity and subsequent loss of ecosystem resilience. (Ryan and Boyer 2012) Pollution has been also shown to alter community structure and the abundance of biota. (Kauppila et al. 2005)

A number of sediment samples were collected from various points in the Gateway NRA by Dr. Mark Ringenary, Natural Resources Specialist in the National Park Service. Samples were collected only from the top level of sediment. The sediments were oven dried overnight at 40c by NPS personnel working at the park's on-site laboratory. The dried samples were shipped to Montclair State University for analysis.

All of the Great Kills (Staten Island) samples were taken from muddy areas with fine sediments including Great Kills Bay and the Fox Creek tidal marsh east of the Oakwood Beach Water Pollution Control Plant. Only one sample was taken on the west side of Staten Island from Saw Mill Creek.

Sandy Hook, as the name implies, is a sandy and narrow peninsula extending into New York Harbor where the Raritan Bay meets the Atlantic Ocean. Sandy Hook is largely preserved in its natural state because it was occupied by the military from 1874 to 1972. Although extensive harbor defense batteries, barracks, mess halls, theaters, radar installations, and other military structures were constructed on the peninsula, much of it was left undeveloped. A new generation of large, breech-loading rifled artillery was developed after the American Civil War. Many of these large cannons were tested at Sandy Hook where the empty beaches served as a 3,000-yard firing range. During the early part of the Cold War, Sandy Hook remained restricted because it hosted anti-aircraft missle batteries and defensive radar installations. After these became obsolete, Sandy Hook was transferred to the National Park Service although the Coast Guard continues to occupy a portion of the peninsula's north end.

The ocean side of the peninsula consists entirely of sandy beaches while the inland side has more diverse habitats including beaches and tidal marshes. Other habitats include salt cedar forest, maritime shrub forest, and stands of both mature holly and red cedar. Some of the holly trees are more than 150 years old. (Geology of National Parks, USGS, http://3dparks.wr.usgs.gov/nyc/parks/loc67.htm, accessed Sept 30, 2013)

All Sandy Hook samples were taken from the inland side of the peninsula from sites in Plum Island, Spermaceti Cove, and Horseshoe Cove. Two additional samples were taken by a team from Montclair State University from a marsh immediately north of Horseshoe Cove. One sample was taken from the fine organic rich sediments at low tide and another from a sand bar below the high tide line. The Sandy Hook samples ranged from very fine to coarse sand.

The Jamaica Bay samples were collected in different parts of the bay and its tributary creeks. Jamaica Bay has a wide range of sediment types. About 50% of the bay's bottom sediments can be characterized as mud. The mean proportion of the silt-clay fraction over the entire bay has been estimated to be between 30.3 and 37.5%. The sediments in the far western part of the Bay contain up to 80% sand and the proportions of silt and clay increases farther to the east (Watershed Protection Plan, p. 62).

Currents in Jamaica Bay run counterclockwise but have been blocked by the extension of John F; Kennedy Airport's runway 4A southwestwards into Jamaica Bay. As a result it now takes three times longer for tidal flushing to remove pollution from the bay than it did 100 years ago (NPS Study 1976, page 46).

Tidal mixing provides the majority of water circulation. Each tidal cycle exchanges approximately one-third of the bay’s water although the degree of mixing varies over time. Freshwater inputs account for only 0.5% of the water in Jamaica Bay. As of 1990 two-thirds of freshwater inputs were from secondary wastewater treatment plants and 10% were from combined sewer overflows (CSO's) (Bopp, Simpson, Chillrud and Robinson, 1993). As of 2005, there were 26 CSO's discharging into Jamaica Bay (Benotti, Abbene and Terracciano 2007).

Detailed descriptions of the park's individual units are presented in the next chapter. The units of the Gateway NRA have provided habitat and recreation for many decades. The story of the present-day park begins in 1938 when the New York State Legislature transferred control of what would become the Jamaica Bay unit to the City of New York. New York City had been acquiring land in Jamaica Bay for park development throughout the 1930s. Jamaica Bay became a wildlife refuge in 1951. By the late 1960s, 50,000 people were visiting the refuge each year (Barlow 1971, 107).

In 1969 Secretary of the Interior Walter Hinckel proposed the creation of the Gateway National Recreation Area to encompass the entire harbor area from Sandy Hook to the Rockaway Peninsula. An early study for the recreation area recommended inclusion of the Jamaica Bay wildlife refuge (Barlow 1971, 109). Even though the bay was degraded it was still good wildlife habitat since the islands, sand islands, sandy shore edges and brackish ponds were still available as of 1970 (Taormina, 1970). Jamaica Bay and the city's lands on the Rockaway Peninsula were turned over to the National Park Service in 1972. At the time the city was facing its fiscal crisis and money for all but the most essential city services was not available. The political issues surrounding the creation of urban national parks in New York, San Francisco, and Boston, were complex but can be summarized briefly, the country's major cities were financially strapped, and urban populations needed recreation areas.

At just one of the park's beaches at Breezy Point, there were 3.4 million visitors in 1975 with peak usage at 90,000 persons a day or 36,000 people on the beach at any one time (General Management Plan 1976, 124). Other major beaches and wildlife habitat is provided by the Sandy Hook Unit.

Tanacredi (1983) described the "paradox" of Gateway NRA. The park's land and waters were subject to severe stresses because of their proximity to a large population center. But this same proximity created a demand for its potential as a recreation resource. The situation is further complicated because throughout the United States demand for shoreline recreation has outstripped public access facilities. In 1975, 54% of the US population lived within 50 miles of the coast but only 2% of the contiguous 48 states' coastlines were in public ownership (Tanacredi 1983).

Ten years after its founding, 10% of the Gateway NRA facilities supported active recreation, softball, paddleball, bicycling, etc, while 90% of the facilities were devoted to passive recreation. Activities such as tent camping, birding, sailing, kayaking, and fishing all fall somewhere between the active and passive and require "delicate management decisions" (Tanacredi 1983).

Gateway is currently facing a crisis in confronting the disappearing marshlands of Jamaica Bay. The problem is especially acute on the islands in the center of the bay. Comparisons with historical aerial photographs have shown several islands marshes reduced by 12% since 1959. Low marsh vegetation loss on the islands in Jamaica bay has averaged 38% since 1974 and vegetation the loss on the smaller islands has been as high as 78%. A combination of factors is believed responsible including a reduced sediment input and localized sea level rise accompanied by land subsidence. Water ponding inside the marshes, marsh edge slumping, and widening tidal channels have also been observed in many places in Jamaica Bay. Park managers are particularly concerned that accretion rates will not keep pace with expected sea level rise in the coming decades. (Hartig, "Anthropogenic and climate-change impacts on salt marshes of Jamaica Bay, New York City," *Wetlands*, 2002)

One approach to the disappearing islands has been habitat restoration using dredged sand from navigation channel maintenance. The scale of the processes is illustrated by the work on Elders Island. Originally 132 acres the marshes in the middle of the island eroded down until it was separated into two islands. At least 70 acres of marsh needed to be restored to replace the resulting mudflats with land suited to "low marsh growth." To complete this work, an estimated 270,000 cubic yards of sand would have to be dredged from the various channels and harbor and placed back on the island. The restored land would be replanted with *Spartina alterniflora* (saltmarsh cordgrass), *Spartina patens* (salt hay), and *Distichis spicata* (spike grass) (*Business Wire*, 2006).

The gateway Study has two purposes. The first is to map broadly the inputs of anthropogenic contamination including sewage, petroleum products, and PAHs. The second purpose is to utilize the abilities of Py-GC/MS to determine the sources of sedimentary organic matter (OM) and map how these vary throughout the Gateway NRA. Sedimentary organic matter forms the basis of many estuarine food webs as well as playing an important role in nutrient cycling. Ideally, the types and distribution of OM in the estuary will shed some light on the biogeochemical processes that are leading to marsh loss in the Jamaica Bay unit.

Significance of Dundee Lake

Dundee Lake is the final section of the freshwater Passaic River. The dam forming the lake is located at the river's head of tide. The distance between Dundee Dam and the Paterson Great Falls is 13.3 kilomteres (8.3 miles). The lake is downstream from the city of Paterson and is surrounded by both industrial sites and communities with high population denstities.

Paterson was founded in 1792 as the nation's first planned industrial city. The 23.5-meter (77 feet) Great Falls of the Passaic provided water-power for the city's mills. Historically, the most important industries in Paterson centered on silk production including weaving, dying, and finishing. Paterson was also home to several locomotive builders, foundries, boilermakers, rolling mills, and the original Colt firearms manufacturing plant. Specialty chemical production centered on the dye industry although pharmaceuticals, personal care products, paints, and cleaning chemicals were also manufactured in Paterson and the surrounding communities. Dundee Lake is significant because it has been exposed to a variety pollutants over the entire timespan of the American industrial revolution. Because the core was taken three decades after the passage of the Clean Water Act, the uppermost portions of the core may have diminishing amounts of pollution.

Although connected to the tidal Passaic River by a canal and lock system, the lake never supported commercial navigation. The pollution from Paterson discouraged recreational use. Recreational rowing, canoeing, and swimming took place above the Great Falls. By 1874 the water downstream of Paterson was described as being "as dark as beer" and was said to contain the sewage of 50,000 persons, oil, coal tar, and the waste chemicals from dye works, textile mills, hat factories, and paper mills. (Olsen 2011)

Much of Dundee Lake's western shoreline is covered by highways including state highways 19, 20, and 46. River Road (county road 507) runs along a portion of the lake's eastern shore. There are a number of industrial sites on both sides of the lake north of the Interstate 80 bridge. There are also multiple brownfields near Dundee Lake including the Garden State Paper Company, Garfield; Prime Energy CoGen, Elmwood Park; and the Marcal Paper Mills, Elmwood Park. (It must be noted that the principle buildings of the Marcal site are still occupied by Soundview Paper Company and are not technically brownfields. Some of the ancilliary buildings are no longer used by the company and thus are listed as brownfields.) There are also a number of smaller brownfield sites near the lake such as gas stations, oil dealers, and automobile service centers. (Brownfields Site Mart) At this time there is little or no research available about how these sites may be contributing to contamination in Dundee Lake.

The sediment core used in this study was donated to Montclair State University by Malcolm Pirnie. The core (number 37) was taken from Dundee Lake as part of a study of the lower Passaic River prior to establishing the river as a Superfund Site and beginning a large-scale cleanup.

Because a large number of analyses were performed by chemists working with Malcolm Pirnie, most of the core has been analyzed for parameters such as Total Organic Carbon (TOC), grain size, heavy metals, radionuclides, and organic priority pollutants. Because Pb-210 has already been measured for this core, the sedimentation rate is available. Many organic pollutants have already been measured in this core but analysis focused exclusively on the EPA Priority Pollutants. While this core was outside the project area, it serves as a comparison to sediments in the lower Passaic and the interpretation of the data was limited to what was relevant for planning the remediation project. Despite the previous analyses, the core still provides ample opportunity for original research.

The information richness of the Py-GC/MS technique also makes it useful for the study of sediment cores. An undisturbed sediment core preserves a chemical record of organic matter inputs to a waterway. They can be used to study the trends of pollution over time as well as the chemical signatures of natural processes. A sediment core can also detect legacy contamination that has been buried under more recent and cleaner deposits. Sediment cores are widely used to map legacy contamination in the three dimensions of latitude, longitude, and depth. Understanding past conditions provides the perspective needed to plan for the future.

Environmental Management and Urban Sediments

Discovering what is in urban sediments is only the starting point for their long-term management. Urban sediments present a number of unique management challenges. Waterways are traditionally commonly held resources so that the legacy contamination is at once everyone's problem and no one's problem. Unlike a hazardous waste site on land where there may be only one responsible party, there are usually multiple responsible parties (RPs) for that have polluted a river of a harbor. There are also conflicting management objectives among the various stakeholders.

Further complicating sediment management is the problem of distribution. Where upstream dams restrict sediment flows downstream regions are often sediment starved. The result is there are no supplies to replenish areas impacted by coastal erosion. The loss of coastal wetlands and the associated ecosystem services is another consequence. Conversely, all of the world's seaports require periodic maintenance dredging to remove sediments carried into shipping channels and dock areas. Maintenance dredging is complicated by the prescence of legacy contamination because the dredged materials require special, and expensive, handling. The cost of this handling is expected to increase in the coming decades because like their counterparts on land, many offshore sediment disposal sites are reaching the limits of their finite capacity. (Envirotools, 2013) The current system of managing sediments has been described by its critics as “dredge and dump.” In contrast, a truly integrated and sustainable urban sediment mangement system has to address three major concerns’ legacy contamination, ongoing contamination, and sediment surpluses and shortages. And it must do all this in a world of complex interactions in and between both human and natural systems. Sustainable sediment management systems will operate in a world of rising costs, increasing coastal populations, growing international shipping, rising sea levels, and a warming climate.

In the United States there are two management approaches that are laying the foundations of a new sediment management regime. Benefical Use is a legal framework that allows dredged materials to be employed in a wide variety of projects. Sediments can be used for landfill cover, habitat or beach restortation, or construction fill. Regional Sediment Management (RSM) is a legal framework that encourages governmental entities to view sediments as a valuable resource. RSM also recognizes that sediments and their management are part of larger hydrographical, geological, and ecological systems.

Where sediments are largely uncontaminated, Beneficial Use and RSM are relatively uncomplicated. In the United States the legal approach for contaminated sediments has been to employ the The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund. Unfortunately, this approach was designed for land-based sites. In harbors and rivers sites do not have clear boundaries because tides and currents redistribute contamination. Many seaports have been heavily industrialized for over a century so there are often multiple responsible parties. Throughout the industrialized world, management of contaminated sediments is further complicated by the large numbers of stakeholders, citizen activists, and governmental agencies with conflicting mandates. Citizens want timely cleanup that restores the recreational and aesthetic values of waterways, responsible parties want cost-effective (ie inexpensive) cleanups, shipping interests want navigation channels maintained, and everyone wants someone else to pay for the process. There is no shortage of innovative and effective technologies available for sediment remediation but there is conspicuous shortage of innovative political thinking. How Norway is attempting to create a new political system for dealing with sediments and how the Willamette River remediation in the city of Portland, Oregon, is hampered by outdated management systems will be explored in chapter 4.

Looking to the future as coastal populations increase there is going to be an associated demand for protecting the shorelines against rising sea levels and a warming climate. Decontaminated urban sediments may provide a valuable raw material for coastal armoring and restoration projects. The suitability of s sediment for any particular remediation or armoring project is largely determined by its grain size. Therefore, the clean sands that are widely used today may not be suited for all projects in the future. The same dams that are trapping sediment flows in upstream areas are also trapping organic materials that are an important component of coastal ecosystems. It is hard to imagine that the mass removal of organic-rich sediments from inland reservoirs, its transport to the sea, and its placement on selected sites offshore will ever be economically feasible. However as we learn more about the role of river to ocean sediment transport organic carbon, we can imagine environmental managers considering the organic matter content of sediments when selecting appropriate uses. The information provided by Py-GC/MS may someday help match sediment source to the appropriate beneficial use.

Case studies in Environmental Management from Jamaica Bay, New York

In environmental management it is appropriate that we consider the nature of human activity in the urban estuaries and ask what insights the emerging field of environmental history might contribute. For this reason two case studies about the history of environmental management and mismanagement of Jamaica Bay are presented.
The origin of these case studies was an attempt to understand what historical events lead to the specific sedimentary conditions observed in this research. Such linkages proved to be highly elusive and conclusively establishing them would require taking multiple sediment cores. However the history of human interaction with the bay was fertile ground for environmental management research.

The author Elizabeth Barlow described Jamaica Bay is a "happy amalgam of many things; salty honky-tonk, serious Ornithology, lazy angling, and jet travel" (Barlow

1971). Located on the southern shore of Long Island and entirely within the borders of New York City, Jamaica Bay is an unique urban landscape. As the city grew, competing demands were placed upon it and clashing stakeholders fought over the bay's resources. From about 1860 to 1930, Jamaica Bay was simultaneously home to commercial fisheries, a place to recreate, a place to live, a transportation hub, a manufacturing center, and a place to dispose of the city's putrescent waste products.

Many cities lie near estuaries but until quite recently few municipal governments knew what to do with them. They were seen as places where miasmas arose and disease carrying mosquitoes bred. City planning, if it was done at all, called for filling them in. The connection between mosquitoes and disease was definitely established in the late 1800s. Progressive-era reformers subsequently had an early public relations success by filling in marshes as public-health measure. (Vileisis, 1999, 117) Ironically the same spirit of reform was simultaneously lamenting the loss of open space and aesthetic values associated with urban growth.

Perhaps this is because to even the most romantic minds of the 1800s, salt marshes were not places to inspire dreams of manifest destiny, spiritual transcendence, or imperial ambitions. In the opening scene of *Great Expectations,* Charles Dickens used the salt marsh to symbolize the loneliness of Pip's orphaned existence and the evil that would soon come into it in the form of the escaped convict Magwitch. Even the painters of the Hudson River School, the first great exponents of the American landscape largely ignored salt marshes. The one exception was of Martin J. Heade (1819-1904). Heade's paintings of the marshes around Newbury Port, Massachusetts are seen by some critics as a celebration of an ordinary landscape where people and nature come together in beneficial ways.

The Backdrop of the Case Studies – The City and the Bay

Although the original towns surrounding Jamaica Bay were established in the mid-1600s, Jamaica Bay first came to the attention of New Yorkers as a vacation destination in the 1830s and 1840s. Loacted at the eastern end of Jamaica Bay where the base of the Rockaway Peninsula meets the Atlantic Ocean, Far Rockaway was one of the first summer resorts in the United States. Among the first reported vacationers in the Rockaways were Philip Hone and his family. The Hones were one of New York City's elite families. They ventured to Rockaway to escape the 1832 cholera outbreak (Aron, 2001, 17). If the Hones' experience was typical, it would not be an exaggeration to say that Jamaica Bay's two main industries, waste processing and tourism, were born in cholera outbreaks. Following a cholera outbreak in the 1840s New York City undertook its first serious efforts at protecting public health. In additon to cleaning up the streets and cleaning privies the city also banished all rendering plants and bone-boiling works from Manhattan. Isolated from the city, Jamaica Bay was seen as the ideal site for disposing butchers' offal, spoiled foods, or animal carcasses. The organic materials were boiled to release oils and greases which had a number of industrial uses including the manufacture of paints, soaps, and candles. The remaining soilids were sold for use as fertilizer. Within a few years there was a thriving waste disposal industry on Barren Island on the west side of the bay even as a tourism industry thrived elsewhere along the bay's shores.

The construction of passenger railaroads increased the number of vistors. Railroads reached Far Rackaway in the 1860s and Canarsie, on the eastern shore by 1865. From Canarsie, a steamboat journey over the bay and past Barren Island allowed tourists to reach the western end of the Rockaway Peninsula. In the 1890s, the New York, Woodhaven, and Rockaway Beach Railroadpushed its tracks over the center of the bay using the existing islands and a series of trestles. This line not only oncreased the number of visitors to the Rockaway Peninsula, it also helped develop the Queens neighborhood of Howard Beach and the smaller vacation resorts of Goose Creek and Broad Channel.

Meanwhile the residents of the original bayside towns carried on their traditional activities of farming and fishing. Because the city of New York had yet to be created from the consolidation of the five boroughs, control of Jamica Bay and its resources was still in the hands of the original townships. In addition to the local fishermen there was also a large menhadden fishery in the New York region and a number of fish oil processing plants had been established on Barren Island. This was seen as an ideal place for them as their odors would not be noticed next to those of the waste processing operations. By the 1880s thousands of recreational anglers came to the bay and spent their money on boat rentals, hotels, and restaurants. The traditional use of nets in the commercial fishery was blamed for wiping out fish stocks and putting the tourist dollars at risk. The response was the 1890 Stadler Bill that passed the state legislature and specifically banned the use of nets in Jamaica Bay. This bill was particularly significant for two reasons. The first time in the history of New York State, local control over fisheries was usurped and secondly, a specific method of fishing was banned in a specific geographical location.

The dispute between the commercial and recreational fishermen was only the first conflict over the bay's fisheries. By the early 1900s the links between disease and contaminated shellfish were well established. As both the permanent population and the number of tourists continued to grow, there was a tension between the baymen who needed clean shellfish beds and the developers who needed more sewer lines. Unlike the earlier dispute that could be resolved through legislative action, the growing pollution in the bay forced the fishery to close in 1924.

On January 1, 1898 five separate counties were consolidated into New York City, Richmond County, Manhattan, The Bronx, Queens, and Brooklyn became one city. A few years after its creation, the consolidated city faced a crisis on its waterfront. The defunct French Panama canal project was acquired by the United States in 1904. With opening of the canal just a few years away, the amount of world shipping was projected to increase. Ships were also growing larger and the docks along New York's shorelines were not. Expanding the seaport into Jamaica Bay seemed like the obvious solution. Planning for the port began in 1906 when Mayor McClellan appointed a commission to study the possibility of creating the port. The commission approved the idea in 1907 ("Jamaica Bay Seaport as City Envisions It", *New York Times*, May 3, 1931).

In 1909 the state ceded title to under-water lands of the bay to the city and one year later the city government and congress made initial appropriations for the work. The federal government began dredging 30-foot channels around the northern and western shores of the bay ("Jamaica Bay Seaport as City Envisions It", *New York Times*, May 3, 1931). The proposal to create the new seaport was the first time that any one governmental agency articulated a coordinated plan for the bay's future. But while the city's eyes were on the future of the bay, for many of the surrounding communities, their noses were still downwind of Barren Island. In 1896 the existing waste processing industries were dramatically expanded and modernized. As part of a new wave of sanitary reforms tons of additional restaurant scraps, kitchen wastes, and organic materials were being processed each day in addition to the existing business of processing animal carcasses and butcher's offal. The sale of recovered materials was financing the collection of garbage in Brooklyn and Manhattan. The resulting conflict would be familiar to generations of environmental professionals. The nearby communities had a LULU (Locally Unwanted Land Use) that was also providing critical services for the larger city. The Jamaica Bay seaport plan had wide political support that did not translate into financial backing. Some shipping channels were dredged. Along the north shore of the bay, tidal creeks were straightned to create boat basins. These projects however would be useless without freight railroad connections to the mainland. These connections could only be provided by a railroad tunnel under Lower New York Harbor that would have linked Brooklyn to Staten Island.

On January 30, 1923, Samuel Rea, President of the Pennsylvania Railroad, sent a letter to New York Mayor Hylan stating that he and a committee of executives of railroads entering New York concluded that a freight railroad tunnel from Staten Island to Brooklyn was "not in the public interest." The letter was signed by representatives of almost all of the major railroads serving New York. A lengthy engineering report accompanied the letter. The report concluded that the traffic projections made by the City of New York were overly optimistic as was the city's estimated cost for the tunnel. The existing system of cross-harbor freight handling system was adequate for the existing traffic and given the traffic volumes, a new tunnel would not pay for itself. (*Engineering News Record* Feb.9, 1923, 88:251.) With so much already invested in the plan, the city government continued to press for new railroad connections. As late as 1931 the Queens Planning Commission and the Borough President were still calling for the necessary extension of railroad facilities to make the port scheme a reality. At the same time the Brooklyn Chamber of Commerce was calling for railroad spurs on each side of Paerdegat Basin coming off the New York Connecting Railroad’s Ralph Avenue Line (“Would Speed Terminals, *New York Times*, Aug. 2, 1931).

Jamaica Bay did become a major transportation hub with the development of aviation. The bay's sheltered waters were ideal for operating sea planes. The US Navy established the Rockaway Naval Air Station so that aircraft could patrol the approaches to New York during the First World War. With the success of the navy air station, there was soon a push for civilian aviation facilities. The waste processing plants on Barren Island had by this time become obsolete and with fewer draft horses working on the streets of the city, there was no longer a pressing need to dispose of carcasses. A new generation of waste processing plants began operations on Staten Island. Barren Island was taken over by the city for the construction of Floyd Bennett field, New York City's first municipal airport. A combination of the great Depression, the failure of the seaport scheme, and a growing demand for recreational facilities ultimately lead to to creation of a city park and wildlife refuge in Jamaica Bay. By this time, the bay had long been a major recreational resource for the city of New York and by the 1920s there was no disputing the importance of parkland in the life of a city. Boaters continued to use the open waters of the bay but its marshy shorelines would not have attracted more than a handful of bird watchers or hunters. It may be assumed that the development of conventional park lands with lawns, play areas, restrooms, waterfront promenades, and food concessions would have required more dredging and filling than the city was willing to pay for. Many parks near the bay were constructed on filled lands. Meanwhile the surrounding communities did not use the accessible marshes for recreation, rather as dumping grounds for old appliances and construction debris.

Another alternative use would have been an expansion of marine aviation. In the 1920s and into the 1930s the world's airports were still largely undeveloped and many aviation experts argued that seaplanes and their larger cousins, flying boats, could provide immediate access to any of the world's seaport cities without the cost of a new airfield. Additionally, having a aircraft that could make a mid-ocean emergency landing was an important safety feature in an era of unreliable engines. In 1937, the city's official marine aviation terminal was constructed instead of the north shore of Long Island at what is now LaGuardia Airport.

The pressing management question was whether planning for the seaport set a precident for the city to consider some kind of unified plan for the future of Jamaica Bay. While some far-sighted municipal planners certainly had a unified vision of the bay's future, Jamaica Bay seems to have become a park because the city had no other use for it.

Jamaica Bay as a Park

There was no more certain symbol that the seaport plans were a thing of the past and that Jamaica Bay was now a park than what happened on Canarsie Pier on the Fourth of July, 1944. Mayor La Guardia made a six-hour tour of New York City's recreation spots including the Pelham Bay Golf Course, the Astoria Pool, and Prospect Park. The July 4th, 1944 tour covered 103 miles and featured twelve scheduled stops. It was intended to promote parks and recreation sites within the city's borders. Crowds surrounded the mayor at Rockaway Beach and Coney Island. Lunch was served on Canarsie Pier, chicken and ham sandwiches, tomato salad, and apple pie with strawberry ice cream. (The mayor declined the pie as he rarely ate desserts) La Guardia said that lunch on the pier was "The first picnic I've had in a long time."("City's Play Sites Toured By Mayor", *New York Times*, July 5, 1944).

Upon winning the mayoral election in 1933, Fiorello La Guardia invited Robert Moses to join his administration. As President of the Long Island State Park Commission, Moses had already directed the development of Heckscher State Park, Jones Beach State Park and the Southern Shore Parkway (Caro p 309).

In staffing Jones Beach and other public parks Moses had further endeared himself to reformers by refusing to use the many jobs they created for political patronage (Caro 1974, 305). Moses would never endear himself to environmentalists because his conception of parks included parkways so that driving to the park would be part of the visitor experience. The parkways that lead to Jones Beach and other Moses parks had a width of 40 feet, extremely generous by the standards of the late 1920s. The roads passed through a landscaped green space. Grade crossings were separated and while there might be tollbooths, there were no traffic lights. At the time a few critics pointed out that by providing only access to private automobiles the parks Moses created would forever be restricted to the relatively affluent. But the critics were in the minority and at that time, the general public regarded Moses as the model of a dedicated public servant.

The combination of Parks Commissioner and Parkway Builder allowed Moses to construct roadways that would soon result in Manhattan being completely encircled by express highways and "ribbon parks" (Rodgers 1952). In 1934 construction began on the Belt Parkway that began in Brooklyn at 68th Street and Colonial Road. The Belt Parkway begins in Owl's Head Park. This park sits on a hill forming the end of the glacial moraine cutting across Brooklyn. The land for the park was acquired in 1928 from the estate of the industrialist Eliphalet Bliss. (The park is still known locally as Bliss Park). Less than half of the newly acquired land went for the construction of the park; the rest was swallowed up by the Belt Parkway and various other uses (Morrone n.d.). Lined with green spaces along its entire length, the Belt Parkway swung inland north of Coney Island and Sheepshead Bay before returning to the shoreline and running along the north shore of Jamaica Bay (Rodgers 1952).

Inside the borders of Brooklyn’s Marine Park, the Marine Parkway leaves the Belt Parkway and extends south over the Marine Park Bridge to connect Brooklyn with the Rockaway Peninsula. This bridge was built in less than a year and gave city dwellers (or at least those with automobiles) direct access to Jacob Riis Park on the Rockaway Peninsula (Rodgers 1952).

The Belt Parkway did create parkland and open space along the Bay Shore but it also had the effect of cutting off the bay from many of the surrounding neighborhoods including Flatlands, Mill Basin, Canarsie, and East New York. This disconnect would have profound implications for the creation of the National Park in later years because a generation of New Yorkers would have to learn a new connection to Jamaica Bay. During the 1930s through the efforts of Robert Moses, at that time the city's Parks Commissioner, the city acquired 9,000 acres comprising the water and islands of the bay. The city also acquired another 3,000 acres of shoreline. It wasn't until 1954 that the city managed to acquire additional land that was combined with existing city property to form Jamaica Bay Park.

Jamaica Bay officially became a wildlife refuge in 1951. For Robert Moses, a wildlife refuge was a low priority in the planning and development of the park but he still responded forcefully when threatened with encroachment. In 1950 the Long Island Railroad wanted to replace the original wooden trestle over the bay. The Transit Authority purchased the bridge and planned to convert the line to handle subway trains. Their plans were to replace sections of the trestle with a causeway built from dredged sand. Moses refused to allow this unless the Parks Department received something in return. The Transit Authority agreed to excavate two freshwater ponds, on the east and west sides of the Cross Bay Boulevard. Six million cubic yards of dredged sand were used to create are two impoundments which were then planted with vegetation by New York City Parks Department. The choice of plantings was determined by their ability to thrive in coastal conditions and to provide food and nesting sites to bird populations (Tanacredi 1983, 143-150). Completed by 1953 these two features were the start of the wildlife refuge. Another project undertaken at that time was to pump sludge from the 26th W Sewage Treatment Plant onto Canarsie Pol where it was mixed with sand and planted with beach grasses by Herbert Johnson (Barlow 1971, 112). The use of sewage solids for topsoil production had been proposed since the first sewage plants were built in Brooklyn and Queens (Scanlon, “Utilization of Sewage Sludge for the Production of Topsoil”, *Sewage and Industrial Wastes,* Vol.29, No.8, Aug.1957, 944-950).

Herbert Johnson, Appointed by Moses to be Resident Supervisor of the refuge in 1951. Prior to coming to the refuge he was working at the Parks Department's soil testing laboratory in the Bronx where he experimented with different types of grasses for golf courses. Johnson's father was an estate gardener. Johnson had a fee hand and propagated autumn Olives, Rosa rugosa, Rosa Multiflora, baybery, and chokeberry. He established a nursery for Japanese Black Pines and sowed wheat oats, and rye to attract land birds (Barlow 1971, 115).

Announcing plans for post-war park development Robert Moses wrote in the *New York Times* that Marine Park would receive a modern boat basin on Jamaica Bay along with a boat house, parking lots, and a launch service to ferry boaters from the shore to moored boats. Facilities to be built at the Deep Creek Basin would provide dock space, moorings, and row boats for hire. Canarsie Pier had a 100-foot long landing barge adjacent to the pier (its purpose was not explained), a yacht anchorage, row boats for hire, a large parking lot, a concession building, lockers, and comfort stations (Moses, “City Park Commissioner, City Plans to Expand and Improve Boat Basins in Various Boroughs”, *New York Times,* Jan.12, 1947).

Writing in 1948 Moses reported that the single greatest problem facing future park development on the waterfront was sewage pollution. Moses was unequivocal when he stated that "this threat has been played down, minimized and dismissed by altogether too many agencies and official bodies. Only certain sections of the press have been told the whole truth about it, because the truth hurts our pride and our pockets." In 1948 one-third of the city was served by six sewage treatment plants, Moses called for the construction of an additional seven plants at a total cost of $57,000.000 (Moses, “New York Reclaims Its Waterfront”, *New York Times,* Mar.7, 1948).

By the late 1960s, 50,000 people were visiting the refuge each year (Barlow 1971, 107). Herbert Johnson, manager of the refuge in the 1960’s is credited with saying that, “I’ll bet I’ve got the only bird sanctuary in the world with a subway running through it” (108). In 1969 Secretary of the Interior Walter Hinckel proposed the creation of the Gateway National Recreation Area to encompass the entire harbor area from Sandy Hook to the Rockaway Peninsula. An early study for the recreation area recommended inclusion of the Jamaica Bay wildlife refuge (Barlow 1971, 109). Even though the bay was degraded it was still good wildlife habitat since the islands, sand islands, sandy shore edges and brackish ponds were still available as of 1970 (Taormina, “Environment: Journal on Jamaica Bay”, *The Conservationist,* 1970, vol.24, no. 5, 16-20). Jamaica Bay and the city’s lands on the Rockaway Peninsula were turned over to the National Park Service in 1972. At the time the city was facing its fiscal crisis and money for all but the most essential city services was not available. The political issues surrounding the creation of urban national parks in New York, San Francisco, and Boston, were complex but can be summarized briefly, the country's major cities were financially strapped, and the urban riots of the late 1960s convinced lawmakers that urban populations needed recreation areas.

As it existed in the mid-1970s the park's Breezy Point Unit on the Rockaway Peninsula exemplified the conflicts and difficulties involved with establishing a national park in the midst of a populated area. The unit consisted of 1,600 acres and four and half miles of ocean beaches (General Management Plan, Sept 1976, 120). The idea of making all of Breezy Point into public parkland was an idea going back to the 1920s (122). The transfer of public lands to the National Park Service proceeded smoothly enough. The unit's popular public beach was conveyed from New York City as it was originally the city's Jacob Riis Park. Other parcels of land were also transferred from the city while the Federal government conveyed Fort Tilden, the surrounding lands, and the fort's facilities (120). Fort Tilden was first constructed in 1917 on land filled by the Army Corps of Engineers. It was decommissioned in 1967 and transferred to the Park Service in 1972 (Stalter, Byer and Tanacredi 1996, 41-51).

Land acquisition from private sources was somewhat more complicated. A beach abutting the private Breezy Point Cooperative was scheduled to be purchased, but to be successful would require the Department of the Interior to waive all future rights to acquire other lands belonging to the Cooperative. This would allow the community to remain one of single-family homes, as indeed it remains to the present day (General Management Plan 1976, 122). The City acquired a complex of half-finished buildings, a remnant of the struggle to preserve the land as a public park, and conveyed them to the Park Service. Two private beach clubs were located on each side of the Breezy Point Cooperative. They were made part of Gateway NRA and allowed to remain operating on a year to year basis. As part of this arrangement they were required to advertise for new members and admit anyone who wanted to join (General Management Plan 1976, 124). The troubles that the Park Service went through to assemble the Breezy Point Unit paid off handsomely. There were 3.4 million visitors in 1975 with peak usage at 90,000 persons a day or 36,000 people on the beach at any one time (General Management Plan 1976, 124). The Park Service expected that once all of the planned land acquisitions were made, the beaches would be able to accommodate easily twice this number of visitors, that is, if the people could get to the beach. In 1975 about 15% of the visitors arrived at Breezy Point via public transportation. This was the highest percentage of any unit in Gateway but it was still insufficient. Automobile traffic was already reaching saturation of peak days and the Park Service did not even own the parking lots. The parking lots at Jacob Riis Park were still owned by the Triborough Bridge and Tunnel Authority and would be conveyed to the Park Service once the bonds sold to build it were repaid (General Management Plan 1976, 120).

Even larger numbers of visitors were expected after the land acquisitions were completed. The Park Service expected 8,000,000 annual visitors and 200,000 persons on a peak day. During a peak day, 80,000 persons would be on the beach at any one time (General Management Plan 1976, 126). The Park Service calculated that accommodating this number of persons would require 1,875 bus transits over the Marine Parkway Bridge and another 750 along the Rockaway Peninsula. Some of the buses would be shuttles operated from the railroad terminals while others would be created by extending existing bus lines. Wherever the busses ran from, the Park Service recommended that local transportation planners make designing such a system a high priority (126).

It was one thing to proclaim that Jamaica Bay proper was now a National Wildlife Refuge, it was another to make the shorelines into suitable bird habitat. Fortunately restoring the bay was a pet project of people like Bernie Blum. For twenty years Blum had been advocating the creation of a park on a point of city land known as Conchs Hole Point. Blum also was a one-man environmental monitoring force, mapping where stolen cars and waste oil were being dumped. Someone had even somebody had dropped a truckload of lawbooks. Otherwise-tidy neighbors were using the point for dumping their rubbish. It was ironic that the neighbors who took pride in the neat appearance of their homes felt no such pride in the nearby land. The city already owned the small peninsula where Blum and his allies wanted to create the park, all that was needed was the political will (Kastner, J. 1990, “The `Miracle' on Jamaica Bay didn't happen overnight.” *Smithsonian*, Jul. 1990).

Blum was pushing for the park from outside the city government and another two individuals were leading the fight from the inside. Marc Matsil was the director of the Division of Natural Resources in the New York City Parks Department. Al Appleton was a former state attorney and volunteer for the New York City Audubon Society. After being appointed the city's environmental commissioner, in 1984 he began working to create the park that Blum had envisioned. The Audubon Society played a critical role in the negotiations. In 1988 the park was created and at the suggestion of Bernie Blum, the land at Conchs Hole Point was renamed Dubos Point Park. Rene Dubos, who died in 1982, was a distinguished microbiologist who made important discoveries in the field of antibiotics but he was also a writer and thinker about environmental issues. He would eventually win a Pulitzer Prize for his ecological writing (Kastner, J. 1990, "The `Miracle' on Jamaica Bay didn't happen overnight." *Smithsonian*, Jul. 1990).

At the time the park was created, the land was covered with goldenrod and poison ivy. There were junked cars, old concrete, broken glass, tires, rotted wood and moldy wallboard. But there were also snowy egrets, great blue heron, periwinkles, and blue crabs. Many cleanup efforts by volunteers slowly returned the point to something resembling a clean ecosystem (Kastner, J. 1990, "The `Miracle' on Jamaica Bay didn't happen overnight." *Smithsonian*, Jul. 1990).

Floyd Bennett Field became one of the most important active recreation areas in the park. The former US Navy hangers and the original Ryan Terminal building were preserved at the same time that the Park Service seeded an area with grass that was larger than Central Park (Strausbaugh, “Where New Yorkers First Took Flight”, *New York Times*, July 10, 2009).

The range of activities at the former airfield is as diverse as the city it serves. The Field is a mecca for radio-controlled model airplane enthusiasts. Gardeners from all five boroughs tend 600 community garden plots growing herbs, vegetables, and flowers. The former runways are used for bicycle racing and land sailing. There is also an archery range and a cricket pitch. A camping area surrounded by trees and shrubs is open to the public by permit. The nearby Ecology Village is home to a two-day, summer camping program for city schoolchildren between the ages 8 and 14. Many of the children in the program have never slept outdoors (Strausbaugh, “Where New Yorkers First Took Flight”, *New York Times*, July 10, 2009).

The current National Recreation Area encompasses the shoreline east and south of the Belt Parkway between Plum Beach and Spring Creek Park, the islands and marshes in the bay and the waters of the bay. The National Recreation Area does not include the communities on Broad Channel Island, most of the mainland in Queens County, Brooklyn, and developed portions of the Rockaway peninsula.

While participating at DredgeFest 2012, Gateway National Park's Chief of Resources, David Avrin stated that one of the most serious problems with operating a National Park in an urban setting is that the Park Service is by nature a very conservative organization. It rules and operating policies were created for managing remote and undeveloped areas. Despite decades of experience with urban parks, many of its rules are the same for both urban areas and wilderness zones. Decision making in an urban park is complicated by the fact that allowing natural processes to function independently, the default mode of operation in a wilderness, is not always a viable option in areas that are heavily impacted by man.

Some of the decisions made about restoring Jamaica Bay's marsh islands provide an example how competing needs complicates working in urban National Parks. As of the fall of 2012 five of the marsh islands in Jamaica Bay were being restored with sands pumped from the navigation dredging operations in the Ambrose Channel. Forty-four acres will be restored on Yellow Bar Hassock alone. Special attention was paid to decisions about the islands' shape, their height above sea level, and goals of habitat restoration. The shorelines of the restored islands will be sculpted to their historic footprints as of 1974. Projections of localized sea level rise were used to determine the ratio of high marsh to low marsh (Baron, “Dredge and the Anthropocene”, *DredgeFest,* September 2012). This balance is critical in determining biodiversity. Jamaica Bay's position on the Atlantic Flyway makes providing bird habitat a high restoration priority, but this conflicts with its role as the home of John F. Kennedy International Airport. The solution was to make the islands farthest from the airport the best habitats. This has resulted in fewer birds nesting near the airport and a reduced risk of bird strikes

(DredgeFest 2012).

The USACE dredgers move tens of thousands of cubic yards of sediments and its earthmoving equipment shifts tens of cubic yards with every minute. Public buy-in and support is critical to the success of restoration projects but there would seem to be little opportunity for members of the public to participate in such a heavily mechanized process. Furthermore, National Parks depend on citizen involvement at many levels. The USACE solved this problem by enlisting volunteers to plant marsh grasses once the heavy equipment had finished sculpting the landforms. In the autumn volunteers collected grass seeds from existing stands of marsh grass and in the spring the same volunteers will plant the seeds. There was a precedent for this activity, a similar project took place in Dubos Point Park in the late 1980s when local science teacher, Lou Siegel, and his students collected the seeds of *Spartina alterniflora* for restoration projects (Kastner, J. 1990, “The `Miracle' on Jamaica Bay didn't happen overnight.” *Smithsonian*, Jul. 1990).

It would be interesting to know if any of the volunteers had a distant ancestor who grazed his livestock on the same species of grasses on the same islands before Jamaica Bay was engulfed by the city.

In thinking about ordinary places like coastal marshes, Emerson said: "I ask not for the great, the remote, the romantic...I embrace the common, I explore and sit at the feet of the low." (Emerson, The American Scholar, 1837) Jamaica Bay may be low-lying and it is hardly remote, but as its history demonstrates, it is anything but common.

Figure and Table

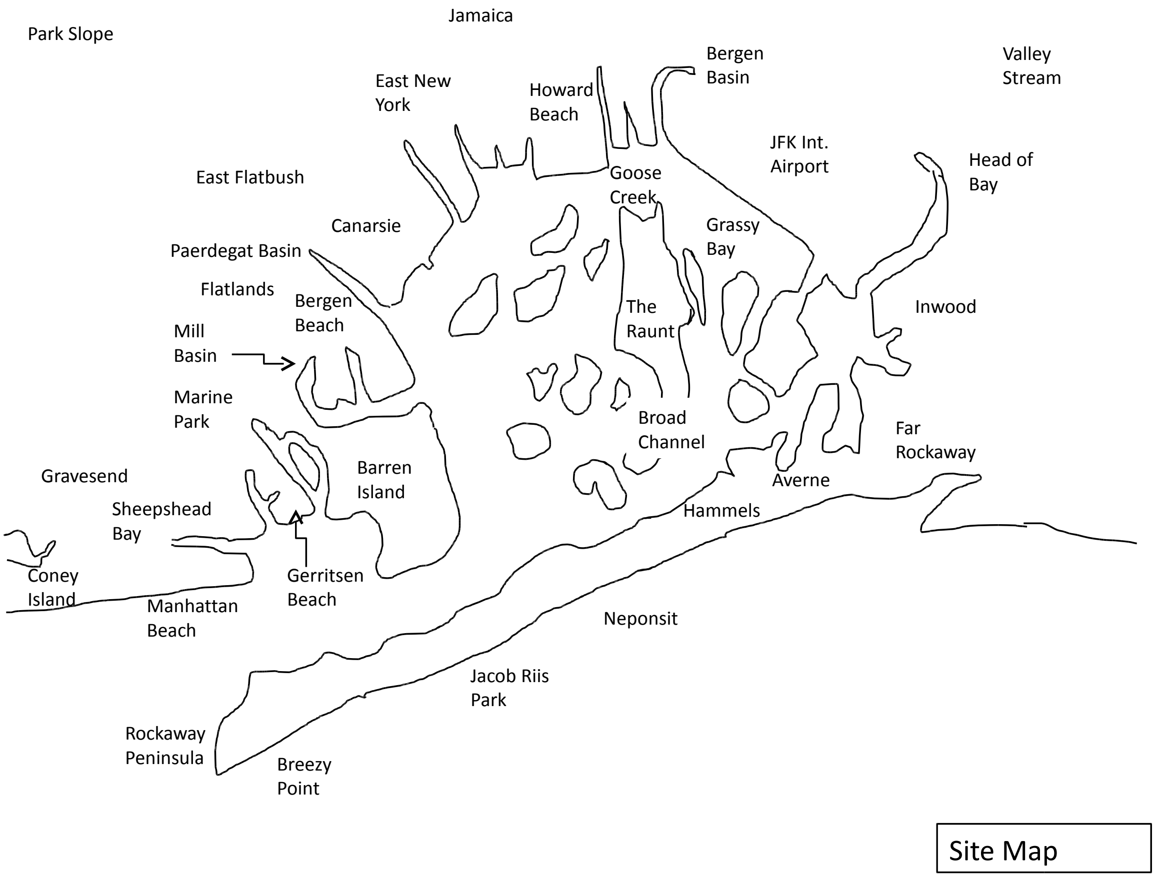


Figure 1-1, The principle neighborhoods in and around Jamaica Bay. Many of the original place names have survived the consolidation of Kings County (Brooklyn) and Queens County into the City of New York.

Table 1-1 Abbreviations of the chemical names and chemical classes used for the figures and tables in chapters 2 and 3.

Code	Compound	Compound class
^11	C11 n-alk-1-ene	Normal and isoprenoid alkenes
^12	C12 n-alk-1-ene	Normal and isoprenoid alkenes
^13	C13 n-alk-1-ene	Normal and isoprenoid alkenes
^14	C14 n-alk-1-ene	Normal and isoprenoid alkenes
^15	C15 n-alk-1-ene	Normal and isoprenoid alkenes
^16	C16 n-alk-1-ene	Normal and isoprenoid alkenes
^17	C17 n-alk-1-ene	Normal and isoprenoid alkenes
^18	C18 n-alk-1-ene	Normal and isoprenoid alkenes
^19	C19 n-alk-1-ene	Normal and isoprenoid alkenes
^20	C20 n-alk-1-ene	Normal and isoprenoid alkenes
^21	C21 n-alk-1-ene	Normal and isoprenoid alkenes
^22	C22 n-alk-1-ene	Normal and isoprenoid alkenes
^23	C23 n-alk-1-ene	Normal and isoprenoid alkenes
^24	C24 n-alk-1-ene	Normal and isoprenoid alkenes
^25	C25 n-alk-1-ene	Normal and isoprenoid alkenes
†10	C10 n-alkane	Normal and isoprenoid alkanes
†11	C11 n-alkane	Normal and isoprenoid alkanes
†12	C12 n-alkane	Normal and isoprenoid alkanes
†13	C13 n-alkane	Normal and isoprenoid alkanes
†14	C14 n-alkane	Normal and isoprenoid alkanes
†15	C15 n-alkane	Normal and isoprenoid alkanes
†16	C16 n-alkane	Normal and isoprenoid alkanes
†17	C17 n-alkane	Normal and isoprenoid alkanes
†18	C18 n-alkane	Normal and isoprenoid alkanes
†19	C19 n-alkane	Normal and isoprenoid alkanes
†20	C20 n-alkane	Normal and isoprenoid alkanes
†21	C21 n-alkane	Normal and isoprenoid alkanes
†22	C22 n-alkane	Normal and isoprenoid alkanes
†23	C23 n-alkane	Normal and isoprenoid alkanes
†24	C24 n-alkane	Normal and isoprenoid alkanes
†25	C25 n-alkane	Normal and isoprenoid alkanes
†26	C26 n-alkane	Normal and isoprenoid alkanes
†27	C27 n-alkane	Normal and isoprenoid alkanes
†28	C28 n-alkane	Normal and isoprenoid alkanes
†29	C29 n-alkane	Normal and isoprenoid alkanes
†30	C30 n-alkane	Normal and isoprenoid alkanes
†31	C31 n-alkane	Normal and isoprenoid alkanes

Pr:1	prist-1-ene	Normal and isoprenoid alkenes
Pr:2	prist-2-ene	Normal and isoprenoid alkenes
Ph	Phytane	Normal and isoprenoid alkanes
Pr	Pristane	Normal and isoprenoid alkanes
EB	Ethylbenzene	Monoaromatic hydrocarbons
B2:	Styrene	Monoaromatic hydrocarbons
B-n3	n-propylbenzene	Monoaromatic hydrocarbons
B-n4	n-butylbenzene	Monoaromatic hydrocarbons
B-n5	n-pentylbenzene	Monoaromatic hydrocarbons
B-n6	n-hexylbenzene	Monoaromatic hydrocarbons
B-n7	n-heptylbenzene	Monoaromatic hydrocarbons
B-n8	n-octylbenzene	Monoaromatic hydrocarbons
B-n9	n-nonylbenzene	Monoaromatic hydrocarbons
B-n10	n-decylbenzene	Monoaromatic hydrocarbons
B-n11	n-undecylbenzene	Monoaromatic hydrocarbons
B-n12	n-dodecylbenzene	Monoaromatic hydrocarbons
B-n13	n-tridecylbenzene	Monoaromatic hydrocarbons
B-n14	n-tetradecylbenzene	Monoaromatic hydrocarbons
B-n15	n-pentadecylbenzene	Monoaromatic hydrocarbons
B-n16	n-hexadecylbenzene	Monoaromatic hydrocarbons
LAB6-11	6-phenylundecane	Linear alkylbenzenes
LAB5-11	5-phenylundecane	Linear alkylbenzenes
LAB4-11	4-phenylundecane	Linear alkylbenzenes
LAB6-12	6-phenyldodecane	Linear alkylbenzenes
LAB5-12	5-phenyldodecane	Linear alkylbenzenes
LAB4-12	4-phenyldodecane	Linear alkylbenzenes
LAB6-13	6-phenyltridecane	Linear alkylbenzenes
LAB5-13	5-phenyltridecane	Linear alkylbenzenes
LAB4-13	4-phenyltridecane	Linear alkylbenzenes
N0	Naphthalene	Naphthalenes
2mN	2-methylnaphthalene	Alkylnaphthalenes
1mN	1-methylnaphthalene	Alkylnaphthalenes
N2	dimethylnaphthalenes	Alkylnaphthalenes
N3	trimethylnaphthalenes	Alkylnaphthalenes
N4	tetramethylnaphthalenes	Alkylnaphthalenes
FLU	Fluorine	PAHs - Parent
PHN	Phenanthrene	PAHs - Parent
ANT	Anthracene	PAHs - Parent
mFLU	Methylfluorenes	PAHs - alkyl
3MP	3-methylphenanthrene	PAHs - alkyl
2MP	2-methylphenanthrene	PAHs - alkyl
MA	Methylanthracene	PAHs - alkyl
9MP	9-methylphenanthrene	PAHs - alkyl
1MP	1-methylphenanthrene	PAHs - alkyl
PHN2	dimethylphenanthrenes	PAHs - alkyl
RET	Retene	PAHs - alkyl

FLA	Fluoranthene	PAHs - Parent
PYR	Pyrene	PAHs - Parent
BAN	benzo[a]anthracene	PAHs - Parent
CHR	Chrysene	PAHs - Parent
PYR1	methylpyrene isomers	PAHs - alkyl
PYR2	dimethylpyrene isomers	PAHs - alkyl
CHR1	methylchrysene isomers	PAHs - alkyl
BbFLA	benzo[b]fluoranthene	PAHs - Parent
BjFLA	benzo[j]fluoranthene	PAHs - Parent
BkjFLA	benzo[k]fluoranthene	PAHs - Parent
BePYR	benzo[e]pyrene	PAHs - Parent
BaPYR	benzo[a]pyrene	PAHs - Parent
PER	Perylene	PAHs - Parent
IPYR	indenol[1,2,3-cd]pyrene	PAHs - Parent
BPER	benzo[ghi]perylene	PAHs - Parent
DBAx	dibenzoanthacene isomer	PAHs - Parent
DBA	dibenzo[a,h]anthracene	PAHs - Parent
HO29	C29 hopane (17a, 21b)	Hopanes (petroleum markers)
HO30	C30 hopane (17a,21b)	Hopanes (petroleum markers)
S27AR	C27 sterane	Steranes
S28AR	C28 sterane	Steranes
S29AR	C29 sterane	Steranes
ST27	Cholestene	Sterenes
ST29	Ethylcholestene	Sterenes
F0	Phenol	Oxygenated compounds
2mF	2-methylphenol	Oxygenated compounds
4-3mF	4&3-methylphenols	Oxygenated compounds
4eF	4-ethylphenol	Oxygenated compounds
F2:	Vinylphenol	Oxygenated compounds
G0	Guaiacol	Guaiacols (Lignin markers)
G1	Methylguaiacol	Guaiacols (Lignin markers)
G2	Ethylguaiacol	Guaiacols (Lignin markers)
G2:	Vinylguaiacol	Guaiacols (Lignin markers)
VAN	Vanillin	Guaiacols (Lignin markers)
G3:a	Eugenol	Guaiacols (Lignin markers)
G3:b	cis iso-eugenol	Guaiacols (Lignin markers)
G3:c	trans iso-eugenol	Guaiacols (Lignin markers)
AVAN	Acetovanillone	Guaiacols (Lignin markers)
S0	Syringol	Syringols (Angiosperm markers)
S1	methylsyringol	Syringols (Angiosperm markers)
S2	Ethylsyringol	Syringols (Angiosperm markers)
S2:	Vinylsyringol	Syringols (Angiosperm markers)
Sald	Syringaldehyde	Syringols (Angiosperm markers)
S3:a	prop-1-enyl syringol	Syringols (Angiosperm markers)
S3:b	cis-prop-2-enyl syringol	Syringols (Angiosperm markers)
S3:c	trans-prop-2-enyl syringol	Syringols (Angiosperm markers)

BA0	Benzaldehyde	benzaldehyde
BA1	benzaldehyde methyl	benzaldehyde
FCA1	Methylfurfural	Polysaccharide pyrolysis markers
Fone1	Methylfuranone	Polysaccharide pyrolysis markers
O1a	2-methylcyclopentenone	Polysaccharide pyrolysis markers
O1b	3-methylcyclopentenone	Polysaccharide pyrolysis markers
AO13	C13-alk-2one	Long Chain Alk-2-ones
AO14	C14-alk-2-one	Long Chain Alk-2-ones
AO15	C15-alk-2-one	Long Chain Alk-2-ones
AO16	C16-alk-2-one	Long Chain Alk-2-ones
AO17	C17-alk-2-one	Long Chain Alk-2-ones
AO18	C18-alk-2-one	Long Chain Alk-2-ones
AO19	C19-alk-2-one	Long Chain Alk-2-ones
CA14	n-tetradecanoic acid	Alkanoic Acids
i-CA15a	pentadecanoic acid isomer	Alkanoic Acids
i-CA15b	pentadecanoic acid isomer	Alkanoic Acids
CA15	n-pentadecanoic acid	Alkanoic Acids
CA16	n-hexadecanoic acid	Alkanoic Acids
CA17	n-heptadecanoic acid	Alkanoic Acids
CA18	n-octadecanoic acid	Alkanoic Acids
CA20	n-eicosanoic acid	Alkanoic Acids
CA22	n-docosanoic acid	Alkanoic Acids
CA24	n-tetracosanoic acid	Alkanoic Acids
Pl2	C2-alkylpyrrole	One Ring Nitrogen Compounds
BCN0	Benzonitrile	One-ring Nitrogen compounds
BCN1	Benzoacetonitrile	One-ring Nitrogen compounds
BCN2	benzenepropanitrile	One-ring Nitrogen compounds
Qu	Quinolone	Two-ring Nitrogen compounds
i-Qu	Isoquinoline	Two-ring Nitrogen compounds
Il0	Indole	Two-ring Nitrogen compounds
Il1	Methylindole	Two-ring Nitrogen compounds
PPd	Phenylpyridine	Two-ring Nitrogen compounds
CBZ	Carbazole	N-PAH's
DKDP	Diketodipyrrole	protein marker
DKPa	cyclo-Pro-Pro-diketopi...	protein marker
AN14	n-tetradecanitrile	aliphatic N compounds
AN16	n-hexadecanitrile	aliphatic N compounds
AN18	n-octadecanitrile	aliphatic N compounds
AM14	Tetradecylamide	aliphatic N compounds
AM16	Hexadecylamide	aliphatic N compounds
AM18	Octadecylamide	aliphatic N compounds
DBT	Dibenzothiophene	Benzothiophenes
4mDBT	4-methyldibenzothiophene	Dibenzothiophenes
1mDBT	1-methyldibenzothiophene	Dibenzothiophenes
3+2mDBT	3-&2-methyldibenzothiophenes	Dibenzothiophenes
BNT	benzonaphthothiophene isomer	Benzothiophenes

S8	elemental sulfur	sulfur

Abbreviations used for plotting compound classes during PCA

n-alkene short	^S
n-alkene long	^L
n-alkane short	†S
n-alkane long	†L
isoprenoid alkene	IA:
isoprenoid alkane	IA
phytadiene	ID
monoaromatic hydrocarbon	MAH
n-alkylbenzene	NAB
linear alkylbenzene	LAB
naphthalene	NPH
alkylnaphthalene	aNPH
PAH - 3-ring parent	PAH3
PAH - 3-ring alkyl	aPAH3
retene	RET
PAH - 4-ring parent	PAH4
PAH - 4-ring alkyl	aPAH4
PAH - 5-ring parent	PAH5
PAH - 6-ring parent	PAH6
hopane	HOP
sterane	STA
sterene	STE
phenolic - simple	FEN
guaiacol	GUA
syringol	SYR
benzaldehyde	BAL
polysaccharide marker	PSM
alkenone	ALO
n-alkanoic acid - short	AAS
n-alkanoic acid - long	AAL
azaarene - 1 ring	AZ1
azaarene - 2 ring	AZ2
indoles	IND
azaarene - 3 ring	AZ3
protein marker	PRO
alkylnitrile	ANI
alkylamide	AMD
alkanamine	AMN
thioarene	THI
isoprenoid thiophene	ITH
sulfur	S

Chapter Two

Estuarine conditions and sediment chemistry, a case study from the Gateway National Recreation Area of Greater New York using Pyrolysis - Gas Chromatography / Mass Spectrometry

Abstract

The surface layer of estuarine sediments from the Gateway National Recreation Area (NRA) was studied by pyrolysis – gas chromatography / mass spectrometry (Py-GC/MS). A comparatively small number of organic molecules can characterize organic matter inputs over a large geographical region and help understand the reasons behind environmental degradation in the Jamaica Bay unit and especially the loss of marshes in the center of the bay. The ratio of two pyrolysis products, vinylguiacol, from terrestrial plant lignin, and indole, from protein, (VGI Index or VGII) is moderately well correlated with the sediment C/N ratios. The VGII suggests that the primary organic matter inputs along the shores of Jamaica Bay is terrestrial while marine inputs dominate where marsh loss has been greatest. In contrast, healthy salt marshes in the Sandy Hook unit had a VGII of 0.82. Throughout the NRA the VGII could also be correlated with other sedimentary organic analyses, the Carbon Preference Index (CPI) (r = 0.54) and the Syringol / Vanillyl (S/V) ratio (r = 0.87). High CPI values indicate contributions from terrestrial plants cutins. Large S/V values are associated with organic matter contributions from grasses. Significant anthropogenic inputs from sewers and combustion-derived polycyclic aromatic hydrocarbons (PAH) inputs are also found in the Jamaica Bay sediments. Taken together, these analyses make a valuable contribution to understanding estuary conditions.

Introduction

Gateway National Recreation Area is divided into three parts, Sandy Hook in New

Jersey, Great Kills on the east shore of Staten Island, and Jamaica Bay/Breezy Point on the southern shore of Long Island (figure 2-1). (All sample points in this study are listed in table 2-1.) This work was undertaken in response to a call from the National Park Service for sediment studies in the Jamaica Bay Unit. Sampling activities were performed under research permit number GATE-2007-SCI-0002. A preliminary report focused on PAH distributions was submitted to the Park Service as Study Number GATE-00174. The authors believe that the present study is the first attempt to use pyrolysis - gas chromatography/mass spectrometry (Py-GC/MS) to create a park-wide survey of the surface layer of sediments. Such a survey will help understand habitat stability and identify areas were contamination is concentrated. There is also an attempt integrate quantities of pyrolysis products (chiefly phenols) with concentrations of other types of molecules (alkanes, polycyclic aromatic hydrocarbons, hopanes, and steroids) in order to create a detailed picture of estuary conditions. A number of earlier sediment studies with a more limited geographic scope were conducted as part of environmental impact statements and academic research (Rhoads, et al, 2001, Barry A. Vittor & Associates 2003).

Site Descriptions

The Gateway National Recreation Area was created in 1972. Creation of the park culminated seven year of efforts to preserve the last undeveloped shorelines in the New York metropolitan region. (NPS 1976) Gateway was one of the first urban parks in the National Park System and quickly became popular with the region's many residents. By

1975 there were 5.1 million annual visits to the park's three units. (NPS 1976) The Gateway National Recreation Area (NRA) encompasses 108 km2 of land and tidal waters and features a number of ecosystem types. Portions of Gateway NRA include the last remnants of the original Hudson – Raritan Estuary (Tanacredi 1983).

The remnants off the original Hudson – Raritan Estuary preserved by the park’s creation included a small swamp white-oak forest on Staten Island, as well as relatively undisturbed sand dunes, salt marshes, and grasslands in other units. (NPS 1976) Other portions of Gateway included areas that were anything but undisturbed. The Sandy Hook Peninsula had been a defensive site for New York Harbor and occupied by the Army from the American Revolution until the creation of Gateway NRA.

Great Kills (Staten Island Unit)

The Staten Island Unit comprises some 11.7 km^2 along the eastern shore of the island and included Fort Wadsworth on its northern end (still occupied by the Army when Gateway was created), Miller Field (an 0.73 km^2 former air base), and Great Kills Park at the southern end. Great Kills had originally been a New York City park. It has a small harbor protected by Crookes Point, a peninsula created using artificial bulkheads. The small salt marsh system at Great Kills is only a tiny remnant of the original marshes that extended northward along the island's eastern shore as far as Fort Wadsworth.

A prominent feature in the landscape of Great Kills 2.3 km^2 is Crooke's Point, a small, triangular, and sandy area that marks the entrance to Great Kills Harbor. An arm constructed of dredged sand connects this point to the rest of the park and forms the eastern boundary of Great Kills Harbor. Dredged sand was used to construct this arm. This arm and Crooke’s Point support a variety of littoral plant communities while recreational beaches line the shore. The area to the northeast of Great Kills Harbor was originally a salt marsh and later was a sanitary landfill. Sand dredged from Great Kils Harbor around 1940 was used to cover the landfill. Present vegetation is dense common reed (*Phragmites australis*). A strip of disturbed hardwood woodland is found along Hylan Boulevard, which forms the area's northwestern border (Stalter et al. 1996). The Staten Island Unit's two islands, Hoffman and Swinburne were created using dredge spoils in the 1870s and had been the site of quarantine hospitals (NPS 1976). Since 1927 the Army Corps of Engineers has maintained a navigable channel in the harbor of Great Kills. A 0.56 km^2 anchorage is dredged to a depth of 2.4 meters. The most recent dredging operation in the channel was in 2003 and removed 94,800 m^3 of sand that was used for beach replenishment (USACE 2008).

Sandy Hook Unit

Sandy Hook, as the name implies, is a sandy and narrow peninsula extending into New York Harbor where the Raritan Bay meets the Atlantic Ocean. The ocean side of the peninsula consists entirely of sandy beaches while the inland side has more diverse habitats including beaches and tidal marshes. Sandy Hook ranges from 100 to 1500 km wide with a total area of about 6.7 km^2. It was formed by the northward transport of eroded beach sand. A variety of littoral and dune vegetation is found on the site. Sandy Hook is also home to American Holly (*Zlex opaca*), red cedar (*Juniperus virginiana*), and some areas of mixed hardwoods (Stalter et al. 1996).

Jamaica Bay Unit

Jamaica Bay measures approximately 52 km^2. It is roughly semicircular with many sandy marsh islands in the center. The sandy Rockaway Peninsula forms the southern boundary of the bay and the Rockaway Inlet is the only opening of the bay to the Atlantic. Eastward flowing currents along the southern shore of Long Island have increased the size of the Rockaway Peninsula. Between1889 and 1980 the peninsula has been extended approximately 4 km westward. A rock jetty was built in 1980 to prevent further growth (Stalter, Byer, Tanacredi 1996, 41-51). Jamaica Bay has eight tributaries of various sizes, Sheepshead Bay, Paerdegat basin, Fresh Creek, Hendrix Creek, Spring Creek, Shellbank Basin, Bergen Basin, and Thurston Basin (Watershed Protection Plan, 36). Today the north shore of Jamaica Bay is dominated by John F. Kennedy International Airport. The airport's southern boundary is Grassy Bay and the Bergen Basin forms its western edge. In Bergen Basin an aviation fuel tank farm is served by four fuel handling wharves. Two of these facilities were active as of 1999 (USACE Port Series 1999). There are about fifteen named marshes forming islands in the bay. These marshes are one to three meters thick and overlie sandy substrates. Shrubs and thickets dominate the uplands on many of the larger islands. Some islands contain peat-rich marshes with meandering tidal channels. Other islands such as Rulers Bar Hassock have a sandy shore tidal marsh with limited channel inlets (Hartig 2002).

Paerdegat Basin, Barbadoes Basin, Conch Basin, Mill Basin, Shellbank Creek, and Mott Hook are straightened and dredged tidal creeks (Barlow 1971, 4).

The Jamaica Bay Wildlife Refuge is the park unit comprising 37 km^2 of marsh, wetlands, ponds, and forested areas within the 52 km^2 inside Jamaica Bay (figures 2-2 and 2-2a). The larger islands of the bay and the shorelines have been the site of landfills, seaport development, subway lines, resort development, two major airports, waste reduction facilities, water pollution control plants, and combined sewer overflows (CSOs). Much of the bay's existing shoreline was created by landfills. The Pennsylvania Avenue Landfill created a man-made 44 ha peninsula on the north shore of the bay between Howard Beach and Canarsie. Generally speaking most of Jamaica Bay’s pollutants have been found in proximity to WPCP outfalls, CSOs, storm sewers, and landfills (NYCDEP 2007).

New York City has a total of 185 km^2 of landfills many were created by filling tidal wetlands. In landfills built prior to the mid-1950s coal ash is abundant and the landfill are generally only 3-7 m thick. Later landfills contain abundant deposits of uncombusted organic matter and range from 16–27 m thick. Their covers have also been sculpted for landscaping purposes. Fine-grained wetland deposits often underlay the landfills and their close proximity to large surface-water bodies results in leachates traveling laterally into both shallow ground water and surface water. This can have a significant effect on sediment quality (Walsh and LaFleur 1995).

The Jamaica Bay unit contains an important example of how anthropogenic changes in Gateway have not always been negative. The construction of a new subway line across the bay in 1953 helped create one of the most important features of the Jamaica Bay refuge. 4.5 million m^3 cubic yards of dredged sand were used to create two impoundments which were then planted with vegetation by New York City Parks Department. The choice of plantings was determined by their ability to thrive in coastal conditions and to provide food and nesting sites to bird populations (Tanacredi 1983).

Even though Jamaica Bay was degraded it still provides good wildlife habitat since the islands, sand islands, sandy shore edges and brackish ponds were still available when Gateway NRA was created (Taormina 1970). The bay contains many diverse habitats, including coastal shoals, mudflats, sand bars, open water (littoral zone), intertidal zones (low and high marshes), and upland areas. Navigation channels in the bay have been dredged to depths of approximately 10 meters. Jamaica Bay provides prime habitat for migratory birds and the intertidal mudflats are recognized as important feeding grounds for migratory shorebirds such as black skimmers, knots, and plovers (Hartig et al. 2002).

Jamaica Bay had a wide range of sediment types. About 50% of the bay's bottom sediments can be characterized as mud. The mean proportion of the silt-clay fraction over the entire bay has been estimated to be between 30.3 and 37.5% (NYCDEP 2007). The sediments in the far western part of the Bay, defined as the area between the Cross

Bay Boulevard (running from Goose Creek to Hammels, see figure 2-2a) and the Rockaway Inlet, contain up to 80% sand and the proportion of silt increases farther to the east. Clay particles show a similar distribution, they comprise less than 10% of the sediments in the Rockaway Inlet and up to 50% in Grassy Bay (NYCDEP 2007).

Earlier research projects found that the mean total organic carbon (TOC) in Jamaica Bay was 2.6%. About 40% of Jamaica Bay sediments had less than 0.5% TOC and another 40% had TOC concentrations greater than 3.5%. When measured in 1985, Jamaica Bay sediments with less than 0.5% TOC appeared clean and yellowish brown to gray. Sediments with 0.5 to 1.0% TOC appeared "dirty" with black organic content. Those with 1.0% or higher were a black, "frothy" mud with an hydrogen sulfide odor. In the sandier western, central, and southern portions of the bay, sediments contained less than 0.5% TOC. Sediment TOC increases to 0.5 to 1.0% at Nova Scotia Bar (near Mill Basin) near JoCo Marsh, and the western side of the Rulers Bar Hassock (this location is also referred to as The Raunt and is the approximate location where sample 5 was obtained.) TOC concentrations between 1.0 and 3.0% are found outside Spring Creek and Fresh Creek as well as areas around Grassy Bay and Grass Hassock Channel. The highest TOC concentrations (>3.0%) were found in Grassy Bay, French and Hendrix Creeks, and near Broad Channel (NYCDEP 2007). Sediment particle size data from earlier research projects is provided in table 2-2. A list of sand fractions and TOC values from this project is provided in table 2-3.

In recent decades the most significant issue facing the Jamaica Bay unit has been the loss of marshlands and especially those comprising the islands in the center of the bay. Comparisons with historical aerial photographs have shown several islands marshes reduced by 12% since 1959. Low marsh vegetation loss on the islands in Jamaica bay has averaged 38% since 1974 and vegetation the loss on the smaller islands has been as high as 78%. A combination of factors is believed responsible including a reduced sediment input and localized sea level rise accompanied by land subsidence. Water ponding inside the marshes, marsh edge slumping, and widening tidal channels have also been observed in many places in Jamaica Bay. Park managers are particularly concerned that accretion rates will not keep pace with expected sea level rise in the coming decades (Hartig 2002).

Pyrolysis and Sediment Geochemistry

Py-GC/MS has been used in a number of sediment studies (Pörschmann et al. 2008, Kruge and Permanye 2004, Deshmukh et al. 2001). Among its advantages are that it requires minimal sample pre-treatment thus saving on the time and costs associated with solvent extraction. It is this ability to process a large number of samples quickly and at low cost that allows a large geographic area to be mapped (Faure and Landais 2001, Kruge and Permanye 2004). The speed of the analysis process coupled with the potentially wide range of organic analytes made Py-GC/MS an ideal method for this project.

At the time of this writing the National Atmospheric and Space Administration (NASA) and the European Space Agency (ESA) also plan to exploit the advantages of Py-GC/MS by employing the Mars Organic Molecule Analyzer (MOMA) on its Mars rover ExoMars scheduled for launch in 2018. The MOMA is a Py-GC/MS system that will be used to explore the Martian soil and has been calibrated with samples taken from the Norwegian arctic (Steininger and Goetz 2012).

Py-GC/MS can provide better recoveries for low molecular weight organic compounds that are often lost during solvent extraction and concentration. However high molecular weight PAH molecules, such as benzo[*b*] & [*k*] fluoranthenes, and benzo[*a*] & [*e*] pyrenes, are not as effectively recovered by Py-GC/MS as they would be by solvent extraction (Faure and Landais 2001). Poerschmann et al. used non-discriminating flash pyrolysis at 750^{o}C to study sediments from Hamilton Harbor, Ontario, and reported results for polycyclic aromatic hydrocarbons (PAHs) comparable to conventional Soxhlet extraction (Pörschmann et al. 2008).

Py-GC/MS allows the study of two types of materials. The first are intact molecules that are desorbed from the sediment particles simply by heating. These intact molecules are mobile and bio-available and thus represent the greatest risk to the environment. The second are the thermal breakdown products from larger molecules. These smaller breakdown products are often more suited to GC/MS analysis than the original molecules (Faure and Landais 2001). The type of materials present in any particular analysis depends largely on the pyrolysis temperature.

Selection of a pyrolysis temperature is often a balance between maximum desorption and minimal thermal degradation. Temperatures in the range 300 to 350 ^{o}C are widely used to desorb lighter materials without creating breakdown products (Medina-Vera 1996, Faure and Landais 2001). Once operating above these temperatures, one of the more common thermal degradation products encountered in pyrolysis are PAHs which can be formed at temperatures between 300 and 600 ^{o}C (Del Rio and Philip 1992). A temperature of 300 ^{o}C was found adequate to thermodesorb saturated hydrocarbons greater than C_{27} (Faure and Landais 2001).

Pyrolysis temperatures in the range of 600 to 750 ^{o}C have been used for sediment studies (Faure and Landais 2001, Pörschmann 2008). However studies of sewage sludge pyrolysis have shown that most biodegradable organic matter volitalizes in the temperature range 150 to 400 ^{o}C and non-biodegradable organic matter volitalizes between 400 to 550 ^{o}C (Barneto et al. 2009). Temperature is not the only variable in desorption. Clay matrices can have sorptive and/or catalytic effects that reduce the yield during the pyrolysis process as reported by Sauer et al. (1988) who performed organic polymer analysis of drilling muds that were rich in bentonite and barite.

Quantitation of pyrolysis products has often been achieved by spiking the samples with known amounts of perdeuterated PAHs. The area of the analyte peaks are compared to the areas of the internal standard peaks (Baumard et al. 1988). A complete description of this process is in Appendix 2.

An important factor that governs the presence of organic materials in sediment is the size of the individual sediment particles. When the percentage of "fines" (defined as clay and silt particles) is less than 20% contamination levels are generally low. The larger particles with a smaller relative surface area to volume do not provide as many binding sites (Lauenstein and Kimbrough 2007). In 1983 it was first observed that high molecular weight PAHs tend to be concentrated on the finest sediment fractions. This observation has been confirmed several times since then (Baumard et al. 1998).

Recent research in soil chemistry has demonstrated that the mineral constituents of the soils can govern how organic matter is partitioned. In andosols (highly porous, dark-colored soils derived from volcanic parent material) from Reunion Island, lipids were mainly associated with PC-AlSi (phosphorus – carbon) complexes but polysaccharides and protiens/amino acids were associated with gibbsite (aluminum hydroxide [$Al(OH)_3$]). Lignins were abundant in free organic matter but not found associated with mineral complexes. A small number of organic compounds were bound to iron oxides. Lipids as well as proteins/amino acids were associated with all organo-mineral complexes polysaccharides were not (de Junet *et al.* 2012). It remains to be seen if organic inputs to existing sediments follow similar partitioning patterns but these findings may be significant for organic matter that arrives in sediments already bound to particles.

Materials and Methods

The National Park Service provided surface sediment samples from all three units of the Gateway NRA. All samples were scraped from the uppermost few centimeters of the sediment and did not involve coring or digging. The majority of samples came from Jamaica Bay. The locations of the sample points are listed in table 2-1 and shown in figures 2-2 and 2-3.

All sampling was performed by Dr. Mark Ringenary, Natural Resources Specialist - National Park Service. Samples were collected by scraping the surface of the top level of sediment. Cleaned sample jars available from IChem were used for all samples. After sampling, the sediments were oven dried overnight at 40 ^{o}C by NPS personnel working at the park's on-site laboratory. The dried samples were shipped to Montclair State University for analysis.

All Sandy Hook samples (figure 2-3) were taken from the inland side of the peninsula from sites in Plum Island, Spermaceti Cove, and Horseshoe Cove. Two additional samples were taken by a team from Montclair State University from a marsh immediately north of Horseshoe Cove. This marsh is notable because its position over time can be determined very precisely. The southern boundary is formed by a roadway and its western edge is formed by a former gun battery whose construction dates to the early 1900s. Topographic maps from the late 1800s show the roadbed was originally a railroad line connecting Sandy Hook Pier with the mainland. A small strip of sand isolated the marsh from Sandy Hook Bay. One sample was taken from this area consisted of the fine organic rich sediments at low tide and another sample came from a sand bar below the high tide line. The Sandy Hook samples ranged from fine and powdery to coarse sand. All of the Great Kills (figure 2-3) samples were taken from muddy areas with fine sediments. Sample 100 came from the northwest end of Great Kills Bay. Sample 101 came from a creek in the Fox Creek tidal marsh east of the Oakwood Beach Water Pollution Control Plant. Only one sample came from the west side of Staten Island, Gateway 102, taken in a mud flat in Saw Mill Creek. This creek cuts through what has been described by New York City's Department of Parks as the "largest expanse of remaining salt marsh along Staten Island’s west shore.”

The analysis was performed using the procedures described in the other chapters. It began with hand-grinding and homogenizing the dried sediments using a mortar and pestle. Small pebbles, shells, and macroscopic plant materials such as blades of grass or leaves were removed at this time. Milligram quantities of the dried sediments were used for the analysis. Approximately 4 to 5 mg of fine, organic rich sediments were loaded into a quartz pyrolysis tube, but if the sediments were sandier approximately 8 to 10 milligrams were used. To determine the amount to weigh out, the relative “fineness” and “sandiness” of the samples were judged by eye and experience. A miniature spatula and Sartorius model CP64 analytical balance were used for the weighing. The dried sediments were spiked with 5 µL of an internal standard solution containing deuterated

PAHs from Cambridge Isotopes, Andover, Ma.. The solution contained naphthalene (D-naphthalene, cat. DLM-365-1), deuterated anthracene (D-anthracene, cat. DLM-102-1), and deuterated pyrene (D-pyrene, cat. DLM-155) in hexane. The spike concentration was manipulated such that each injection introduced 24.50 ng of D-naphthalene and 27.00 ng of D-anthracene into the chromatographic system. D-pyrene was the only compound used for quantization.

The chromatographic system used for the study was a Thermo Electron Focus GC and Thermo Electron DSQ quadralpole type mass spectrometer. A CDS model 1500 pyrolysis system was used to heat the samples at 610 ^{o}C for 20 seconds under a helium atmosphere. The thermally extracted molecules and pyrolysis products are swept onto the GC column by a stream of helium gas. The GC column used for organic geochemical determinations was a 30 m J&W Scientific DB-1MS column, with a 0.25 mm i.d. and 0.25 µm film thickness. The PAH determinations were performed using a 60m J&W Scientific DB-1MS column, with a 0.25 mm i.d. and 0.25 µm film thickness. All GC temperature programs began at 50 ^{o}C for 5 minutes and rose at a rate of 5 ^{o}C per minute until reaching 300 ^{o}C and holding for 25 minutes. Gas pressure at the column head was 228 kPa with a split ratio of 1 to 25.

When operated in the full scan mode the mass spectrometer was set to 50-550 Da, 1.08 scans/sec., 70 eV ionization voltage. In the SIM mode the MS was also set to 70 eV ionization voltage and identification was based on a combination of molecular weight and retention time window.

The output files of the chromatography system were converted to ISIS format and imported into EasyQuant for peak identification. Compound identification was through a combination of retention time window and one or more characteristic ions. Concentrations of analyte molecules were estimated using the following formulas:

$$\text{ng analyte} = \frac{(\text{ng internal std / area counts internal standard peak})}{(\text{area counts analyte peak})}$$

$$\text{ng/mg analyte} = \frac{\text{ng analyte}}{\text{mg dried sample}}$$

A correction factor was applied to each result. This factor was based on the ratio in the peak area obtained in the total ion chromatogram and the peak area obtained from integrating only the ion used for quantitation.

The PAH analysis was conducted in the selected ion monitoring (SIM) mode. Compound identification was again based on a combination of molecular weight and retention time window. A correction factor was not applied for this class of compounds because both the internal standard and analytes were chemically very similar.

The percentage of "fines," defined as the percentage of inorganic silt and clay in each sediment sample was determined using a simple settling method. The sample was digested with hot, 30% hydrogen peroxide, allowed to cool, and treated with dilute HCl. The sample was then rinsed with distilled water and allowed to settle in a graduated cylinder. The amount of sand is determined by a simple volume ratio calculation (Marczak 2012). No attempt was made to resolve the finer sediment fractions into the percentages of silt and clay.

The loss on ignition (LOI) value was determined by weighing the sample before and after heating the sample to 400 °C overnight. This temperature was recommended by the USEPA to prevent destruction of carbonates and a resulting positive error (Schmacher 2002).

Carbon/nitrogen analysis was performed using a Carlo Erba NA1500 CNHS elemental analyzer. Sediments were loaded into tin capsules subjected to flash combustion in a quartz column containing chromium oxide and silvered cobaltous/cobaltic oxide at 1000 °C. The instrument's reduction column was set to 650 °C and oxygen was removed from the gas stream by reduced elemental copper. Water was removed in a magnesium perchlorate trap. A 2 m column operated at 55 °C separated the N_2 and CO_2 which were then sent to a thermal conductivity detector.

Principle component analysis (PCA) was performed using JMP 9 (SAS Software, Cary N.C.) and correlation coefficients (r values) were calculated with Microsoft Excel. All of the correlation results presented in the text are r values and not r^2. Prior to PCA calculations the sample concentrations were first normalized so that each chemical constituent was represented by a percentage of the total of all measured compounds. All values that were not detected were assigned a random concentration below 0.001 mg/kg, i.e. several orders of magnitude below the measured values. To prevent large concentration values from skewing the PCA results the square root of each normalized concentration value was used.

Results and Discussion

It is important to remember that the samples were taken from the top layer of the sediment and as such only represent the most recent depositional history. The most abundant compounds in Jamaica Bay were vinylphenols, phenols, methyl- and ethyl-phenols, vinylguaiacols, indole, and styrene (figure 2-4). Elemental sulfur is most abundant at sample points 4, 8, 10m, 26, 27, and the Norton Basin (figure 2-2). Phenol is a common pyrolysis product which can be produced from cellulose, tyrosine, and altered lignins (Santin et al. 2009). Methyl phenols and guaiacyl derivatives such as ethylguaiacols and vinylguaiacols can be produced by the pyrolysis of terrestrial plants and especially grass ligands (Saiz-Jimenez and De Leeaw 1986). Styrene can be formed by the pyrolysis of humic organic matter (Fabbri 2001). Faire and Landais (2001) observed that most of these materials were only formed during high temperature pyrolysis suggesting exclusive formation through organic macromolecule breakdown. Structures of these molecules are provided in the appendix 3.

Sewage Inputs

In 2007 the New York City Department of Environmental Protection reported that Jamaica Bay's freshwater input comes "almost exclusively from combined sewer overflows (CSOs), storm sewers, and WPCPs." Such point sources can have dramatic impacts on estuary systems. During dissolved oxygen measurements in Narragansett Bay, Deacutis et al. (2006) found that increased organic matter loadings from point sources can lead to anoxic conditions even during periods of drought.

Cholestenes are steroid compounds that can be used as a biomarker for sewage contamination in sediments (Kruge and Permanyer 2004). Concentrations of cholestene and ethylcholestene ranged from not detected (ND) to 0.51 to 0.22 mg/kg respectively. The highest concentrations were found at sample point 27 that is near the 26th Ward Water Pollution Control Plant, which as of 2011 has been in operation since 1944 and serves a population of 283,428 in eastern Brooklyn (NYCDEP 2013). Other high concentrations of these compounds ranging from 0.03 to 0.05 mg/kg were found at sample points 3,12, 24, 28, and 29. All but sample points 24 and 28 are located near WPCPs. Sample 24 came from Grassy Bay and is close to the outlet of Bergen Basin. Sewage may have been carried out of the basin. Another possibility is a leaking sewer line associated with John F. Kennedy Airport. Sample 28 came from the Shellbank Basin where there are many recreational boats and limited water circulation. It may be that some combination of indifferent use of marine pump-out facilities and leaking residential sewer lines can account for the sterenes.

In the majority of instances where sterenes were detected, C_{27} (cholestenes) compounds were more abundant than C_{28} (methylcholestenes) and C_{29} (ethylcholestenes). This preference is typical of sewage inputs and samples 12, 24, 28, and 29 had clear $C_{27}>C_{29}>C_{28}$ patterns. A notable exception was the Norton Basin sample where C_{29} was the most abundant. This may be indicative of waterfowl feces from the new park created on the old Edgemere Landfill (Kruge et al. 2010).

In 1989 McClurg reported that there had been accumulations of sediments near some of the creeks opening onto Jamaica Bay as these were also the locations of major CSO discharge points the sediment mounds were rich in both organic and inorganic wastes. Three sewage-containing mounds were identified at Spring Creek, Fresh Creek, and Hendrix Creek. Because of the low current velocities in the bay there was little subsequent flushing immediately downstream of the CSO discharge points (McClurg 1989). An early example of using chemical amendments to remediate sediments in place was implemented in Bergen Basin in the 1960s. A three-pipe CSO discharged into the head of basin. The basin was typical of the tidal basins surrounding Jamaica Bay in that its banks had been straightened for commercial navigation and where water flows were confined to tidal exchange. The sewer plant operating at the site dated to 1943 and had a design capacity of 230,000 cubic meters/day but could not handle overflows created by storm conditions. The city's goal was to construct a storm water treatment plant but until that could be accomplished some method had to be found to control the odors resulting from a combination of untreated sewer discharges and hot summer weather. The presence of sulfur-reducing bacteria in the effluents was in large part responsible for the problem. Sodium nitrate was added to the sediments to create aerobic conditions and hydrogen sulfide in the waters of the basin was destroyed with the addition of sodium hypochlorite (Lang 1996).

Cholestene concentrations were also low in the Staten Island Unit. The highest concentration was 0.03 mg/kg in the Fox Creek tidal marsh sediments (sample point 101). The latter result is especially encouraging as the creek surrounds the Oakwood Beach WPCP.

On Sandy Hook, two samples were taken by students from Montclair State from the marsh north of Horseshoe Cove. One sample was taken in the muddy banks of a creek that ran through the marsh (Sandy_Hook_MSU_1). Another sample came from a sandbar in the center of the creek (Sandy_Hook_MSU_3). The sample from the bank had a cholestene concentration of 0.02 mg/kg and no cholestene was found in the sample from the sandbar.

Biomarkers

Pyrolysis of material from terrestrial plants produces a number of useful biomarkers. Both phenols and o- & c- cresols can be produced from cellulose, tyrosine, and altered lignin derivatives (Santin et al. 2009). Both lignin and degraded lignin produce methoxyphenols in pyrolysis including methylguaiacol, ethylguaiacol, vinylguaiacol, isoeugenol, and methoxyeugenol. In particular, methylphenols and guaiacol derivatives (ethylguaiacol and vinylguaiacol) point to a predominance of grass lignins (Saiz-Jimenez and De Leeuw 1986). Faure and Landais (2001) concluded that all of these molecules are exclusively thermal degradation products of pyrolysis because they were not observed when sediments are heated at 300 ^{o}C. Other sources of phenols and alkyl phenols include pine needles, leaves, seeds, kerogen, and industrial by-products (Faure and Landais 2001). Indole is recognized as a protein biomarker and has been associated with both marine algae and bacteria (Kruge et al. 2010).

The vinylguaiacol / indole index (VGII) combines the peak areas for indole (I) as a marine algae biomarker and vinylguaiacol (VG) as a terrestrial plant biomarker can provide an indicator of the relative contribution of marine and terrestrial plants to the organic matter of a particular sediment (Micic et al. 2010). In estuaries, the carbon/nitrogen ration (C/N) can reflect the degree to which conditions are either marine or freshwater and the corresponding organic matter inputs, i.e. algal or terrestrial plants (Lamb et al. 2007). The C/N ratio in estuary sediments reflects the relative inputs of terrestrial organic matter (Goñi et al. 2003). By focusing exclusively on compounds that are linked to the specific sources of the organic matter, terrestrial plants and algae, the author believes that the VGII is less prone to interferences from nutrient runoff, tidal variation, or anthropogenic sources of these elements.

$$\mathrm{VGII} = \mathrm{VG} / (\mathrm{I} + \mathrm{VG})$$

It will be seen from the equation above that the index decreases with a high indole (algal) contribution but rises with higher vinylguaiacol (terrestrial) contributions. The result of this and other sediment chemistry ratios are presented in table 2-4. A disussion of the PCA is presented at the end of this chapter. The VGII was tested against carbon – nitrogen data and was found to have a r value of only 0.52 (figure 2-5).

Another useful means of detecting the input of terrestrial plants to sedimentary organic matter is to use the Carbon Preference Index (CPI). The CPI is a numerical calculation that determines an odd-over-even predominance for n-alkanes in a certain carbon number range. Killops and Killops (2005) state that immature higher plant contributions to the sediments are represented by CPI values greater than 1 and that values significantly higher than 1 represent undegraded higher plant contributions. However, they do not say how much higher than 1 is "significantly higher." The CPI value calculation uses alkanes with even carbon numbers from 26 to 32 and alkanes with odd carbon numbers from 25 to 33. (Killops and Killops 2005)

$$\mathrm{CPI} = \frac{(A/B) + (C/B)}{2}$$

Where A = Sum C25 to C31 (odd only)
Where B = Sum C26 to C32 (even only)
Where C = Sum C27 to C33 (odd only)

However chromatographic limitations precluded the quantitation of alkanes with a carbon number greater than 31 so the CPI calculated for these samples will not include the contributions from either C_{32} or C_{33} alkanes (figure 2-6).

Despite this limitation, the VGI Indexes and the CPI are moderately correlated in the Jamaica Bay samples (r = 0.57) and for all samples in the study area the correlation is r = 0.54 (figure 2-7).

In the Jamaica Bay unit, the mean VGII is 0.33 and the median value is 0.25. This can be attributed to a predominance of marine algae input to the sediment organic matter. Only six of the 22 Jamaica Bay sample points (1, 3, 8, 12, 22, and 28) have a VGII greater than 0.51, ranging from a low value of 0.51 at Elder's Point Marsh (sample point 22) to a high value of 0.79 at Gerritsen Creek (sample point 8). The majority of samples associated with the disappearing marshes in the center of the bay (11, 16, and 18) all had VGI Indexes of 0.25 or less. A very different situation was found at Sandy Hook where the marsh sediments had a VGII of 0.82 and a large CPI value of 2.18.

The samples with high VGI Indexes (1, 3, 8, 12, 22, and 28) all fall into a terrestrial plant cluster identified by PCA (table 2-5). A detailed discussion of the PCA analysis is provided at the end of this chapter. This illustrates an important distinction between biomarker ratio and PCA approaches to analyzing data. If excessive inputs of nutrients from sewage treatment plants were the cause of excessive algae growth, then sample points with low VGI Indexes should be grouped with sample points associated with anthropogenic contamination. This is not the case as several samples (3, 12, 29) associated with treatment plants have high VGI Indexes. Nutrient loadings and plant growth is more complex than would anticipated just from a single biomarker ratio. When the VGII values for Jamaica Bay were compared with the CPI values, two distinct clusters of points emerged. One cluster represents sample points whose VGI Indexes and CPIs averaged 0.70 and 2.68 respectively. This means that these points (1, 3, 8, 12, 22, and 28) have high inputs of relatively undegraded higher plant matter of terrestrial origin. Significantly, only sample 22 from Elder's Point Marsh is from an area in the center of the bay where the islands are disappearing. Sample point 1 is located in the Rockaway Inlet but the remainder of these samples came from the shores of the bay. The other cluster, which includes many of the other sample points, had VGI Indexes and CPIs of 0.19 and 2.01 respectively.

Because of the small number of samples a simple Student T test was performed. There was a significant difference in the VG/I values of these two clusters at the 99% confidence interval but for the CPI values the differences were only significant at the 95% confidence interval.

The VGI Indexes for Great Kills sediment were 0.19 in the sandy mud of Great Kills Harbor (sample point 100) and 0.34 in the Fox Creek tidal marsh (sample point 101). The CPI numbers for these sample points were 2.1 and 2.6 respectively. In both cases the relatively low VG/I numbers can be attributed to marine algae being a predominant source of the sediment's organic matter and yet the CPI indicates a simultaneous contribution of higher plant inputs.

Another useful ratio calculation uses the concentrations of syringols and vanillins (S/V). While all vascular plants contain vanillyl phenols only angiosperms contain syringol phenols (Steinberg et al. 2009). Thus the S/V ratio indicates what types of vascular plants are contributing organic matter to the sediments (Louchouarn et al. 1999, Goñi and Thomas 2000). Values for the ratio of Syringol/vanillin in the Jamaica Bay samples ranged from 0.0 to 1.4 with a mean of 0.37 and a median of 0.21. A higher ratio is linked to increased organic inputs from grasses (Steinberg et al. 2009). With one exception, sample point 1, all of the sample points where the S/V ratio was greater than the mean, (1, 3, 8, 12, 26, 27, and 28) are located along the shores of the bay and in the basins that extend inland. As with the VGI Index, assignments based on the S/V ratio do not correspond with the cluster assignments listed in table 2-4. None of the samples from the center of the bay, or areas close to the remaining islands, exceeded the mean S/V value and only one exceeded the median value. In contrast, the sample taken from the marsh at Sandy Hook had a S/V ratio of 0.99, almost 5 times higher than in marshy areas of Jamaica Bay. The Great Kills samples also had a low S/V ratio indicating that the inputs of grasses are small while the VG/I suggests that the predominant inputs originate in the marine environment. The samples from the islands in the center of the bay also have low concentrations of guaiacols that can be indicative of grasses (Saiz-Jimenez and De Leeuw 1986).

Recent field studies have shown that In Jamaica Bay, the dominant green algae is *Ulva* *sp*.. The greatest population densities are found in the center of the bay where the waters are their shallowest. In some areas the algae covers more than 98% of the bottom. Wastewater is believed to be this algae's primary source of nitrogen. (Wallace 2012) *Ulva lactura* has been observed on mudflats and between stands of *S. alterniflora*. At the Big Egg Marsh (sample point 11) *S. alterniflora* is being replaced by *Ulva sp*.. (Gordon, et al. 2001)

The samples from the islands in the center of the bay also have low VGI Indexes and low concentrations of guaiacols that can be indicative of grasses. (Saiz-Jimenez and De Leeuw 1986) Ecological stresses on marsh grasses, including excess nutrient loadings, have been linked to marsh losses although the exact causes of marsh loss are not limited to plant stresses and can vary widely over similar geographic regions. (Nyman et al. 2006) The expansion of tide pools is closely associated with the decline of Jamaica Bay's marsh vegetation. (Gordon, et al. 2001)

Overall there is a very good correlation between the above ratios with each other and the CPI. The CPI and S/V are correlated at r = 0.64, the CPI and VG/I are correlated at r = 0.57, and the VG/I and SV are correlated well at r = 0.88 (figure 2-7). This last number suggests that inputs of grasses, higher plants, and terrestrial plants generally track one another quite closely (figure 2-8).

It should be noted that the relative inputs of these materials vary with the amounts of organic matter carried by rivers, which of course also varies over time. There can be significant variations even over very short time scales and this will most likely not be reflected in the composition of surface sediments. In the Hood Canal catchment area in Washington State, there was an increase in the dissolved C/V ratio (cinnamyl/vanyllin), the dissolved S/V ratio, and the dissolved Ad/Al (vannilyl acids/vannilyl aldehydes) ratio over months-long time scales. Ward et al, 2010 concluded that during dry summer months reservoirs of organic particulate matter accumulate on the catchment's forest floors. The study area was primarily coniferous or mixed deciduous forest with low population densities. As rains increased over the fall and winter there was a clear positive correlation between stream flow and concentrations of dissolved organic matter (DOM), dissolved organic nitrogen (DON), particulate organic carbon (POC), particulate organic nitrogen (PON), and inorganic nutrients as the reservoir of these materials emptied. However as rains continued through the winter and into the spring the correlation became less strong. The lignin phenol concentrations also changed over this time scale C/V increased with discharge, the S/V ratio fell, and the Ad/Al ratio rose. As this last ratio can be a measure of degradation, it suggested that the last material to be washed into the rivers was the most degraded (Ward et al. 2012).

Another issue that can be investigated by using biomarkers is hypoxia. Research by Fukushima at al (1992) demonstrated how three species of methylthiophenes, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene, and 3-(4,8,12-trimethyltridecyl)-thiophene can be found in sediments when hydrogen sulfide can react with phytol under reducing conditions (Fukushima at al 1992). Phytol is created from the breakdown of chlorophyll. It can react with polysulfides under anoxic conditions to yield a 5- member thiophene ring with a highly branched isoprenoid. Although photo-sensitization has been confirmed as part of this reaction, there is doubt that this would occur in deeper waters. Thus a bacterial mechanism is amont those proposed to account for the formation of these compounds. (Amrani and Aizenshtat 2004). A similar reaction occurring at low temperatures and in the presence of trimethylaminewas reported by Rowland et al. (1993). This reaction involved elemental sulphur and unsaturated phytyl derivatives.

In Jamaica Bay the greatest total concentration of these compounds (397 mg/kg) is found in Grassy Bay (sample 24). Grassy Bay's depth and limited water circulation has lead to seasonal hypoxia. (Beck et al. 2009) Isoprenoid compounds in sample 24 also include several that originate in cyanobacteria and green algae and are derivatives of phytadiene. Cyanobacteria and green algae are both linked to eutrophic and hypoxic conditions as well as algal blooms.

The average concentration of these compounds is 118 mg/kg and the other Jamaica Bay locations with concentrations of diagnostic methylthiophenes above the average value include, in descending order, sample points NB, 26, 29, 27, 12, 10M, 13A, and 3, Concentrations ranged from 123 mg/kg to 326 mg/kg. With the exception of sample points 12, 10M, and 3, all of the remaining points are associated with areas of limited water circulation. Sample points 12, 3, and 27 are all associated with WPCPs.

Hopanes and Petroleum Markers

The largest amounts of C_{29} and C_{30} hopanes that serve well as markers for petroleum contamination are found at Bergen Basin (sample point 27, 0.38 mg/kg) and Praedegat Basin (sample point 29, 0.32 mg/kg). There is a jet fuel depot serving John F. Kennedy Airport on Bergen Basin. Neither of these sample points has a particularly low CPI (1.67 for sample 27, and 2.37 for sample 29) which would unambiguously confirm the presence petroleum. The remaining samples with hopane concentrations above 0.1 mg/kg are 3, 12, 24, 26, and 28. Of these samples, only number 26 was taken from an area where petroleum products are delivered by barge. However completely unambiguous petroleum signatures from these samples are not available because of the presence of so many other classes of compounds.

The use of PAH concentration ratios for as a means of confirming the origin of the origins of PAH contamination is discussed in the next section. It should be mentioned at this point, that samples 5, 8, 13a, and 23 all showed some inconclusive evidence that petroleum discharges were responsible for the PAH contamination at these sites. However, hopane petroleum markers were not found at these sites.

PAH Contamination

PAH contamination is an important subject for urban estuary studies. Although these materials may originate in industrial wastes the two primary sources are combustion and petroleum contamination. Once released into the environment they can persist in the atmosphere and be deposited into the aquatic environment by rain, snow, or particulate fallout. They quickly adsorb onto sediments and other types particulate matter. This property is allows these molecules to bioconcentrate in the aquatic food chain. Many PAH molecules are known human carcinogens (Kennish 2000). Commercial, industrial, residential, and undeveloped land uses are associated with different levels of PAH accumulations (Menzie et al. 2002).

Another factor which governs the distribution of PAH molecules is the size and nature of the sediment grains. PAHs are not readily soluble in water and tend to adhere to particulate matter.

PAH concentration in sediments is linked to the organic matter content. Those PAH molecules with low aqueous solubilities and high affinity for carbon rich particulates will typically be found associated with high levels of organic carbon. However there is not always a clear correlation between the enrichment of a particular PAH molecule, organic carbon, and grain size (Stange 1997). The sediment characteristics at each sample point are provided in table 2-1.

Organisms in closest contact with sediment tend to have the greatest PAH accumulation. These include the deposit-feeding bivalves, burrowing organisms, and animals living in zones of high turbidity (Baumard et al. 1998). It was first observed in 1983 that a given PAH's bioavailability will vary with the molecule's origin. Petrogenic PAHs tend to be more readily bio-accumulated than pyrogenic. But this is only a rough guide, the actual bio-availability is related to physiochemical characteristics of the sediments, the properties of the specific PAH, and the characteristics of the organism (Baumard et al. 1998). In the Venice Lagoon, Venice, Italy, sediment PAH concentrations ranged from 0.065 to 0.46 mg/kg and could account for 70 to 80% of the potential mutagenic effects on marine life (La Rocca et al. 1996). Poerschmann found that PAH source indicator ratios in harbor sediments were similar for conventional solvent extraction, pyrolysis at 750^{o}C and thermochemolysis at 500^{o}C. This observation lead to the conclusion that the PAH enrichment due to the degradation products from humic organic matter may be minor (Pörschmann et al. 2008).

Except where Environmental Impact Assessments have been required for specific wetlands restoration or channel dredging projects there has been very little published about PAH concentrations in the Gateway NRA. The Environmental Impact Assessment for the Norton Basin / Little Bay restoration project in Jamaica Bay reported total PAH concentrations for surface sediments. The highest concentration, 11.8 mg/kg, was inside a containment boom at the JFK outflow pipe number two. Grassy Bay was another area of high PAH concentrations. Total PAH's in the southeast and southwest parts of Grassy Bay were 9.4 mg/kg and 0.5 mg/kg respectively. The remaining areas of Grassy Bay, Black Bank Marsh, East Broad Channel, and Ruler's Bar all had total PAH levels less than 0.1 mg/kg. The Rockaway Inlet had the lowest PAH concentrations at 0.004 mg/kg (Rhoads et al. 2001). Other sediment contamination studies in Jamaica Bay have also reported high levels of PAH contamination in Grassy Bay and the northeastern side of Nova Scotia Bar. PAH contamination is generally higher along the northern and eastern portions of the bay (NYCDEP 2007).

Results of the PAH analysis are shown in table 2-6. When all of the PAH concentrations for a particular sample point are added together the most contaminated sections of Jamaica Bay are shown to be sample points 26, 27, 29, Norton Basin, and 13a. All of these points had more than 10 mg/kg total PAH content. A detailed evaluation of PAH distribution and probable effects on marine life is provided in the author's report to the National Park Service (Olsen 2007). The lowest PAH concentrations in Jamaica Bay were found in samples 5 and 6 from the Rockaway Inlet and number 18 from the JoCo Marsh. This result is not surprising because the Rockaway Inlet has always been subject to flushing by swift currents and tidal circulation. Generally speaking, the eastern part of the bay, especially Grassy Bay where JoCo marsh is situated, has been more stagnant with lower water quality (NAS 1971). Thus the result from sample 18 is harder to explain.

Areas of Jamaica Bay with the highest PAH concentrations were those with fine grain sizes and organic rich sediments. Sandy samples had a relatively narrow range of 0.39 to 1.9 mg/kg total PAH content. Samples from the Rockaway Inlet were both the sandiest and had the lowest PAH concentrations. Conversely the PAH content of the fine, organic rich samples ranged from 2.1 to 20 mg/kg total PAH content. In other studies of the bay contamination was strongly correlated with the TOC content of the sediment (NYCDEP 2007).

The most contaminated sample in the entire study was from the Norton Basin (NB) where levels of acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, Benzo[*a*]anthracene, and Chrysene all exceeded levels that NOAA estimates as being harmful to marine life according to the NOAA Sediment Quality Reference Tables (NOAA SQRT Card). Levels of benzo[a]anthracene, and chrysene exceeded the median levels where adverse effects have been observed. Sample 13a was taken on the other side of the peninsula formed by the Edgemere Landfill. This landfill was not closed until 1998 (*Civil Engineering* 1998) and forms a peninsula with the Sommerville Basin (site of sample 13a) on the west. Levels of acenaphthene, fluorene, phenanthrene, and benzo[*a*]anthracene in sample 13a exceeded levels at which NOAA estimates that there will be adverse effects on marine life. PAH contamination was generally higher in samples taken from the basins and shoreline of the northern portion of Jamaica Bay. Between 18% and 73% of PAH observations at sample points 24, 26, 27, and 29 were above levels at which there would be either a probable effect on marine life or the median concentrations at which adverse effects have been observed.

The PAH content of the Sandy Hook samples from Spermaceti Cove and Plum Island were low in total PAH content with a total content only slightly higher than 1 mg/kg. However the sample from Horseshoe Cove had a total PAH level just over 10 mg/kg. The difference may be attributable to sediment grain size as Horseshoe Cove was less sandy than the other sample points.

All of the Great Kills samples were somewhat higher than those of Sandy Hook. The sample from Saw Mill Creek had a total PAH content of 5.2 mg/kg. The samples from Great Kills harbor and the Fox Creek tidal marsh had total PAH concentrations of 15.6 and 12.0 mg/kg respectively.

The ratio of anthracene and phenanthrene and the ratio of fluoranthene and pyrene can both be used to indicate if the primary input of PAH contamination was petrogenic or pyrogenic (Budzinski et al. 1997, Yunker et al. 2002). It is possible to use these ratios because 3-ring PAH molecules are the most thermodynamically stable and will preserve a record of the conditions of formation (Pörschmann et al. 2008). However Vane et al. (2008) caution that the use of these ratios are "merely indicative" of the source and do not provide an "unequivocal" assignment. One source of uncertainty is differential degradation of PAH molecules. Research on PAH degradation in San Diego Harbor revealed that under sulfate-reducing conditions, fluorene, fluoranthene, and methylnaphthalene were anaerobically oxidized to carbon dioxide but pyrene and benzo[*a*]pyrene were not (Coates et al. 1997).

An/Ph = anthracene / (anthracene + phenanthrene)

A ratio greater than 0.1 indicates that the materials are most probably pyrogenic in origin. Similarly, if the ratio of fluoranthene / (fluoranthene + pyrene) is greater than 0.4, then the materials are most probably pyrogenic in origin. The fluoranthene / (fluoranthene + pyrene) ratio allows some additional source determinations. A ratio below 0.4 is thought to reflect petrogenic origins, 0.4 to 0.5 from the combustion of liquid fossil fuels, and greater than 0.5 from combustion solid fuels including coal, wood, or grass (Budzinski 1997, Yunker 2002).

Fl/Py = fluoranthene / (fluoranthene + pyrene)

The An/Ph ratio is greater than 0.1 for each of the Jamaica Bay samples, ranging from 0.11 to 0.93 with a mean value of 0.36. Only one sample was close to a value of 0.1, sample 16 from the Pumpkin Patch Channel between some of the islands in the middle of the bay.

The Fl/Py ratio also points to a pyrogenic origin for most of the *PAH contamination* within Jamaica Bay. These calculations do not preclude the possibility of petroleum contamination but merely indicate the most likely source of PAH contamination. Samples 5, 8, 13a, and 23 could all be classified as petrogenic by this ratio but in the case of 13a, a value of 0.38 is very close to the 0.4 petrogenic / pyrogenic border line. Sample

8 was taken in an area where petroleum products have unloaded from barges. Among the samples with pyrogenic origins, the PAH content of eight of these can be attributed to liquid fossil fuels combustion and that of sample 6 to solid fuels combustion. Tables 2-7 and 2-8 shows the results of these ratio calculations.

Although there have been good correlations with these ratios and source apportionment by $\delta^{13}C$, (Yan et al. 2006), there are some limitations to using parent compound ratios for PAH source determination. Multiple PAH sources and heavy pollutant concentrations may obscure the results. (Yan et al. 2006) Among the other limitions is that low molecular weight PAHs in the petroleum are the first to be weathered. This creates a bias in favor of a pyrogenic interpretation unless preservation conditions are good. Other ratios using including alkylated PAHs have been proposed. These include the CPI, the C_{17}/C_{29} ratio, and the ratio of UCM/total alkanes (Wagener et al. 2010).

The ratio of methyl phenanthrenes to phenanthrenes can also be used to determine the source of PAH contamination.

$$\text{Sum MP/P} = \text{Total methylphenanthrenes / phenanthrene}$$

Ratios in excess of 2 indicate petrogenic contamination and those less than 2 are an indication of pyrogenic origins (Garrigues et al. 1995).

Within the Gateway area there are a number of sample points where all three ratios indicate a pyrogenic source, 1, 3, 4, 9, 10, 18, 24, 26, 27, and 29 in Jamaica Bay and on Staten Island, 100 and 102. Within Jamaica Bay water mixing is generally restricted to tidal exchanges through the navigable channels (Benotti 2007). Areas within the bay's tributaries and dead end basins have reduced water quality due to contaminated surface runoff and poor flushing (NYCDEP 2007). Areas characterized by this type of restricted flow regime and fine sediments have had the highest levels of PAH contamination. Although it has not been conclusively demonstrated in the present study, a likely cause of the pyroenic PAH contamination is automotive. In more than 400 particulate samples collected from throughout the Chesapeake Bay between 1991 and 1998, motor vehicles were found to be a major source of combustion derived PAH's. Benzo[*a*]anthracene, benzo[*a*]pyrene, and benzo[*b*]fluoranthene from automobiles were found in the air, rain, and surface waters of the bay. About 53% of PAH molecules in the sea surface microlayer were from automobiles and about 47% were coal derived (Dickhut et al. 2000).

In a study of the Elizabeth River, Virginia, wetland sediments the largest total PAH concentrations were found near commercial land uses and appeared to be from automobiles. Automotive sources include exhaust, crank case oil, and brake dust. These are all deposited on impervious surfaces (Kimbrough and Dickhut 2006). PAHs are among the mist toxic constituents of roadway runoff (Malty et al. 1995).
Kimbrough and Dickhut (2006) found in wetlands sites in the Elizabeth River PAH

variability within a site are greater than variability between sites (commercial, industrial, residential, undeveloped, and urban) and they were forced to conclude that a few or even a single PAH source was dominant. The dominant PAH inputs (52 to 69%) to wetlands were automotive regardless of adjacent land use (Kimbrough and Dickhut 2006). A similar result was found in the Iko River estuary in Nigeria. Comparisons of PAH concentrations in epipelic and benthic sediments demonstrated a comparative enrichment in the epipelic zones. The PAH molecules were primarily pyrogenic although there was also a slight petrogenic signature. This had lead to the conclusion that PAH accumulations in that estuary were from industrial sources via runoff (Essien et al. 2011).

In 2006 Yan et al. published staple carbon isotope results from carbon-13 ratios in New York Harbor sediment cores. They concluded that between 1970 and 2000 combustion provided an increasingly important source of PAH contamination throughout the entire harbor (Yan 2006). The predominance of pyrogenic PAH contamination in Gateway National Recreation Area is entirely consistent with these results.

Multivariate Cluster Analysis

Multivariate cluster analysis grouped the sample points into three distinct groups based on the principal input of organic matter. The Jamaica Bay samples in the group dominated by terrestrial organic matter were 1, 3, 8, 12, and 28. Most of these samples were taken along the bay's shoreline although some in this first group (3 and 12) were also WPCPs. Sample SH1 (Sandy Hook 1) was also in this group and came from a thriving and healthy marsh in a protected setting (table 2-5 and figure 2-9).

The second grouping consisted of samples dominated by aquatic organic matter. Eight Jamaica Bay samples were included in this group (4, 9, 6, 10m, 16, 18, 22, and 23s) and four of them (6, 18, 10m, and 23s) were from the center of the bay where marsh loss is greatest. The third grouping (11, 13a 24, 26, 27, 29, and NB) is dominated by organic matter originating in pollution. Samples 24, 27, and 29 are associated with water pollution control plants (WPCPs) while 13a and NB are associated with landfills. Sample number 11 was taken Big Egg Marsh near Broad Channel and about 1 km from the Rockaway WPCP. Sample 12 was also in close proximity to the Rockaway WPCP but we may safely assume that it was the either the flow of currents carrying material away from the plant, or the prescence of terrestrial vegation on the peninsula that caused the latter sample to be grouped in the “terrestrial” cluster. Sample 26 was taken at the Head of Bay an area of limited circulation and feed by urban streams that are subject to stormwater runoff.

It is not clear why sample 1, which was collected near the outlet of the Coney Island WPCP in the Rockaway Inlet, was clustered with the “terrestrial” locations. The reasons for this may be connected somehow to a very high proportion of sand and that it came from a location where tidal currents are stronger than almost any other point in the study area.

The PCA grouped the Staten Island samples, 102 and 101 into an area between the "contaminated" and "aquatic" clusters. Sample 101 was grouped more clearly with the contaminated cluster and this may have something to do with the PAH concentrations. The values of the eigenvectors that were assigned to each chemical species in the first principal component showed a clear grouping of terrestrial biomarkers syringols, guaiacols, and phenols with average loadings values between -1.0 and -0.6. Most of the indicators of anthropogenic contamination had loadings values between 0.0 and 0.8, while those from and aquatic biomass had loading values from 0.4 to 1.0. Within the first principal component the loading values for alkylated PAHs were generally above 0.6. Although there are natural sources of these compounds, there is a possibility that petroleum contamination heavily weights the first principal component. This is supported by the presence of methynaphthalenes, methylphenanthrenes (Garrigues et al. 1995), and methylpyrenes (Maher and Aislabie 1992) near the top of the loadings.

The second principal component proved more useful in distinguishing aquatic biomarkers and anthropogenic contamination. Sterenes, hopanes, azarenes, linear alkylbenzenes, alkanamines, and 3- and 4-ring parent PAHs had loading values ranging from 0.4 to 0.8. Sewage markers have high loading values within the second principal component including C_{27}, C_{28}, and C_{29} sterenes (Kruge et al. 2010). Other sewage markers in this component include several linear alkylbenzenes that originate in detergents (Kruge et al. 2010).

The various organic analytes were grouped into compound classes based on their origins and chemical characteristics. The greatest contributions to most of the classes came, in descending order, from sample points 3, 27, 12, 29, 1, and 28. The sediments from these sites have the largest loss on ignition (LOI) values. Most of these samples are associated with WPCPs and generally speaking they contribute the largest proportions of syringols, two and three ring nitrogen compounds, parent PAHs, polysaccharide pyrolysis markers, surfactants, alkanes and alkenes, linear alkylbenzenes, nitriles, and alkanoic acids.

Conclusions

The study of the Gateway National Recreation area can be regarded as an example of natural processes operating in an un-natural environment or of anthropogenic processes operating in a natural environment. Perhaps the truest interpretation is that it is about the intersection of natural and man-made forces operating in a small geographic area.

This study has confirmed that a lack of terrestrial organic matter is linked to the Jamaica Bay locations where marsh loss is greatest. However, it has not determined whether this can be linked to potential causes of marsh loss (diminished land plant productivity) or whether it represents a symptom of marsh loss. The entire question of where land plant productivity fits into the complex interplay between the causes and effects of marsh loss is well beyond the scope of sediment chemistry. A potentially useful contribution to the field might be to apply these techniques to sediment cores and track changes to marshes over longer periods of time.

Biomarker ratios VG/I and S/V, taken together with the CPI can shed light on estuary conditions over a large geographic area. They are well suited to rapid screening but are limited in that they reflect the outcomes, but not necessarily the mechanisms of ecological processes.

This study has also confirmed the importance of sewage discharge inputs to Jamaica Bay as a source of organic matter. The most important implication of this finding may be that freshwater inputs to urban estuaries cannot be left to the vagaries of sewer plants and storm water flows. It is possible that the future protection of urban creeks and groundwater flows will be an important aspect of urban estuary management.

PAH contributions from combustion sources clearly dominate this class of contaminants. This is not a surprising result for Sandy Hook. Given the long human history of Jamaica Bay and Great Kills, it is odd that there is not a greater indication of PAH contamination originating with petroleum. This may be because in recent years there has been a greater emphasis on spill prevention and cleanup. The evidence of earlier petroleum spills may be buried deeper in the sediments. If this is the case, it remains to be seen what other forms of legacy pollution are buried. Another possibility is that a petroleum-based PAH signature is being overwhelmed by pyrogenic PAHs being deposited from the atmosphere or by street runoff. In such a complex system, hopanes and other petroleum markers may provide a far more reliable indication of petroleum contamination.

The greatest concentrations of PAHs in Jamaica Bay were found in areas associated with former landfills and where there is restricted water circulation. Detection of PAHs do not address some larger questions. Are PAHs escaping from landfills and thus increasing in concentration? Or are the concentrations building up at an accelerated rate because they are not being flushed out? Are both of these factors somehow working together? An excellent follow up study either Jamaica Bay or Great Kills would be to search for sediment contamination that can be specifically linked to landfills.

Figures and Tables

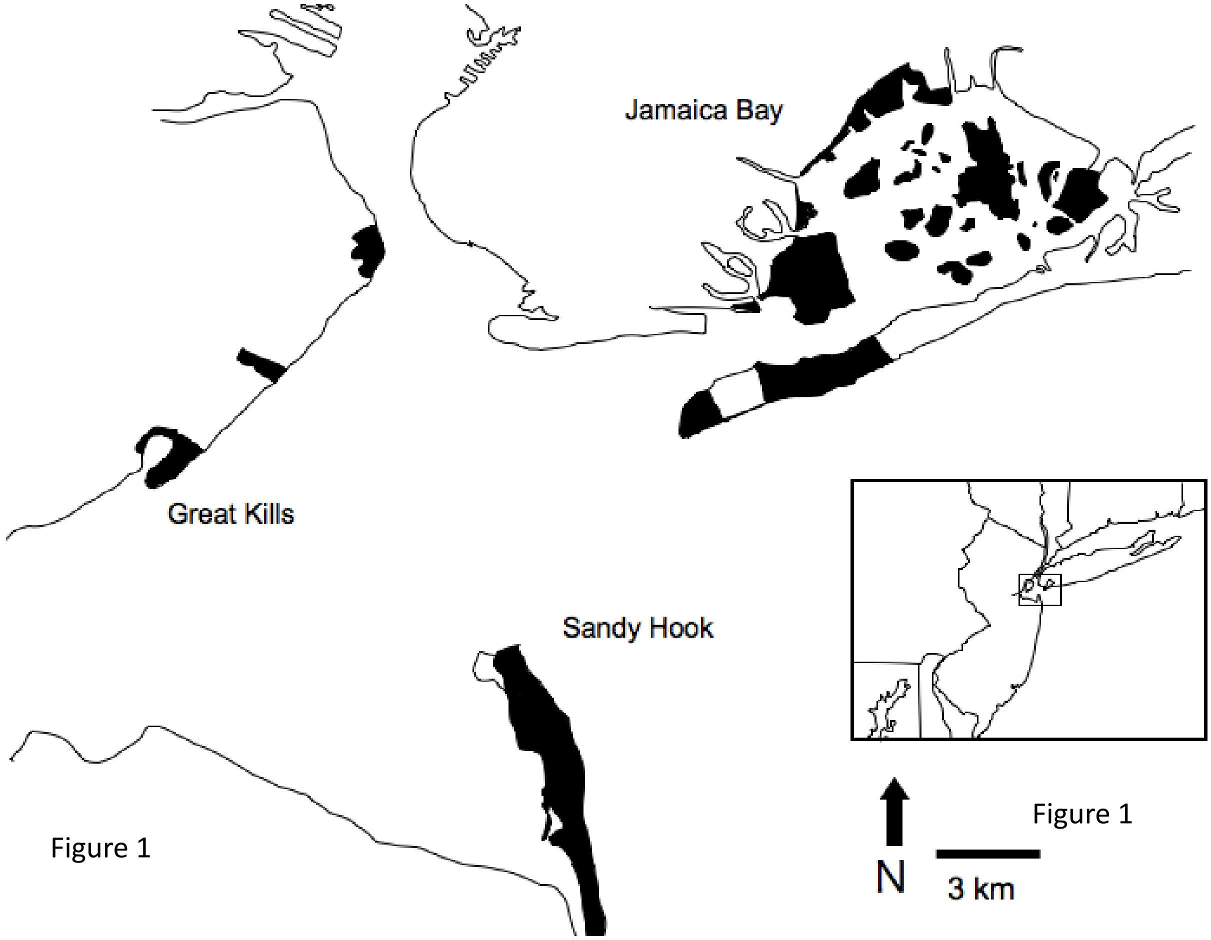


Figure 2-1. Map of New York Harbor showing the location of the three units of the Gateway National Recreation Area.

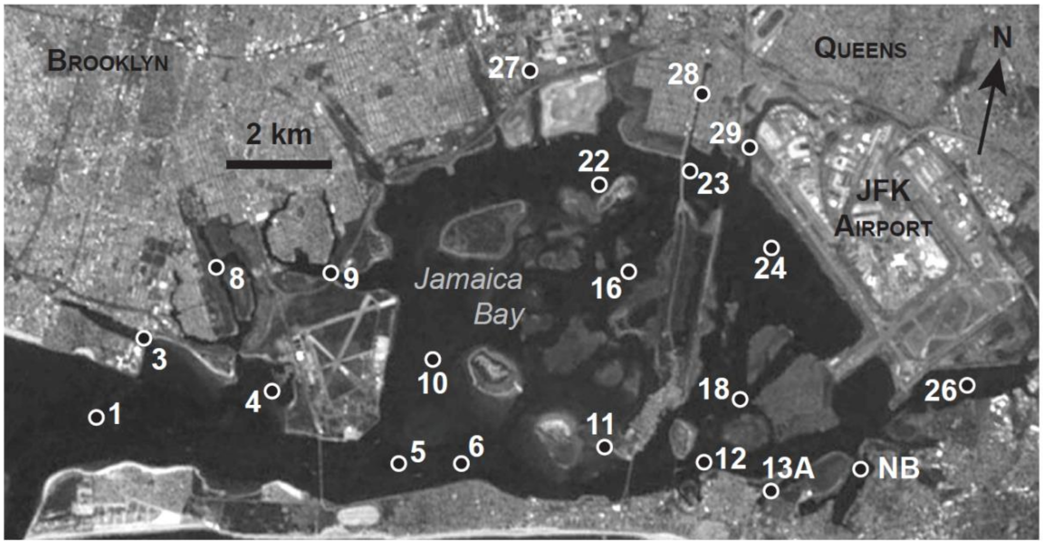


Figure 2-2. The center of Jamaica Bay and some portions of the shoreline comprise the Jamaica Bay National Wildlife Refuge. The Rockaway Peninsula that forms the southern boundary of the bay is heavily urbanized and primarily residential. Portions of the western end of this peninsula were still undeveloped when the park was created. These are now popular bathing beaches.

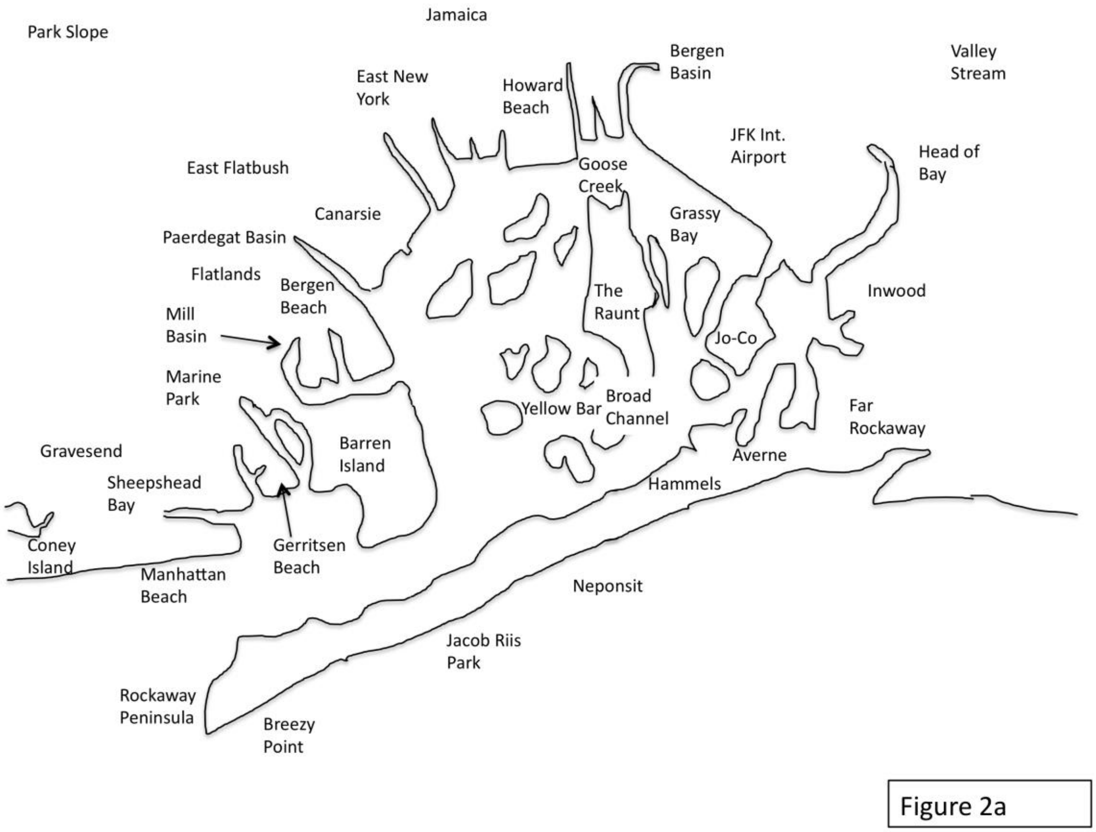


Figure 2-2a. The place names of the major geographical features of Jamaica Bay and the surrounding neighborhoods.

Figure 3

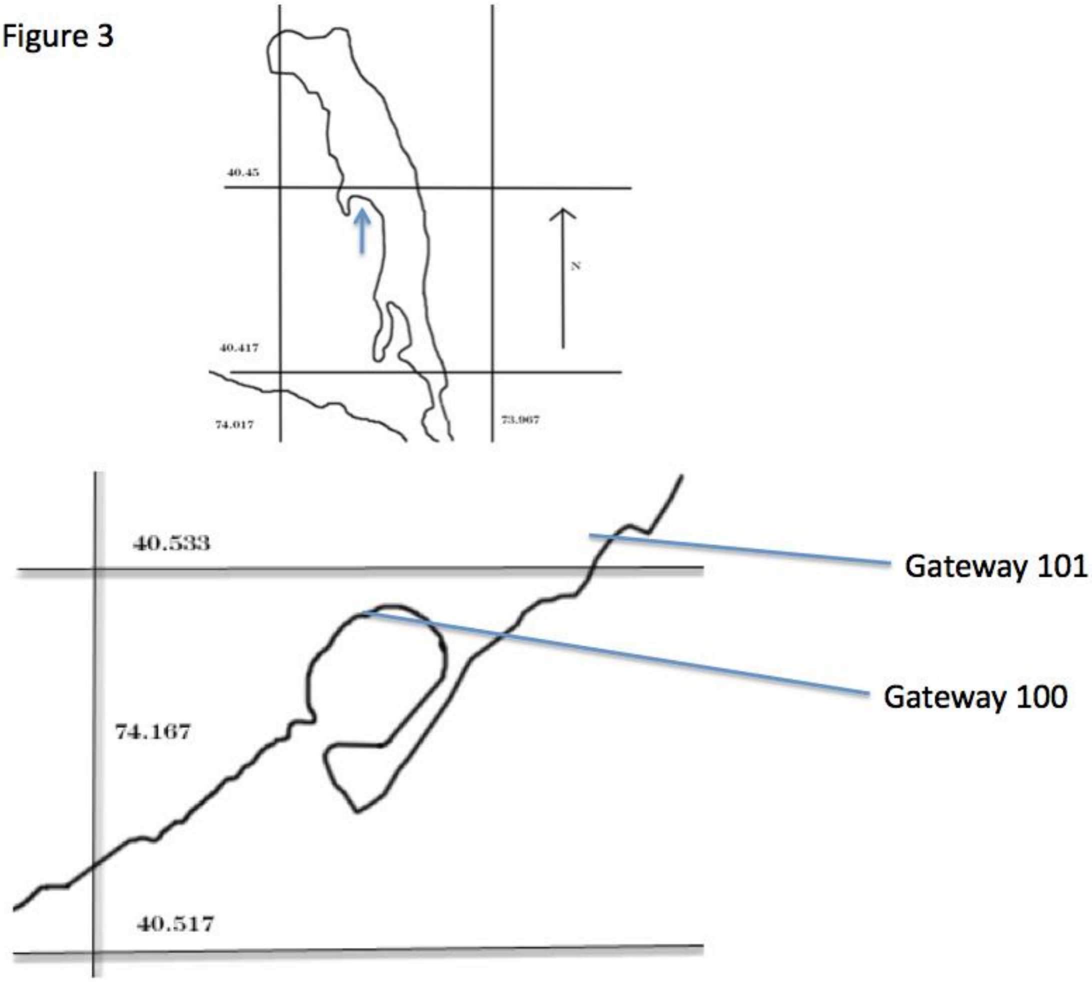


Figure 2-3. The Great Kills (bottom) and Sandy Hook (top) units. The location of the marsh where the Sandy Hook MSU samples were taken is marked by an arrow. The location of Gateway 102, which was collected on the west side of Staten Island is not shown.

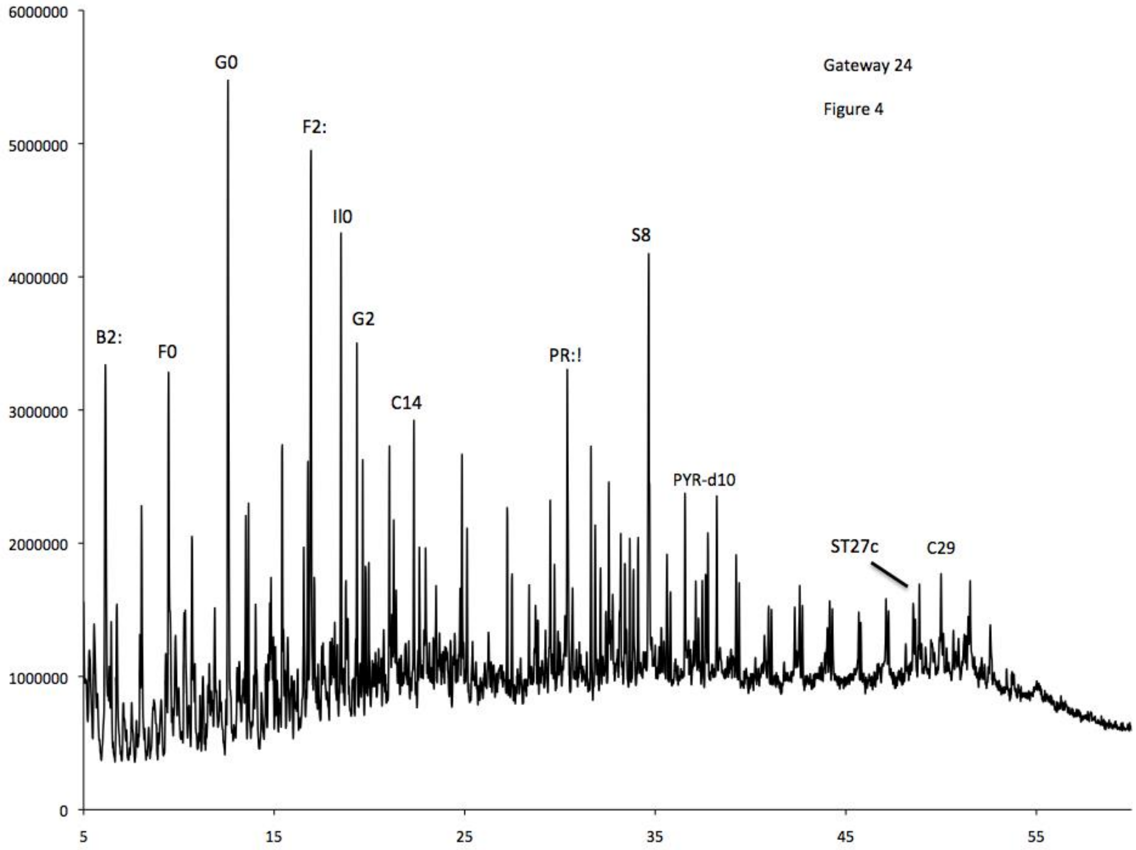


Figure 2-4. Chromatogram from sample point 24. This chromatogram is fairly typical of the organic-rich Jamaica Bay samples. Major components are identified as follows: B2: - styrene; F0 - phenol; G0 – guaiacol; F2: - vinylphenol; Il0 – indole; G2: - vinylguaiacol; PR:1 – prist-1-ene; S8 – sulfur; PYR-d10 – deuterated pyrene; ST27c – C27 sterane.

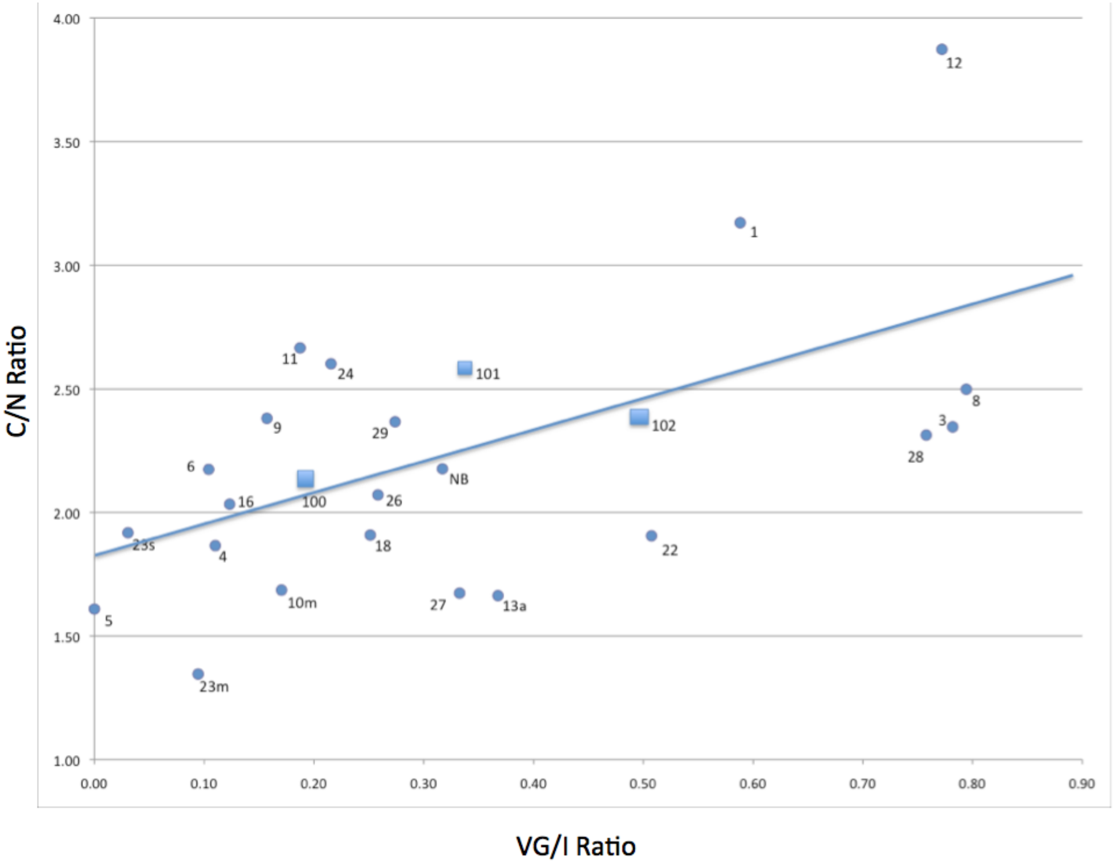


Figure 2-5. The VGII (X axis) and the C/N ratio (Y axis). The VGII which is derived from the pyrolysis breakdown products of terrestrial plants and algae and the C/N ratio are moderately well correlated. Jamaica Bay sample points are shown as round dots and samples from Staten Island are shown as squares.

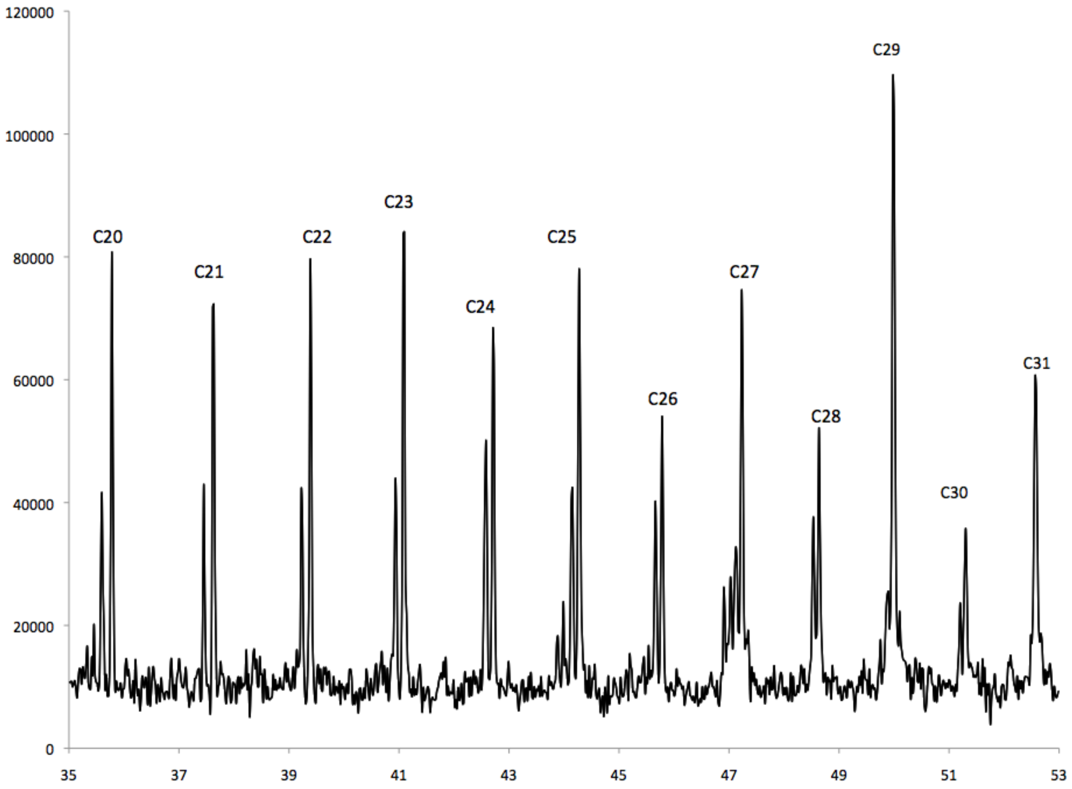


Figure 2-6. The extracted ion chromatogram for mass 71 and showing the major alkane peaks from the Sandy Hook organic rich sediments. The odd-over-even predominance among the longer chain lengths is clearly visible.

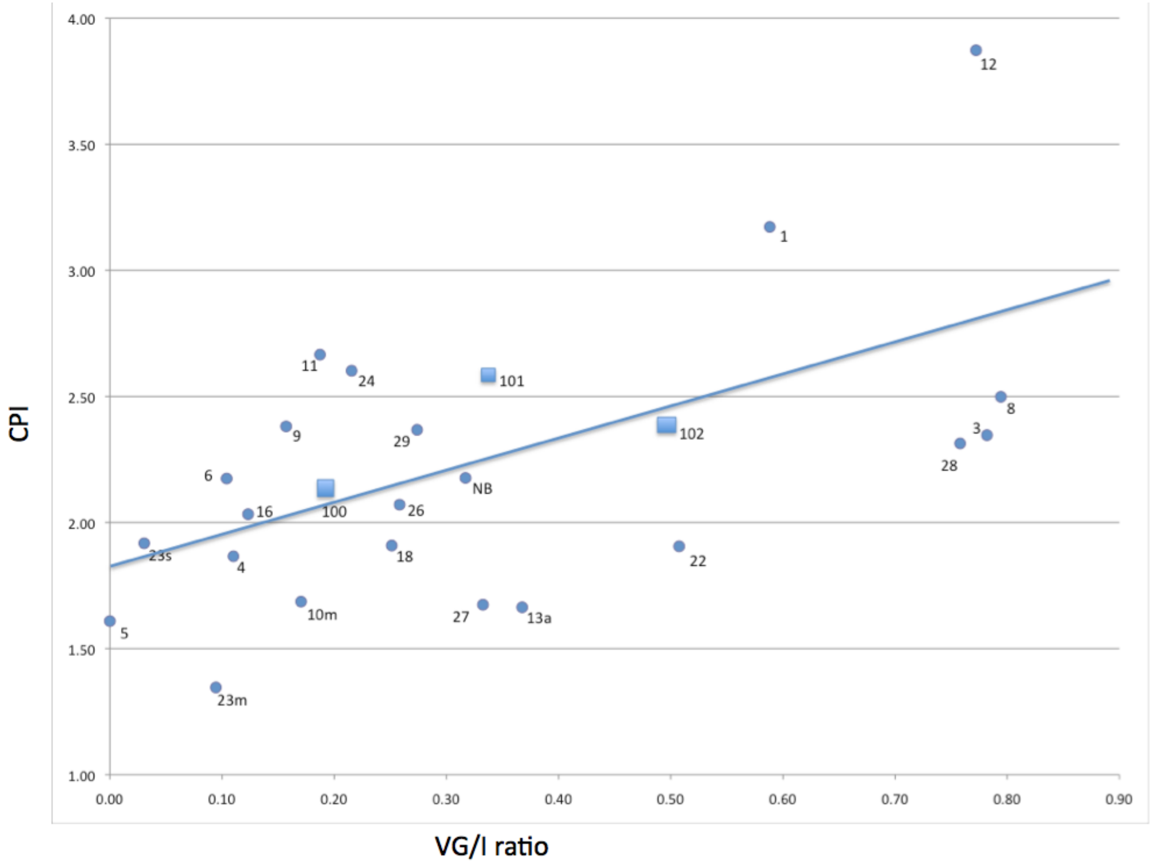


Figure 2-7. The VGII (X axis) and CPI (Y axis). These two idices should track one another closely as a high VGII indicates a large terrestrial plant input and high CPI values are indicative of undegraded terrestrial plant inputs. The Jamaica Bay sample points are shown as round dots and samples from Staten Island are shown as squares.

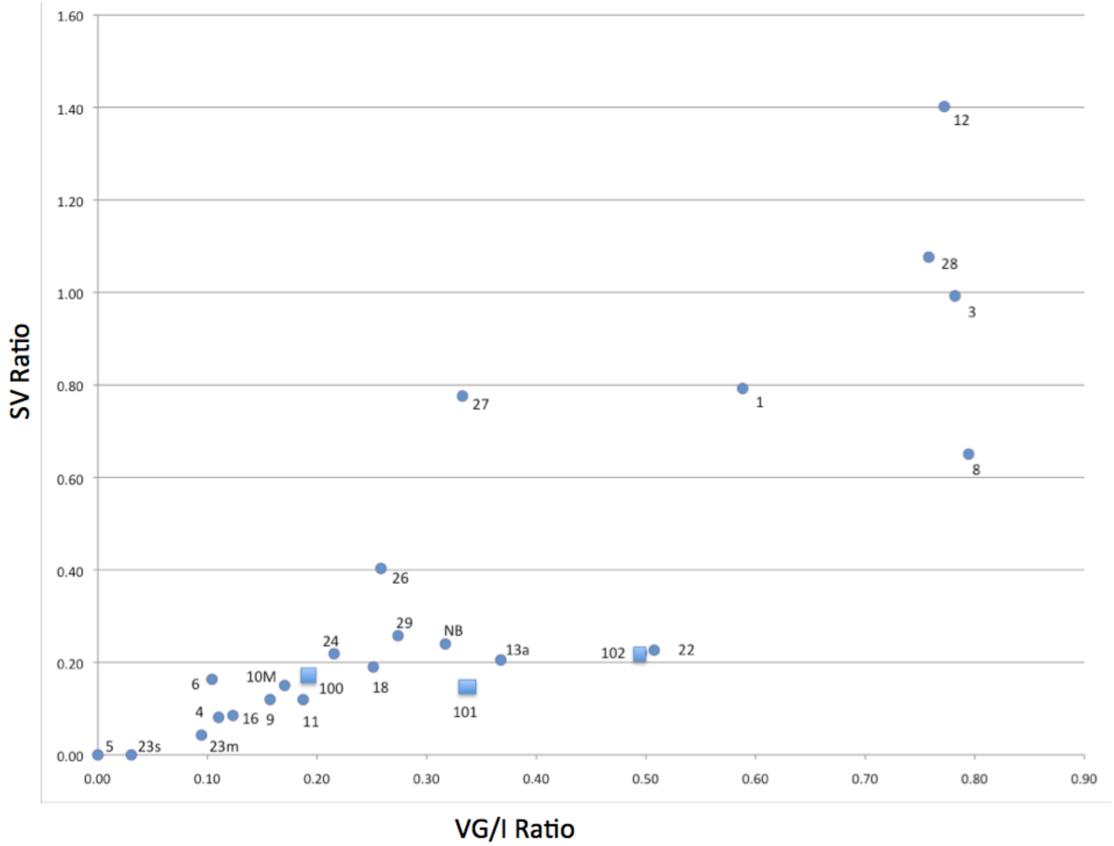


Figure 2-8. The VGII (X axis) and SV (Y axis) ratios. These indices are well correlated. Jamaica Bay sample points are shown as round dots and samples from Staten Island are shown as squares. A high SV ratio indicates organic matter input from grasses. The regression line has been omitted for clarity.

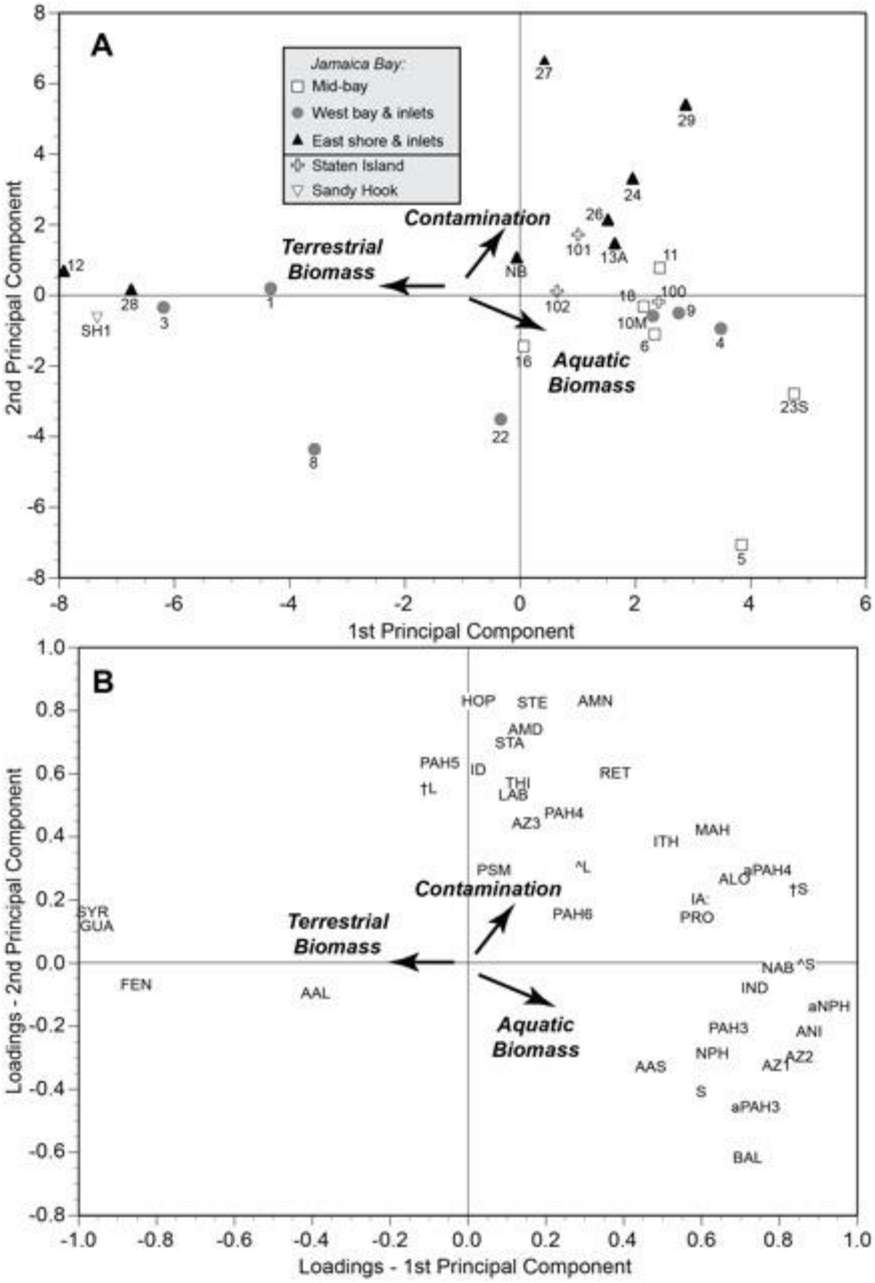


Figure 2-9. PCA Analysis clustering of the Gateway samples. The clusters are representative of the dominant input of organic matter (A). The relative postions of varous classes of compounds with in the PC loadings are shown in part B.

Table 2-1, Decimal latitude and longitude locations of the sampling points with sediment descriptions.

Sample Point	Lat	Long	Description and location
Gateway 100	40.5462	74.13607	Sandy mud, Great Kills Harbor at end of creek
Gateway 101	40.54882	74.11399	Mud flat, Oakwood Beach, Fox Creek Tidal Marsh
Gateway 102	40.60828	74.188896	Mud flat, Saw Mill Creek
Jamaica Bay 1	40.56736	73.93529	Fine sandy, Center of Rockaway Inlet
Jamaica Bay 3	40.582333	73.933445	Fine organic rich, Mouth of Sheepshead Bay
Jamaica Bay 4	40.584471	73.902597	Fine organic rich, Dead Horse Bay
Jamaica Bay 5	40.577706	73.870286	Course sand, Nova Scotia Bar
Jamaica Bay 6	40.58201	73.856054	Sandy, Beach Channel
Jamaica Bay 8	40.597972	73.924756	Fine organic rich, Gerritsen Creek near Mill Creek
Jamaica Bay 9	40.604798	73.900527	Fine organic rich, Mill Basin
Jamaica Bay 10	40.597852	73.870668	Fine organic rich, Island Channel near Ruffle Bar
Jamaica Bay 12	40.598561	73.803597	Fine organic rich, Beach Channel
Jamaica Bay 11	40.595603	73.825911	Fine sandy, Big Egg Marsh
Jamaica Bay 13	40.60171	73.77528	Sandy, Norton Basin
Jamaica Bay 13a	40.59879	73.78885	Fine organic rich, Sommerville Basin
Jamaica Bay 16	40.62384	73.8385	Fine sandy, Pumpkin Patch Channel
Jamaica Bay 18	40.611389	73.801417	Sandy, Winhole Channel
Jamaica Bay 22	40.634734	73.849788	Fine organic rich with sand, Elder's Point Marsh
Jamaica Bay 23	40.643734	73.834962	Fine sandy, north end of Cross Bay Blvd bridge
Jamaica Bay 24	40.637497	73.810692	Fine organic rich, Grassy Bay
Jamaica Bay 26	40.628833	73.75667	Fine organic rich, Head of Bay
Jamaica Bay 27	40.64854	73.87505	Fine organic rich, Hendrix Creek
Jamaica Bay 28	40.656981	73.838336	Shellbank Basin
Jamaica Bay 29	40.652448	73.823524	Fine organic rich, Bergen Basin
Jamaica Bay NB	40.60872	73.7728	Fine organic rich, entrance to Norton Basin
Sandy Hook 1	40.4048	73.9793	Course powdery, Plum Island
Sandy Hook 2	40.42401	73.98576	Sandy, Spermaceti Cove
Sandy Hook 3	40.44884	73.9993	Fine powder, Horsehoe Cove
Sandy Hook MSU 1	40.448875	73.999072	Fine organic rich, Salt marsh at low tide line
Sandy Hook MSU 3	40.448694	73.999136	Sand, Sand bar in intertidal zone

Table 2-2, Sediment characteristics and locations within Jamaica Bay, from *Jamaica Bay Watershed Protection Plan, Volume I – Regional Profile*. All values in percent.

Location	Sand	Silt	Clay	MSU sample number (if applicable)
Rockaway Inlet	80	10	10	1
Grassy Bay	20-30	20 – 30	50	24
The Raunt	50-60	0-30	20-40	N/A
Grass Hassock Channel	25	25-45	30-50	N/A

Table 2-3, Sediment types and TOC values from this project.

Sample Point	LOI (%)	silt/clay (%)
Gateway 100	37.5	2.00
Gateway 101	12.1	>95
Gateway 102	5.43	75.0
Jamaica Bay 1	4.53	40.0
Jamaica Bay 2	8.85	66.7
Jamaica Bay 3	7.39	83.3
Jamaica Bay 4	4.41	74.0
Jamaica Bay 5	0.38	3.81
Jamaica Bay 6	1.77	22.2
Jamaica Bay 8	5.45	57.1
Jamaica Bay 9	6.03	66.7
Jamaica Bay 10	6.73	13.0
Jamaica Bay 11	1.46	29.0
Jamaica Bay 12	34.8	>95
Jamaica Bay 13A	7.82	76.9
Jamaica Bay 16	1.47	15.8
Jamaica Bay 18	1.31	35.0
Jamaica Bay 22	2.77	61.5
Jamaica Bay 23	1.09	9.09
Jamaica Bay 24	15.7	>95
Jamaica Bay 26	15.2	94.7
Jamaica Bay 27	21.9	95.0
Jamaica Bay 28	28.0	88.9
Jamaica Bay 29	19.5	>95
Jamaica Bay NB	12.3	82.6
Sandy Hook MSU 1	17.8	95.0
Sandy Hook MSU 3	1.52	<5

Table 2-4, Results for various sediment characteristics and significant biomarker ratios.

Sample Point	C/N	CPI	% LOI	Percent Silt & Clay	S/V	VG/I
Gateway 1	12.8	3.17	0.00	0.00	0.79	0.59
Gateway 3	11.5	2.35	0.00	0.00	0.99	0.78
Gateway 4	No data	1.87	4.41	74.0	0.08	0.11
Gateway 5	14.0	1.61	0.38	3.81	0.00	0.00
Gateway 6	10.4	2.17	1.77	22.2	0.16	0.1
Gateway 8	13.8	2.50	5.45	57.1	0.65	0.79
Gateway 9	12.8	2.38	6.03	66.7	0.12	0.16
Gateway 10 M	No data	1.69	6.73	13.0	0.15	0.17
Gateway 11	No data	2.67	1.46	29.0	0.12	0.19
Gateway 12	16.9	3.87	34.8	95.0	1.4	0.77
Gateway 13A	9.33	1.66	7.82	76.9	0.21	0.37
Gateway 16	No data	2.03	1.47	15.8	0.09	0.12
Gateway 18	No data	1.91	1.31	35.0	0.19	0.25
Gateway 22	13.3	1.91	2.77	61.5	0.23	0.51
Gateway 23M	8.46	1.35	No data	No data	0.04	0.09
Gateway 23S	11.3	1.92	1.09	9.09	0.00	0.03
Gateway 24	11.2	2.6	15.7	95.0	0.22	0.22
Gateway 26	12.0	2.07	15.2	94.7	0.4	0.26
Gateway 27	13.7	1.67	21.9	95.0	0.78	0.33
Gateway 28	16.2	2.31	28.0	88.9	1.08	0.76
Gateway 29	14.2	2.37	19.5	95.0	0.26	0.27
Gateway NB	11.8	2.18	12.0	83.3	0.24	0.32
Gateway 100	No data	2.13	2	37.5	0.17	0.19
Gateway 101	13.3	2.59	12.1	95.0	0.15	0.34
Gateway 102	16.5	2.39	5.43	75.0	0.22	0.5
Sandy Hook W1	No data	2.18	17.8	95.0	0.99	0.82
Sandy Hook W3	No data	0.95	1.52	5.00	0.11	0.1

Table 2-5. Jamaic Bay sample clustering from PCA.

Sample	Cluster Assignment	Location
1	Terrestrial Biomass	Center of Rockaway Inlet
3	Terrestrial Biomass	Sheepshead Bay near outfall of the Coney Island WPCP
4	Aquatic Biomass	Dead Horse Bay
5	Unclassified	Open water on western side of the bay
6	Aquatic Biomass	Open water west side of the bay and near Rockaway WPCP
8	Terrestrial Biomass	Gerritsen Creek near Mill Creek
9	Aquatic Biomass	Mill Basin
11	Anthropogenic	Big Egg Marsh
12	Terrestrial Biomass	Brant Point, west of Rockaway WPCP and CSOs
16	Aquatic Biomass	Pumpkin Patch Channel
18	Aquatic Biomass	Winhole Channel
22	Aquatic Biomass	Elder's Point Marsh
24	Anthropogenic	Grassy Bay
26	Anthropogenic	Head of Bay
27	Anthropogenic	26th Ward WPCP on Hendrix Creek
28	Terrestrial Biomass	Shellbank Basin
29	Anthropogenic	Entrance of Bergen Basin site of the Jamaica WPCP
10m	Aquatic Biomass	Island Channel near Ruffle Bar
13a	Anthropogenic	Sommerville Basin, near Edgemere Landfill
23m	Unclassified	North end of Cross Bay Blvd bridge
23s	Aquatic Biomass	North end of Cross Bay Blvd bridge
NB	Anthropogenic	Entrance to Norton Basin

Table 2-6. PAH Concentrations determined by selected ion monitoring (SIM) or full scan analysis. All results in mg/kg. Values of zero represent not detected.

Sample Point	Mode	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene
Gateway 1	SIM	0.6	0.23	0.07	0.07
Gateway 3	SIM	0.37	0.13	0.14	0.08
Gateway 4	SIM	1.71	0.17	0.14	0.22
Gateway 5	SIM	N.D.	0.03	N.D.	0.02
Gateway 6	SIM	0.03	0.02	N.D.	0.01
Gateway 9	SIM	0.01	0.49	0.18	0.07
Gateway 13a	SIM	8.79	1.19	0.19	0.16
Gateway 18	SIM	0.02	0.02	0.02	0.01
Gateway 23	SIM	0.34	0.28	0.06	0.05
Gateway 24	SIM	1.29	1.19	0.02	0.16
Gateway 26	SIM	0.07	0.35	0.06	0.47
Gateway 27	SIM	0.11	0.34	0.25	0.09
Gateway 29	SIM	0.18	1.51	0.37	0.12
Gateway NB (Norton Basin)	SIM	3.09	1.21	0.2	N.D.
Gateway 102 (Staten Isl)	SIM	1.11	0.16	N.D.	0.45
Sandy Hook 1	Full Scan	0.31	N.D.	N.D.	N.D.
Sandy Hook 2	Full Scan	N.D.	N.D.	N.D.	N.D.
Sandy Hook 3	Full Scan	1.28	N.D.	N.D.	N.D.
Sample Point	Mode	Phenanthrene	Anthracene	Fluoranthene	Pyrene
Gateway 1	SIM	0.24	0.06	0.23	0.27
Gateway 3	SIM	0.31	0.19	0.33	0.35
Gateway 4	SIM	0.44	0.19	0.51	0.65
Gateway 5	SIM	0.12	0.04	0.05	0.27
Gateway 6	SIM	0.22	0.23	0.16	0.11
Gateway 9	SIM	0.55	0.24	0.8	0.93
Gateway 13a	SIM	0.67	0.53	1.09	1.79
Gateway 18	SIM	0.13	0.03	0.07	0.09
Gateway 23	SIM	0.14	0.1	0.09	0.32
Gateway 24	SIM	0.45	0.28	1.24	1.14
Gateway 26	SIM	1.07	0.54	1.61	1.99
Gateway 27	SIM	1.37	0.42	4.53	4.23
Gateway 29	SIM	0.76	0.44	3.32	3.26
Gateway NB (Norton Basin)	SIM	0.57	0.27	1.54	1.75
Gateway 102 (Staten Isl)	SIM	0.71	0.44	0.49	0.58
Sandy Hook 1	Full Scan	0.13	0.1	0.21	0.24
Sandy Hook 2	Full Scan	0.19	0.15	0.43	0.31
Sandy Hook 3	Full Scan	1.2	1.34	3.15	3.33
Sample Point	Mode	Benzo[a]anthracene	Chrysene	Benzo[b+j]fluoranthene	Benzo[k]fluoranthene
Gateway 1	SIM	0.10	0.10	0.33	0.04
Gateway 3	SIM	0.08	0.11	0.05	N.D.
Gateway 4	SIM	0.3	0.37	1.57	2.25
Gateway 5	SIM	0.08	0.07	N.D.	N.D.
Gateway 6	SIM	0.17	N.D.	N.D.	N.D.
Gateway 9	SIM	0.18	0.22	N.D.	N.D.
Gateway 13a	SIM	0.71	0.8	2.57	0.2
Gateway 18	SIM	0.01	0.01	N.D.	N.D.
Gateway 23	SIM	0.12	0.14	0.13	0.02
Gateway 24	SIM	0.63	0.69	1.51	0.12
Gateway 26	SIM	1.48	1.72	4.96	0.25
Gateway 27	SIM	1.23	1.98	4.01	0.17
Gateway 29	SIM	1.53	1.74	5.82	0.12
Gateway NB (Norton Basin)	SIM	0.85	1.06	4.48	0.35
Gateway 102 (Staten Isl)	SIM	0.25	0.33	0.95	0.09
Sandy Hook 1	Full Scan	0.08	0.14	0.25	0.05
Sandy Hook 2	Full Scan	0.11	0.18	0.21	0.02
Sandy Hook 3	Full Scan	1.04	1.4	2.25	0.17
Sample Point	Mode	Benzo[a]pyrene	Dibenzo[a,h]anthracene	Indino[1,2,3-cd]pyrene	Benzo[g,h,I]perylene
Gateway 1	SIM	0.12	N.D.	0.04	0.04
Gateway 3	SIM	N.D.	N.D.	0.09	0.23
Gateway 4	SIM	0.63	N.D.	N.D.	0.15
Gateway 5	SIM	N.D.	N.D.	N.D.	N.D.
Gateway 6	SIM	N.D.	N.D.	N.D.	N.D.
Gateway 9	SIM	N.D.	N.D.	N.D.	N.D.
Gateway 13a	SIM	0.78	N.D.	0.06	0.06
Gateway 18	SIM	N.D.	N.D.	N.D.	N.D.
Gateway 23	SIM	0.05	N.D.	N.D.	N.D.
Gateway 24	SIM	0.17	N.D.	N.D.	N.D.
Gateway 26	SIM	0.86	N.D.	N.D.	N.D.
Gateway 27	SIM	1.21	N.D.	N.D.	N.D.
Gateway 29	SIM	0.87	N.D.	N.D.	N.D.
Gateway NB (Norton Basin)	SIM	1.62	N.D.	0.23	0.13

Gateway 102 (Staten Isl)	SIM	0.26	N.D.	N.D.	N.D.
Sandy Hook 1	Full Scan	0.07	N.D.	N.D.	N.D.
Sandy Hook 2	Full Scan	0.08	N.D.	N.D.	N.D.
Sandy Hook 3	Full Scan	0.25	N.D.	N.D.	N.D.

Table 2-7 Jamaica Bay petrogenic v pyrogenic source determination based on Anthracene – Phenanthracene and Fluoranthene – Pyrene ratios. Note that for samples 5, 8, 13a, and 23, the interpretations are not in agreement.

Sample Point	an/(an+ph)	Interpretation
Gateway 1	0.20	Pyrogenic
Gateway 3	0.38	Pyrogenic
Gateway 4	0.30	Pyrogenic
Gateway 5	0.25	Pyrogenic
Gateway 6	0.51	Pyrogenic
Gateway 8	0.24	Pyrogenic
Gateway 9	0.30	Pyrogenic
Gateway 10	0.52	Pyrogenic
Gateway 11	0.93	Pyrogenic
Gateway 13a	0.44	Pyrogenic
Gateway 16	0.11	Pyrogenic
Gateway 18	0.19	Pyrogenic
Gateway 23	0.42	Pyrogenic
Gateway 24	0.38	Pyrogenic
Gateway 26	0.34	Pyrogenic
Gateway 27	0.23	Pyrogenic
Gateway 29	0.37	Pyrogenic
Gateway NB	0.32	Pyrogenic

Sample Point	fl/(fl+py)	Interpretation
Gateway 1	0.46	Liq fossil fuels
Gateway 3	0.49	Liq fossil fuels
Gateway 4	0.44	Liq fossil fuels
Gateway 5	0.16	petrogenic
Gateway 6	0.59	Grass, wood or coal
Gateway 8	0.28	petrogenic
Gateway 9	0.46	Liq fossil fuels
Gateway 10	0.52	Grass, wood or coal
Gateway 11	0.52	Grass, wood or coal
Gateway 13a	0.38	petrogenic
Gateway 16	0.50	Liq fossil fuels
Gateway 18	0.44	Liq fossil fuels
Gateway 23	0.22	petrogenic
Gateway 24	0.52	Grass, wood or coal
Gateway 26	0.45	Liq fossil fuels
Gateway 27	0.52	Grass, wood or coal
Gateway 29	0.50	Liq fossil fuels
Gateway NB	0.47	Liq fossil fuels

Table 2-8, Sandy Hook and Staten Island petrogenic v pyrogenic source determination based on Anthracene – Phenanthracene and Fluoranthene – Pyrene ratios

Sample point	an/(an+ph)	Interpretation
Sandy Hook 1	0.43	Pyrogenic
Sandy Hook 2	0.44	Pyrogenic
Sandy Hook 3	0.53	Pyrogenic
Sandy Hook_MSU_1	0.53	Pyrogenic
Sandy Hook_MSU_3	ND	N/A
Gateway 100 (Staten Isl)	0.52	Pyrogenic
Gateway 101 (Staten Isl)	0.45	Pyrogenic
Gateway 102 (Staten Isl)	0.49	Pyrogenic

Sample point	fl/(fl+py)	Interpretation
Sandy Hook 1	0.47	Liquid fossil fuels
Sandy Hook 2	0.58	Grass, wood or coal
Sandy Hook 3	0.49	Liquid fossil fuels
Sandy Hook_MSU_1	ND	Grass, wood or coal
Sandy Hook_MSU_3	0.50	Liquid fossil fuels
Gateway 100 (Staten Isl)	0.53	Grass, wood or coal
Gateway 101 (Staten Isl)	0.55	Grass, wood or coal
Gateway 102 (Staten Isl)	0.45	Liquid fossil fuels

Chapter Three

Pyrolysis GC/MS Investigations of a Distrurbed Sediment Core from the Passaic River's Dundee Lake, Athropogenic Influences and Inputs to the Organic Geochemisty

Abstract

Analysis of a sediment core taken from Dundee Lake on the Passaic River was performed by pyrolysis/gas chromatography/massspectrometry. The core was collected in 2005 as part of a Passaic River sediment project conducted by Malcolm Pirnie prior to the designation of the tidal portion of the river as a part of the National Priority List. It was the only core from Dundee Lake and the also the only one from a non-tidal section of the river. The total depth of the core was approximately 200 cm and it was collected immediately downstream of the Route 46 highway bridge.

Dundee Lake is the name given to a fresh water section of the Passaic River between the head of tide at the Dundee Dam and the city of Paterson. The surrounding area has a high population density and was home to many industries, including dye works, general manufacturing, and papermaking. It was thought that this core would provide a record of pollutant inputs over long periods of time and would reflect the changing composition of upstream industries. However measurements of ^{137}Cs strongly suggested that the core was taken from an highly disturbed environment. Clear temporal trends were not discernible.

Ratios of diagnostic PAH molecules, sewage markers, and biogenic pyrolysis biomarkers suggested that the organic inputs to the core did not vary greatly with depth and were of recent origin. There was a consistent increase in hydrocarbons and sewage markers at 30 cm and another consistent, though smaller, increase at 80 cm. Compounds of the same

chemical class showed clear patterns of co-occurrence and correlations (r values) were frequently 0.9 or higher among petrogenic compounds. These results suggest related co-deposited compounds tend to remain together despite subsequent disturbance.

This core serves as a case study that illustrates that indices created from PAH ratios, pyrolysis product ratios, and hydrocarbon inputs can work together to illuminate sediment conditions even in highly disturbed area.

Introduction

The core analyzed in this project was collected in 2005 as part of a Passaic River sediment project conducted by Malcolm Pirnie prior to the designation of the tidal portion of the river as a part of the USEPA's National Priority List of Superfund sites. Core 37 was the only one taken in Dundee Lake and also the only one from a non-tidal section of the river. The core was a high-resolution core from a location in the Dundee Lake immediately downstream of the Route 46 highway bridge (figures 3-1 and 3-2). The core was analyzed by Py-GC/MS.

Site Description

Dundee Lake is the name given to a fresh-water section of the Passaic River between the head-of-tide at the Dundee Dam and the city of Paterson. The first of several dams at the site was built in the 1840s for water power purposes and the present dam between the cities of Garfield on the east bank and Passaic on the west bank was constructed in the

1860s. The dam is 137 meters feet across, 2 meters wide at the top and 24 meters wide at the base (Clayton and Nelson 1882). The 1900 Report of the Chief of Engineers U.S. Army lists the lake as being navigable for vessels drawing six feet of water and the total length of the lake was 5.6 kilometers (Report of the Chief of Engineers U.S. Army, 1900).

Dundee Lake is surrounded by many industries and areas with a high population density. Most of the industries were located in the city of Paterson and included dye works, general manufacturing, and papermaking. The majority of the sedimentary studies from the Upper Passaic River have focused on dioxin concentrations. Ehrlich, et. al. (1994) report finding a fingerprint pattern for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) that is consistent with recycled pulp and paper mill effluents in sediments from both the upper Passaic River and Kill Van Kull. Cooper et al. (1993) report dioxin concentrations in the Dundee Lake sediments below 57 ng/kg. A study published in 1985 by the New Jersey Department of Environmental Protection revealed that eel and carp taken from regions above the head of tide or above Dundee Dam had no detectable levels of TCDD and that dioxin contamination of fish and crustaceans is only ocuring on the tidal section of the Passaic River. (Hazen et al. 1985) The Dundee Lake sediments are very organic rich. Uchrin and Ahlert (1985) report Sediment Oxygen Demand (SOD) ranging from non-detectable to 2.43 g m^{-2} day^{-1}. The demand did depend on temperature and the the measured values were comparable with historical data from comparable locations.

Very little has been published about the sediments of Dundee Lake which is in stark contrast to the sediments of the tidal portions of the river. Barabás et al. (2004) report that the USEPA studied 351 sediment cores from the lower Passaic. In Dundee Lake a search of the Science Direct database returned only two results. Searching the American Chemical Society (ACS) only returned a single paper tangentally dealing with the upper Passaic sediments.

The concrete-arch Route 46 highway bridge (Figure 3-2) immediately upstream of the core's location was constructed in the 1930s as part of the expansion of the state highway system west of New York City (HAER). Bidding on the bridge construction contracts began in September of 1930. An existing bridge had to be replaced and a new temporary bridge was erected to accommodate traffic (*New York Times*, 1930). The highways along the west shore of Dundee Lake date to the 1970s.

Some idea of the scale of sediment movements and currents near the core's location can be determined from the results of an experimental bridge pier scour monitoring system installed by Rutgers University on the Route 46 highway bridge. At the bridge piers, weekly fluctuations in the range of 0.30 meters of sediment depth were observed over a 23-month period beginning in 2001. Daily fluctuations of approximately the same magnitude were observed after rainstorms (Nassif et al. 2002).

The river is approximately 137 meters wide at the bridge site. The strong currents and intense sediment movements in the area are attributed to the river's 45-degree bend and the placement of the bridge piers (Nassif et al. 2002).

Additional evidence of sediment movement and a disturbed core comes from a photograph recently obtained from Google Earth ®. There are clear sediment plumes extending downriver from the piers of the Route 46 bridge and extending directly into the area where the core was taken (figure 3-3).

An additional 9 pairs of cores were taken in 2007 as part of the USEPA's Remedial Investigation (RI) sampling program. In 8 of the 9 locations there was visible petroleum product contamination ranging from 8 to 18 cm thick at depths between 10 and 79 cm below the sediment-water interface. It was thought this petroleum layer might represent a single time horizon. Only four of the nine locations were identified as undisturbed silt deposition sites and thus suitable sites for detailed study (Dundee Lake Narrative 2008). Core 37 did not contain the petroleum layer or undisturbed sediments. This was the only core donated to Montclair State University and therefor the only one available for study.

Materials and Methods

The core was collected by the staff of Malcolm Pirnie using vibracoring equipment. The sediments were dried, and hand-ground using a motor and pestle. Small pebbles, shells, and macroscopic plant materials such as blades of grass or leaves were removed at this time. Milligram quantities of the dried sediments were used for the analysis. Approximately 4 to 5 milligrams of fine, organic rich sediments were loaded into a quartz pyrolysis tube. A miniature spatula and Sartorius model CP64 analytical balance was used for the weighing. The dried sediments were spiked with 5 µL of an internal standard solution containing deuterated PAHs from Cambridge Isotopes, Andover, Ma.. The solution contained naphthalene (D-naphthalene, cat. DLM-365-1), deuterated anthracene (D-anthracene, cat. DLM-102-1), and deuterated pyrene (D-pyrene, cat. DLM-155) in hexane. The spike concentration was manipulated such that each injection introduced 24.50 ng of D-naphthalene and 27.00 ng of D-anthracene into the chromatographic system. D-Pyrene was the only isotope actually used for quantization. Chromatography was performed on a Thermo Electron Focus GC and Thermo Electron DSQ quadrapole type mass spectrometer. A CDS model 1500 pyrolysis system was used to heat the samples at 610 ^{o}C for 20 seconds under a helium atmosphere. The GC column was a 30m J&W Scientific DB-1MS column, with a 0.25 mm i.d. and 0.25µm film thickness. The temperature program began at 50 ^{o}C for 5 minutes and rose at a rate of 5^{o}C per minute until reaching 300 ^{o}C and holding for 25 minutes. Gas pressure at the column head was 228 kPa with a split ratio of 1 to 25. The mass spectrometer was set to 50-550 Da, 1.08 scans/sec., 70 eV ionization voltage.

Concentrations of analyte molecules were estimated from the peak areas of the internal standard. A correction factor was applied to each result. This factor was based on the ratio between the peak area obtained in the total ion chromatogram and the peak area obtained from integrating only the ion used for quantitation. The output files of the chromatography system were converted to ISIS format and imported into EasyQuant for peak identification. Principal Component Analysis (PCA) was performed using JMP 9 (SAS Software, Cary N.C.) and correlation coefficients (r values) were calculated with Microsoft Excel. All of the correlation results presented in the text are r values and not r^2.

Prior to PCA calculations the sample concentrations were first normalized so that each chemical constituent was represented by a percentage of the total of all measured compounds. All values that were not detected (ND) were assigned a random concentration below 0.001 mg/kg, i.e. an order of magnitude below that of detected materials. To prevent large concentration values from skewing the PCA results the square root of each normalized concentration value was used.

The ^{137}Cs results were obtained from Malcolm Pirnie. The analysis was performed by gamma-ray spectroscopy according to the standards set forth in the EML Procedures Manual, *HASL-300.*

Loss on ignition (LOI) values were obtained by heating dried sediments to 600 ^{o}C overnight and determining the weight loss. The proportion of fine-grained clay and silt particles in the sediment was determined by visual examination.

Results and Discussion

The ^{137}Cs results did not show a single peak that might have been used to date the sediments; rather there were five peaks at depths from 5 to 80 cm (figure 3-4). Results ranged from not detected (1.5, 7.5, 46.5 and 56.5 cm deep) to a high of 0.077 pCi g^{-1} per gram at a depth of 41.5 cm. This result is consistent with other highly disturbed areas of the Passaic River. Barbara, et. al. 2010 presented examples of three undisturbed sediment cores from the lower Passaic River where the ^{137}Cs showed a distinct single spike, 1.1 pCi g^{-1} at river kilometer 20.6, 0.7 pCi g^{-1} at river kilometer 6.84, and 0.19 pCi g^{-1} at river kilometer 0.66. Barbara et al. (2010) also cited examples of highly disturbed sediment (river kilometer 12.6, river kilometer 0.24, and the Saddle River) where the ^{137}Cs concentrations could not be used to date sediment cores. A mechanism for explaining these specific disturbances was not proposed. (Barbara, et. al. 2010) In an undisturbed core, spikes in the ^{137}Cs concentrations correspond to specific historical events. There is usually a large peak corresponding to above-ground nuclear weapons testing in the late 1950s and early 1960s. A smaller peak is often observed that corresponds to the Chernobyl reactor accident. A lack of these peaks therefore strongly suggests that the core was taken from a highly disturbed environment.

The LOI data for the upper meter of the core showed a remarkable lack of variation (figure 3-4). LOI values ranged from 13.9% to 21.9% with a mean value of 17.3% and a standard deviation of 2.3%. When the LOI vales were plotted against depth, the slope of the resulting least squares regression line was only 0.02 percent LOI per centimeter of depth. Inspection of the sediments after LOI determination revealed that the core consisted entirely of fine-grained sediments with no sand present.

The cesium results suggest disturbance and the LOI results suggest uniformity, but there is no contradiction. High energy environments can result in well-sorted sediments because the fine-grained sediments are also the most easily transported. The most likely scenario is that high-energy areas are found where the river makes its bend and flows around the bridge piers. A lower-energy depositional environment seems to be located immediately downstream of the bridge where the core was taken. It is also possible that earlier sediments may have been removed during the construction of the Route 46 bridge.

The PCA results on the sample points are shown in figure 3-5 and table 3-1. The first PC accounts for 40.7% of sample variation while the second PC accounts for 14.5% of sample variation. The cross plot of principal component 1 and 2 show three clear groupings of samples based on depth.

A cross-plot of the loadings within the first and second principal components also shows distinct compound groupings (figure 3-5). Guiacols, phenols, and vanillin are all produced in the pyrolysis of plant matter and these are clustered toward the top of the plot area. Both parent and methyl forms of three-ring PAHs are clustered near the left of the cross plot. Four- and five-ring PAHs are clustered to the right of the three-ring molecules. Linear alkylbenzenes (LABs) are found toward the center of the plot while straight chain hydrocarbons are clustered along the right-hand side.

Within the loadings of the principal components certain classes of compounds appeared abundant in the upper quartile of each PC. Among the first twenty compounds in the loadings of the first PC, 18 were either alkanes or alkenes. *n*-Alkylbenzenes and alkanones were also prominent in the first quartile of the loading. In the lower quartile of the first PC's loading, there were abundant parent and methylated PAHs present as were anthropgenic sewage markers including a smattering of linear alkylbenzenes and C_{27} and C_{29} sterenes. Botanical pyrolysis products (syringols, guiacols, vanillin) were clustered around the middle of the loadings. This is a clear separation by compound class.

The loadings of the second PC also are clustered by compound class. Fifteen of the first twenty compounds at the top of the loading were botanical pyrolysis markers with a clustering of guiacols being particularly prominent. As with the loadings of the first PC, the bottom of the loading also contained many PAHs but these were interspersed with a greater variety of compounds including monaromatic hydrocarbons, and a few straight-chained alkanes. Methylnaphthalenes were also prominently clustered. Within the third PC there was a cluster of methylated PAHs at the top of the loading with a few alkylamides, and methylated dibenzothiophenes.

The principle sewage markers used in this analysis were cholestene, ethylcholestene, and a suite of linear alkylbenzenes (LABs) ranging in size from 6-phenylundecane (LAB6-11) to 4-phenyltridecane (LAB4-13). LABs came into widespread use after the Second World War. Wartime shortages of the oils and fats needed to make soap prompted their development (Adami 2008). Like most compounds in this study the concentrations of these materials vary with depth. When plotted on the same graph, sewage markers and LABs appear to be tracking one another (figure 3-7). Examining the concentrations closely, spikes in the both materials coincide at 141.5, 111.5, and 81.5 cm.. However sewage markers spike with no corresponding LAB spike at 161.5 and 28.5 cm. while LABs spike at 21.5 and 10.5 cm. with no corresponding increase in sewage concentrations.

Because at some depths these one or both of these materials were not detected, the correlation calculated over the depth of the entire core is quite poor (r = 0.23) but the correlation improves dramtically if the non-detected samples are excluded (r = 0.61). If LABs and total fatty acids are both indicative of sewage inputs then they would be expected to be correlated but the actual correlation was only (r = 0.27) even when the non-detected values are excluded from the calculation.

To determine the nature of organic inputs to sediments, there are a number of useful ratios that can be determined using the quantitation of pyrolysis products. The ratio of syringol to vanillin is an indication of the input of angiosperms and an increase in the ratio is often linked to an increase from the input of grasses. (Steinberg et al. 2009) The VGI Index (VGII) (see chapter 2) is determined from the relative inputs of indole as a marine algae biomarker and vinylguaiacol as a terrestrial plant biomarker (Micic et al. 2010). The third ratio considered in this work is the Carbon Preference Index (CPI). The CPI is a numerical calculation that determines an odd-over-even predominance for n-alkanes in a certain carbon number range. Immature higher plant contributions to the sediments are represented by CPI values greater than 1. Values significantly higher than 1 represent un-degraded higher plant contributions (Killops and Killops 2005). It is important to remember that the CPI is related to chain lengths of alkanes and not their absolute concentration. Throughout the depth of the core the CPI is consistently above 1. In the top meter, the index has an average value of 2.12 and a low of 1.56 at the 30 cm depth. In the first meter of the core, the VGII shows a significant input of algae having an average value of 0.19 and no value greater than 0.32. The largest value in the entire core is 0.54 at a depth of 180 cm.

Throughout the depth of the core, the three ratios appear to track one another and all increase with depth (figure 3-8). The appearance of the traces is similar and the correlations between them are fairly good. (VGII and S/V r = 0.60, CPI and S/V r = 0.41, VGII and CPI r = 0.63) At a depth of 30 centimeters where the inputs of sewage, alkanes, and PAHs spike, these indices all reach a nadir as if the inputs of contamination exclude the inputs from natural sources. In support of this interpretation, throughout the entire depth of the core, the VGII and the total hopane concentrations have a good negative correlation of r = -0.73. As the CPI reaches its low point at around 30 cm, it seems possible that the corresponding spike in alkanes might be attributable to petroleum but it should be remembered that alkanes can be created from the pyrolysis of naturally occurring materials such as algaenan, cutin, and suberan (Deshmukh, et. al. 2001).

Although a graphical representation of these three ratios suggests that they are tracking together, the actual correlations are variable. Through the entire core, the VG/I and S/V are fairly well correlated at r = 0.60, the CPI and S/V at r = 0.41, and the CPI and VG/I at r = 0.63. However in the first 100 cm of the core, the correlations are quite poor. The VG/I and S/V are correlated at r = 0.43, the CPI and S/V at r = 0.09, and the CPI and VG/I at r = 0.06. Within the diagnostic limitations of the these ratios and depending on the depth, there may be monolithic inputs of naturally occurring terrestrial organic matter, or the organic matter inputs may be largely independent of each other. Unfortunately these calculations cannot shed any light on the question of what portion of this material originated in the upper Passaic watershed and what portion originated locally.

Alkanes, hopanes, and petrogenic PAHs are often associated with petroleum. A plot of their concentrations with depth shows concentrations of hopanes and alkanes spiking at 28.5 and 81.5 cm but otherwise not significantly varying with depth. (Figure 3-6) There was a corresponding spike of petrogenic PAH concentrations at these depths as well. Correlations for the total concentations of each class of compounds are shown in table 3-2. A complete list of all compounds and their concentrations is provided in Appendix 5.

PAHs in the environment can originate as either products of combustion, as constituents of petroleum, or as by-products of industrial processes. The Pyrogenic Index (PyI) is a method of determining the relative inputs of pyrogenic and petrogenic PAHs. While there are several versions of the index, they are all fundamentally similar. The concentrations of the common pyrogenic PAH molecules are placed in the numerator and the total PAH concentrations are placed in the denominator. The index used in this study was taken from a paper by Carls (2006). Carls attempted to address common problems in petroleum idenification by creating a combined nonparametric model. Firstly, there is broad range of hydrocarbon sources including natural seeps. Secondly, once released into the environment, petroleum composition can be modified by physical and biological processes.

$$\text{PyI} = \text{Pyro} / \text{Petro}$$

Where:

$$\text{Pyro} = \text{ANT} + \text{FLU} + \text{PYR} + \text{BaA} + \text{BbF} + \text{BkF} + \text{BeP} + \text{BaP} + \text{PER} + \text{IDP} + \text{DBA} + \text{DBZ}$$

$$\text{Petro} = (\sum (\text{naphthalenes}) + \sum (\text{fluorenes}) + \sum (\text{dibenzothiphenes}) + \sum (\text{phenanthrenes}) + \sum (\text{chrysenes})$$

The PyI ranges from 0.18 at 91 cm to 1.23 at 215 cm. It increases dramatically below 181 cm. Hopanes and petrogenic PAHs are not abundant in the lower part of the core.

The PyI shows some variation within the first 150 cm of the core but the other parent PAH diagnostic ratios are largely unchanged throughout this depth range. There are some limitations to using parent compound ratios for PAH source determination. One source of uncertainty is differential degradation of PAH molecules. Coates et. al. (1997) found that in certain sediments, fluorine, fluoranthene, and methylnaphthalene were found to be vulnerable to anaerobic oxidation but pyrene and benzo[*a*]pyrene were not. Other research has shown that low molecular weight PAHs in petroleum are the first to be weathered. This creates a bias in favor of a pyrogenic interpretation. Other ratios using including alkylated PAHs have been proposed. These include the CPI, the C_{17}/C_{29} ratio, and the ratio of UCM/total alkanes (Wagener et al. 2010).

Other lines of evidence suggest a significant petrogenic input. Methylated PAHs are common to petroleum. Among the dibenzothiophenes (DBT) 4-methyldibenzothiphene is a good indicator of un-combusted petroleum (Simcik and Offenberg, 2006) The larger the ratio of 4-mDBT to other DBT molecules, the more un-combusted petroleum is contributing to the organic matter in the sediments. We would expect the Pyrogenic and the 4-DBT/Total DBT indices to be negatively, or at least poorly, correlated. The overall correlation is $r = 0.37$. This PyI has negative correlations with several methylated to parent PAH ratios that are used to determine the relative petrogenic to pyrogenic inputs. These include the following; ($\sum$ MPh)/Ph, $r = -0.43$; mPYR + dmPYR / PYR, $r = -0.44$; mCHR / CHR, $r = -0.45$). These correlations suggests that pyrogenic and petrogenic PAH inputs might be somewhat mutually exclusive.

In some instances there seems to be a strong association between concentrations of related PAH compounds at different depths in the core. Methylated PAH concentrations which are indicative of either weathering parent PAH molecules or petrogenic inputs, track each other very closely (methylanthracenes with methylpyhenanthrenes (r = 0.99), methylnaphthalenes with methylchrysenes (r = 0.91), methylnaphthalenes with methylpyhenanthrenes (r = 0.88), and methylpyhenanthrenes with methylchrysenes (r = 0.88). There are also strong associations with dibenzothiphenes and methylated PAHs, dibenzothiophenes with methylanthracenes (r = 0.97) and methylchrysenes with dibenzothiophenes (r = 0.91). (Figure 3-9) These last two correlations suggest that methylated PAH molecules are present as a result of petrogenic inputs. Figures 3-10 and 3-11 show extracted ion chromatograms of selected parent and daughter PAHs.

Among the more common ratios of PAHs used to determine petrogenic and pyrogenic inputs are the ratios of anthracene to phenanthrene An/(Ph + An) and the ratio of fluoranthene to pyrene Fl/(Py + Fl) (Budzinski et al. 1997, Yunker et al. 2002). An An/(Ph + An) ratio greater than 0.10 indicates that the materials are most probably pyrogenic in origin. Similarly, if the Fl/(Py + Fl) ratio is greater than 0.40, then the materials are most probably pyrogenic in origin. This ratio allows some additional source determinations. A ratio below 0.4 is thought to reflect petrogenic origins, 0.4 to 0.5 from the combustion of liquid fossil fuels, and greater than 0.5 from combustion solid fuels including coal, wood, or grass. (Budzinski et al. 1997, Yunker et al. 2002) The ratio of methylphenanthrenes to parent phenanthrenes (mP/P) can also be used to determine the source of PAH contamination. Values in excess of 2 indicate petrogenic contamination and those less than 2 are an indication of pyrogenic origins. (Garrigues et al. 1995) Boonyatumanond et. al. 2006 used this ratio to source PAH contamination in riverine, estuary, and coastal sediments of Thailand also states that petrogenic sources have a ratio value of 2 or higher and pyrogenic sources have a ratio of 0.5 or lower (Boonyatumanond et al. 2006).

Tracing the Fl/Py ratio with depth gives a surprising result (figure 3-12). The values above 0.5, suggesting inputs from solid fossil fuels, are in the top 50 cm of the core whereas the values between 0.4 and 0.5, suggesting inputs of liquid fossil fuels, are from 50 to 80 cm. It is almost as if coal combustion products are deposited in the recent sediments and petroleum combustion products are deposited in the older sediments. At no point in the first meter of the core, are any of these ratios indicative of petrogenic inputs. This situation may have resulted from sediments with older forms of contamination eroding from stream banks and covering recently deposited materials.

Figure 3-12 also shows why there is also a weak negative correlation with An/Ph (r = -.21) and a very poor correlation with Fl/Py (r = 0.08). Ideally these two parent PAH ratio values should closely track the PyI index as they both rise when pyrogenic inputs increase. This may be due to the exclusvice use of parent PAHs in the An/Ph and Fl/Py ratios and methylated PAHs in the PyI.

It is clear that this core does not represent an undisturbed record of pollution history. Without some means of dating the sediments, there is only the chemical evidence that the core is a recent deposit downstream of an area of strong currents and deposition of fine-grained sediments. This in not typical situation because strong currents and rapid sediment movement normally create a zones of coarse sediments. If there are other sources of radio nucleotides in the sediments, then there might have been measuring errors in the ^{137}Cs values. This would render any arguments based on ^{137}Cs values moot. Industrial deposition of radio nucleotides may be present in such a densely developed region. But because reports of such materials do not appear in the literature, this possibility may be safely discarded.

There is amble evidence that using ^{137}Cs for dating sediment cores is far from straightforward. In 1984 Mc Call et. al demonstrated that in urbanized watersheds erosion can carry sediments containing both ^{210}Pb and ^{137}Cs so that the accumulation rates of these isotopes greatly exceeds what would be possible by direct atmospheric deposition alone. Robbins et. al (1977) found that bioturbation was far more important than molecular diffusion in the post-depositional mobility of ^{137}Cs. Another mechanism for mobility was found in Southwest England’s shallow coastal lagoons. The hydrostatic pressure between sea level and the lagoon standing water can force sea level up through the sediments and cause replacement of ^{137}Cs by Na^+ and K^+. (Foster et. al 2006) Another complicating factor is found in high salinity environments and halite-saturated sediments. Adsorption sites in clay lattices may be saturated by Na^+. The distribution coefficient of ^{137}Cs can shift from ∼3600 at 0% NaCl to ∼600 at 26% NaCl. This has lead to the conclusion that ^{137}Cs may not be useful for dating sediments in highly saline environments. (Longmore et. al 1986)

Are there any other potential causes of the variability or organic molecule concentrations within the core? One explanation is that preservation conditions for organic matter or chemical contaminants vary with depth. Anoxic conditions are known to be optimal for the preservation of organic molecules. There are also other conditions can lead to variable preservation although they do not necessarily operate on buried sediments. On mud flats, exposure to sunlight can accelerate degradation (Reuss et al. 2005). Differences in trapping conditions for different types of silts and clays can also lead to variations in measured pollutant fluxes to sediment cores (Wickstron and Tolonen 1987).

The concentration of elemental sulfur may resolve the question. In most of the upper core it is low or not detected. It spikes at 5.3 mg/kg at 30 cm and then returns to its previous low values. The concentration rises abruptly to 5.2 mg/kg at 70 cm and remains approximately at this level for the remainder of the first 100 cm. Elemental sulfur can be indicative of anaerobic conditions. The sulfur spikes at 30 cm and 70 cm may explain the elevated concentrations of sewage biomarkers and linear alkylbenzenes as depletion of oxygen may have created good preservation conditions (figure 3-13).

But there is another explanation for the sulfur concentrations in that there is also a fairly good correlation between elemental sulfur and total dibenzothiophenes (r =0.61). Dibenzothiophenes can originate in uncombusted petroleum and shoule not be confused with the isoprenoid thiophenes. However when samples where the sulfur concentration is zero or greater than 200 mg/kg are excluded from this calculation, the correlation rises dramatically (r = 0.87). The implication is that sulfur may be more useful as an indicator of DBTs than of anaerobic conditions that lead to good preservation (figure 4-13). There are a number of bacterial species that can desulfurize thiophenes in sediments although the actual mechanism operating in this core is not clear (Aragon et al. 2005).

The most abundant organic acid in the samples was n-hexadecanoic acid followed by *n*-heptadecanoic and *n*-octadecanoic acids. The concentrations of these biomarkers might be expected to change with varying amounts of bacteria. However, there is no strong correlation between the concentrations of fatty acids and any other types of organic material, except alkanes (r = 0.64) but this might merely represent the long carbon chains present in organic acids breaking apart.

Conclusions

Despite variations in individual compound concentrations, consistent PAH ratios, CPI ratio, and PyI the organic materials in the core appear to be fairly uniform. LABs are present throughout the core and as these materials have only been widely used in detergents since the 1950s, it may be concluded that the entire core is no older than the mid-twentieth century. Variations in organic compound concentrations might represent episodic deposition events and the tendency of one class to compound to occur together suggests that once bound to sediment particles, these compounds remain together and are not subject to a mixing process.

Core 37 serves as a case study of the sort of confusion that can result from disturbed sediments. It also illustrates that indices created from PAH ratios, pyrolysis product ratios, and hydrocarbon inputs can work together to illuminate sediment conditions even in highly disturbed areas.

Future work might include incorporating better grain size data into the interpretation. Although variable preservation conditions have been ruled out as an explanation for variation within the core, it would be helpful to look for biomarkers that conclusively demonstrate variations in the bacterial communities that arose either because of, or gave rise to, varying chemical preservation conditions.

Figures and Tables

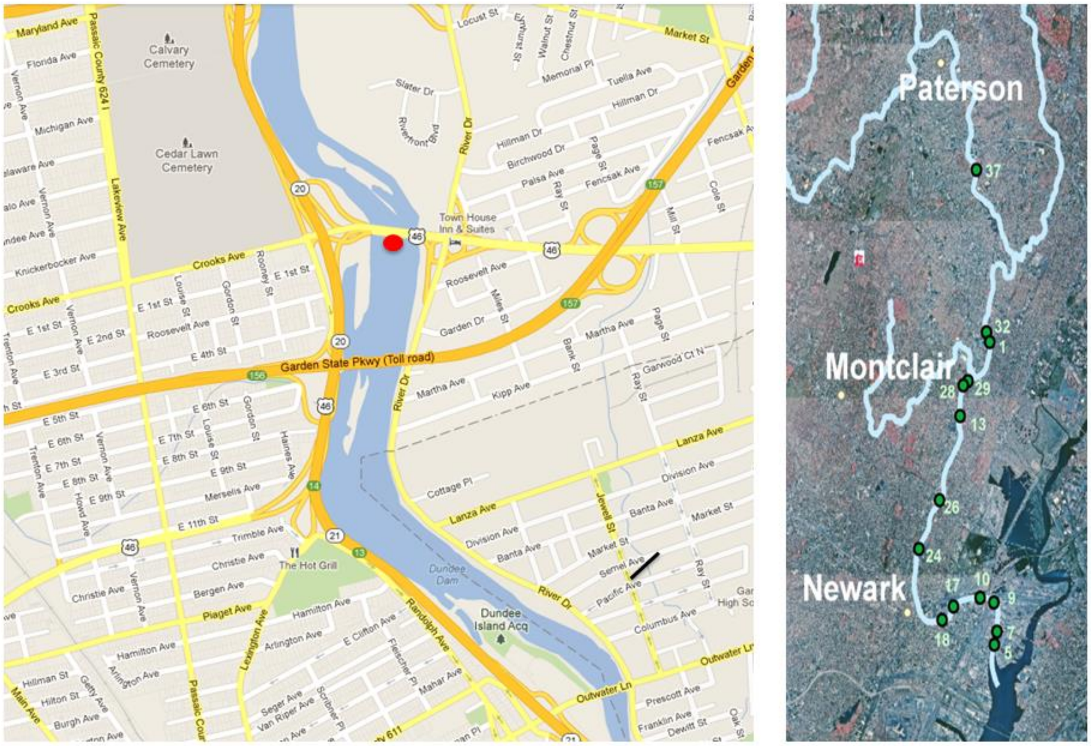


Figure 3-1. The location of Core 37. The core was taken at a site where the river makes a 45-degree bend and the location is characterized by strong currents and significant sediment movement. (Google Maps)

Figure 3-2. Looking Upstream at the Route 46 Highway Bridge. Due to the significance of its concrete arch construction, the bridge was placed on the National Register of Historic Places in 1991. (Library of Congress)

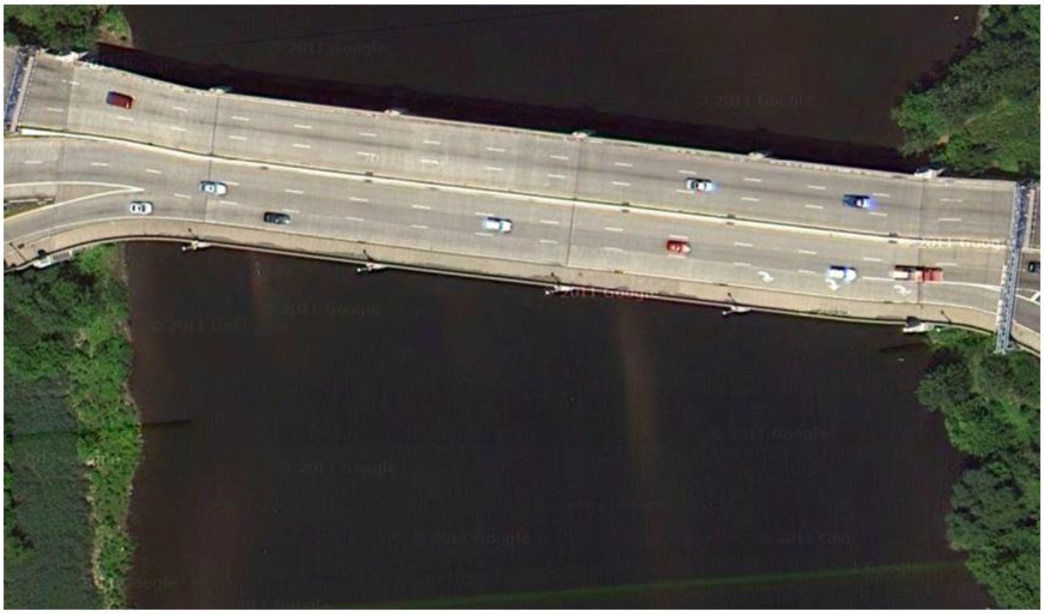


Figure 3-3. A Google Earth ® photograph of Dundee Lake and the Route 46 highway bridge. This image clearly shows sediment plumes entering the area where the core was taken. (Google Earth)

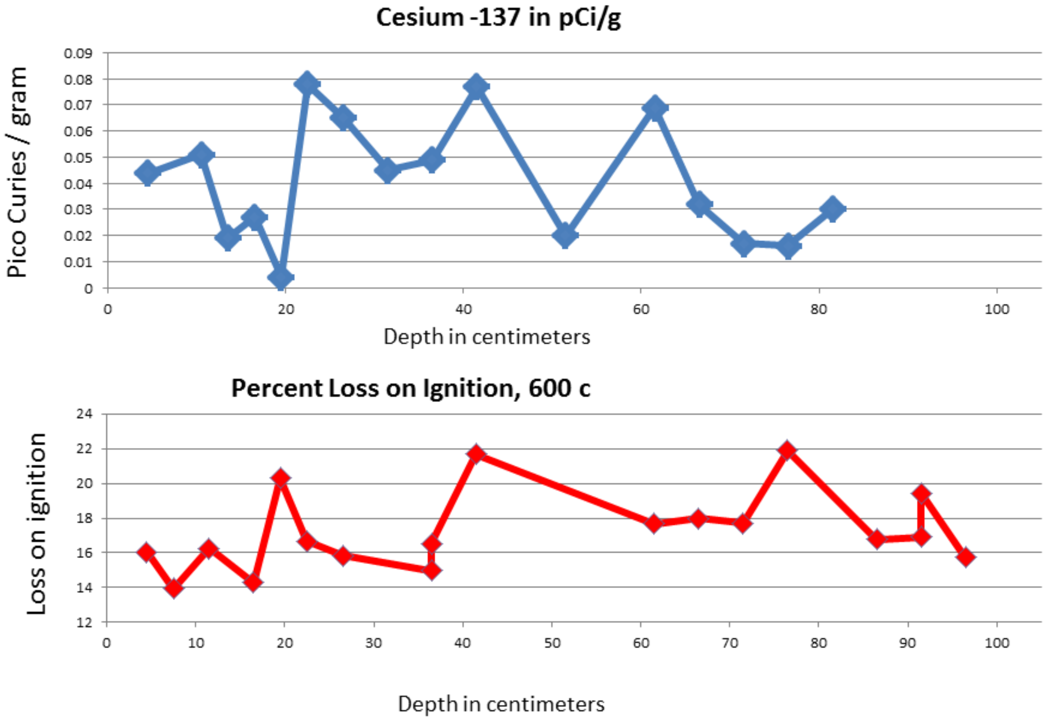
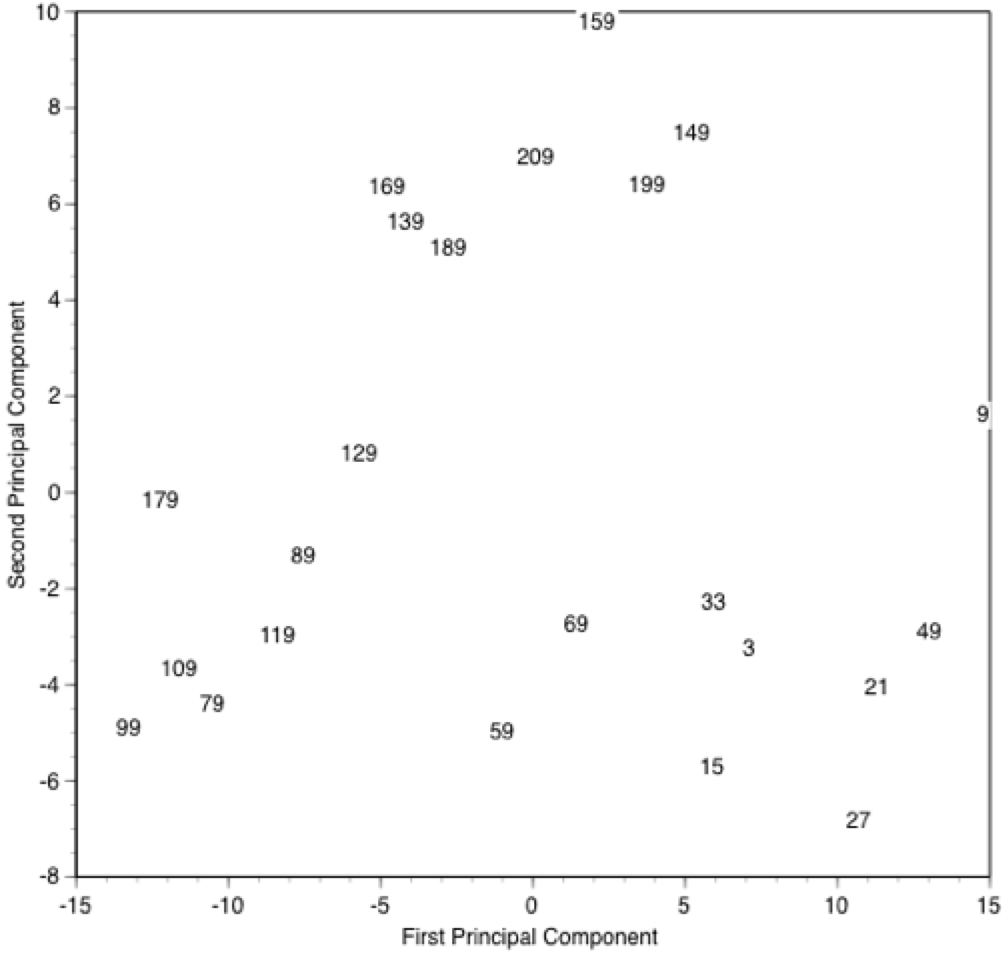


Figure 3-4. The ^{137}Cs (pCi/g) and LOI (% loss) values are plotted on the same X axis scale. The X axis is depth in centimeters. Note that both show a seemingly random distribution with depth and neither has any prominent peaks.


Second Principal Component
First Principal Component
10
8
6
4
2
0
-2
-4
-6
-8
-15
-10
-5
0
5
10
15
159
149
209
169
199
139
189
9
129
179
89
33
69
49
119
3
109
21
79
99
59
15
27

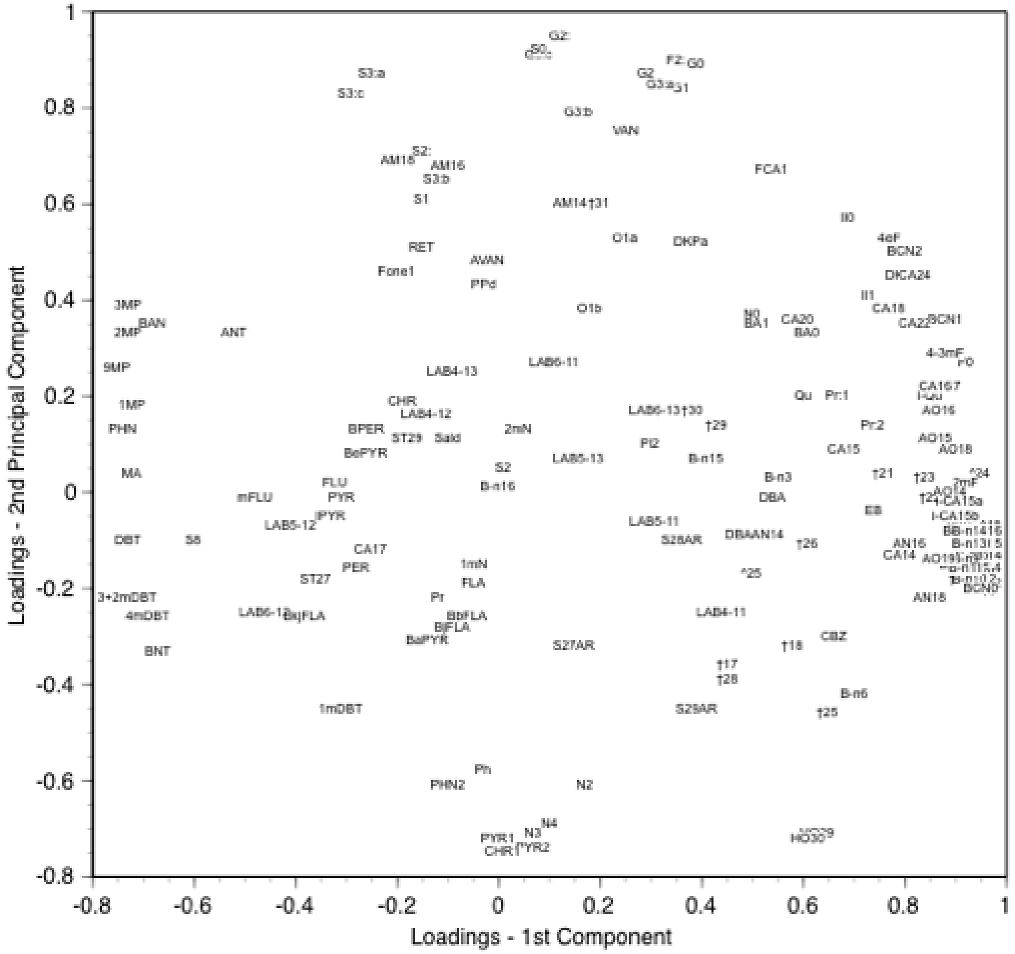


Figure 3-5 Cross plot of the first and second principle components (top) and the compound loadings within the principle components (bottom). The top graph shows clear clustering of the sample points by depth. A list of compound abbreviations is provided in table 1-1 and loading values are provided in table 3-1.

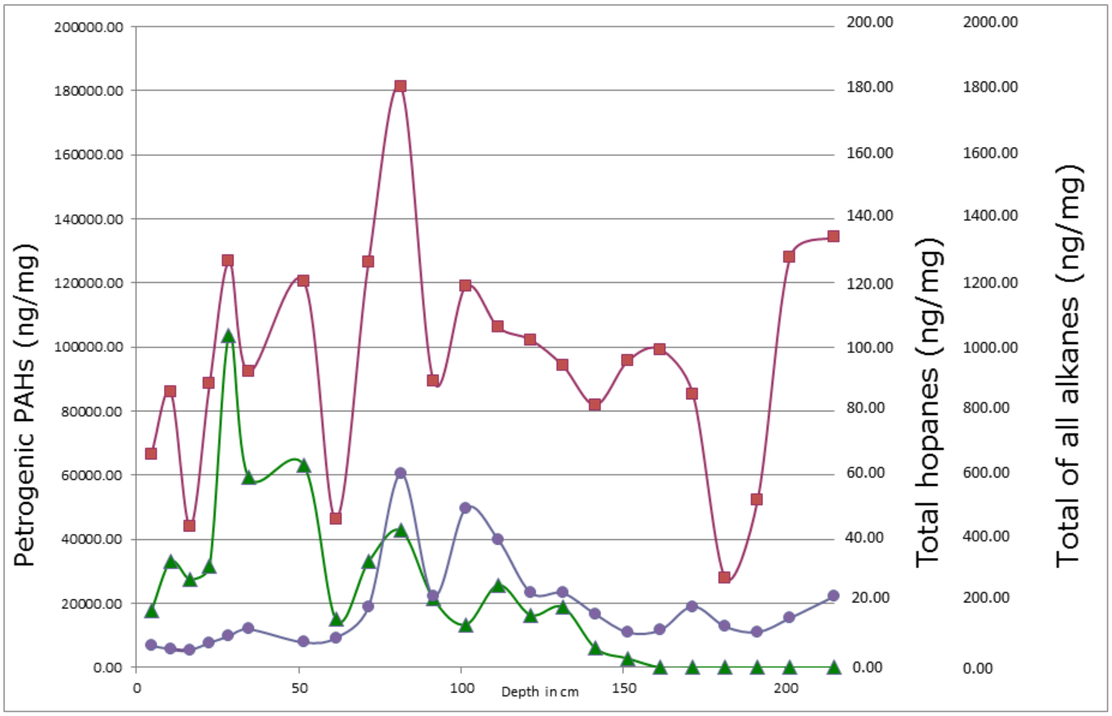


Figure 3-6 The main classes of petroleum markers are plotted against the depth in the core. The Hopanes are shown by a dark green line with diamond-shaped markers. The other inputs are as follows: total alkanes – red – squares, total petrogenic PAHs – light blue – squares

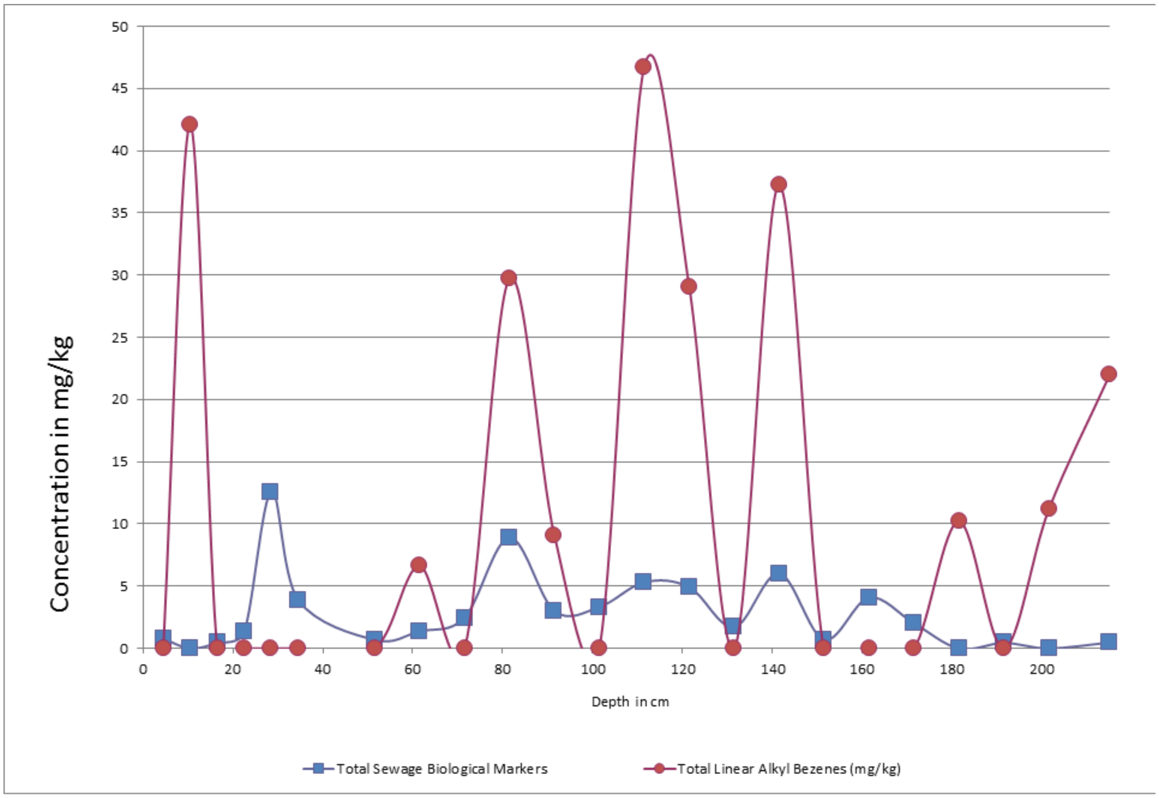


Figure 3-7 The concentration of all biological sewage markers plotted alongside linear alkylbenzenes. Because at several depths one or more of these compounds are not detected, the correlation of the two is somewhat low.

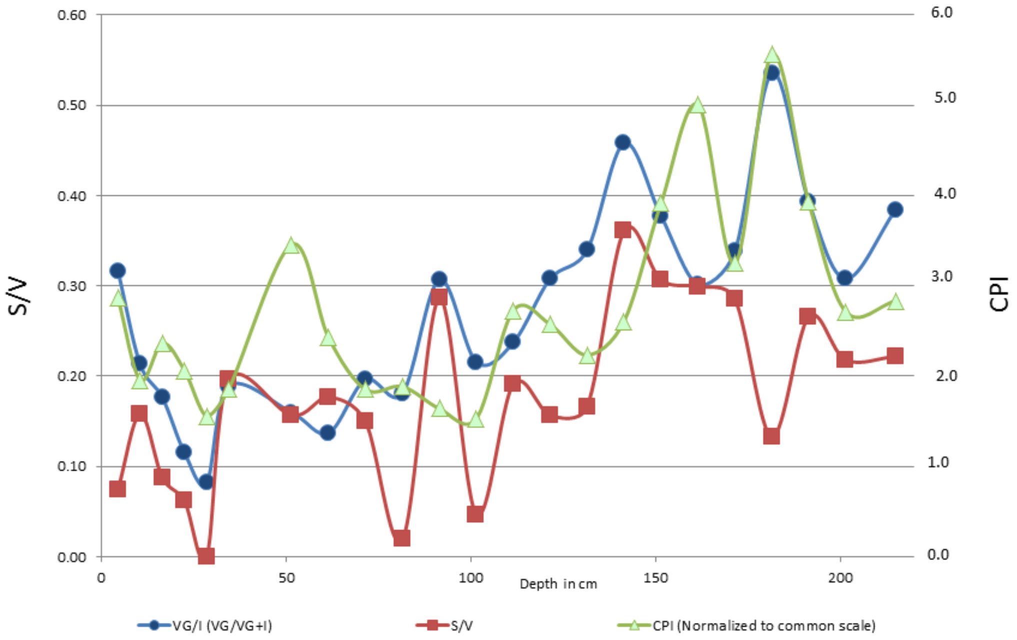


Figure 3-8 The inputs of the principle biogenic pyrolysis products are plotted with depth. The VG/I and S/V ratios are on a common scale.

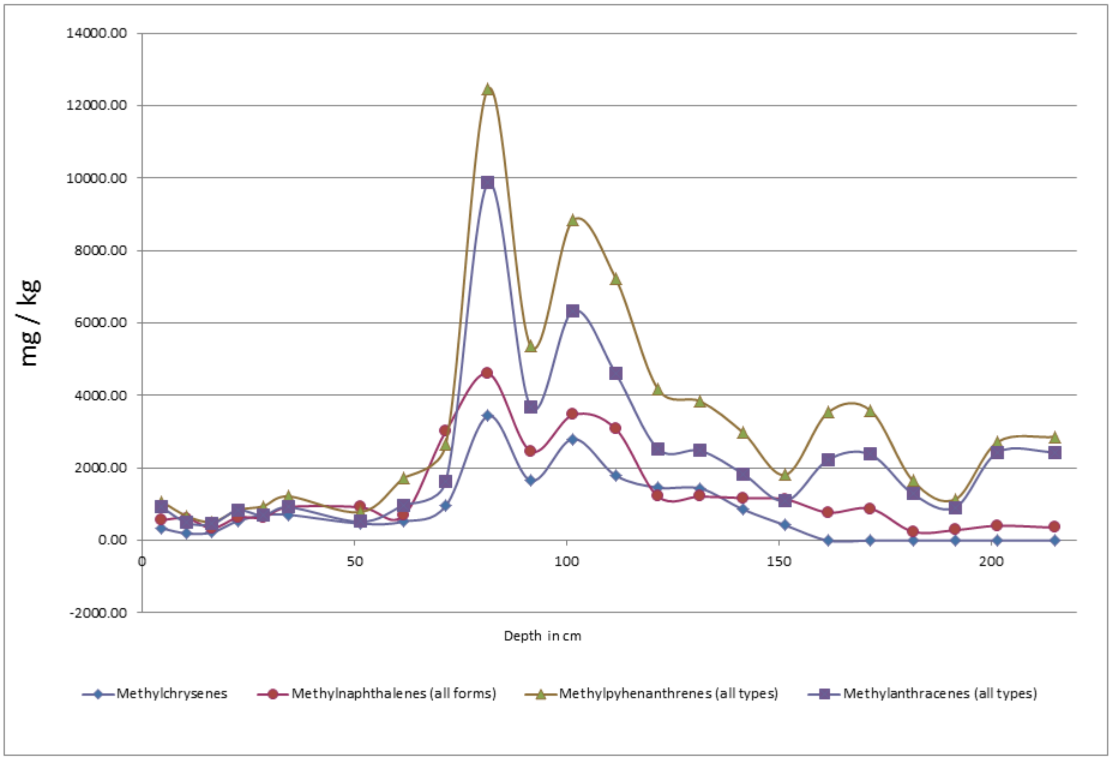


Figure 3-9. Methylated PAH concentrations with depth. Despite the disturbed nature of the area, certain methylated PAH concentrations track one another quite closely and it is likely that spikes in concentration probably represent unique depositional events.

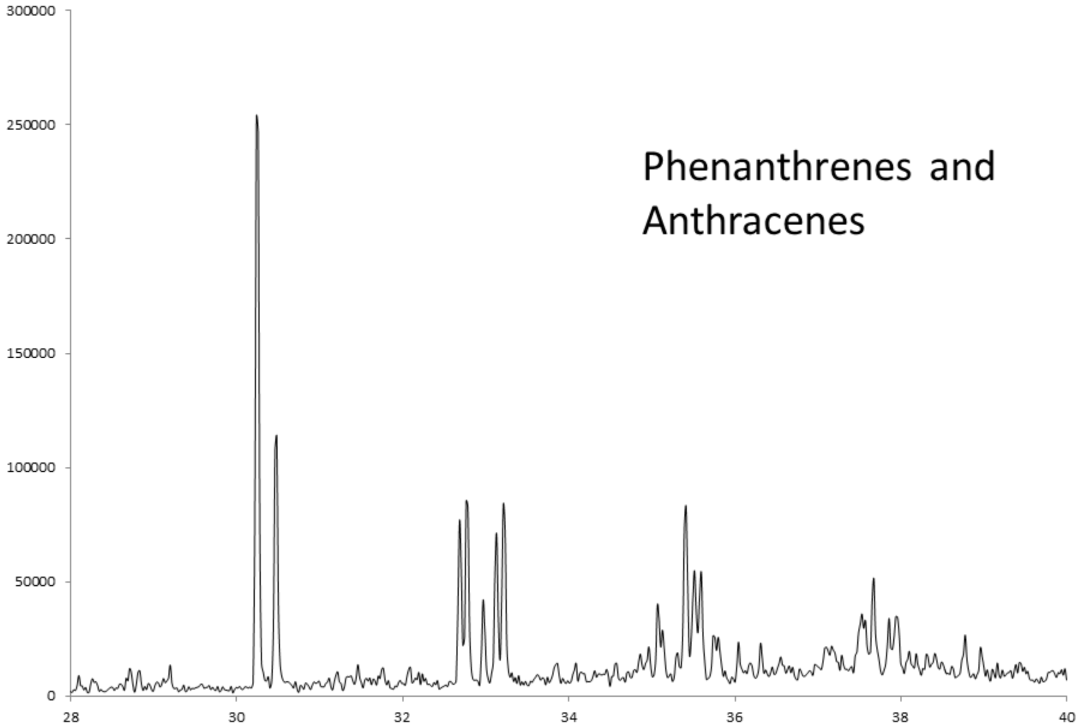


Figure 3-10. Extracted ion chromatogram of Phenanthrene and Anthracene. These appear at 30 minutes and groupings of their methylated, dimethylated, and trimethylated daughter compounds appearing at 33, 35, and 37 minutes respectively.

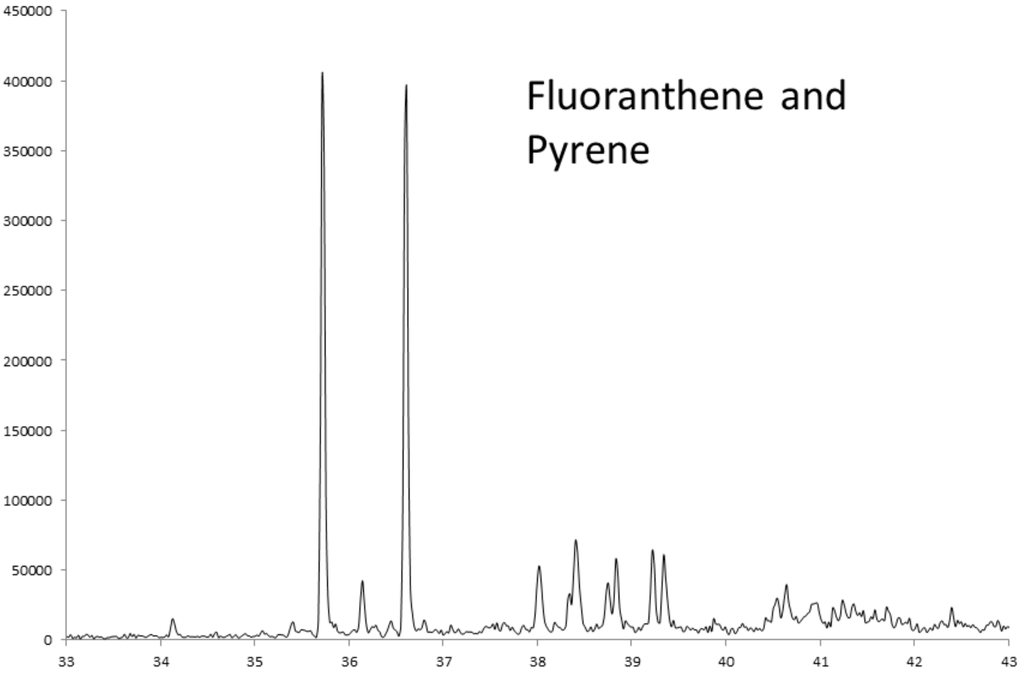


Figure 3-11. Extracted ion chromatogram of Fluoranthene (35.5 minutes) and Pyrene (36 minutes). Methylated and dimethylated daughter compounds appear at 37 - 40 minutes and dimehtylated daughter compounds at 40 to 42 minutes.

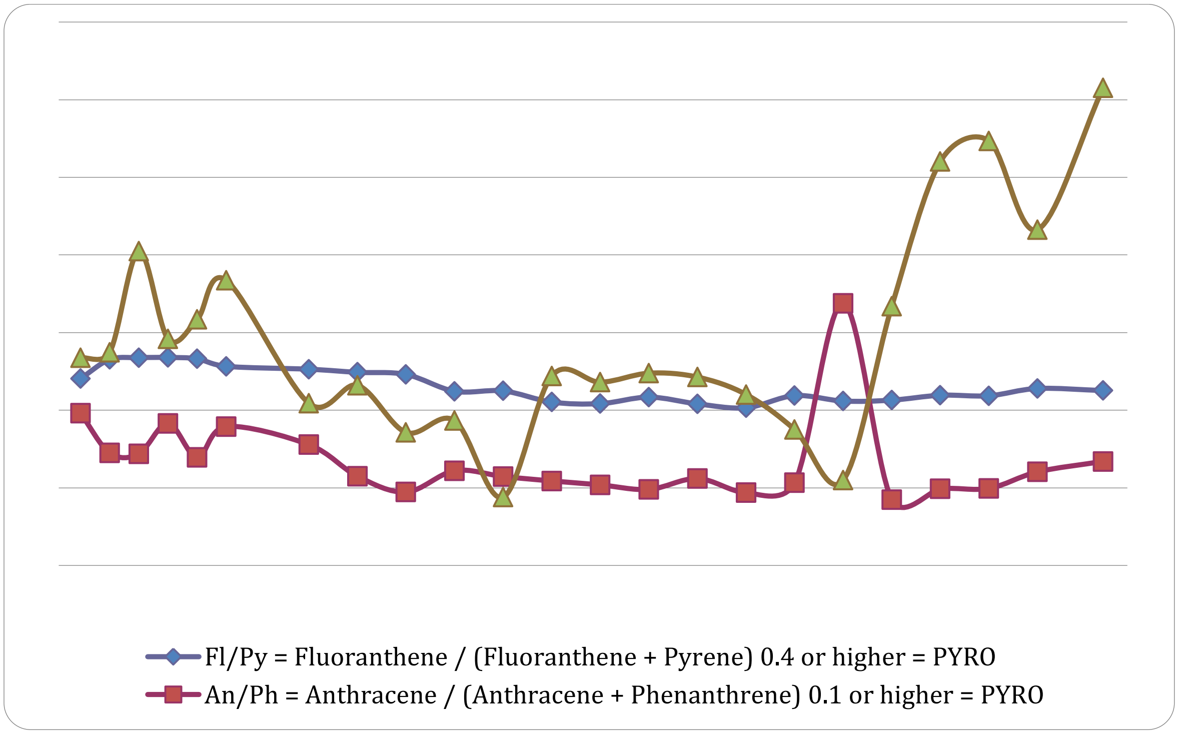


Figure 3-12 The ratios of common pyrogenic PAH moleculeswith depth. These are fairly stable throughout the depth of the core but the pyrogenic index varies widely with depth. The drop in phenanthrene concentrations that caused a spike in the anthracene/phenanthrene ratio is unexplained. The pyrogenic index is shown as a trace with triangular markers.

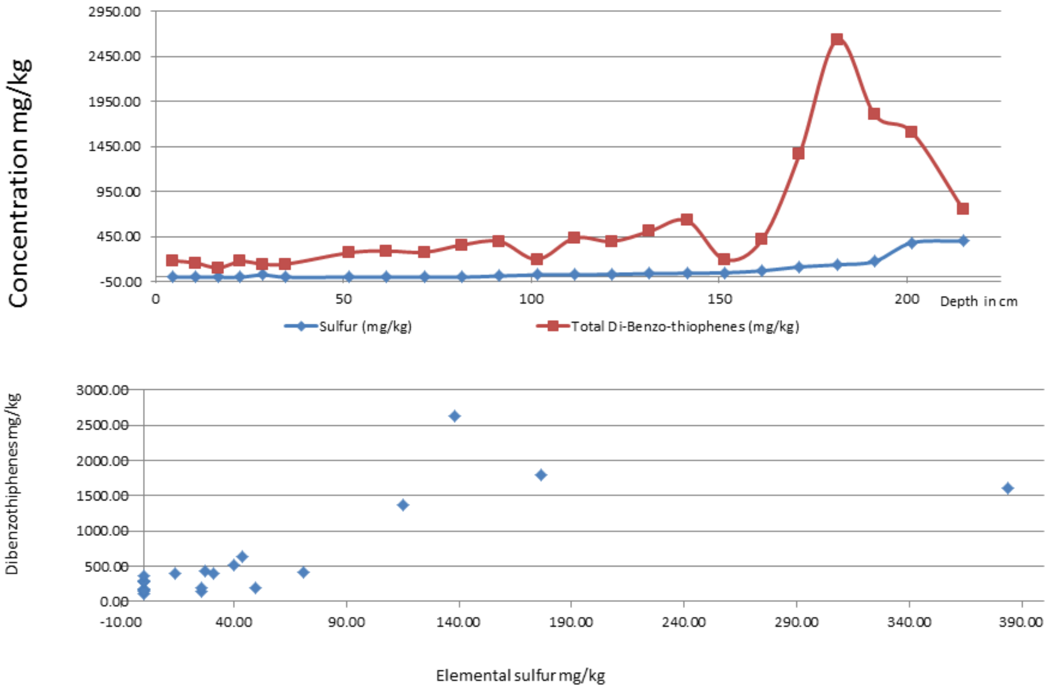


Figure 3-13, The concentrations of elemental sulfur and dibenzothiophenes are shown as a function of depth and are also cross plotted.

Table 3-1. Ranking of compounds by Principle Component Analysis.

cmpd	Prin1		cmpd	Prin2		cmpd	Prin3
^14	0.97		G2:	0.95		mFLU	0.68
†16	0.97		S0	0.92		AM16	0.62
^19	0.97		G3:c	0.91		Fone1	0.61
†14	0.97		F2:	0.90		S2	0.58
^18	0.97		G0	0.89		1mDBT	0.58
†15	0.97		G2	0.87		ST29	0.58
†13	0.97		S3:a	0.87		1mN	0.55
^12	0.97		G3:a	0.85		AM18	0.54
^11	0.96		G1	0.84		N3	0.54
†12	0.96		S3:c	0.83		ST27	0.53
^17	0.96		G3:b	0.79		Qu	0.53
^16	0.95		VAN	0.75		PHN2	0.53
†10	0.95		S2:	0.71		PYR2	0.52
^15	0.95		AM18	0.69		CHR1	0.52
BCN0	0.95		AM16	0.68		N2	0.51
†11	0.95		FCA1	0.67		N4	0.51
†20	0.95		S3:b	0.65		PYR1	0.50
^24	0.95		S1	0.61		AVAN	0.48
B-n5	0.94		†31	0.60		Il1	0.47
^13	0.94		AM14	0.60		BbFLA	0.47
B-n4	0.93		Il0	0.57		Pr	0.46

^20	0.93		O1a	0.53		CBZ	0.46
B-n8	0.93		4eF	0.53		2mN	0.46
B-n13	0.93		DKPa	0.52		FLU	0.45
B-n10	0.93		RET	0.51		BkjFLA	0.45
^21	0.93		BCN2	0.50		AM14	0.44
B-n14	0.93		AVAN	0.48		4mDBT	0.44
B-n9	0.92		Fone1	0.46		3+2mDBT	0.42
B-n11	0.92		CA24	0.45		Ph	0.42
^23	0.92		DKDP	0.45		BjFLA	0.42
F0	0.92		PPd	0.43		PPd	0.40
2mF	0.92		Il1	0.41		B-n16	0.39
B-n7	0.91		3MP	0.39		B-n3	0.36
†19	0.91		CA18	0.38		i-Qu	0.36
^22	0.91		O1b	0.38		Pl2	0.34
B-n12	0.91		N0	0.37		†17	0.34
†24	0.91		BCN1	0.36		Il0	0.34
i-CA15a	0.91		CA20	0.36		†18	0.33
AO13	0.90		CA22	0.35		G3:b	0.33
i-CA15b	0.90		BAN	0.35		LAB6-12	0.32
AO18	0.90		BA1	0.35		B-n7	0.31
AO14	0.89		BA0	0.33		BaPYR	0.31
B2:	0.89		2MP	0.33		IPYR	0.31
AO17	0.88		ANT	0.33		S1	0.31

BCN1	0.88		4-3mF	0.29		S27AR	0.31
4-3mF	0.88		F0	0.27		4eF	0.30
AO16	0.87		LAB6-11	0.27		S8	0.30
AO19	0.87		9MP	0.26		S3:b	0.29
AO15	0.86		LAB4-13	0.25		DKPa	0.29
CA16	0.86		CA16	0.22		PER	0.29
i-Qu	0.85		AO17	0.22		G3:a	0.29
AN18	0.85		i-Qu	0.20		G3:c	0.28
†22	0.85		Qu	0.20		LAB5-12	0.28
†23	0.84		Pr:1	0.20		4-3mF	0.28
CA24	0.82		CHR	0.19		1MP	0.27
CA22	0.82		1MP	0.18		LAB4-13	0.26
AN16	0.81		AO16	0.17		DBT	0.25
DKDP	0.80		†30	0.17		BCN2	0.25
BCN2	0.80		†27	0.17		G1	0.24
CA14	0.79		LAB6-13	0.17		MA	0.24
CA18	0.77		LAB4-12	0.16		O1a	0.24
4eF	0.77		†29	0.14		2mF	0.23
†21	0.76		Pr:2	0.14		†28	0.23
Pr:2	0.74		PHN	0.13		9MP	0.23
EB	0.74		BPER	0.13		2MP	0.22
Il1	0.73		2mN	0.13		3MP	0.20
B-n6	0.70		Sald	0.11		S3:a	0.20

Il0	0.69		ST29	0.11		S3:c	0.19
CA15	0.68		AO15	0.11		EB	0.19
Pr:1	0.67		Pl2	0.10		B2:	0.19
CBZ	0.66		CA15	0.09		B-n4	0.19
†25	0.65		AO18	0.09		HO29	0.18
HO29	0.63		BePYR	0.08		F2:	0.18
†26	0.61		LAB5-13	0.07		B-n9	0.18
HO30	0.61		B-n15	0.07		G2	0.17
BA0	0.61		S2	0.05		S29AR	0.17
Qu	0.60		^24	0.04		B-n15	0.16
CA20	0.59		MA	0.04		†27	0.16
†18	0.58		†21	0.04		B-n11	0.16
B-n3	0.55		†23	0.03		†10	0.15
DBA	0.54		B-n3	0.03		F0	0.15
FCA1	0.54		FLU	0.02		B-n8	0.15
AN14	0.53		2mF	0.02		HO30	0.14
BA1	0.51		B-n16	0.01		B-n5	0.14
^25	0.50		AO14	0.00		†12	0.14
N0	0.50		†22	-0.01		G2:	0.14
DBAx	0.48		DBA	-0.01		N0	0.13
†28	0.45		PYR	-0.01		†14	0.13
†17	0.45		mFLU	-0.01		S0	0.12
LAB4-11	0.44		^22	-0.02		B-n10	0.12

†29	0.43		i-CA15a	-0.02		BNT	0.11
B-n15	0.41		AO13	-0.02		BCN0	0.11
G0	0.39		EB	-0.04		†20	0.11
S29AR	0.39		i-CA15b	-0.05		†15	0.11
†30	0.38		IPYR	-0.05		†16	0.10
DKPa	0.38		^21	-0.05		LAB6-13	0.10
S28AR	0.36		†24	-0.05		O1b	0.10
G1	0.36		B-n7	-0.06		B-n13	0.10
F2:	0.35		LAB5-11	-0.06		†11	0.09
†27	0.33		^18	-0.07		LAB5-13	0.09
G3:a	0.32		LAB5-12	-0.07		B-n6	0.09
LAB5-11	0.31		†16	-0.08		VAN	0.08
LAB6-13	0.31		^13	-0.08		^12	0.08
Pl2	0.30		B-n14	-0.08		†24	0.08
G2	0.29		B-n12	-0.08		DKDP	0.07
VAN	0.25		DBAx	-0.09		†13	0.06
O1a	0.25		AN14	-0.09		^13	0.06
†31	0.20		DBT	-0.10		BPER	0.06
O1b	0.18		S28AR	-0.10		†23	0.06
N2	0.17		S8	-0.10		CA24	0.05
G3:b	0.16		†15	-0.11		RET	0.05
LAB5-13	0.16		B-n13	-0.11		^19	0.05
S27AR	0.15		^19	-0.11		BAN	0.04

AM14	0.14		†20	-0.11		^11	0.04
G2:	0.12		†26	-0.11		BePYR	0.04
LAB6-11	0.11		AN16	-0.11		AO19	0.04
N4	0.10		†13	-0.12		BCN1	0.03
G3:c	0.08		^23	-0.12		†26	0.02
S0	0.08		CA17	-0.12		B-n14	0.02
N3	0.07		B-n4	-0.12		†29	0.01
PYR2	0.07		†11	-0.12		AN16	0.01
2mN	0.04		B-n8	-0.13		AN18	0.01
S2	0.01		CA14	-0.13		^14	0.01
CHR1	0.01		B-n5	-0.13		G0	0.00
B-n16	0.00		†14	-0.13		^18	-0.01
PYR1	0.00		AO19	-0.14		B-n12	-0.01
AVAN	-0.02		B-n9	-0.14		^23	-0.01
PPd	-0.03		1mN	-0.15		S2:	-0.03
Ph	-0.03		B2:	-0.15		^15	-0.03
FLA	-0.05		PER	-0.16		†19	-0.04
1mN	-0.05		^14	-0.16		^22	-0.04
BbFLA	-0.06		^15	-0.16		AN14	-0.04
LAB4-13	-0.09		B-n11	-0.16		^17	-0.04
BjFLA	-0.09		†10	-0.17		DBAx	-0.05
PHN2	-0.10		^17	-0.17		Pr:2	-0.05
Sald	-0.10		^25	-0.17		†30	-0.05

AM16	-0.10		^20	-0.17		FCA1	-0.05
Pr	-0.12		†12	-0.18		^20	-0.05
S3:b	-0.12		ST27	-0.18		AO18	-0.06
LAB4-12	-0.14		B-n10	-0.18		BA0	-0.06
BaPYR	-0.14		†19	-0.18		†25	-0.08
S2:	-0.15		FLA	-0.19		†21	-0.08
S1	-0.15		^16	-0.19		†22	-0.08
RET	-0.15		^12	-0.19		CA20	-0.11
ST29	-0.18		BCN0	-0.20		^16	-0.12
CHR	-0.19		^11	-0.21		Sald	-0.13
Fone1	-0.20		3+2mDBT	-0.22		^24	-0.13
AM18	-0.20		Pr	-0.22		Pr:1	-0.14
CA17	-0.25		AN18	-0.22		^25	-0.18
S3:a	-0.25		LAB4-11	-0.25		AO13	-0.18
BePYR	-0.26		LAB6-12	-0.25		i-CA15a	-0.18
BPER	-0.26		BbFLA	-0.26		CA22	-0.19
PER	-0.28		BkjFLA	-0.26		LAB4-12	-0.20
S3:c	-0.29		4mDBT	-0.26		LAB6-11	-0.20
1mDBT	-0.31		BjFLA	-0.28		CA16	-0.21
PYR	-0.31		CBZ	-0.30		i-CA15b	-0.22
FLU	-0.32		BaPYR	-0.31		AO17	-0.23
IPYR	-0.33		†18	-0.32		AO14	-0.23
ST27	-0.36		S27AR	-0.32		^21	-0.23

BkjFLA	-0.38		BNT	-0.33		AO16	-0.24
LAB5-12	-0.41		†17	-0.36		CA17	-0.24
LAB6-12	-0.46		†28	-0.39		CA18	-0.24
mFLU	-0.48		B-n6	-0.42		BA1	-0.26
ANT	-0.52		1mDBT	-0.45		AO15	-0.26
S8	-0.60		S29AR	-0.45		†31	-0.29
BNT	-0.67		†25	-0.46		CA15	-0.31
BAN	-0.68		Ph	-0.58		S28AR	-0.32
4mDBT	-0.69		PHN2	-0.61		LAB4-11	-0.33
MA	-0.72		N2	-0.61		DBA	-0.33
1MP	-0.72		N4	-0.69		CHR	-0.34
3+2mDBT	-0.73		HO29	-0.71		CA14	-0.42
3MP	-0.73		N3	-0.71		ANT	-0.46
2MP	-0.73		HO30	-0.72		PHN	-0.47
DBT	-0.73		PYR1	-0.72		LAB5-11	-0.65
PHN	-0.74		PYR2	-0.74		PYR	-0.82
9MP	-0.75		CHR1	-0.75		FLA	-0.87

Table 3-2. Correlations between total concentrations of each compound class in the Dundee Lake core.

	Alkanoic Acids	Benzothiophenes	Dibenzothiophenes	Elemental Sulfur	Guaiacols	Hopanes	Linear alkylbenzen	Long Chain Alk-2-ones	Loss On Ignition	Monoaromatic	Nitriles	Normal and isoprenoid	Normal and isoprenoid
Alkanoic Acids	1.00	0.90	0.60	0.04	0.86	0.62	0.88	0.59	0.61	0.70	0.88	0.91	0.92
Benzothiophenes		1.00	0.56	0.09	0.76	0.58	0.80	0.62	0.43	0.56	0.80	0.80	0.84
Dibenzothiophenes			1.00	0.47	0.33	0.71	0.74	0.69	0.61	0.70	0.77	0.72	0.73
Elemental Sulfur				1.00	-0.23	0.12	0.15	0.16	0.11	0.09	0.21	0.09	0.12
Guaiacols (Lignin markers)					1.00	0.28	0.63	0.34	0.55	0.50	0.69	0.75	0.72
Hopanes (petroleum markers)						1.00	0.86	0.80	0.69	0.84	0.76	0.79	0.82
Linear alkylbenzenes							1.00	0.71	0.74	0.91	0.92	0.95	0.96
Long Chain Alk-2-ones								1.00	0.65	0.70	0.73	0.75	0.79
Loss On Ignition									1.00	0.83	0.80	0.83	0.79
Monoaromatic hydrocarbons										1.00	0.83	0.89	0.87
Nitriles											1.00	0.96	0.97
Normal and isoprenoid alkanes												1.00	0.99
Normal and isoprenoid alkenes													1.00

	Not Otherwise	One-ring Nitrogen	Oxygenated compounds	PAH's - Dueterated	PAHs - Daughters	PAHs - Parent	Percent Silt & Clay	Polysaccharide	Sterenes	Surfactant	Syringols (Angiosper	Three-Ring Nitrogen	Two-ring Nitrogen
Alkanoic Acids	0.95	0.82	0.89	0.79	0.95	0.95	0.51	0.90	0.42	0.80	0.81	0.93	0.87
Benzothiophenes	0.94	0.77	0.80	0.70	0.93	0.93	0.37	0.95	0.32	0.77	0.71	0.85	0.81
Dibenzothiophenes	0.66	0.77	0.37	0.58	0.66	0.63	0.59	0.50	0.53	0.77	0.30	0.65	0.76
Elemental Sulfur	0.19	0.22	-0.18	0.17	0.13	0.06	0.40	0.05	0.07	0.12	-0.26	0.02	0.14
Guaiacols (Lignin markers)	0.79	0.58	0.99	0.64	0.78	0.79	0.26	0.80	0.12	0.57	0.99	0.80	0.67
Hopanes (petroleum markers)	0.67	0.85	0.34	0.50	0.70	0.70	0.64	0.48	0.82	0.87	0.23	0.71	0.82
Linear alkylbenzenes	0.88	0.95	0.68	0.69	0.91	0.89	0.61	0.77	0.75	0.96	0.59	0.94	0.96
Long Chain Alk-2-ones	0.71	0.74	0.39	0.64	0.73	0.69	0.61	0.49	0.44	0.73	0.31	0.61	0.75
Loss On Ignition	0.64	0.75	0.58	0.64	0.64	0.63	0.78	0.40	0.52	0.75	0.55	0.73	0.77
Monoaromatic hydrocarbons	0.69	0.87	0.51	0.60	0.76	0.73	0.64	0.51	0.79	0.89	0.51	0.82	0.88
Nitriles	0.93	0.97	0.75	0.79	0.93	0.88	0.68	0.76	0.52	0.92	0.65	0.95	0.98
Normal and isoprenoid alkanes	0.92	0.94	0.79	0.73	0.93	0.89	0.64	0.75	0.57	0.93	0.72	0.95	0.97
Normal and isoprenoid alkenes	0.94	0.95	0.77	0.79	0.96	0.93	0.67	0.80	0.58	0.94	0.69	0.95	0.97
Not Otherwise Indexed	1.00	0.88	0.84	0.82	0.98	0.95	0.59	0.90	0.37	0.83	0.74	0.91	0.91
One-ring Nitrogen compounds		1.00	0.64	0.67	0.90	0.84	0.63	0.71	0.66	0.95	0.53	0.93	0.98
Oxygenated compounds			1.00	0.67	0.82	0.82	0.32	0.83	0.15	0.62	0.96	0.84	0.71
PAH's - Dueterated				1.00	0.79	0.82	0.73	0.75	0.25	0.64	0.62	0.74	0.73
PAHs - Daughters					1.00	0.96	0.54	0.89	0.45	0.86	0.74	0.93	0.93
PAHs - Parent						1.00	0.56	0.92	0.47	0.84	0.75	0.92	0.88
Percent Silt & Clay							1.00	0.36	0.41	0.60	0.25	0.53	0.62
Polysaccharide pyrolysis markers								1.00	0.29	0.73	0.76	0.85	0.77
Sterenes									1.00	0.73	0.09	0.56	0.62

	Not Otherwise Indexed	One-ring Nitrogen	Oxygenated compounds	PAH's - Dueterated	PAHs - Daughters	PAHs - Parent	Percent Silt & Clay	Polysaccharide pyrolysis	Sterenes	Surfactant	Syringols (Angiosperm markers)	Three-Ring Nitrogen Compounds	Two-ring Nitrogen compounds
Surfactant										1.00	0.53	0.93	0.96
Syringols (Angiosperm markers)											1.00	0.77	0.63
Three-Ring Nitrogen Compounds												1.00	0.96
Two-ring Nitrogen compounds													1.00

Chapter Four

Environmental Management of Urban Sediments: Moving From Dredge and Dump to Sustainable Sediment Management in Three Easy Steps

Abstract

It is currently estimated that 53% of the United States population lives in coastal areas and worldwide an estimated 44% of the world's population lives within 150 kilometers of the coasts. One of the many challenges facing the coatal regions is the management of sediment resources. Many areas of the world are sediment starved because large dams are trapping an estimated 25% of global suspended sediment loads. Conversely, world seaports require continued mainteance dredging for the fleet of 45,000 oceangoing merchant ships that move 90% of global trade. Many dredged materials are already being re-used for beach replenishment, habitat restoration, and landfill capping. As sea levels rise in the coming decades, sediments will be an increasingly important resource required for armoring the coasts and habitat restoration.

Creating a system of sustainable sediment management system will require several steps. One of the most pressing concerns will be to address legacy contamination. The U.S. Environmental Protection Agency (US EPA) has estimated that there is approximately 1.2 billion cubic yards of contaminated sediment under the surface waters of the United States. The cost of disposing sediments that meet the criteria for hazardous waste can be as much as $100 per cubic yard and costs can reach $250 per cubic yard if sediment meets the criteria for hazardous waste. In sediment remediation projects timelines are often stretched over decades and costs have been known to vary by more that 1000% from their estimates. Because of the long timelines and high costs new approaches are

needed for engaging stakeholders and managing the risks associated with legacy contamination.

An integrated and sustainable sediment management system is needed to replace a current system of “dredge and dump.” This system would consider the total environmental costs of dredging, feature operational decontamination facilities, and address the problems of ongoing recontamination. In such a regimine sediment re-use for armoring the coastlines against rising sea levels and a warmer climate will consider grain size, hydraulic conductivity, and organic material content. The information provided by Py-GC/MS can be used to characterize the sediments and help match sediment source to the appropriate beneficial use.

Introduction

In June of 1805 the residents of Philadelphia saw a strange machine emerge from the workshop of Oliver Evans. Thirty feet long and twelve feet wide, it consisted of a scow’s hull mounted on four wheels. In its hull, the machine’s inventor had mounted a high-pressure steam engine that was linked to a bucket chain of the type that was used to dredge muck and silt from the city’s waterfront. High-pressure steam was a new and exciting technology that promised to revolutionize transportation and industry. In addition to a paddle wheel at the stern, the steam engine was also connected to the machine’s wheels so that instead of being towed to the waterfront, the first automobile in the United States drove itself to the Delaware River. The *Orukter Amphibolos* or

"Amphibious Digger" had been built for the Philadelphia Board of Health for cleaning the city’s waterways. At about the same time, England’s foremost high-pressure steam advocate was constructing his own high-tech dredger. Richard Trevithick had already pioneered railway locomotives and steam-powered road carriages when in 1806 he proposed dredging stones for use as ship ballast from the bottom of the Thames. To power the dredge machinery, a 4.5 kW engine was mounted on the former Royal Navy brig *HMS Blazer*. Although a technical success, the engine was not powerful enough to raise the ballast at the rate required. A larger, commercially successful steam-powered bucket dredge was put in operation in 1807. These were the first times in history that modern technology would be applied to the centuries-old problem of dredging, but it would be almost another 170 years before modern ideas about sustainability would be haltingly applied to the equally old problem of what to do with the dredged materials.

Dredging management and engineering is a mature discipline but truly integrated sediment management is a relatively new discipline and encompasses marine physics, chemistry, biology, and microbiology. Integrating these disciplines and carefully manipulating multiple inputs is not a simple task and experts are only beginning to come to grips with it. One environmental consultant was quite blunt when he said that, “Notably, no port in the world currently has a sediment management plan suited to the modern era.” (Kirby 2012)

For much of history, dredging operations were largely the province of civil engineers, ship owners, and port officials. Sediment management consisted of dredging in one location and dumping in another. The container revolution caused urban waterfronts to become increasingly de-industrialized and issues related to their management now include real estate development, the needs of boaters and fishermen, commercial navigation, urban habitat preservation, historic preservation, and questions of public access. The modern urban waterfront is an area of competing uses and clashing stakeholders. To complicate matters, there are about 80 government agencies in the United States that have some involvement with coastal zones (Seavitt, 2012). Adding even more to the complexity is a collection of non-governmental organizations (NGOs), citizen advocacy groups, and trade associations. In New York City, the Metropolitan Waterfront Alliance provides a forum where no fewer than 620 separate institutions with ties to the waterfront can come together, discuss issues of mutual concern and find a balance between the conflicting demands. Modern sediment management in urban areas has four unique characteristics:

1. The continuous need for maintenance dredging in shipping channels.
2. The need to confront legacy contamination from historic industrial activities.
3. The ongoing inputs of contamination from storm water runoff, combined sewer overflows (CSOs), and industrial activities.
4. The increasing human populations placing multiple demands on urban waterways and stresses on coastal ecosystems. There are also multiple management goals and regulatory agendas.

In New York Harbor alone, there are 240 miles of maintained shipping channels and many of these will be deepened to a 50-foot (15.2 meter) depth by 2014. The cost of this work will be $1.6 billion and it will generate 42,000,000 cubic yards of sedimentary material. (Baron 2012) At one time this material would simply have been dumped in the ocean but there has long been concern over the ecological effects of their near-shore ocean disposal (Albrecht et al. 1981, Bray et al. 1996). In 1972, the United States prohibited ocean disposal of dredged materials if laboratory testing revealed them to be toxic or if they contained pollutants likely to accumulate in the tissues of marine organisms. Changes to the testing protocols and enactment of the Marine Protection Research and Sanctuaries Act have since reduced the amount of material eligible for ocean disposal although near shore disposal in confined sites is still permitted (O'Connor 1999).

Increasingly stringent environmental regulations on both the national and international levels combined with the ever-increasing sediment disposal costs have placed new demands on sediment management. In many urban systems with legacy sediment contamination, the essential challenge consists of balancing the cost of a remediation (which ideally should be as low as possible) with considerations such as long-term liability, sustainability, regulatory or public challenges, the maturity of alternative treatment options, and the long-term management needs of the ecological system (Stern and Peck 2012) (figure 5-1).

Beneficial Use, Innovative Reuse, and Life Cycle Assessments

One of the primary components of sediment management is the concept of reuse. This idea can be broadly subdivided into Beneficial Use and Innovative Resuse. Beneficial use is defined by the US Army Corps of Engineers as “Utilizing dredged sediments as resource materials in productive ways which provide environmental, economic, or social benefit.” (USACE 2013)

The US Army Corps of Engineers (USACE) Guidance Document ER 1105-2-100, issued in December of 1990 encouraged regional districts to “consider options that provide opportunities for aquatic ecosystem restoration when determining an acceptable method of disposal of dredged material.” If it were found feasible to use dredged materials for restoration projects, then that activity would be specifically authorized as part of the project. The document also included an economic incentive. If beneficial use was lowest cost, environmentally acceptable method of disposal, then it could be cost shared with navigation. Two years later, Section 204 of the Water Resources Development Act (WRDA) of 1992 granted authority to employ beneficial use in aquatic restoration or environmental remediation projects.

Beneficial Use as it is currently practiced matches the level of contamination to the intended use. Contaminated, organic-rich sediments might be blended with other materials (biosolids, yard wastes, or storm debris) to create topsoil that can be used in landscaping. However if the intended use is the production of food, uncontaminated sediments must be used. (USACE 2013) Sediments do not undergo decontamination as contaminants are “diluted” to safe levels with amendments. Generally, sediment treatment is minimal but dewatering or stabilization is often used to prepare materials for reuse.

For the purposes of this discussion “Innovative Reuse” will be defined as a process that involves a decontamination step. This can be thermal treatment, sediment washing, or some sort of advanced biological treatment. The end product is sometimes very different than the original material. The most obvious example is the production of construction aggregates by the thermal treatment of sediments.

Obviously there can be considerable overlap between these two categories with some projects defined as “innovative” that would more correctly fit the “beneficial” category. In a project where sediment preparation prior to beneficial use is a complicated process, the boundary to “innovative” resuse might be crossed.

It might well be asked if “reuse” is the same thing as sustainable? Stern and Peck (2012) define sustainable sediment management as an integrated approach that addresses long-term management issues within a watershed so as to maintain current uses while promoting beneficial use of sediments.

At first glance, reuse appears synonymous with sustainable. However a true measure of sustainability requires making Life Cycle Assessments (LCA). This consists of considering the total effects a product will have on its environment from its creation to its ultimate disposal. For sediments this means from the moment of their creation in an inland erosive environment to their ultimate deposition. Preventing erosion in upland river basins is not normally considered part of urban sediment management so as a practical matter, we need only consider the activities that begin with dredging. Expanding on the ideas of Stern and Peck (2012) we can postulate:

sustainability = (value created when sediments are used as a resource) - (total costs) – (future liabilities)

Sustainability is like any other endeavor, if the value of a product equals or exceeds the costs, then a positive outcome is achieved. In a simple navigation maintenance project the value of the shipping channel only needs to equal or exceed the costs. But sustainability also considers the issue of future liabilities so that the positive outcome is lost or diminished unless these remain small.

Whether it is done for shipping channel maintenance or as part of an environmental remediation project, dredging is expensive. It also requires a great deal of energy, generates pollution, may damage marine life, and creates greenhouse gasses. All of these financial, energy, and environmental costs can be grouped together under the total costs as both direct financial outlays and externalities. If the dredged sediments are contaminated, they may merely be placed in a Confined Disposal Facility (CDF), Confined Aquatic Disposal Facility (CADF, or sometimes a CAD cell), or perhaps shipped to a distant landfill. In this instance, the sustainability is negative or at best very small because the resource value created is zero and the future liabilities are potentially large. If the dredged materials are relatively uncontaminated they can be used for any number of purposes such as beach replenishment. In this case, the value of the restored beach is large and the future liabilities are small. (Though it must be allowed that the sustainability of beach replenishment is itself subject to debate.)

If polluted sediments removed during the project are decontaminated through some method of innovative reuse, then the future liabilities become small. If the decontaminated sediments are subsequently put to some beneficial use, then the overall sustainability of the project is large even though the financial outlays were large.

An example of how Life Cycle Assessment is applied to a sediment remediation project comes from the Grenland Fjord in Norway. The fjord had been contaminated with polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) from industrial activities. One remediation alternative was natural recovery. The other alternative was capping although whether to employ active and/or passive thin-layer capping was still being debated. When only the immediate site contamination was considered, then capping emerged as the preferred alternative. However when all of the energy use, greenhouse gas emissions, and other resource uses were taken into account, the total environmental footprint increased by more than an order of magnitude. There was, however, an exception to this overall conclusion. If the capping material was biomass-derived activated carbon, and if the carbon dioxide produced during its production was sequestered, then the binding of the contaminants to the cap and their subsequent immobilization would more than compensate for the extra costs and lower the overall environmental costs until they were comparable to natural recovery (Sparrevik et al. 2011).

It should be noted that activated carbon caps are effective only if the material does not become ineffective due to competitive binding or pore blockage from naturally occurring organic compounds (Cornelissen et al. 2008).

In recent years the beneficial uses of dredged sediments have expanded to include the construction of artificial reefs and shoals, habitat restoration, intertidal marsh restoration, and the filling of dead-end basins. They have also been used in the remediation of landfills and brownfields (Yozzo et al. 2004). In the 2011 fiscal year (FY), the US Army Corps of Engineers (USACE) spent $586 million for ecosystem restoration projects. This is 12% of the Civil Works budget. If sediments are needed for any of these projects, there will be no shortage, the FY 2011 budget for navigation projects was $1.65 billion (USACE 2011).

Sadly, the same cannot be said of innovative reuse because of the added costs of the decontamination steps. In 2011, the Maryland Port Association (MPA) concluded that for projects that involved contaminated dredged material, there was “no demonstrated innovative reuse option" that was "cost competitive with nearshore confinement. " (Francingues et al. 2011)

Step One, Coming to Grips With the Legacy Contamination

Writing in the Portland, Oregon, web-based news site, *Willamette Week*, about the debates over sediment remediation in Portland harbor, Aaron Mesh presented a series of questions and answers. Two of the questions and answers were:

"Doing nothing seems to make no sense—so the obvious choice is to dredge it out, right?"

"Sure, if you're not the one paying for it. "

"So the deciding factor will be based on science, right?"

"Sure, if you mean political science" (Mesh 2012).

There are many river, harbor, or estuary systems where contaminated sediments are being either investigated or remediated. The Hudson River is just one of many large river systems undergoing investigation or remediation for contaminated sediments. Other large rivers include the lower Passaic River in New Jersey, the Kalamazoo and Tittabawassee Rivers in Michigan, the Lower Fox River in Wisconsin, the upper Columbia River and Duwamish River in Washington State, and the Housatonic River in Massachusetts and Connecticut (Francingues et al. 2008).

The Cost of Sediment Removal and Disposal

In the United States alone, the U.S. Environmental Protection Agency (US EPA) has estimated that there is approximately 1.2 billion cubic yards of contaminated sediment under the country's surface waters (Interstate Technology & Regulatory Council 2011). Using current average costs for managing contaminated sediments, this volume of material could cost several trillions of dollars to remove and dispose of. State regulatory agencies are increasingly responsible for the identification, investigation, and management of contaminated sediments. By 2011, more than 25% of the contaminated sediment projects in the United States were instigated by state agencies and this percentage will likely grow (Interstate Technology & Regulatory Council 2011).

In many cases urban sediments have been polluted throughout the industrial era and this legacy contamination is so bad that full remediation will be required before any beneficial reuse is even possible. Aside from any potential risk to fish, humans, and wildlife, contaminated sediments have a reduced capacity for biological purification and an associated loss of biodiversity (Ramaroson et al. 2012).

Costs can escalate dramatically when sediments require special handling. In a wetlands restoration project in Huntington Beach, California, the sediments from the project were not hazardous and these costs were somewhat low compared to more polluted waterways. Estimates for "traditional" sediment disposal, i.e. re-use on site for constructing berms or rebuilding islands, were $5.00 per cubic yard. However disposal in a sanitary landfill would cost $7.30 per cubic yard. For off shore disposal, the cost rose to $9.44 per cubic yard (Moffatt and Nichol 2004). In contrast the dredging of the highly contaminated Ottowa River near Toledo, Ohio, was completed in late 2010 at a cost of $194.20 per cubic yard. The project involved removing 242,000 cubic yards of sediment from a 5.5 mile section of the river. The $47 million cost of the project was shared between the U.S. Environmental Protection Agency and the Ottawa River Group. The Ottawa River Group included Allied Waste North America Inc., E.I. du Pont de Nemours and Co., GenCorp Inc., Honeywell Inc., Illinois Tool Works Inc., United Technologies Corp., Varta Microbattery Inc., The Mosaic Co., Perstorp Polyols Inc. and Grand Trunk Western Railroad. The City of Toledo is also a partner in the group and furnished space in its municipal landfill as its share of the cost. The dredged sediments contained more than 7,500 pounds of PCBs and 80,000 pounds of PAHs, and over a million pounds of heavy metals. Some 15,700 cubic yards of the most heavily PCB-contaminated sediments were sent to a hazardous waste landfill in Michigan (Environmental News Wire 2010). For the Fox River project in Wisconsin, as of 2001, the unit cost for dredging, dewatering, and landfilling PCB-contaminated sediments was $366 per cubic yard (Montgomery 2001). The Jersey Gardens Mall is the third largest mall in the state. Its site in Bayonne, New Jersey, was originally a landfill that was capped with sediments excavated from shipping channels in the Port of New York/New Jersey. A total of 500,000 cubic yards of sediments were treated with binders and used at the site. The cost per cubic yard was $48.00 and included dredging, processing, transport, and placement (Myers 2005). The estimated costs of dredging material handling in dollars per cubic yard are in table 5-1. A similar analysis is presented in figure 5-2.

Strategies for Managing Heavily Contaminated Sediments – Entering the Decision Matrix

There is a long-standing debate whether sediments should be decontaminated before beneficial use or if they can be used as is. In the latter instance, the beneficial use would obviously have to be in an application where the contamination does not pose a risk to human or ecological health. Resolving the decontaminate vs. use directly question is complex and the answer often hinges on the balance between economic needs and social benefits against the costs of using either treated or untreated sediments. This balance must take into account the ecological limitations imposed by the presence of contaminants and even the public's perception that all dredged materials are, by definition, waste materials (Deibel et al. 2007). Each of the options available for treatment of heavily contaminated sediments has advantages and disadvantages beyond simple, though contentious, questions of cost. One thing they do have in common is that they operate in a very complex legal and political environment.

One of the complicating factors of sediment management is that the management decision matrix contains what Stern and Peck (2012) call the judgment zone. Badly contaminated sediments fall into the hazardous waste zone where their removal and subsequent treatment is governed by the Resource Conservation Recovery Act (RCRA) or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or more commonly Superfund). This extreme is characterized by high costs and limited management options. At the other end of the scale are situations were sediment contamination is low or absent. This is a zone of low costs and multiple management options. The judgment zone is where contamination is moderate and management options are constrained by the local situation and available funds (Stern and Peck 2012).

At this point it is worth pausing to distinguish two types of contaminated sediment remediation, mass removal and risk-based. A mass removal approach consists of simply removing all of the contaminated material from a river or harbor. A risk assessment approach differs from a mass removal in that the planning begins with determining the total risk to human and ecological health as opposed to simply calculating total contamination loading. Risk assessments, based on the site's unique characteristics, are used to determine what percentage of the total risk can be eliminated through selected remedial actions. For example, cleaning up a hot spot that is a source of contamination spreading through the system might reduce the total risk by 50% whereas remediating an equally contaminated area not exposed to strong tidal currents might do little to reduce total risk. This approach allows certain areas can be prioritized for immediate action. Areas that present lower risks can be capped, actively remediated in place, or allowed to undergo monitored natural attenuation. Conversely, if any of these approaches were to achieve maximum risk reduction, then they could be chosen over remedial dredging. A highly idealized diagram of how this works is shown in figure 5-3.

A risk-based approach is a form of adaptive management. Adaptive Management begins with the assumption that in any system as complex as those at the intersection of the natural world and human activities, uncertainties and surprises are inevitable. Previously the response from environmental managers took one of several forms as explained by Gunderson (1999). Wishful thinking simply ignored the uncertainties. Another approach was to divide the problem into what promised to be manageable pieces. But without a means of putting it back together, this did nothing but create a collection of correct answers but not an effective response. A technocratic approach attempts to banish uncertainties and forestall surprises by finding the right governmental policy, or the best scientific advisors, or the most detailed studies (Gunderson 1999).

At the core of adaptive management is a willingness to learn. Johnson (1999) sees this as a process where each management action is seen as an experiment. What is learned then informs the next action, and what is learned in that step informs the next and so on. Uncertainties, rather than being banished, are an expected part of the process and the goal is to reduce them continually by a process of continuous learning by doing (Johnson 1999). However if the learning process is going to be effective, then the management actions must be rigorous experiments. They have to be scientific in the sense that they provide testable hypotheses and measureable outcomes (Muray and Marmorek, 2004).

Whatever the advantages of risk-based remediation, when dealing with the most severely contaminated sediments, remediation as a mass removal under CERCLA remains the preferred alternative. The Superfund process has several phases, discovery, listing on the National Priority List (NPL), site characterization and remedial investigation (RI), feasibility study (FS), development of a proposed remedy, issuance of a decision document that defines the selected remedy, implementation of the remedy, and five year reviews to insure the effectiveness of the remedy. With contaminated sediments in urban waterways, it has always been difficult to keep all of these steps progressing at a timely pace. The problem is complicated because there are multiple contamination sources operating over multiple decades and the contaminants are spread over large areas. Often there are multiple responsible parties and several government agencies with jurisdiction over the project area. Another aspect of the problem is that the Superfund program was created at least 30 years before the complexities of sediment management were understood. Each site has its own unique characteristics such as the natural sediment load and environmental stressors that are outside the project area and beyond the control of the responsible parties. These stressors include CSOs, runoff, and industrial activities (Bridges et al. 2012).

Portland had been a major industrial center and seaport for 150 years. The city's port can serve as an example of Murphy's Law as it applies to Superfund. Anything that could possibly go wrong, went wrong, and it also cost a tremendous amount of money. When a

Superfund site is on land, three basic assumptions can be made. Firstly, there is usually only one responsible party, or at most a small number of them. The second assumption is that the site is usually confined to a small area and the boundaries of the site do not change. (This assumption is not entirely valid if contamination spreads to groundwater) Since the site is confined to a specific area, in theory at least, a mass removal of contamination will resolve the problem. Lastly, once the site is clean, it will not be re-contaminated.

None of these assumptions can safely be made for a sediment site. Portland Harbor was placed on the National Priority List in December of 2000. As of 2013 the study area extended from River Mile 2 to River Mile 11 on the Willamette River (USEPA 2013). The Willamette River's journey to Superfund began in the 1970s, when Governor Tom McCall campaigned on a platform to clean up Oregon's defining waterway (Jacklet 2010).

The first assumption can be discarded. The nine river miles have been home to numerous industries for about 150 years. Some of these industries are still in operation and are large employers. Others have closed but the parent companies are still in business. Another category are companies that have gone out of business and therefore the associated sites are "orphaned" with no responsible party. At this time there are about 100 businesses and property owners that can be targeted as responsible parties (Jacklet 2010). While a site that extends nine miles along a river may technically be "confined" to a specific geographic region, as a practical matter the site cannot reasonably be considered as confined, especially since the sediments can move. The final assumption, that the site once cleaned, it will remain clean, is far from valid in Portland. Erosion from legacy sites along the Willamette is a significant source of new sediment contamination (Jacklet 2010). A number of riverside industries, such as shipyards, continue to be a source of pollution.

When the Superfund process began in 2000 there was a great deal of optimism that in Portland, things would be different. A number of key players promised to "avoid the delays and bickering that have turned so many other Superfund cleanups into multi-decade wars of attrition" (Jacklet 2010). The Lower Willamette Group (table 5-3) was established as a consortium of port officials, the city government, and a dozen key businesses located in the harbor. The group predicted that that a Record of Decision (ROD) would be complete by 2006. Eight years and $75 million later, the study was complete but work on the cleanup plan had barely begun (Jacklet 2010). Key milestones in the project are listed in table 5-4.

According to Oregon Public Broadcasting (OPB 2013) as of January 2013, $100 million dollars had been spent on the studies. (Other sources state that the actual cost was higher.) The USEPA announced in January of 2013 that the initial draft of the feasibility study prepared by the Lower Willamette Group had several serious flaws. It failed to identify hot spots, overstated the benefits of capping, and minimized the benefits of removing contaminants by dredging. The EPA announced that it would ask for yet another study.

For sediment disposal, the EPA proposed a Confined Disposal Facility. However this aspect of the plan had always been unpopular. There were ten letters from the public opposed to the facility for every one letter of support (Jacklet 2010).

It is worth pausing at this point to compare and contrast "traditional" mass removal with adaptive management and also to ask if the latter approach would have worked better in Portland. Mass removal waives away the uncertainties in that it assumes the extent of the contamination can be mapped and understood before the project begins. In Portland, over $100,000,000 has been spent on studies and consultants yet no cleanup plans are even ready. Mass removal next assumes that project plans can be created at the outset that will address the entire problem. Superfund is financed through the concept of "polluter pays." Therefore the more dangerous assumption is that the polluters (aka responsible parties) can be reliably identified and made to pay a fairly determined share of cleanup costs. This has not been the case in Portland. There is also an assumption that once project plans are announced, the public, other stakeholders, and the lawyers will not have their own ideas about the cleanup. This is certainly not a safe assumption because Portland has an engaged and politically active population as well as a thriving marine industry that depends on the port.

It is difficult to imagine where the adaptive management process might begin in Portland given that the problems are found on both the land and in the waterways. Bridges (2011) suggests that a starting point might be in determining the Value of Information (VOI). A VOI analysis is designed to determine which decisions are sensitive to a particular source of uncertainty. This allows environmental managers to prioritize which uncertainties should be addressed. Finally it allows managers to determine how much should be spent on eliminating or reducing the uncertainties (Bridges 2011). Because adaptive management is designed to treat each step in the remediation process as an experiment, the succession of experiments can be designed according to the priorities identified in the VOI process. And if adaptive management should fail, there is still the option of surrendering to mass removal.

And what has Portland gained for the $100,000,000? As of 2010 approximately 38,400 people were employed by the industries of Portland Harbor. However the Portland Bureau of Planning and Sustainability estimates that 3,600 jobs have been lost since 2000 in part due to the uncertainties around the clean up efforts and the stigma of Superfund. Several significant industrial property sales have been canceled or are on hold. The Portland Development Commission estimated that these types of delays have cost the region $320 million in investment, $81 million in annual payroll, and 1,450 jobs. Meanwhile the shipping channel in the Willamette River is filling in and the EPA has forbidden maintenance dredging. At this time this has not been a problem due to the worldwide slowdown in maritime traffic but it is expected to put limits on the growth of the port (Jacklet 2010).

Even in the best cases, a single RP and a clearly defined problem, projects can stretch over long time periods. The case of the Hudson River PCB remediation is an excellent example. The portions of the Hudson River that were contaminated with PCBs were placed on the NPL in 1984. The phase one report was issued in 1991 and the remedy was selected in 2002. Phase one dredging began in 2009. In this instance, much of the delay between 2002 and 2009 is due to the Responsible Party's (General Electric’s) resistance to implementing the remedy. However the majority of significant delays are attributed to the uncertainties inherent in these projects. Uncertainties can be found in the risk assessments, the effectiveness of remedial actions, how exposure is calculated, and site characterization. This leads to protracted debates over risk assessments and models as well as setting unrealistic clean up goals. Time is consumed in these debates while risks continue and costs escalate. The twenty-year delay between the first inspections of the Hudson River and the remediation is typical of these projects. In the Portland Harbor project the feasibility study lasted ten years and cost $75 million. The entire Boston Harbor project lasted ten years (Bridges et al. 2012).

Such delays might be tolerable if cleanups based on mass removal were universally effective. Dredging often releases contamination back into the environment, in the case of the Hudson River PCB removal about 3% of the PCBs were released into the water column and distributed to downstream areas. (Bridges 2011) The National Research Council has concluded that they often fail to achieve meaningful risk reduction. A more integrated approach using a combination of remediation technologies might achieve more effective risk reduction (Bridges et al. 2012).

Accelerating the cleanup process may begin with understanding that in any urban environment there will be limits on what level of contaminant reduction can be achieved. All stakeholders, including the responsible parties, should be engaged as early as possible so that agreed-upon and realistic goals with meaningful metrics can be implemented. Risk assessments can be based on the site's characteristics can then be used to guide the remediation. Responsible parties can be encouraged to take early action in the high-risk areas. The regulatory agencies can help move the project to its conclusion by meaningful promises to keep any disputes out of the courts. (Translation: get moving and you don't get sued.) All of these ideas were developed at a meeting of the US Army Corps of Engineers Research and Development Center and the Sediment Management Work Group and summarized in a paper by Bridges et al. 2012.

The approach of encouraging responsible parties to get out in front of the project and voluntarily remediate high priority areas was the essence of a proposal made at a recent meeting at Montclair State University. Representatives of Responsible Parties in the Passaic River remediation argued that rather than engage in a mass removal extending through much of the lower river, the hot spots should be addressed. This would be followed by a reevaluation and risk reassessment prior to a decision whether to conduct additional remediation. This approach embraces the concepts of adaptive management because each cycle of remediation-reevaluation-risk assessment, not only reduces the total risk to human and environmental health, it gives the project managers the data they need to plan effectively and select the best solutions for maximum risk reduction in the next cycle.

Interaction with the Stakeholders and the Larger Pubic

The question remains whether the public and other stakeholders would embrace a cleanup strategy that does not entail the mass removal of all contaminated sediments. It is the author's impression, that as Responsible Parties resist mass removal because of the costs, projects drag on, the public grows increasingly frustrated, and political demand for mass removal increases. In theory, adaptive management could reduce the project timelines but if the reevaluation and risk assessment steps are not handled in a completely transparent fashion, the fighting and political delays common to these projects could be endlessly repeated after every cycle.

Better stakeholder involvement is widely believed to be a solution to the problem of fighting and political delays. What occurred during a tunnel construction project in Oslo's harbor may prove an instructive case study. Construction of a new road tunnel under the harbor required disturbing contaminated sediments. Remediation activities took place between 2006 and 2009. Before work began there was an Environmental

Impact Assessment. The remediation plan was approved both by Norway's Pollution Control Authority and the local city council. The solution was placing dredged material in a confined aquatic disposal facility (CADF) approximately 3 km from the dredging site but still within the larger Oslo Fjord. Other portions of the contaminated area were going to be capped. The proposal immediately came under fire from non-governmental organizations that objected to placing the CADF in the fjord. Essentially the problem was that the public's perception of risk was very different than that of the experts. Despite an otherwise far-sighted national sediment management strategy, about half of Norway's remediation plans still lacked adequate consideration of stakeholder perceptions and beliefs about site's hazards, or more succinctly, "Concern Assessment" (Sparrevik and Breedveld 2010). Another analysis of the Oslo project concluded that the wider public perceived risk based on the transparency of the decision making process and the controllability of the disposal options (Sparrevik et al. 2011).

Norway did not intend to create a sediment management process that lacked transparency. Indeed the country had made a national commitment to a clean marine environment. Unlike other parts of the world, sediment remediation was not driven by the need for navigation channel maintenance but by environmental awareness and urban redevelopment. Beginning in the late 1990s the country undertook an investigation of sediment contamination at 120 sites along its coast. A set of Sediment Quality Guidelines (SQG) was developed and sites were ranked from background (class 1) to severe contamination (class 5). Because of concerns over the transfer of contamination from sediments to the marine chain, seafood consumption restrictions have been issued for 32 coastal areas. By 2009 management plans for 29 of these areas were in place and remediation plans were created for 17 of them. Some of the remediation options included Remediate in Place (RIP) and capping as opposed to mass removal (Sparrevik and Breedveld 2010).

The transparency problems resulted because management plans were heavily influenced by what could otherwise be perceived as good decision-making tools, eco-toxicity-based SQGs and site-specific risk assessments. This approach takes advantage of current scientific advances and allows for *ad hoc* decision making. But scaling it up to create national guidelines is difficult. Additionally, 70% of the risk management strategies used in the remediation projects were developed on an *ad hoc* basis. This did nothing to enhance the perceived transparency of the decision making process (Sparrevik and Breedveld 2010). In response to these issues, Norway created the Sediment and Society initiative. It attempted to create a more collaborative approach that incorporated both local and scientific knowledge. The project seeks to explore new methods of stakeholder involvement which are more informative, consultative, and participatory (Oen et al. 2010).

The Sediment and Society initiative also addressed what could best be described as the problems that lie beyond the limits of technical knowledge such as striking the balance between project costs, regulatory obligations, economic viability, ecosystem preservation, and protecting human health. There is also the unequal distribution of project costs, which often are quite high. Scientific uncertainties and differing stakeholder perceptions complicate further the issues. As of 2010 three important challenges were identified, encouraging stakeholders to participate in the early phases of the planning process, securing the resources needed to support widespread participation, and including individuals who possess useful local or management knowledge but little influence over the decision-making process (Oen et al. 2010).

Every project must confront the problem disposing of the heavily contaminated sediments. Despite the availability of innovative treatment technologies, this largely remains a mass removal process of dredging, dewatering, and landfilling. This is the approach taken on the Upper Hudson River PCB-remediation project, the Fox River Project, and the Lower Passaic River Project. (Although a portion of the more heavily contaminated Passaic sediments will be incinerated in Utah) The great advantage of dredge-dewater-landfill is that it is a proven technology with no real siting or permitting problems as would be encountered with a thermal treatment facility, sediment washing facility, or plasma arc process. However the problem with this approach are that it is extremely expensive, landfills do not offer permanently secure storage, and the practice is not particularly sustainable when factors such as the green house gas emissions from haulage and the limits of landfill space are considered (Stern and Peck 2012). It had been argued at the 2012 DredgeFest symposium (and the author has been unable to confirm the truth of the assertion) that the State of Connecticut is unable to undertake any dredging projects in its harbors and waterways because of a shortage of landfill capacity. Even if completely untrue, the fact that such a claim could be made, and taken seriously, in a room full of engineers, port planners, and scientists, says something about the state of the art.

Advanced treatment technologies promise to provide an alternative to landfills and confined aquatic disposal. They have been proven to be effective so their wider adoption has become a "people issue" (Kirby 2012). *New Jersey Monthly* reported on a public meeting between federal officials and residents of Newark's Ironbound neighborhood about alternatives to landfilling contaminated Passaic River sediments. Because the total volume of contaminated sediments from the current project is estimated to be as much as 11 million cubic yards, almost five times more than the 2.6 million cubic yards from the Hudson River PCB remediation, some form of local treatment may be required as an alternative to long distance transport to landfills. At this particular meeting, there were hints that a leading citizens' advocacy group, the Passaic River Coalition, favored thermal destruction. This technology was successful demonstrated during an earlier pilot-dredging project. The Coalition's allies in the neighborhood were not so enthusiastic. The ironbound is already home to a municipal solid waste incinerator, and residents had recently opposed proposals for both a medical-waste incinerator and a pet crematorium. Said one community leader, "No matter what you call it, it's an incinerator, and if it's going to go anyplace, it will end up being jammed down our throats here, like everything else" (DePalma 2012).

While it is tempting to dismiss community resistance to infrastructure projects, including environmentally beneficial sediment remediation, as nothing more than NIMBY and BANANAs (Not In My Back Yard and Build Absolutely Nothing Anywhere Near Anyone) the actual situation is far more complicated. As Norway discovered, the existing processes for engaging stakeholders and local communities are often responsible for creating unnecessary project delays and yet such delays are almost inevitable given the problem of mismatched time scales.

Sparrevik et al. (2011) points out that the different groups enter the process at different times. In a study of PCB remediation in the sediments of Bergen harbor, Norway, three different groups were identified. The "problem owners" are active in the problem formulation and approval phase. For Bergen harbor this meant mapping PCB contamination and seeking regulatory approval for a preliminary remediation plan. The problem owners become less active in the project once the second group, the consultants, begins its work. This group gathers detailed data and evaluates remediation alternatives. The consultants then go on to seek regulatory approval and prepare environmental impact statements. As the consultants work winds down the last group, the stakeholders, enter the process. Stakeholders are defined by Sparrevik as the people, organizations, and groups who are affected by the problem and who have the power to make the decision, support it, or oppose it (Sparrevik et al. 2011).

The problem is that the stakeholders are not involved until the remediation plans are far advanced and that these plans are often based on technical feasibility, budget constraints, time scales, and political realities. The response of the stakeholders is to see the decision and planning processes as lacking transparency. Stakeholders get involved only after many decisions have already been made, the project has a certain momentum, and there is a lack of negotiating space. The natural response from the stakeholders is a distrust of the planning process. In response, the problem owners grow increasingly resistant to making any type of change and avoid a meaningful dialog with the stakeholders. The problem is further complicated because the stakeholder response is qualitative, making it hard to prioritize which concerns to address (Sparrevik et al. 2011). The entire process has taken on the name, “decide and defend” (Oen et al. 2010).

The solution explored by Sparrevik was to engage in a process that employed the principles of multi-criteria decision analysis that allowed all participants to learn through "qualitative participatory methods." Three advisory groups were formed consisting of local residents, local stakeholders, and nonresident sediment experts. All of these groups were engaged in a process through which they learned from each other as the complex remediation alternatives were examined. The multi-criteria decision analysis process gave provided structure, robustness and transparency. While the overall process worked well in the Bergen harbor project there was some difficulty coming to grips with the idea quantitatively scoring potential impacts (Sparrevik et al. 2011).

As we have seen in the discussion of Newark, New Jersey's, debates over a thermal treatment facility, a major impediment for contaminated sediment management remains the ability to implement a treatment technology with minimal permitting and siting delays. It may be that the solution to this problem is going to be creating temporary treatment facilities that are permitted only for the duration of a project. This approach was successful for the dewatering and transfer station at Fort Edward, New York used in the Hudson River PCB remediation.

The other approach would be a permanent innovative resuse facility that would serve multiple projects over long time scales. Severly contaminated sediments could be treated before reuse and less contaminated materials would be processed before beneficial use. The Maryland Port Association (MPA) created a list of issues surrounding the creation of such a facility. Assuming such a facility would be suitable for the port, the most fundamental question was whether the operators of the ports were willing to make the necessary long-term financial commitment. The sale of materials recovered or created from sediment remediation would be expected to help pay for the facility and its continued operation. Therefore the next question is whether there a demand for such materials and at a cost that is competitive with the current treatment strategies? A complicating factor is that the costs of re-use are expected to vary not only with the extent of contamination but with the grain size of the sediment. Costs increase as grain size diminishes. From all that we have seen thus far, any hope that the sale of recovered materials will offset the costs of processesing is unrealistic purely on a direct cost per cubic yard basis. (Francingues et al. 2011) (Another example of this issue is explored in detail in the Jamaica Bay waste management case study) As we have postulated earlier, only if all sustainability and future liabilities are included in the calculation will the costs be competitive.

Such a facility would have to process a wide range of sediment types and ideally should support several innovative reuse technologies. Fortuneately these can share screening and dewatering machinery. However the providing the estimated 20 or more hectares (50 acres) of land for stockpiling materials awaiting treatment will be a problem in a busy port. (Francingues et al. 2011)

The most pressing political issue is whether the regulatory agencies, in this case the Maryland Department of Environment will issue a general permit for multiple innovative reuse projects. Individual permits issued on a project-by-project basis would be expected to slow down the pace of remediation and increase the overall costs. Another political question concerns stakeholder support. Would such as facility receive support or opposition? (Francingues et al. 2011) From the experience of the thermal treatment facility proposed for the Passaic River, we might expect that regional and state level environmental advocacy groups might support the facility but the host community will not.

As an intermediate measure, the use of sediment separation could be stepped up so that the volume of materials either land filled or sent to CADs can be decreased and the pool of clean sand for beneficial use increased. How this was done for the Port of Hamburg is explained in the next section. If smaller volumes of heavily contaminated fine sediments are being produced, a centrally located, ex-situ sediment washing or incineration facility could be created that serves multiple remediation projects.

It would be a fallacy to conclude that once legacy sediment contamination has been addressed, there will be no further need for worry. However Cornelissen et al. 2008, measured PAH, TBT (Tributyltin) and PCB particles in existing Oslo harbor sediments (i.e. legacy contamination) and "future" sediments (i.e. riverine and urban runoff particles). They found that the future sediments were much less contaminated. Therefore a harbor remediation strategy of dredging followed by capping the current sediments would be of immediate benefit. The catch is that because the "future" sediments are not uncontaminated the strategy would only be effective for about ten years. The contaminant levels above and below the dredged depth would be comparable, especially if bioturbation mixed the older, capping, and new materials (Cornelissen et al. 2008). In other urban centers ongoing sediment contamination comes from street runoff, industrial activities, contaminated industrial sites, sewers, and combined sewer overflows.

Sustainable sediment management plans need to be created because the problem of sediment contamination may improve, but will never completely go away.

Step 2, Learn to Cope With the Complex Interactions Between Human, Ecological, and Sedimentary Systems

There is an apocryphal story about how sediment management remains in a “one size fits all” mentality. An environmental scientist wanted to test a new sediment remediation method. He called the local office of the USACE and asked if they could supply him with ten cubic yards of contaminated sediment from a local river. The Corps official on the other end of the phone was delighted to help and said that the USACE could provide 10,000 cubic yards immediately. “No,” said the scientist, “I only need ten cubic yards.” There was a long pause before the official replied,

“I don’t think we can do that.”

In the 1930s the USACE first began seriously examining the interrelationship between navigation projects and contiguous beaches. The typical port city had two problems, there was too much sediment in the port’s navigation channels and not enough sediment on the city’s recreational beaches. The concept of Regional Sediment Management (RSM) was an attempt harness natural forces to solve engineering problems on a regional scale. The first project to use long-shore sand transport was at Santa Barbara, California and the South Lake Worth Inlet, Florida during the mid-1930s. Sand removed during navigation projects was placed so that it would be carried by currents to nearby beaches. What distinguishes modern RSM projects from simple maintenance dredging projects are that they collaborations with multiple state and local governments to manage sediments over large geographic areas and accommodate multiple stakeholder needs. Notable RSM projects in undertaken since the year 2000 have occurred in the Northern Gulf of Mexico, Northeastern Florida, at the New Jersey Shore, the South Shore of Long Island, Southeast Lake Michigan, Southern California, and Honolulu (USACE 2013). The important principles of RSM as articulated by the USACE Mobile, Alabama , office are listed in table 5-2.

Several successful RSM projects have been completed in the Gulf of Mexico using dredged materials obtained from navigation projects or from nearby dredged material disposal sites. A report detailing 11 of these projects was prepared by Byrnes and Berlinghoff (2011). The dredged materials were used for shoreline protection, habitat restoration, and filling behind bulkhead structures. It is significant however, that sandy materials were preferred for these projects and none of them required dealing with contamination (Byrnes and Berlinghoff 2011).

In its current form, regional sediment management is not equal to the task of dealing with the complexities of urban systems. Urban sedimentary systems have a convergence of conflicting demands, an abundance of feuding stakeholders, and uncertainties created by growing coastal populations at a time of sea level rise and warming climates.

A good starting point for coming to grips with the complexities of urban sediment management would be recognizing that most urban waterways are not natural systems. Wetlands at the urban margin have been filled to create land for agricultural, residential, or industrial development. Stream channels have been straightened and banks have often been reinforced. Where multiple channels may have existed, many rivers have been directed into a single channel. Deep navigation channels have been excavated, for example, the Lower Rhine at Rotterdam had a depth of about 5 m in the 1880s, but is currently approximately 24 m deep. Deep harbor basins can act as sediment traps. Shorelines are left unprotected from storm surges (Kirby 2012). It would be a severe understatement to say that in such a system natural sediment dynamics have been disrupted.

Knowing how best to manage this disrupted system requires us to first ask, “where do sediments come from?” and “how much of them are natural to this particular system?”

Natural and Anthropogenic Influences on Sediment Budgets

Rivers worldwide are currently transporting over long distances an estimated 24 gigatons of clastic and dissolved materials to oceans or interior basins each year. Creation of localized meanders accounts for an estimated movement of another 39 gigatons each year. However in the absence of disturbance from agriculture, logging, and construction-related earth moving activities, the amount of clastic and dissolved materials would only be 14 gigatons per year. Estimates of soil loss from agriculture are 5 tons per hectare per year for pasture lands and 15 tons per hectare per year for cultivated lands (Hooke 2012).

The European Union Freshwater Fish Directive has created a guideline standard for annual mean suspended sediment concentration of 25 mg/L. Setting any such sweeping standards and expecting them to be valid over diverse geographical areas is always problematic. Catchment-specific sediment guidelines have been proposed for parts of England and Wales. These could take into account factors such as climate, the re-suspension of sediments caused by aquatic animals, and local geological conditions. But before these alternative guidelines can be put in place, it will be necessary to determine the “natural” or background sediment loads. No management strategy can hope to lower sediment loads below this value since it is intrinsic to the regional conditions. Unfortunately modern, highly intensive, agricultural activity has largely obscured this background signal, also referred to as the “modern background sediment delivery to rivers” (MBSDR). Scientists looking to establish MBSDR have turned to palaeolimnological reconstruction (Collins et al. 2012). Assisting in this process may provide yet another application for Py-GC/MS sediment analysis.

Measuring sediment loads within watersheds can be performed remotely but there are special considerations when interpreting the data. Turbidity sensors and hydrophones are useful tools for field observations. But turbidity sensors do not directly monitor loads within the water column nor do hydrophones directly measure bed loads. A sediment load study in Japan’s Gifu Prefecture demonstrated that it is possible to estimate sediment transport during rain events by combining turbidity and hydrophone data from separate locations. It was also possible to estimate the sediment source area using the relationship between turbidity and water level (Tani 2012).

While integrated sediment management in downstream urban areas such as ports and coastal estuaries requires knowing upstream sediment loads, there are several other practical reasons to make these measurements. River sediments can negatively impact both water quality and quantity in drinking water reservoirs and excess sediment loads have been identified as a major cause of impairment. Although some pollutants can be transported while sorbed to sediment particles Galster (2013) lists more direct source of impairment including a loss of storage capacity in reservoirs and behind dams, altered aquatic habitat, and decreased channel capacity leading to increased flooding.

Sediment Starvation and Shortages: the Problem and Potential Solutions

While port managers spend millions of dollars removing sediments from harbors and navigable rivers, the ability of many exurban coastal regions to provide ecosystem services is compromised by a shortage of sediments and the nutrients that they bring from upland areas. Many of these shortages have been created by upland navigation improvements or dams. There are an estimated 45,000 large dams in the world storing approximately 7000 cubic kilometers of water and trapping an estimated 25% of global suspended sediment loads (Takeuchi 2004). Coastal cities depend on these upstream dams but they also depend on the nearby coastlines for recreation, fishing, and protection from major storms.

One of the most famous examples of sediment starvation is in the Grand Canyon where according to the Glen Canyon Institute, about 95% of the natural sediment load is retained behind the Glen Canyon Dam. Sediment loads in the Grand Canyon prior to dam construction are estimated to have been 275,000 tons every day (Glen Canyon Institute). Not only has the canyon's environment been adversely affected, the entire northern end of the Gulf of California is considered to be sediment-starved (Carriquiry et al. 2001).

In areas where there is active navigation dredging, sediment starvation can be addressed through the mechanized transport of materials to starved areas. The islands in Jamaica Bay, a shallow coastal estuary located on the southern shore of Long Island and entirely within the city of New York, have been shrinking for many years. It is widely suspected that one of the principle reasons is sediment starvation. In the fall of 2012 five of the marsh islands in Jamaica Bay were being restored with sands pumped from the navigation dredging operations in the Ambrose Channel. Forty-four acres will be restored just on one island (Baron 2012). An earlier project restoring 70 acres of marsh on Elders Island required placing 270,000 cubic yards of sand before the area was ready to be replanted with *Spartina alterniflora* (saltmarsh cordgrass) , *Spartina patens* (salt hay), and *Distichis spicata* (spike grass) (Business Wire 2006).

There are situations where attempts to use natural forces to direct sediments for one purpose can create sediment shortages in another. River diversions can be used to deliver sediments to locations to coastal marshes. Diversion structures are usually associated with flood control activities but diversions from the Mississippi River have been used to deliver fluvial sediments and nutrients to coastal marshes. However diversions will deprive the originally fed locations of sediment loads. This effect may be significant in small riverine systems although the size of the diversions off the Mississippi were considered trivial compared to the total riverine resource (Reed et al. 2012).

Because sediment type must be matched to the intended beneficial resuse, it is not always a simple matter to move material to where it is needed from where it is not needed. Sand is the appropriate material for beach restoration but its large grain size means that it may not be suited to projects where a muddy texture is needed. With the changes in climate creating stronger storms and sea levels rising, new emphasis has been placed on creating "soft" infrastructure for coastal protection. In regions where the foreshore is relatively high, a muddy coast can be protected from erosion simply by planting marsh vegetation. Hard defenses such as seawalls and other barriers may be needed for low-lying areas. If space permits, they can be situated inland so the remaining shoreline serves as a buffer zone. Where this is not possible new tidal flats can be created using muddy dredged materials (Kiby 2012).

A similar set of choices was encountered by the State of Louisiana where clean sand is preferred for beach restoration and the building up barrier islands. This is of particular local concern because of the narrowing and overtopping of barrier islands threatens both coastal properties as well as the back barrier bay and interior marshlands. But for restoring marshlands, mixed sediments are preferred.   The cost of transporting the desired type of sediment increases with distance and an especially significant engineering challenge has been to locate suitable deposits of sand (Syed et al. 2010). In Japan a shortage of beach sand for coastal construction projects has lead to the widespread adoption of a technology where soft dredged materials are combined with a special mixture of clay, water, and cement. This creates a material that has many of the mechanical properties of sand and can be modified depending on the needs of a particular project. An additional advantage of the process is that Japan has limited capacity for the disposal of soft dredged materials (Saitoh 2013).

If clean sand can be separated from the more contaminated sediment fractions a much larger pool of potential material could be exploited. It has been argued (Olin-Estes and Palermo 2001) that improved separation technologies could create sources of sediments for beneficial use such as ecological restoration based on grain size or other desired criteria. This is the approach taken at the Port of Hamburg, Germany, where the sand fraction of the dredged material is separated from the silt fraction. The sand fraction is relatively clean and can be reused without additional treatment while the silt fraction contains most of the organic contamination and is sent for separate treatment or disposal

(Detzner and Knies 2004). A similar approach was evaluated by the USEPA at the Saginaw Bay CDF, located on the shore of Lake Huron in Michigan. Approximately 400 cubic yards of sediment were processed in an hydrocyclone that separated sand and fine-grained particles. The process succeeded in producing a sand fraction suited for beneficial reuse. The sand made up approximately 75% of the sediment mass. The projected costs of using this approach on future projects is between $39 and $224 per cubic yard depending on the volume of sediments treated (USEPA 2013).

It is well-known that high temperature incineration of sediments can destroy organic pollutants and immobilize inorganic materials. But it can also cause the sediment particles to undergo physical changes. In a study involving the high temperature chemical reactions as part of a decontamination process Ramaroson et. al., found that organic chemicals on sediment particles degraded at 600c. Total destruction of organics was achieved at 700c. Between 500 and 600c specific surface area increases as organics are lost or destroyed and water is removed. However, between 700 and 800c, the particles are calcinated and sintering can occur. As particles are bound together by the sintering, the overall surface area decreases. This is significant for re-use because larger particles with less surface area will hold fewer contaminants. Also significant is that environmental managers can control the physical characteristics of the sediments by the treatment temperature and residence times (Ramaroson et al. 2012).

Habitat Restoration Considerations

In many instances where sediment is needed for habitat restoration, the solution has been active pumping or dredging and transport. An instructive case history of using water currents to move materials occurred in the Eastern Scheldt on the coast of The Netherlands. In this estuary, an estimated 50 hectares of mud and tidal flats are disappearing annually. This figure is expected to rise to rise to 100 hectares annually. Aside from creating a serious habitat loss, the flats also serve as a barrier against waves running up the dikes. Construction of a storm surge barrier has changed the tidal regimen and is contributing to the problem. Tidal channels are too wide relative to the reduced tidal flows and are infilling with sediments drawn from the adjacent tidal flats. This sediment movement primarily takes place during storm events. The reduced tidal flows cannot move materials back onto the tidal flats and even if it could, the system is sediment-starved because of the storm surge barrier. The solution used by the Dutch engineers at the Galgeplaat, an island in one of the tidal channels was to construct a circular sand ring about 450 meters in diameter in 2008. Called a “nourishment”, it stood about a meter high, it was allowed to fill with available sand during flood tides. Sediments from maintenance dredging operations were also added to the nourishment. Earth-moving equipment spread the sands during low tides. The total volume of sediments in the nourishment was 130,000 cubic meters. The nourishment was positioned so that it would supply sediments to the tidal currents that would in turn, deliver the sand to the depleted areas (Borsje et al. 2012).

Unfortunately the location of the nourishment was not in a sufficiently energetic area and after two years the amount of sediment moved to the flats was minimal. The nourishment itself developed as a coastal habitat and here the engineers learned valuable lessons about topography and biomass. Where the nourishment was submerged during at least part of the tidal cycle, biomass was greater and species diversity was richer. The dry areas had between 7 and 9 species, depending on the time of year, while the wet areas has between 11 and 15. Irregularities in the nourishment's surface such as elevation differences, gullies and gentle slopes, provided variable drainage patterns with effects on water supply. This allowed variations in species re-colonization rates and ultimately greater biodiversity (Borsje et al. 2012). In Jamaica Bay, the specific goals of habitat creation informed decisions about the restored islands' shape and their height above sea level, and goals of habitat restoration. The islands' shorelines will be sculpted to their historic footprints as of 1974. Projections of localized sea level rise were used to determine the ratio of high marsh to low marsh. This balance is critical in determining biodiversity. Jamaica Bay's position on the Atlantic Flyway makes providing bird habitat a high restoration priority (Baron 2012).

The experience with the Galgeplaat is an example of how using dredged materials for habitat restoration raises a number of issues. Each individual issue is well understood but when they are considered in the aggregate, it becomes clear that using sediments for effective habitat restoration requires an interdisciplinary approach. In any habitat restoration project the first question is what is the existing habitat and will it be enhanced or is the goal to replace it with another? In choosing an appropriate sediment, one of the first considerations is grain size because the tendency for materials to consolidate will have an impact on species composition. Sandy sediments suited for sea grass are ideal habitat for many types of fish but other species, including southern flounder and gulf sturgeon, prefer muddy bottoms. The slope of beaches and marshes will affect species composition as will the resulting salinity gradients. In beach replenishment projects sustainable plant growth will not result if the created landforms that are not in keeping with prevailing beach and dune profiles (Reed et al. 2012). Viable marsh plant communities cannot be established unless the restoration is not at least a minimum elevation above sea level.

Another consideration is that the hydraulic conductivity of wetlands sediments. This is controlled by particle size, packing, and organic matter content (Mann and Wetzel 2000). The clear implication is that the sediments used for restoration may not create the desired hydraulic conductivity.

One of the many proposals for habitat creation for urban areas has been to partially fill disused dead-end basins. Clean sediments can be used to elevate the basin bottom into the photic zone. This would this increase primary productivity and encourage benthic invertebrates. New sediments would also serve as a cap on the undesirable organic materials that accumulate in the ends of dead-end basins. However there would have to be careful consideration of transport dynamics to insure that there is no opportunity for contaminant dispersal. Development of shallow sub tidal and intertidal habitat in dead-end canals and basins of NY/NJ Harbor could potentially provide a use for up to 5,000,000 cubic yards of dredged material. At $35 per cubic yard however, the cost of this option is comparatively high (Yozzo et al. 2004).

The Use of Organic-Rich Sediments for Ecological Restoration

One of the more exciting developments relating to sediments and habitat restoration has been attempts to use organic-rich materials and take advantage of their complex geochemistry. An excellent example is the attempt by Japanese engineers to restore seaweed beds in coastal areas that are characterized as barren ground. There are a number of contributing factors to the growth of barren grounds including rising water temperatures and excessive grazing by sea urchins. One major contributor can be traced to sediment starvation. The dissolved iron necessary for plant growth is the Fe(II) form but that quickly is oxidized to Fe(III) and precipitated as insoluble $Fe(OH)_3$. Humic substances serve as naturally occurring chelating agents and bind Fe(II) (Fukushima, et al. 2011).

The construction of dams on rivers often prevents the transfer of the necessary humic substances from the terrestrial to the marine environments. Silt removed from reservoirs during maintenance dredging was mixed with iron-containing slag and applied to coastal areas (Yamamoto et al. 2006, Toyota et al. 2009, Yamamoto et al. 2010).

The ability of humic acids to bind to iron was found to increase with the O/C molar ratio and with a decrease in the sediment's amino acid content. However, TMAH-Pyro-GC/MS did not prove useful in identifying oxygenated compounds that might serve as binding sites. Binding capacity rose with anaerobic microbial action and the only reliable predictor of the increase was the ratio of C16:0 / C16:1w7 resulting from microbial action (Fukushima et al. 2011). A test was made on the coastline of the Japan Sea in Hokkaido. Slags and composts were applied to shallow-water barren ground. Subsequent measurements confirmed that supplying a source of iron significantly contributed to kelp bed growth (Yamamoto et al. 2010).

Nutrient content generally is a somewhat neglected aspect of sediment reuse. Surface erosion of bedrock releases trace nutrients and valuable organic components are created during the soil-forming process. Trace nutrient, nitrogen, phosphorus, and potassium content will influence the types of beneficial reuse projects that any particular sediment is suited for. A complicating factor however is the variation with depth that results from changes in erosion rates, transport phenomena, and patterns of fertilizer use (Junakova and Balintova 2012). Significant changes in nutrient and organic matter composition in Apalachicola Bay, Florida, have been linked to three factors, land use changes, anthropogenic alterations to river flows, and sea-level rise. Overall the inputs of organic matter are increasingly marine (Surratt et al. 2008). In situations such as these, where sediment composition and nutrient content changes with depth, the potential for any one beneficial use might reasonably be expected to change as well. Using Py-GC/MS to characterize sediment cores would be an effective way to identify such changes.

If the practitioners of sediment management have to cope with the uncertainties of complex natural systems, it is worth remembering that human society is also a complex system, as two British researchers demonstrated in 2006. Restoring an urban river is at face value a relatively uncomplicated concept. But it should be no surprise that restoration professionals, policy workers and the general publics all have different expectations. But a recent study in the United Kingdom showed that not everyone could even agree on whether the activity should be regarded primarily as a scientific / practical process or a social one. The restorationists are perceived as being radical in the scientific sense in that they challenge to the tradition of the 'hard engineering' of rivers. Though the same restorationists are hardly radical in the social sense in that they are part of a tradition of technocratic environmental management. Confusion arising out of such complexities might be addressed through more emphasis on and integration of social science within urban restoration projects (Eden and Tunstall 2006).

Step 3, Anticipate A Changing World

"The future ain't what it used to be."

Yogi Berra

Coastlines are one of the few places were people can witness geologic changes within human lifetimes but the 21st century, the rate of change, its causes, and the impacts of change on both humans and ecosystems may be unprecedented. Although it is hard to make specific predictions about the future, we can reasonably identify the most factors likely to exert the greatest changes on coastal areas. These include human population pressure, larger ships carrying increased amounts of foreign trade, sea level rise, climate change, nutrient run off, energy extraction, invasive species, and topsoil erosion.

According to NOAA, over half the population of the United States lives within 50 miles of the seacoasts. Coastal counties account for only 17% of the land area, (not including Alaska) but house 53% of the population. Between 1980 and 2003, population in coastal regions increased by 28% with the largest gains in the Pacific region (NOAA 2013). In some coastal communities, such as Florida’s St. Johns River Water Management District, more than 60% of homes and businesses are within 500 feet of the shoreline (Arc User Online).

Of the long-term sediment management issues, climate change will have a number of effects. To determine what these will be, the most important variable is the Relative Sea Level Rise (RSLR) that is the combined rise in sea levels along with localized geologic subsidence. The effects of rising sea levels are relatively easy to foresee. If estuary systems are sediment-starved, such as Jamaica Bay, they will not accrete vertically faster than RSLR and coastal marshes may be lost. An additional complication is that other coastal habitats such as coastal freshwater marshes and coastal forests will be experiencing salt water intrusion. Prediction becomes more complicated if regional rainfall patterns are also considered. More precipitation will raise flushing rates and reduce the salinity of brackish estuaries and increased erosion may lead to excess sedimentation with resulting stress on marine life (Reed et al. 2012). In some estuary systems the diversion of fresh water for human use has increased salinity and this has altered plant communities (Watson and Byrne 2012). Microbial communities are also affected by salinity changes. In some freshwater tidal marshes this accelerates organic carbon mineralization and accelerates the loss of salt marshes (Weston et. al. 2011).

An increase in global sediment loads has been predicted in regions where climate change is expected to lead to increased rainfall and more intense rain events (Takeuchi 2004). A drier climate will reduce sediment and nutrient loads to some coastal systems (Reed et al. 2012) but other areas will experience an increase in sediment as more lands are lost to desertification (Takeuchi 2004). Changes in sediment flux are comparatively easy to measure on small scales but catchment-wide changes are harder to measure and can be substantially different from what might be predicted based solely on plot-scale measurements. Despite this problem, such catchment-wide measurements can provide complimentary measurements of the extent of desertification (Vanmaercke et al. 2011).

Sea level rise is one of the factors that will complicate future sediment management. The effects of sea level rise can be divided into three main categories, inundation (including storm events), morphological (including changes to wetlands, beaches, and cliffs), and hydrological (encompassing salt water intrusion and altered drainage patterns) (Parry et al. 2009). To cope with these and other changes, all types of sediments (not just sand) will have to be regarded a resource by policy makers, engineers, and coastal stakeholders.

Sediment starvation created by upstream dams and channelization projects combined with sea level rise already threatens many river delta systems. While the problems with the Mississippi and Nile Deltas are well documented, there are also threats to the Rhone delta in southern France (Paskoff 2004) and Spain's Ebro River (Rovira and Ibàñez 2007). In the case of the Ebro, the delta has experienced an estimated 99% reduction from its original sediment inputs. Based on current estimates of sea level rise and land subsidence, 45% of the delta is expected to be below mean sea level by 2100 (Rovira and Ibàñez 2007).

A number of authors have expressed concern that sediment starvation caused by large dams will deprive coastal regions of an important resource required for maintaining defenses, restoring estuaries, and other coastal adaptations (Day et al. 1995, Nicholls 2006, Ferreira 2008, Reed et al. 2012). Another issue related to large dams is the overall reduction in stream flow and consequent reduction in the ability of the downstream river reaches to carry sediments. This results in river bottom elevation and increased risk of flooding (Takeuchi 2004, Nicholls 2006, Day 1995, Reed et al. 2012, Ferreira 2008).

Some natural sedimentary systems are able to accommodate sea level rise. Because of a continual production of vegetal debris, a mature mangrove forest off the coast of Brazil's Rio de Janeiro State has been accumulating sediment at a rate of approximately 1.7 mm/y for about 100 years. Inputs of marine organic matter have been minimal. Geological stability means that the land is not subsiding and so the accumulation rate has kept pace with the sea level rise (Sanders et al. 2008). In many regions, the response of natural systems is expected to be coastal retreat and the landward expansion of estuaries.

The landward expansion of estuaries will not be a welcome development. Estuaries along the coast of the United Kingdom are already experiencing what has been described as the "coastal squeeze." While the shape of an estuary governs whether it will retain or export sediment, the area immediately beyond the water's edge also plays an important role. This area is known as the "accommodation space." Larger than normal waves and periodic storm surges invade this space where their energy is dissipated. Less energetic water carries less sediment so that an estuary with a large accommodation space becomes a sediment sink. The coastal squeeze results when the accommodation space is reduced by seawalls, navigation canals, or other barriers. This results in the wave energy being redirected back out to sea and carrying sediments along with it. Estuaries are not the only areas affected by hard coastal defenses such as seawalls. Seawalls and other types of hard defenses can also rob beaches of the replacement sediments that would normally be furnished by erodible cliffs or interior sand deposits (Morris 2012).

The coastal squeeze is only one example of what can happen when the irresistible force of inland-moving estuaries and rising seas encounter immovable objects in the shape of existing roads, housing, and other human structures. The historic response to this has been the construction of sea walls and other hard defenses. The advantage of this approach is that despite high initial costs, the benefits are immediate (Andrews et al. 2006). Another advantage identified by Morris (2012) is been that constructing or maintaining hard defenses is politically popular, especially if managed coastal realignment is seen by the public as retreat. In the aftermath of Hurricane Sandy, a number of coastal towns in New Jersey are actively considering seawalls to protect their boardwalks.

Using sediment to protect coasts through soft defenses operates over longer time scales but confers multiple benefits. Andrews et al. (2006) states that it is cost effective only when considered on timescales of 25 years or more. Following the progress of biological re-colonization of constructed soft defenses through biomarker analysis may be a useful application of Py-GC/MS. The benefits of soft defenses are made clear by life cycle analysis and they include water purification by aquatic plants, habitat creation, and carbon sequestration. From the viewpoint of coastal communities however, the most important benefit is the dissipation of wave energy (Morris 2012).

If sea level rise complicates sediment management from the water, then population pressure will complicate it from the land. It is well known that the much of the world’s population lives near the coast and that the proportion doing so will increase in the future. The first coastal systems to suffer adverse environmental impacts from population pressures are estuaries (USEPA 2009). They are among the most threatened ecosystems in the world as they are vulnerable to damage from eutrophication, sediment starvation, polluted runoff, freshwater diversion, invasive species, and human encroachment (Kennish 2002). These threats are especially acute in urban areas.

Even in countries where the importance of these ecosystems is understood and appreciated, threats persist. An example is Australia’s Gulf St. Vincent near Adelaide in the State of South Australia. This coastal ecosystem includes diverse habitats, tidal wetlands, sea grass meadows, mangroves, and saltmarsh. Approximately 95% Adelaide's population lives near this estuary system and depends upon it for commercial and recreational fishing, tourism and aquaculture. Yet the coast remains under threat from coastal development, storm water runoff, and industrial discharges with a consequent and the water quality decline and contamination of the food-chain (Edyvane 1999). In the United States, the Gulf Coast contains approximately 41% of the nation’s remaining wetland habitat. Despite legal protections this region is subject to the same threats. Harmful algal blooms resulting from eutrophication are well documented in the region (Steffen et. al 2010).

Aside from the sediment starvation already discussed, rising populations will have several effects on sediment management. In coastal and river cities, there will be increasing amounts of contaminated street runoff, sewage, and industrial activity. As construction and agricultural activities increase in the upland regions there will be increased sediment loadings from erosion. Expanding trade will mean larger ships with greater drafts that require deeper navigation channels.

As of 2006 approximately 90% of global trade moved by sea in a fleet of 45,000 oceangoing merchant ships. American ports are handling 2 billion tons annually and this was expected to double by 2020 (Sharma 2006). The expansion of the Panama Canal is expected to be completed by 2015 and container ships with 50-foot drafts and capacities of 12,000 containers will begin using the world's seaports.

All of the issues related to coastal population growth are under active investigation but at the moment the most intensely investigated topic is sea level rise and how it relates to the future of coastal cities. Understanding sediment dynamics in those coastal cities is an area where there are many opportunities for original research.

Conclusions

"Success is not final, failure is not fatal: it is the courage to continue that counts."
Winston Churchill

Sediment management is an ongoing process.

Sediment management is a mature field with a deep base of both theoretical and applied knowledge. There have been many success stories with RSM, beach replenishment, habitat restoration, and coastal defenses. It is fair to say that many aspects of the field have become routine.

All of the previous statements are true as long as they are describing uncontaminated materials.

When dealing with urban sediments, in the short term, the greatest obstacles are political. They include a lack of interagency cooperation, uncertain risk assessments, and ineffective engagement with both local stakeholders and responsible parties. There are abundant technical solutions but little apparent progress in moving beyond “dredge and dump.” It is hard to predict what form the political solutions may take. Certainly, Norway’s Sediments and Society initiative may prove an effective model but there remain unresolved issues. In the United States the most obvious sediment management problem is long project timelines. These are due at least in part to the limitations of the Superfund process at it applies to sedimentary systems. Risk-based remediation holds some promise for reducing project timelines but there has been little apparent progress in overcoming political opposition to this approach. Even various beneficial and innovative reuse scenarios face their own political obstacles although at first glance they would appear to be purely technocratic solutions. Embracing a life cycle anslysis mind set and appreciating that there will be limitations on both CADF cell and landfill capacities, may provide the impetus for creating integrated and sustainable sediment management systems.

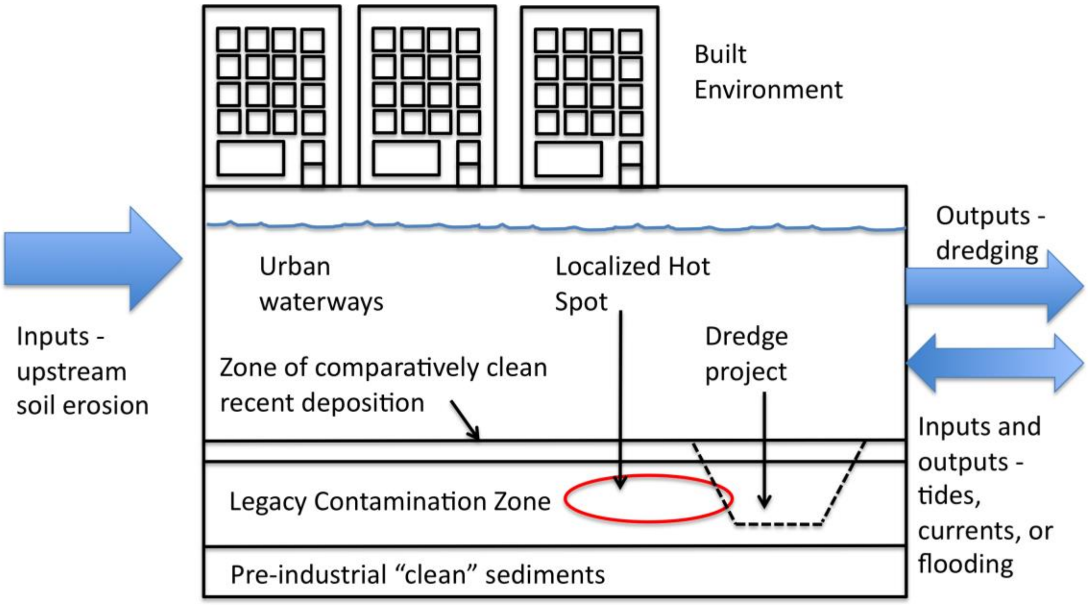
Looking at the long-term future of contaminated sediment management it is clear that as sea levels rise, having sustainable source of dredged materials for coastal defenses and habitat restoration will become increasingly important. Widespread adaptation of advanced treatment technologies may no longer be a luxury.

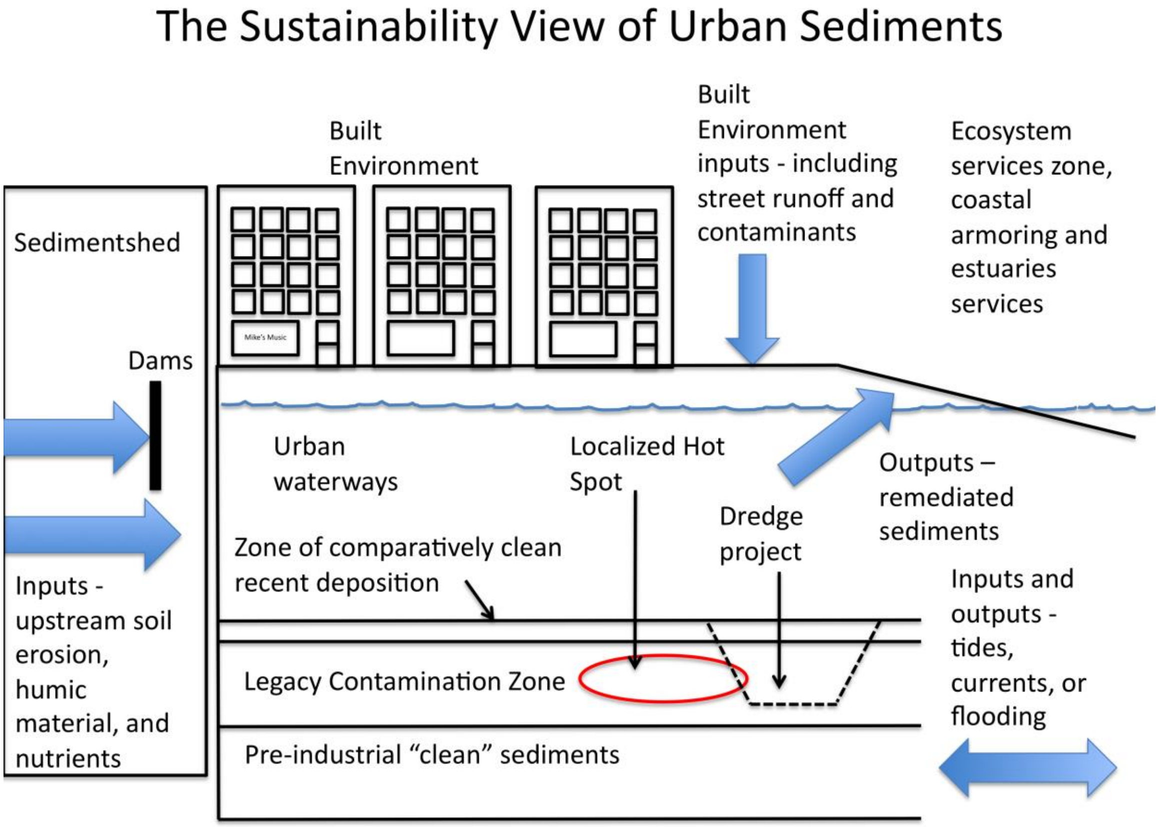
The selection of sediments for use in various beneficial projects is now chiefly a function of grain size. In the future we may see equal attention paid to nutrient content and humic substances so that sediments sources are more closely matched to specific habitat needs. In an ideal world, the materials required for a specific habitat or coastal estuary restoration project might be blended from a mixture of sources. These might include decontaminated dredged materials, sediments from upland reservoirs, and additives selected for organic carbon, trace nutrient, hydraulic conductivity, or other characteristics.

As long as there have been people living by the seas, there have been challenges of sediment management. In today's rapidly changing world, the challenges are greater than ever before but the incentives to create a sustainable management system are greater as well.

Figures and Tables

The Simple View of Urban Sediments





Figures 5-1 and 5-1a. A simplified diagram of how urban sediments are traditionally viewed and what how a system of sustainable sediment management would be different.

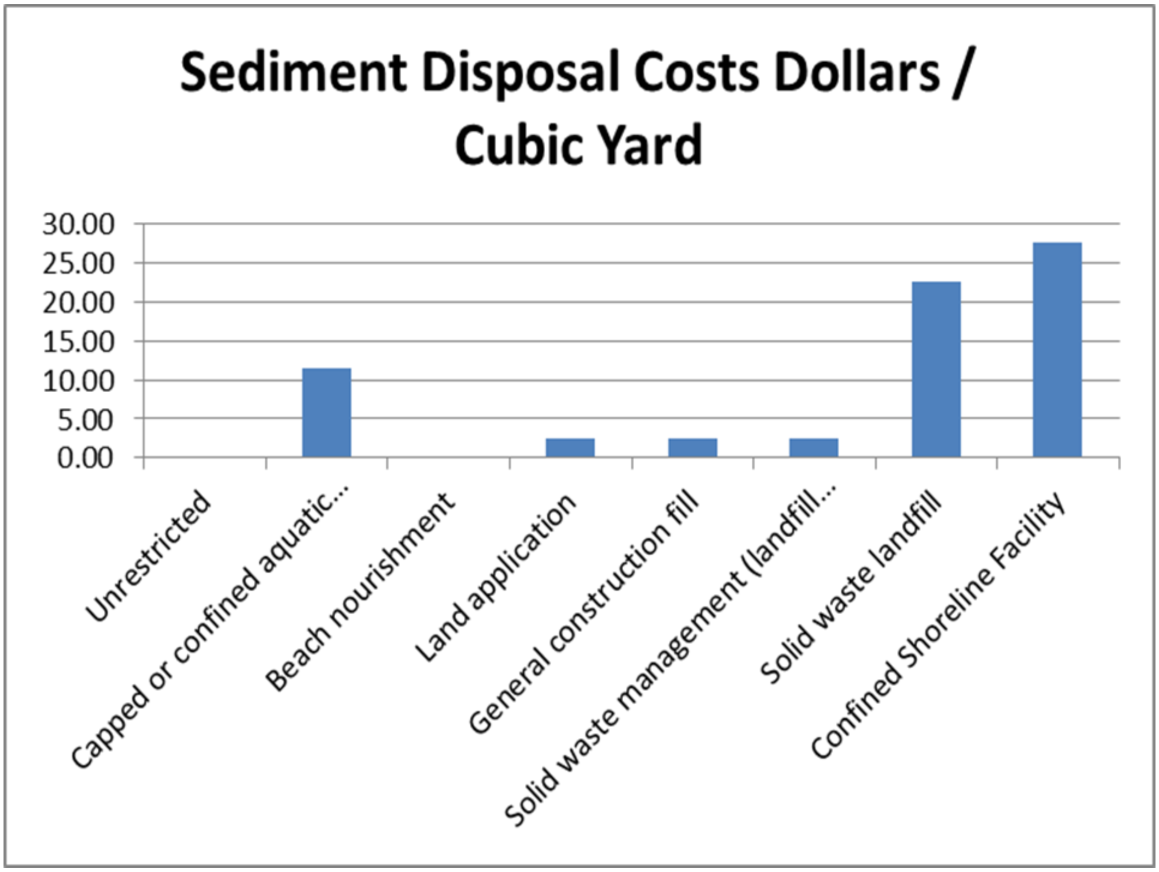


Figure 5-2. The costs of sediment disposal options. Costs rise with increasing amounts of contamination that demands increasingly stringent disposal mechanisms. If the sediments must be handled as RCRA wastes the cost of disposal can average $175.00 per cubic yard. If the sediments meet TSCA criteria, the average cost can rise to $250.00 per cubic yard. The data is from the US Environmental Protection Agency. ARCS Remediation Guidance Document, EPA 905-B94-003, 1994, table 8-4.

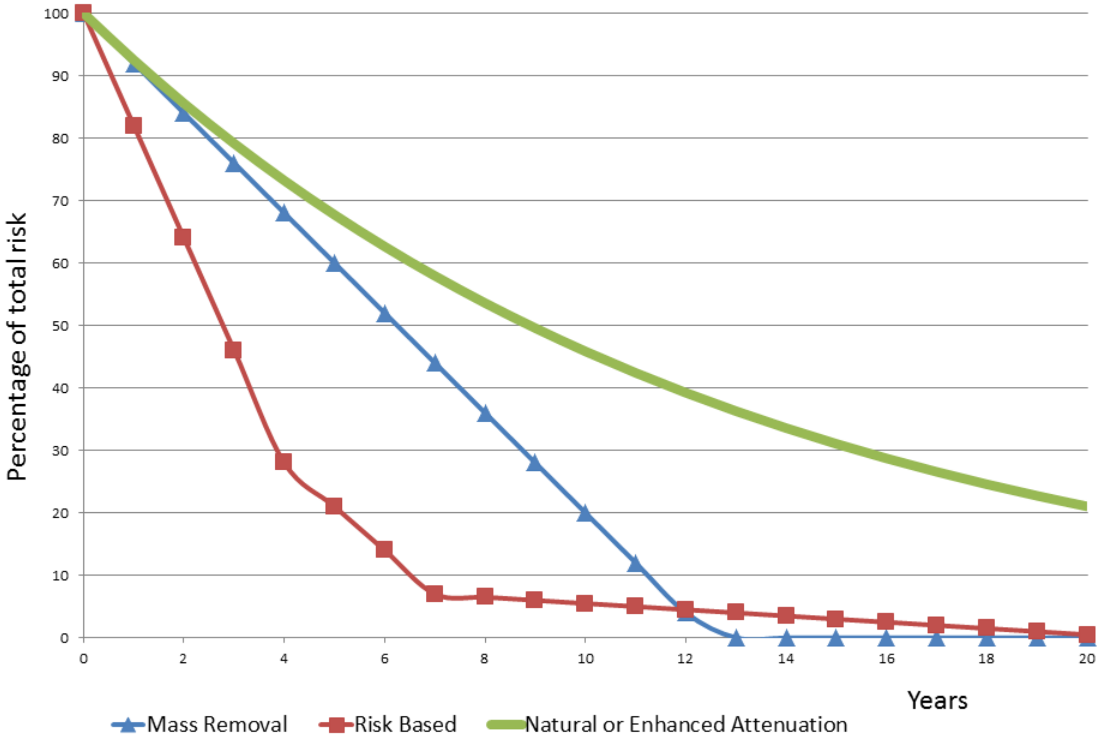


Figure 5-3. An *idealized* risk assessment approach. Mass removal reduces the overall risk in a linearly decreasing trend. The risk assessment approach is a series of distinct steps that are each designed for maximum risk reduction. Note that this approach reduces the total risk much earlier than the more linear mass removal approach. If natural or enhanced attenuation is the selected option, the risk would decrease but on a much longer timescale. Meanwhile, the actual and external costs of dealing with the problem are increasing. In actual practice, mass removal actions are prioritized based on risk so that the actual decline would more closely resemble that of the risk assessment approach.

Table 5-1, A study prepared for the US Navy on dredging costs included the following figures in dollars per cubic yard for various material handling options.

Dredging alone (no treatment)	<$10
Pretreatment options:	
Air drying (passive)	$4 to $7
Filtration	$8
Centrifuge	< $8
Gravity thickening	<$8
Size separation, dewatering and wastewater treatment	$15 to $75
Decontamination Options:	
Thermal desorption, incineration, vitrification,	$110 to $1,350
Sediment washing	$81 to $330
Solidification/stabilization	$81 to $392
Biopile/composting, phytoremediation	$20 to $270
Landfill and Confined Disposal Options	
Commercial landfill	$30 to $300
On-site landfill	$3 to $20
Confined disposal facility (CDF)	$15 to $50
Confined aquatic disposal (CDF)	>$50

(Figures from: Contaminated Sediments at Navy Facilities: Cleanup Alternatives, TDS 2092-ENV, TechData Sheet, Naval Facilities Engineering Command Washington, DC 20374-5065, December 2002)

Table 5-2.The USACE, Mobile District developed seven principles of RSM.

1. Recognize sediment as a valuable resource that is integral to the economic and environmental vitality of the area. Evaluate the use of all sediment resources for implementing sound RSM practices.

2. Seek opportunities to implement RSM practices and procedures to improve sediment management. Strive to achieve balanced, sustainable solutions to sediment-related issues.

3. Coordinate with project partners and stakeholders when evaluating, formulating, and implementing RSM plans, practices, and procedures. Partner with stakeholders to balance objectives and leverage resources.

4. Make local project decisions in the context of the sediment system and consider the regional implications beyond the local site, beyond project-intended effects, and over longer time scales (decades or more). Evaluate the impacts of individual projects on adjacent projects and the regional system.

5. Integrate a systems approach to management of sediment from upland sources, through river systems, into estuaries, and along coastal regions. Apply RSM principles to the entire watershed and include watershed impacts in the evaluation of coastal projects.

6. Monitor projects to evaluate the physical, environmental, and social impacts at the local and regional scale. Seek opportunities to improve project efficiencies and minimize negative impacts.

7. Apply technical knowledge, tools, and available resources to understand the dynamics of local and regional systems prior to and following actions to improve management of sediment.

Source: Byrnes and Berlinghoff 2011.

Table 5-3. Members of the Lower Willamette Group

Arkema Inc. (priority area former pesticide mfg facility, land cleanup began in 2012)
Bayer CropScience, Inc.
BNSF Railway Company
Chevron U.S.A., Inc.
City of Portland
EVRAZ Oregon Steel Mills
Gunderson LLC
Kinder Morgan Liquids Terminals
NW Natural Gas
Phillips 66 Company
Port of Portland
Siltronic Corporation
TOC Holdings Co.
Union Pacific Railroad Company
Source: USEPA, Portland Harbor Superfund Site,
http://yosemite.epa.gov/r10/cleanup.nsf/sites/ptldharbor, accessed April 1, 2013

Table 5-4. Key milestones for the Portland Harbor Superfund project.

2000 to 2010	Research, sampling, and analysis
2011	Remedial investigation and risk analysis
2013	Draft feasability study
2014	Expected date when cleanup plan will be ready for public comment
2015	Record of decision

Source: USEPA, Portland Harbor Superfund Site,
http://yosemite.epa.gov/r10/cleanup.nsf/sites/ptldharbor, accessed April 1, 2013

Part Two

Case Studies in Environmental Management

Case Study 1
Jamaica Bay and the New York City's Waste Management Infrastructure.

Abstract

New York City's sanitary reforms of the 1890s were a significant because for the first time in the city's history every street was cleaned and all neighborhoods had regular trash collection. Critical to the success of the reforms was a system of waste disposal. Since the 1850s, companies on Brooklyn's Barren Island, in the western portion of Jamaica Bay, converted offal and animal carcasses into grease and fertilizer. This system was expanded to accommodate the waste flows created by the city-wide sanitation reforms. The industry was established when Barren Island was unpopulated and isolated but the eastward growth of the city made the waste industry increasingly unwelcome even as the city depended on it for financing trash collection. These industries illustrate the importance of having an effective waste management technology, a market for recovered materials, and an isolated location for processing operations.

Intoduction

In the 1800s New York City was never a particularly clean place. The Common Council had the authority to oversee sanitary conditions since the start of the century. (Burrows, Gotham, page 588) But enforcement of the sanitary laws was infrequent at best. By the 1830s heaps of mud, rotting food, and animal excrement piled up on the streets forming a foul mass dubbed "Corporation Pudding." To this mass were added the waste streams from tanneries, slaughterhouses, dyers, distilleries, glue works, bone boilers, and stables. In the absence of regular garbage collection pigs were allowed to roam the streets and convert at least a portion of the wastes to food (Burrows and Wallace 1998, 588).

Although the city had a master plan, there was no effective planning authority. (Spann page 160). While individual neighborhoods might protest against the presence of slaughterhouses, stables, bone boilers, and other nuisances, the protests were usually ineffective. In such disputes the city government tended to side with property owners and merchants (Spann page161).

An 1832 cholera epidemic swept through Europe and fears that it would cross the Atlantic lead to a call by the city's Medical Society to establish a system of emergency hospitals and begin disinfecting cesspools and privies using quicklime. They also called on the city government to clean up the streets, yards, and vacant lots (Burrows and Wallace 1998, 590). Although the Medical Society represented two-thirds of the city's practicing physicians, the city government largely ignored their suggestions. In writing about the 1832 outbreak Burrows and Wallace assert that the city government believed that the outbreak would bypass the "virtuous parts of town and descend, like God's wrath, on the sin-infested quarters" (590). By June 15th word reached the city that cholera has crossed the ocean and had broken out in Montreal and Quebec. The first confirmed cases in the city were reported by the end of June (590). About half the population, an estimated 100,000 people eventually fled the city. A total of 3,513 persons died during the course of the epidemic, mostly in the poorer neighborhoods (591) During the epidemic, the city's Bellevue Hospital admitted 2,000 cholera patients of which about 600 died (592).

Eventually the Board of Health took the lead in fighting the epidemic. The clothes and bedding of the sick were taken out and burned. Streets were swept clean as were the vacant lots, docks, and other places where years of filth had accumulated. Working people laid off in the epidemic were paid to clean their dwellings. The city's wealthier citizens established soup kitchens, and set up a system for distributing food and clothing (Burrows and Wallace 1998, 591). In August the number of new cases began dropping and by the 29th medical authorities declared the city safe (593).

After the epidemic subsided, the physicians, civic leaders, and the clergy took stock and tried to make sense of the event. They had little information to go on. It would be another decade and a half before Dr. John Snow of London (1813-1858) would firmly establish the link between contaminated water supplies and the spread of cholera. The first edition of his groundbreaking *On the Mode of the Communication of Cholera* was published in 1849 and an expanded edition came out in 1855. The germ theory of disease would not be well established among the medical community for another five decades (Olsen, 2011). About the only thing that could be said with any certainty was that the disease struck most often in the poorest and dirtiest parts of the city. Opinion was divided as to whether the disease was divine retribution for slovenliness, breaking the Sabbath, indulging in drink, or some other vice. An only slightly more charitable view held that the poor were naturally slovenly and thus brought the disease on themselves (Burrows and Wallace 1998, 593).

The majority of these explanations allowed affluent New Yorkers the comforting thought that the poor had largely brought the disease on themselves and therefore they had little to fear from any future epidemics.

In New York City of the 1800s the filth and mess on the streets was about as evenly distributed as the city's wealth. The more affluent residents paid for regular garbage collection, street sweeping, and frequent privy cleaning. (Nagel, MSU lecture, 2010)

Cholera broke out again in 1848, and after 5,000 deaths, the calls for sanitary reform could no longer be ignored (Burrows and Wallace 1998, 786). What was worse, this time the disease was spreading beyond the slums and infecting both rich and poor alike. On Friday, July 13, James Reyburn, a well-known 55-year old cotton broker and Wall Street lawyer began exhibiting the first symptoms cholera. Despite the efforts of his physicians Reyburn was dead by Saturday night. Reyburn was well known and respected in the city and his death threatened to set off a panic. Newspapers reported that several of the recent cholera victims were members of the "respectable classes, including even ladies" (Miller 2000).

One of the most far reaching reforms after the outbreak was the construction of a sewer system. The city's Croton Aqueduct Department had recently been reorganized so that they would also be responsible for sewer construction. The city had spent millions to build the original aqueduct and having satisfied its responsibilities to provide drinking water, balked at the cost of providing sewers (Spann, n.d., 133). For many years the city saw the purpose of what few sewers it did have as carrying off rainwater and not human wastes. Tubmen, the workers who emptied the privies, were specifically prohibited from placing wastes into the sewers and in 1819 the Common Council went so far as to require grates installed on the sewers to keep fecal matter out (Burrows and Wallace 1998, 589). In the wake of the outbreak however the situation changed. Between 1850 and 1855, 70 miles of new sewers were laid. It was only a start. In 1856 the city had 500 miles of streets and in a city of 600,000 people there were only 10,384 water closets and a mere 1361 baths (Spann n.d., 133).

There were numerous other sanitary reforms in the wake of the epidemic. The city seized up an estimated five to six thousand hogs from individual homeowners. Another 20,000 hogs were driven to the still undeveloped northern parts of Manhattan. Bounties were paid for stray dogs and 3,520 were killed mostly by club-wielding boys. The reform with the greatest impact on the future of Jamaica Bay was the decision in 1851-2 to banish all bone boiling works from Manhattan. (Burrows and Wallace 1998, 786)

In 1850 it was estimated that New York had 748 places where there was a "greater or lesser amount of animal matter undergoing decay." These places included 206 public markets, 11 slaughterhouses, and 531 butcher shops (Spann n.d., 129).

The state of private abattoirs on Manhattan Island was described by Mary Trautmann of the Women's Health Protective Association in 1898. The association was formed in 1884 by eleven women from the exclusive Beekman Hill neighborhood overlooking the East River. The association took on the problem of foul air in their neighborhood. They did not have to look far for one of the causes, 20,000 tons of manure were stored by a one Michael Kane, a fertilizer dealer whose brother-in-law was a State Senator. The women brought Kane to court and unlike previous efforts to force Kane to remove the manure, they would not be ignored (Trautmann, *Women's Health Protective Association, Municipal Affairs*, vol.2, no.2, June 1896).

The Association next toured the private abattoirs in an area known as the "Abattoir District" along First Avenue from 43rd to 47th streets. The earlier legislation that moved bone boiling and rendering works out of the city only covered the southern part of Manhattan Island. The abattoir operated by Rafferty and Williams had 55 "dirty little pens." The slaughtering was done "in the presence of children" who stood by and watched the entire process. The walls and floors of the pens reeked with filth. The meat was hung on hooks over the curbs, exposed to swarms of flies, and whatever dirt and dust was swirling in the air. Animals awaiting slaughter were kept in basement pens, often crawling over one another to reach the gratings and a breath of fresh air (Trautmann, *Women's Health Protective Association, Municipal Affairs*, vol.2, no.2, June 1896).

The odors from the bone boiling works were described as "overpowering." One of the problems was that bones were not collected on a regular schedule and those that had been awaiting collection were often putrid. The simple expedient of requiring bones and offal to be collected and processed daily was enough to eliminate the problem (Trautmann, *Women's Health Protective Association, Municipal Affairs*, vol.2, no.2, June 1896).

The Waste Industry Moves to Barren Island

City Inspector Alfred White established a franchise system to handle the city's waste in 1849 and using a dummy partner as a front, arranged for himself to have a monopoly on waste disposal. He and co-owner William B. Reynolds selected Barren Island in the east end of Jamaica Bay as the site of a plant that would turn the city’s putrescible waste products into grease and fertilizer (Miller 2000).

Shortly before the 1870s the firm of P. White's Sons won a contract with the Board of Health for removing dead animals from the streets of New York. The primary product of the company was the products of the rendering process. In one five-day period in August of 1896 the company removed 1,256 dead horses from the streets of New York. The company had its own pier on the Hudson River and two steam boats to carry carcasses to Barren Island (“To Use New York Garbage”, *New York Times*, Sept.27, 1896).

If the nuisances were removed from the city, they were still smelly and disease-breeding. In 1870 an unidentified writer in *Punchinello* noted that the New York Rendering Company, which at the time was located near the Hudson River, was an odiferous nuisance to its neighbors. In the summer months the odors drifted over the river and enveloped the excursion boats filled with passengers seeking relief from the city. The writer stated that the rendering company's vats were kept filled by the dead horses from the street railway companies. New York Mayor Abraham Hall (1829-1898) made a complaint against the company and an indictment was expected from the grand jury in the early fall of 1870. The writer hoped that the "boiling nuisances" would soon be seized and that the company would soon "render up the ghost, and go out sputtering, like a dip candle from one of their own rancid renderings – and so an end of them." The writer it should be noted, did not propose an alternative disposal site or method (*Punchinello* 1870).

Moving New York's waste processing industries to Barren Island solved the problem of recycling organic wastes but did not solve the problem of the odors that the industry created, it only shifted them to Jamaica Bay. As the bay became increasingly popular as a tourist destination and population grew in the surrounding communities, the odors associated with Barren Island were growing increasingly unwelcome. The *Brooklyn Daily Eagle* reported in August of 1899 that steamboat passengers on Jamaica Bay were exposed to a belt of smells from horse-boiling works, menhaden oil works, offal baking works, and garbage drying plants (“Barren Island”, *Brooklyn Daily Eagle*, Aug. 14, 1899).

For the first fifty years, the city concentrated on using the waste recycling process to dispose of animal carcasses, butcher's offal, and slaughterhouse wastes. It was not until 1897 that the city attempted to collect all food wastes from home and commercial kitchens, markets, butcher shops, slaughter houses, hotels, and restaurants and recover marketable products from them (Waring, “Great Business Operations III, the Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405).

The grease recovered had a number of important industrial uses. Tallow was used in leather tanning, as a lubricant, and in the manufacture of soap and candles.

Making good quality candles careful preparation of the tallow. The first step was rendering the animal fat. Rendering fat was simply melting it in a vessel for two or three hours. It was then passed through a sieve. After being allowed to cool, the remaining solids were separated out. The mass was loaded into a perforated pail and the tallow squeezed out by use of a screw press. The remaining solids were often used as swine food while the tallow was re-melted and became purer and whiter (*Manufacturer and Builder* Oct.1873, 235).

Processing animal fats for soap manufacture used a slightly different process. In addition to animal fats, coconut oil, palm, and olive oils were widely used. A number of improvements on the basic rendering process were in use by 1870. The Wilson Process used a sealed tank. The typical tank was an upright cylinder holding 1200 to 1500 gallons with a pipe for the admission of steam. Valves allowed condensed steam and the processed fat to be drawn off. The tank was loaded through a manhole at the top. Suet was steamed at 50 psi for up to 15 hours. More time was required for processing lard. The residual material in the tank was reported to be rich in nitrogen and phosphorous and it was probably sold for fertilizer (*Manufacturer and Builder* Aug.1870, 232).

Residual water in process often contained dissolved remnants of the original animal tissues. These were subject to bacterial decay and caused the processed fats to have an unpleasant odor. These impurities were removed by subsequent washing steps (*Manufacturer and Builder* Aug.1870, 232).

During the 1800s it was important to recycle food waste products back into fertilizer because without massive inputs of nutrients the sandy soils of Long Island would not have been able to sustain a large urban population. While some food stuffs such as grains could be transported long distances, until the twentieth century, there was no technology that could fresh fruits and vegetables from distant farms. Recycling the city’s organic waste products; food scraps, offal, night soil, manure, dead animals, and bones allowed the farmers on Long Island to use twice the amount of fertilizer as farmers in other parts of the country. It also removed smelly, disease-breeding nuisances from the city.

Despite competition from western corn, wheat, and cattle, farming in the New York and New Jersey regions increased dramatically. Between 1840 and 1860 the value of crops produced in region's market gardens for urban consumption increased by eight times.

Tomatoes, asparagus, cabbages, cauliflower, peas, beans, carrots, and potatoes flowed into the city by boat, market wagon, and railroad (Spann n.d., 122).

A number of persons pointed out the tremendous waste of resources that discharging sewage into the oceans represented. At an 1853 meeting of the City Farmer's Club, Robert Ellis of Ulster County, claimed that in one year, the sewage that New York City discharged into the oceans contained enough nitrogen to raise 180 million pounds of wheat (Spann n.d., 30).

It was not however, that New York was neglecting this resource. The city's night soils were sold to fertilizer manufacturers like the Lodi Manufacturing Company of New Jersey. As early as 1840 the Board of Aldermen was advocating new railroad construction so that the market for manure would be expanded (Spann n.d., 131). The city realized considerable amounts of revenue through the sale of manure. In 1845 the proceeds reached $45,000 (460). But as the supply increased, the price went down. In 1856 there were 22,500 horses pulling just the public conveyances such as omnibuses, streetcars, and cabs. The number of horses kept for private carriages and wagons was uncounted (129). By 1857 the revenues from the sale of manure disappeared completely (460).

Municipal studies from the Department of Sanitation in 1889 and the office of the Mayor 1894 concluded that large scale refuse combustion was both uneconomical and unproven.

Early experience with this technology (at the time employing mostly low-temperature combustion under 675 C) supported these conclusions. Staten Island's three-year old municipal incinerator was closed by court order in 1898 after repeated complaints about the odors. The incinerator which replaced it failed after only one year. Of 180 waste incinerators built in the United States after 1885, 60% were closed by 1908. Once high temperature burn technology became available after 1908, 200 successful incinerators were in operation within ten years (Walsh, "Incineration, What Lead to the Rise and Fall of Incineration in New York City?", *Environmental Science and Technology*, Aug.1, 2002, vol.36, no.15, 317A – 322A).

Waste Reduction and the Future of City Garbage

It was the threat of disease and the nuisance odors from putrescible food wastes that continued to dictate the city's waste management policies. In 1896 the city adopted waste management laws that would feed the plants on Barren Island a seemingly inexhaustible stream of waste (figure CS1-1). It became mandatory for householders to separate moist food wastes, rubbish (defined as dry wastes), and ashes. Writing in 2002, Daniel C. Walsh of Columbia University concluded that this decision delayed New York City's adoption of incineration technology for at least three decades (Walsh, "Incineration, What Lead to the Rise and Fall of Incineration in New York City?", *Environmental Science and Technology*, Aug.1, 2002, vol.36, no.15, 317A – 322A).

The problems with incineration were obviously well known among the public and seem to have preceded their construction. In 1896 some of the bidders for garbage removal contracts in Brooklyn announced that they would build an incinerator on Barren Island. In response to this announcement, the Citizens' Association of Flatlands announced that it would take legal action to prevent construction of an incinerator on Barren Island, or "anywhere within smelling distance of the homes along Jamaica" (“Object to Cremators Near Them”, *New York Times*, Oct.14, 1896).

Writing about the relative merits of incineration, or as it was known at the time, cremation, George E. Waring did note that incinerators had lower labor costs since they required fewer operators (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405). The American and English experience with incineration were very different. English operators generally succeeded in running their incinerators at a higher temperature. Observers at the time attributed this to two factors, the use of soft coal for heating, and secondly that the English diet had fewer vegetables. When fireplace ashes were comingled in the waste stream the un-burnt chunks of coal provided significant extra fuel. Fewer vegetables in the waste streams meant less water in the incinerator.

Tests of incineration technology by the City of New York showed that regardless of the operating conditions there was always some unburned vegetable matter and even unburned paper (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405).

Having settled on waste reduction, the city had to choose between several competing waste reduction companies and each had a slightly different process. The Pierce and Merz companies used a mixture of steam and light hydrocarbons in a tightly closed vessel to extract the usable grease. The Merz system was used in Buffalo and Saint Louis it used a mixture of benzene and naptha for the extraction. The Pierce process used only naptha.   The Arnold, Holthaus, and Preston companies used processes were described as being "purely mechanical" and used no naptha (Waring, "Great Business Operations III., The Utilization of City Garbage", *Cosmopolitan*, vol.24, 1898, 405).

After a careful examination of companies using each of these competing technologies, the city decided that steam without naptha extraction would be adequate for the city's needs and invited bids for the new waste reduction plant. In the first round of bidding Arnold bid $169,000, Holthaus $175,000, and Merz $144,000. At the next round of bidding Merz did not lower its bid, Holthaus dropped out, and Arnold lowered its bid to $89,990. Arnold thus won a five year contract that would require them to build the largest waste reduction plant in the world. The $89,900 that would be paid by the city each year was estimated to be approximately equal to what it would cost the company for the barge transport of garbage between Manhattan and Barren Island. The Arnold Company would make its profits entirely from the sale of grease and tankage. At the time that the contract was awarded, the plant was expected to receive about 600 tons of garbage every day. Since the price crude grease was 3 cents per pound and tankage was

$6 a ton, the Arnold Company could expect to make $1,000 a day from grease and another $600 from in tankage. Shortly after the contract was awarded the price of grease dropped to 1.5 cents per pound but the volume of garbage increased and it was hoped that these two trends would cancel each other out and the company would continue to make money (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405).

The technology of waste reduction was fundamentally no different than that used for rendering but had to be scaled up if it to process the garbage of an entire city. By 1900 the waste reduction works were recovering 1000 tons of marketable grease every day and 1500 tons a day at peak times. A report made to the Institute of Civil Engineers said that the 48 digesters each had a capacity of 10 tons, stood 14 feet high, and had a diameter of 5' 6". The bottoms of the digesters were conical and the top were dome-shaped. The digester was first filled with water to a depth of three or four feet and then filled with garbage. The hatches were closed and steam was admitted into the jacketing. This raised the temperature inside to boiling and the pressure was allowed to stand at 30 to 80 psi for eight hours (“The Barren Island Garbage-Reduction Works, Greater New York”, *The Institution of Civil Engineers*, Sess.1889-1900,Pt.III, Sec.1, Feb.6, 1900, 389).

After digestion the tankage was pressed to remove the last amounts of recoverable grease and any residual water. On Barren Island the tankage was loaded in thin layers into crates that were surrounded by gunny sacking. The stack was pressed at 240 tons of pressure although it is not recorded how this pressure was achieved, with hydraulics or some system of gears and screws (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405) (figure CS1-2). After pressing, the tankage was sent into driers, large steam jacketed cylinders equipped with revolving arms that kept the material stirring. The fumes from the driers were a source of noxious gasses and were not easily destroyed. A combination of a water spray, heated retorts, and finally a tyre directed them into the "hottest part" of the furnace that supplied heat for the steam boilers (405). However Waring admitted that some gasses remained and as will be seen complaints about the waste processing plants on Barren Island would continue for some years (405).

The residual liquids squeezed from the tankage were described as being a "dark-colored caramel refuse" was piped into the Rockaway Inlet. Waring claimed that the discharge could "do no harm whatsoever" because the volume was small compared to the tidal currents. However it was possible to trace the effluent 100 feet back to the discharge pipe by its color (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405). Waring may well have believed that the effluent was harmless but his attitude is somewhat naive. The effluent pipe would have sent the discharge toward Coney Island when the tide was going out, and towards Rockaway and Canarsie when it was flowing in. The ultimate solution was to send the liquid to an evaporator so that the water would be boiled off and the thick, organic-rich remainder added to the tankage (405).

In scaling up rendering technologies for waste reduction one of the most important changes was the adoption of improved material handling technologies so the barges would be unloaded faster (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405) (figure CS1-3).

Looking forward to the future of the industry Waring predicted that a system of continuous pressing would need to be adopted along with other labor saving machinery so that a city as small as 50,000 persons might profitably operate a waste reduction plant (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405).

The waste reduction system conceived by the City of New York was only valid for food wastes "garbage" and left the other waste streams, street sweepings, ashes, and "rubbish" untreated. "Rubbish" was generally defined to mean items like paper, rags, bottles, and cans that could be recycled. In the mid-1890s New York generated 950,000 cubic yards of waste rubbish annually. The city was offered $245,000 dollars annually for the privilege of culling this waste stream. The cost of culling this material was estimated to be $6,000 annually for every 50,000 city residents (Waring, “Great Business Operations III., The Utilization of City Garbage”, *Cosmopolitan*, vol.24, 1898, 405) (figure CS1-4).

The requirement for sorting garbage came just before the opening of the garbage reduction plant of the New York Sanitary Reduction Company. The company had been incorporated in New Jersey with $1,000,000 in capital. The New York Sanitary Reduction Company would have a five-year contract with the city. The President was David Martin, a famous Philadelphia political boss, the Vice President was Thomas F. White of New York, Secretary William W. Gooch, and the treasurer was W.V. Cranford who was affiliated with a Brooklyn contracting firm. Vice President White was co-owner with his brother Andrew J. White in the firm of P. White's Sons. P. White's Sons already had a large plant on Barren Island. The company was the largest landowner on the island and its largest employer. At the time that the New York Sanitary Reduction Company was founded P. White's Sons had already signed contracts with a number of the city's leading hotels for the removal of garbage ("To Use New York Garbage", *New York Times*, Sept., 27, 1896).

The plant of the New York Sanitary Reduction Company was designed with 48 cylindrical cooking vessels, each one five feet wide by fifteen feet high. Steam for cooking the garbage was let into the tanks from a pipe at the bottom. Each tank could hold six tons of garbage and operating three cycles each 24 hours the total capacity of the plant was 864 tons. The tanks were capable of reaching a temperature of 300 F. They were designed with openings at top and bottom. They were loaded at the top from conveyors that brought the garbage from the boats. The cooked materials were dropped out the bottom opening and into a sheet-iron receiving tank. Water would then drain out the bottom of the tank. At this point the garbage should, in theory at least, be odorless.

Any noxious gasses released during the heating cycle would be captured and sent into the steam boiler's firebox. The cooking process was also expected to kill bacteria. The receiving tanks in turn emptied their contents into bags about 30 inches square which were then closed and stacked in one of 12 screw press each about four feet square. Pressing removed the last of the grease and waster. The grease was sent for washing with water to remove impurities while the dry tankage was sent to driers (“To Use New York Garbage”, *New York Times,* Sept., 27, 1896).

The first step in the process was a trip on a tram car to the drying house. The tankage was dumped into a pit where a masticating machine kept it stirred. There were more than a dozen driers. These were steam-jacketed horizontal tanks, 16 feet long with stirring arms attached to a rotating shaft. The drying operation lasted three to six hours. When the moisture content reached 10% the tankage was screened before being bagged for sale as fertilizer (“To Use New York Garbage”, *New York Times,* Sept., 27, 1896).

At the time that the New York Sanitary Reduction Company plant was opened, New York generated about 800 tons of garbage each day. There was obviously little or no excess capacity so landfilling and ocean disposal would continue to be used (“To Use New York Garbage”, *New York Times,* Sept., 27, 1896).

In writing about the new plant the New York Times took pains to reassure its readers that the plant would not be a problem for the city. Barren Island was "so remote" that "few

New-Yorkers would know how to find it." Works of this type, so readers were assured, when properly operated would not produce offensive odors. It seems not to have occurred to the writer in the *Times* that Barren Island was only a short distance from Coney Island, Rockaway Point, and Canarsie (“To Use New York Garbage”, *New York Times*, Sept., 27, 1896).

When reduction plants joined the rendering works in the mid-1890s, a whole new class of public nuisance was introduced to Jamaica Bay. When the New York State Department of Health held hearing on reduction plants in 1916, the report identified twelve reasons why garbage reduction created nuisances. These are listed in table 1.

In 1899 it was reported that the plant managers did attempt to make the process less odiferous. Refuse was unloaded from the scows quickly and brought immediately into the plants instead of being allowed to pile up on the docks. The processing technology was described as being "quick and thorough" and deodorizing compounds were freely used (“Barren Island”, *Brooklyn Daily Eagle*, Aug.14, 1899).

An editorial in the *Brooklyn Daily Eagle* noted that the State Legislature in Albany would be conducting hearing about the odors coming from Barren Island. The editorial noted that there was no "healthful and inoffensive way" to dispose of refuse. Science, they wrote, stands "helpless before this elementary problem." The sewage of cities was being poured into streams where they would foul the drinking waters of downstream cities.

Refuse had to be recycled into agricultural fertilizer and this is what happens on Barren Island. The owners and managers of the plants claimed that this was done without "injury to health or offense to the senses." Indeed one of the plant managers claimed the only odor was like that of chocolate. The *Brooklyn Daily Eagle* pointed out that the plants have tall chimneys which carry the fumes into the air. In theory this should have solved the problem but by the time that the plume of smoke reached the other side of the bay, it had descended to ground level. The newspaper gleefully predicted that it would not be long before the State Legislature would learn that the residents near the plants did not find the fumes very much like chocolate (“The Barren Island Zephyrs”, *Brooklyn Daily Eagle*, Feb.14, 1900).

If the plants were producing a nuisance, could they actually be closed? Shutting down the plants would not be easy. As of 1899 the sale of recovered materials from Barren Island was netting $2,000,000 a year. The revenues were used to finance garbage collection. Should this revenue stream dry up, the city would be forced to finance its own collection routes. It was also noted that in addition to resource conversion, there was the business of recovering tin cans, rags, and paper. The oil was still an important industrial feedstock and used to manufacture soap, hair oil, candles, lubricants, and other products (“Barren Island”, *Brooklyn Daily Eagle*, Aug.14, 1899).

But these considerations did not prevent the State Legislature from trying to shut the plants down. A law provided that after May of 1901 it would be illegal to render or boil, garbage, swill, or offal in the borough of Brooklyn (“Constitution Extends Even to Barren Island”, *Brooklyn Daily Eagle*, Nov.10, 1900).

However the contracts between the city of New York and the New York Sanitary Reduction Company had more than a year to run beyond the May 1901 date. The company then brought suit against the city restraining it from enforcing the law. Justice Francis M. Scott of the Manhattan Supreme Court heard the case and ruled that the act violated the constitution in that it did not declare the business to be a nuisance (which under common law would entitle injured parties to injunctive relief) or prohibited the activities in any other part of the city. Lastly, Justice Scott ruled that even if the legislature did have the right to cancel a contract whose purpose was the preservation of public health, it could not do so without providing compensation for the injured party (“Constitution Extends Even to Barren Island”, *Brooklyn Daily Eagle*, Nov.10, 1900).

In considering alternatives to the process it was noted that ocean dumping was wasteful and the way it was practiced was not very effective. Instead of going the required forty miles out to sea, the scows were only going six to eight miles. Incoming tides brought the garbage onto the beaches of Coney Island, Rockaway, and even Long Beach. The materials fester in the sun and breed "maggots and flies by the millions" (“Barren Island”, *Brooklyn Daily Eagle*, Aug.14, 1899).

Alternative disposal sites on the New Jersey Shore and Staten Island were considered.

The former location was rejected due to anticipated community opposition while the latter seemed preferable since it was already under a constant cloud of smoke from the oil refineries in New Jersey. Even so, it was noted that the borough was developing rapidly and new residents would certainly object to garbage processing plants in the community. Another option was an artificial island twenty miles off shore. Such a scheme was already under consideration as a gambling resort (“Barren Island”, *Brooklyn Daily Eagle*, Aug.14, 1899).

In the late 1890s, Brooklyn also decided to adapt waste reduction technology. Brooklyn's City Works (Theodore Willis) and Health (Emory) commissioners signed a five-year garbage removal contract with the Brooklyn Sanitary Company (H. Cranford President) in December of 1896 (“Garbage Contract Awarded”, *Brooklyn Daily Eagle,* Dec.11, 1896).   The contract called for daily collection of kitchen wastes and also for the immediate removal of the garbage which had been accumulating in empty lots and on the streets. But it did not specify the means of ultimate disposal, only calling for a disposal plant with a capacity of 500 tons every 24 hours and that construction of the plant would start within thirty days of the contract being signed (“Garbage Contract Executed”, *Brooklyn Daily Eagle*, Dec.12, 1896). A few weeks before the contract was signed the Brooklyn Sanitary Company announced that they would use the plants already on Barren Island until their own plant was ready. As the contract moved forward the company announced that it would adopt the Arnold system of waste reduction when it built its own plant. Responding to concerns about potential odor problems Mayor Wurster personally contacted officials in Philadelphia to ask whether the system was a nuisance. Philadelphia at the time was one of the largest cities using the process (“Wurster and Garbage”, *Brooklyn Daily Eagle*, Nov. 21, 1896).

The city of Brooklyn was understandably eager to sign the contract since the federal government ordered that ocean dumping of garbage cease after June 1, 1896. Brooklyn's mayor Frederick W. Wurster was urged to act in conjunction with Mayor William L. Strong of New York to request a delay at least to the end of the year, the cities having no better means of disposal (“The Garbage Question”, *Brooklyn Daily Eagle*, Feb.5, 1896).

The New York Sanitary Reduction Company and other operators on Barren Island would be joined by the Brooklyn Sanitary Company which was owned and operated by F.L Cranford, President, W.V. Cranford, secretary, and their father J.P. Cranford, a well-known Brooklyn contractor. The announced their plans in November of 1896 promising to spend $200,000 for a waste processing plant that would have a capacity of 500 tons per day and be operational by May of 1897. Their bid for the five year contract was $605,000 which according to J.P. Cranford would mean operating at a loss. The revenue would be made up by the sale of grease and fertilizer. Most of the latter was expected to be sold in the southern states for cotton growing (“Sanitary Company's Plans”, *Brooklyn Daily Eagle*, Nov. 18, 1896). The plant was operational in 1897 and the odors coming from it were described as being no worse than would be experienced in a "large hotel kitchen" (“The City's Garbage Plant”, *Brooklyn Daily Eagle*, Dec.1, 1897). The tankage not sold for fertilizer was used as fuel for the boilers and as with the other plants on Barren Island, the syrupy waste water was treated in vacuum evaporators so the last remaining waste materials could be recovered and added to the fertilizer. The company's chemist, Dr. Terne, developed this process. The tankage was sold to fertilizer manufacturers who, after enriching the material with phosphates and other nutrients, sold it to cotton cultivators. As the final sifting of the tankage took place, the operator of the sieves, described as a "boy" but his age was not given, claimed the silverware that "careless servants" threw into the garbage pails ("The City's Garbage Plant").

By 1902 the Brooklyn Sanitary Company was established on Barren Island and was even able to sponsor an excursion for 200 of the island's children to Steeple Chase Park on Coney Island. The outing was supervised by Reverend T.F. Horan of the Holy Family Roman Catholic Church of Canarsie ("Children Enjoy Outing", *Brooklyn Daily Eagle*, Sep.4, 1902).

Although the 1896 contract between the City of Brooklyn and the Brooklyn Sanitary Company was to run five years, consolidation terminated that arrangement and the Brooklyn Sanitary Company began the new century with a day-to-day contract that could be terminated at any time by the Commissioner of Street Cleaning. In 1902 the first five-year garbage disposal contract for Brooklyn would be awarded to the New York Sanitary Utilization Company. The company underbid three rivals with a low bid of only $47,990. The Brooklyn Sanitary Company did not bid on the contract. No explanation was given for this decision in the press reports. However the low bid did not include street cleaning or collection of garbage. The City's Street Cleaning Department was supposed to supervise those activities (“Nagle Plan Carried Out by Successor Woodbury”, *Brooklyn Daily Eagle*, Apr.15, 1902).

Barren Island served three functions, waste disposal, fertilizer production, and industrial chemicals, particularly grease and glycerin. As early as the 1700's farms in the surrounding countryside produced cash crops for New York's urban market. By the mid-1700's large areas of farmland in New Jersey were already abandoned as soil fertility was exhausted (Olsen, n.d., *Hadrosaurs*). As New York's population grew even faster throughout the 1800s, it became clear that without an effective means of replenishing the soil the farmers would be faced with ever decreasing crop yields (Miller 2000, 47).

For many decades farms close to the major cities successfully used manures as fertilizers. The same carts, wagons, boats, and even railroads that carried crops to the urban centers carried manures back to the countryside. An 1842 report of the King’s County Agricultural Society noted the positive correlation between manure use and farm income (Linder and Zacharias 1999, 29). The shift to more “manure-intensive” vegetable production in western Long Island corresponded to the rise of horse-drawn transportation in Brooklyn and New York (50). All of the stable manure from Brooklyn, most of New York’s, and even a portion of Albany’s were used to fertilize farms on western Long Island (47). In addition to horses, manures were available from the city’s dairy cows and pigs. In 1878 the U.S. Census Office observed that Brooklyn had 75,000 homes and 25,000 privies that provided 20,000 cubic feet of night-soil to farms in Kings County each year (49). In time, a group of dealers arose who collected manures, composted them into light and friable manure, and sold them at premium prices to farmers (48). In 1872, the typical market gardener near a large city would use as much fertilizer on one acre as other farmers used on 50 acres (49).

But by the late 1800s and early 1900s the limitations of manure were becoming obvious. The tradition of returning manure from the city this would not be enough to stem the loss of soil fertility. Manure scooped off the streets was contaminated with other wastes. Even when it is pure, manure's high water content made transport inefficient. Manure also lacked sufficient amounts of potassium and phosphate for it to fulfill the needs of the region's farmers (Miller 2000, 49).

In 1907 the City of New York reported the results for the analysis of their street sweepings and found that using them as agricultural fertilizer was unrealistic. In street sweepings, the nitrogen, phosphoric acid, and potassium were almost entirely from animal excrement. The amounts of nitrogen, phosphoric acid, and potassium varied considerably. On average in every one ton of street sweepings, there were 8.52 pounds of nitrogen, 8.40 pounds of phosphoric acid, and 7.32 pounds potash. The other 98.8% of the sweepings were considered inert. Additionally, as much as half of the phosphates were sometimes present in an insoluble form *(Report of Commission on Street Cleaning* *and Waste Disposal,* City of New York, 1907).

The total value of these nutrients varied with fluctuations of the fertilizer markets so that the costs that the city could recover were never guaranteed. In the first years of the 1900s, the value of the nitrogen, phosphoric acid, and potassium was just over 2.00$ per ton. And while there were 550,000 tons of street sweepings produced annually in the city, the approximately $1,000,000 in agricultural value was not enough to offset the problems associated with the material *(Report of Commission on Street Cleaning and Waste Disposal,* City of New York, 1907).

The fundamental problem was that 98.9% of the material was inert. This made transport, distribution, and spreading inefficient when compared to other types of fertilizers. At best, street sweepings had less than half the fertilizing value of stable manure, which itself was getting harder and harder to sell to farmers *(Report of Commission on Street Cleaning and Waste Disposal,* City of New York, 1907).

The cities were reluctant to use street sweepings as landfill material because they fermented underground and generated ammonia and other noxious gases. The City government was also concerned about disease causing bacteria breeding in this organic-rich stew *(Report of Commission on Street Cleaning and Waste Disposal,* City of New York, 1907).

Fortunately for New York the street sweepings could be used as landfill material because they were collected in the same carts as the ashes from coal and wood fires. Since only 20% of the mass consisted of sweepings the total organic matter was relatively low. When used as landfill, it was thought that the antiseptic properties of the ashes would prevent putrescence *(Report of Commission on Street Cleaning and Waste Disposal,* City of New York, 1907). In New York around 1910 the majority of the ashes, rubbish, and street sweeping were used a fill at Riker's Island (Baskerville 1911) (figure CS1-5).

Because of the limitations of manure as a fertilizer for the exurban farmer, the tankage from rendering operations filled an important need. In 1857 advertisements appeared in agricultural magazines promoting an "animal fertilizer" that was manufactured on Barren Island from the offal of New York City. This product was claimed to be a "very powerful and lasting manure." It could be purchased from George W. Mayher for $50 per ton in either barrels or bags. It was sold through the United States Agricultural Warehouse and Seed Store on Water Street in New York (*The Cultivator*, vol.5, no.4, Apr.1857, 135). The Brooklyn Fertilizer Manufacturing Company advertised its "ammoniated tafeu" for $25 a ton and claimed that it contained phosphates, potash, "ammoniacal and organic substances." Because the company had been manufacturing fertilizer from the night soil, blood, and butchers' offal of Brooklyn for ten years they were guaranteed a steady supply of good quality wastes. Prospective purchasers were invited to send for a circular which included a chemical analysis of the material. It is not clear if this company was located in Barren Island but it did maintain offices in both New

York and Brooklyn (135).

Once the food wastes were separated from the other refuse, the extraction of grease proceeded by one of three different methods. In all cases the result was the recovery of two material streams, grease and the remaining solids, referred to as the dry tankage. The simplest method was cooking under pressure with steam. Wet garbage was loaded into a pressure vessel and heated. Both water and fats were then pressed out and the oils were skimmed off the surface of the water. The dry tankage was sometimes extracted with gasoline to recover the last of the grease. Another method began with crushing and drying the food wastes in a rotary hot-air drier. The dried materials were extracted with gasoline and the remaining tankage was ground for a final time. The third method was to extract wet wastes with gasoline at a temperature equal to the boiling point of gasoline. The advantage of this approach was that both water and grease were removed in the same step (Schroeder, “The Fertilizer Value of City Wastes Part Two, Garbage Tankage, Its Composition; the Availability of its Nitrogen, and its Use as a Fertilizer”, *J. Industrial and Engineering Chemistry*, May 1917, vol.9, no.5, 513).

At the time that the operations were moved to Barren Island waste recovery was smelly. The starting materials were butcher's wastes, rotting meats, bones, and animal carcasses. Any carcasses that were acquired whole were first skinned and then chopped into smaller pieces. All of these materials were boiled in a large iron vat equipped with a tightly fitted cover that did not eliminate the escape of noxious gasses. The pressure was not allowed to rise above a few pounds per square inch. Boiling separates meat from the bones, and recovers most of the grease. The larger bones were charred and used as a filter medium in sugar refining. Smaller bones were cut up for button manufacturing. The meat became a feedstock for the manufacture of ammoniated superphosphate of lime. The recovered grease used for manufacturing soap and candles (Sharples Oct.1874, 234).

One of the main drawbacks to boiling was that the water used became a smelly soup. It also contained 5 to 6 % glycerine. The soup, along with any blood, was simply disposed of (Sharples Oct.1874, 234).

The use of closed tanks for the recovery of grease was a step designed to allow higher pressures and as a side benefit allowed noxious gasses to be captured. Higher pressures also caused bone to disintegrate. One of the earliest types of a grease rendering tank was the Wilson Patent Tank, described in 1856 as “a cylindrical vessel of boiler iron, about ten feet high, and four feet in diameter; it is made steam tight, having openings which can be closed at pleasure near the top and bottom, for the admission and discharge of fatty matters to be melted. Heat is applied by introducing steam through a pipe opening into the bottom of the tank; the pressure used is about fifty pounds to the square inch (equal to 280 degrees F). The heat is applied from six to nine hours in succession” (Seaman 1873, 23) A later type of tank was Perry's. This was a cigar-shaped vessel with a steam jacket and a port on the top from which grease could be drawn off (Sharples Oct.1874, 234).

By 1874 technologies were introduced that would direct any noxious gasses created during the digestion process and direct them into the same fires that were used to create the steam. However before this could happen any steam in the gas stream had to be superheated so that it would not extinguish the flames. The Lockwood and Everett system used 500 feet of iron piping arranged into a coil and placed over the fire. The steam from the digester was passed through the coil which was heated to red hot. A similar method was to condense the steam in the gas stream and then blow the noxious gases, which were not condensed, up through grates into the fire (Sharples Oct.1874, 234).

The oil and grease were sold on both American and European markets at a price that varied between 2 to 4 ½ cents per pound. The purchasers refined them into commercially valuable oils the chief constituents of which were glycerine, stearine, and red oil (Report of the Commissioners on Street Cleaning 1907) (figure CS1-6).

In some instances sulfuric acid was used in fat extraction. Typically the acid could be up to 12% of the weight of the fats to be rendered. After extraction the acid was removed by washing with water at a high temperature. But if the tallow was used as a lubricant in a steam engine any remaining acid would be liberated by the heat and pressure of the steam. The acid would attack the metal and cut grooves into the surface. The grooves resembled the tracks of wood-boring worms in timber leading machinists to describe the damage as “worm-eaten.” An 1869 textbook cautioned that pure grease or beef tallow “rendered by heat alone” should be used for lubrication (Watson 1869, 192).

After the grease extraction was complete, the tankage was used as fertilizer although it is not clear from the contemporary descriptions of the process how the material was processed prior to application. If it was not applied directly to fields, the next step might be treatment with sulfuric acid. This has been mentioned as one means of making the phosphates soluble. Another approach would have been to compost the material but the author has seen no mention of this being done, at least not deliberately.

Accounts of the Scandinavian and Newfoundland whale fisheries of the late 1800s describe processing whale flesh and blubber in a process similar to that used to process food wastes on Barren Island. After the oil was extracted the meat was placed in a rotating drum with “swinging” knives. While the knives cut in the meat the drum was heated to dry it. The resulting dried material was said to make an excellent fertilizer and in Scandinavia was used as cattle feed (Boston Society of Natural History 2006, 232).

In 1917 the typical load of food and kitchen waste analyzed ant the results are presented on table 2. From the table it will be seen that the nutrients are enriched by a factor of 3.6 but in terms of overall percentage they remain fairly low in comparison to many commercial fertilizers. It was recognized at the time that the fertilizer value of garbage tankage was low, containing only 3 to 4% "ammoniacal tankage" which made the product a high volume but low cost material that made an excellent filler. (Terne, Dec.1904, 421).

An alternative source of agricultural nitrogen was the production of gas from coal. Gas for heating and lighting was manufactured by heating coal to release flammable hydrocarbons. The process of creating gas from 100 pounds of coal will yield 65 pounds of coke, 500 cubic feet of gas, 0.6 gallons of tar, and between 0.23 and 0.32 pounds of ammonia (Coit, Peck and Colby 1903, 128). In 1904, writing in the Journal of the Franklin Institute, the industrial chemist Bruno Terne estimated that the total US production of ammonium sulfate (NH4)2SO4 from coke ovens and manufactured gas plants was between 25,000 and 30,000 tons (Terne, Dec.1904, vol.158, no.6, 421).

Bruno Terne also experimented with an alternative method of producing agricultural ammonia from garbage which used destructive distillation of pressed garbage in coke ovens. In 1897 he approached the Semet-Solvay Company in Syracuse, New York, with his idea. The company was interested enough for a trial run and allowed Bruno to process a railroad car full of pressed garbage from Barren Island. The initial results were encouraging and a series of tests were conducted. Each ton of moist garbage yielded about 61.3 pounds of ammonium sulfate and 6,800 cubic feet of gas of which 8 to 10% was methane and 33 to 36% hydrogen. However with just under 25% water the pressed garbage was difficult to heat. Believing that the water could be successfully pressed out of the garbage once the operation was operated on an industrial scale, a deal was brokered between the New England Sanitary Product Company that would operate the plant, the Semet-Solvay Company that would design and build the equipment, and the

City of Boston whose garbage would be converted to ammonia. The agreement was reached in April of 1898 and the plant was ready by the late fall of that year. Excess water in the garbage proved to be fatal to the process. Pressing in huge rollers succeeded in removing both water and grease but was subject to frequent mechanical failures. Heating in a rotating drier was more successful. However the Boston plant burned down in February 1899 and was never rebuilt (Terne Dec.1904, 421).

In 1885, P. White's Sons were described as "manufacturers of Barren Island Fertilizers, Superphosphate of Lime; Dried Blood, Bone and Meat, &c." The company was managed by Thomas F. and Andrew J. White. It maintained an office on Peck Slip in Manhattan and a small plant near New Brunswick, New Jersey, but had its main plant on Barren Island. They had no shortage of raw materials in the form of blood, bones, and meat as their company controlled the dead animal and offal contracts for both New York and Brooklyn. In addition to the fertilizer sold under the name "Farmers' Pride", the company manufactured a number of specialty fertilizers including sulfate of ammonia, dried blood, and dried fish scrap (Edwards and Critten 1885).

P. White's Sons sold horsehair, hides, and glue stock. They rendered large quantities of tallow and grease (Edwards and Critten 1885).

In 1905 the population of Barren Island was 1,400 the majority of whom were described as Poles. The island had several factories and the New York Sanitary Utilization

Company’s plant. Some of the island’s population was boatmen and fishermen. There were three hotels and a public school (“Part of Barren Island Sinks”, *New York Times*, Nov.26, 1905). The Reverend Father Horan of Canarsie was the pastor of the island’s church (“Building Cut in Two to Save it from the Sea”, *New York Times*, Nov.28, 1905).

By 1910 Barren Island was home to some 2,000 workers, mostly Italian and Polish but also Russian and African American. Four saloons catered to this diverse clientele and a two-man police station, described as “a small yellow hut” was in the island to keep order among the “unruly foreign population” (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910) (figure CS1-7).

Kitchen waste from the Street Cleaning Department scows was loaded onto four-wheeled trucks that were wheeled up an iron spiral ramp into the third-floor pressing room. Twelve cast iron digesters ten feet high and four feet wide were located in the room. Doors on the top of each of the digesters were loaded from the trucks as they moved past. As the tanks were filled, the doors were locked, and steam at 100 psi was admitted from the bottom. Two products resulted, the grease that was drawn off and the dry tankage (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910).

As of 1910 the dry tankage was used as landfill along the Barren Island (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910). It may be supposed that the sinking of the eastern end of the island and the need to shore up the land precluded recycling the tankage into fertilizer.

In 1910, the New York Sanitary Company's plant on Barren Island was three stories high, had a sloping metal roof, and a 150-foot high yellow brick chimney. Beside the plant was a crematorium owned by a company that held the contract for cremating the city's dead animals. These facilities were on the eastern side of the island while the remaining plants and several hundred worker-huts were clustered on the western side of the island ("Fatal Explosion on Barren Island", *New York Times*, May 10, 1910).

Floods, Fires, and the Dangers of Waste Processing

In November of 1905 one of the New York Sanitary Utilization warehouse and docks disappeared into the waters of the Rockaway Inlet. It was reported at the time that three powerful currents met at that point. On Saturday, November 25th, 1905 workers in the factories heard a roaring underfoot. Running to the windows they saw the Sanitary Utilization Company's 150-foor long, two story warehouse, and the company's dock sinking into Jamaica Bay. The steamboat *Fanny McKane* had just arrived at the dock and a line had been put ashore to make her fast. When the Captain saw the warehouse totter, he rang the engine room for full speed astern. The boat was about fifty feet from shore when the land gave way. The warehouse roof was last seen floating seaward and about 5,000 barrels of oil were lost ("Part of Barren Island Sinks", *New York Times*, Nov.26, 1905).

The population of the island was thrown into a panic and an estimated 500 men and women rushed to the other side of the island. Several men apparently believed that the entire island was about to sink had jumped into the bay. It is thought that all were eventually rescued. Charles Yousesky was carried several hundred yards from shore before being rescued by a boat sent from the *Fanny McKane*. Captain Reimels of the Canarsie Police Station saw the warehouse disappear and sent two tugboats to the scene ("Part of Barren Island Sinks", *New York Times*, Nov.26, 1905).

The area that sank measured about 400 feet long by 200 feet wide, or 80,000 square feet. The water depth at the site was between 75 and 85 feet ("Part of Barren Island Sinks", *New York Times*, Nov.26, 1905). In the days that followed more land was lost. A second piece of "apparently solid" land sank and minor losses continued. People speculated that some shift in the three currents that met at the site caused the land to be undermined. Another possible contributing factor may have been a sandbar that formed between Barren Island and the Rockaway Peninsula. Water channeled by the sandbar may have been responsible for wearing away at the island. Whatever the cause, a whirlpool was visible on the surface and could be seen cutting into the island ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

An office building fell into the bay but was not drawn into the whirlpool. Cables secured it to the remaining shore until it could be towed out into the bay and beyond danger. Another building was being undermined but was cut in two and the half that was being undermined was allowed to drop into the bay ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

Boatmen throughout the bay began collecting the floating barrels for which the Sanitary Reduction Company paid between 15 and 25 cents each. Workmen worked double shifts driving piles in an effort to stabilize the shoreline. Father Horan was the pastor of the island's Catholic Church although he lived in Canarsie. He made several trips from his home to comfort his flock. He was quoted as saying that "I do not think there is any danger of any extensive destruction. There have been several landslides of this sort on the island, although those of the last few days have been more destructive than any for some years" ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

Father Horan may have been referring to the collapse of the fertilizer plant of the Wimpfheimer Company that had sunk into the bay seventeen years earlier. That building was also on the eastern end of the island. The company's owner, Mr. Wimpfheimer, was quoted as saying that he had thought the building was located on quicksand. Following Wimpfheimer's building collapse a stone jetty was built around the end of the point. It was thought that the jetty would prevent another accident from occurring ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

Less than one year after the collapse a serious fire broke out in the digester building. It caused $1,500,000 worth of damage, destroyed fifteen buildings, and left the city without refuse processing capacity. In 1906, the digester building was a three-story brick structure at the east end of the island. The building was 500 feet long by 200 feet wide and contained 150 digester tanks ("$1,500,000 Fire Loss on Barren Island", *New York Times*, May 21, 1906).

The fire broke out around 1:00 pm on Sunday, May 20, 1906. Watchman Christopher Behlin was making his rounds when he noticed flames in the digester building. Before he could sound the alarm the flames had penetrated the building's roof and were jumping to the adjacent pump building. The pump building was a three story frame structure and housed the company's firefighting apparatus. By the time the island's volunteer fire department arrived, the pump building was engulfed in flames ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

The fire spread to the plant's other buildings. The fireboat *Seth Low* was sent to fight the fire but was delayed because the crew had no experience in Jamaica Bay and no pilot could be found to steer her through the Rockaway Inlet. When the boat finally arrived on the scene the crew began pumping water on the fires along the island's southern shore. Nothing else could be done. The Sunday crowds on the nearby beaches watched fascinated, believing large ships were burning ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

The flames spread to the hydraulic press plant and destroyed 52 pressed valued at $3,800 each. The two drying building, each a city block long, were destroyed as were the company's warehouses ("Building Cut in Two to Save it from the Sea", *New York Times,* Nov.28, 1905).

Half-a-mile away from the Sanitary Utilization Company were the "horse buildings." These were owned by the company that disposed of animal carcasses. Despite the distance from the flames, their roofs were catching fire. The *Seth Low* was able to direct streams of water onto them, preventing the "horse buildings" from burning ("Building Cut in Two to Save it from the Sea", *New York Times*, Nov.28, 1905).

When the fire began to consume the buildings of the Brooklyn Refuse Company the 600 families living on the island began to think about evacuation. Fleeing with hastily packed belongings the families raced to the boats tied up to the island's docks. The scows, rowboats, launches, small sailboats, and yachts filled with refugees. They were described as carrying clocks, bedding, carpets, mirrors, and household pets. One woman fell into the water and let go of a caged parrot and a marble clock. After fishing her out, her husband scolded her in Bohemian for letting go of them. The parrot was rescued and taken to Canarsie. Later, the couple found fishing-tackle, and were seen attempting to recover the clock. Several other fleeing persons also fell into the water but no persons drowned.

The McKeever brothers, owners of one of the other fertilizer plants on the island, raced to the scene aboard a chartered steamboat. Finding their buildings had not yet caught fire, the McKeevers collected an estimated 400 men and began to wet the roofs of their buildings. The fire was still burning at midnight when it spread to the docks, derricks, and rigging along half a mile of shoreline. These were all consumed and the remains fell into the bay. The fire damage was later estimated to have spread over 16 acres (“Building Cut in Two to Save it from the Sea”, *New York Times*, Nov.28, 1905).

The effect on waste disposal was immediately felt. New York once again began dumping garbage at sea outside Sandy Hook. Bathing beaches on Long Island between Coney Island and Smith's Point and along the Jersey Shore from Sea Bright to Atlantic City were said to be "literally covered with garbage" (Baskerville 1911).

Four years later another fire broke out on the island. Shortly after noon on May 9, 1910, one of the 12 digesters exploded at the New York Sanitary Company’s plant on Barren Island. One worker was killed and five were injured. The explosion could be heard as far away as Canarsie. The dead worker, Antonio Carditz, described simply as “a Russian,” was killed by shock after a cast iron piece broke his leg in three places and his body was enveloped in steam. Three of the five injured workers were listed as Wernier Service, a Russian; Cyprien Carewitch, a Russian; and Matthew Hubbard, “negro.” John Waters and Carl Moggs were listed as injured but were not described. Some 2,000 Polish and Italian workers were said to be thrown into chaos (“Fatal Explosion on Barren

Island”, *New York Times*, May 10, 1910).

At the time, the New York Sanitary Company was described as processing “Practically all the garbage which the City’s Street Cleaning Department collects in Brooklyn every day” (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910).

The steam gauge on the digester was later found and it read 65 psi. A ten foot hole was torn through the roof and a cloud of steam rose fifty feet over Jamaica Bay. Pieces of the digester struck the workers and the force of the blast threw them off the loading ramp and into the corners of the pressing room (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910).

The floor of the pressing room collapsed under the exploded tank and splattered the workers below with parboiled waste. The 400 workers inside the building, some blinded by the explosion and exposed to scalding steam, were sent into a panic. Witnesses on boats in Jamaica Bay reported seeing many jumping from the windows and sliding down the spiral ramps (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910).

Ironically the only person who did not hear the explosion was a one Snyder, the company’s licensed boiler engineer who was on duty in a noisy boiler room located an adjacent building. Snyder only realized that the boiler had exploded when he noticed a drop in steam pressure. Snyder shut off the steam and went outside where he saw the chaos. He then began going to the other plant boilers and securing them against additional explosions ("Fatal Explosion on Barren Island", *New York Times*, May 10, 1910).

The real heroes of the day were the New York City Police officers who were stationed at the island's two-man police station. They had seen the explosion through the station's windows. Rushing through the fleeing workers, Officer Isaac Van Houten and Sergeant Atkinson, entered the building. They found Carditz lying on the second floor and improvised a tourniquet from a handkerchief. While carrying the injured man from the building another portion of the ceiling collapsed and cut a deep gash in Van Houten's leg. The foremen had already carried out the other injured men ("Fatal Explosion on Barren Island", *New York Times*, May 10, 1910).

The company's launch had still not returned from a trip to Canarsie but the crew of Police Boat C had seen the explosion and brought their boat to the company's dock. Carditz, Service, and Carewitch were loaded aboard the launch but the cockpit was so small that Carditz had to be laid on the floor while Carewitch's head rested on one bench, his feet on the other, and his body over Cartditz's. The police boat headed for Canarsie at fifteen miles per hour when they met the company's launch coming back. Three doctors from St. Mary's Hospital and one from Kings County Hospital were on the company's launch. The tourniquet on Carditz's leg did not completely stop the bleeding and the doctors put another bandage on the wound. Carditz later died in the hospital ("Fatal Explosion on

Barren Island”, *New York Times*, May 10, 1910).

The explosion had caused an estimated $5,000 worth of damage (“Fatal Explosion on Barren Island”, *New York Times*, May 10, 1910).

The Waste Industry Expands

At the time the collection of garbage and transportation to scows was handled by the city under the direction of the Commissioner of Street Cleaning. On January 2, 1914 a new contract was signed between the city and John J. Hart of the New York Disposal Corporation. New York Disposal leased the plant on Barren Island belonging to the New York Sanitary Utilization Company. The process used was by New York Disposal was largely unchanged except that naphtha was used as a solvent after pressing the tankage to extract the last of the grease (“37th Annual Report of the New York State Dept of Health”, *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751).

The contract provided that the garbage of Manhattan, the Bronx, and Brooklyn be processed by the company. These three boroughs were generating 412,000 tons of garbage annually. On Staten Island and in Queens, garbage was mixed with ashes and rubbish and sent for incineration (“37th Annual Report of the New York State Dept of Health”, *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751).

A separate collection system existed for rubbish (“37th Annual Report of the New York

State Dept of Health", *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751).

The expansion of the garbage processing operations beyond Barren Island and into other portions of Jamaica Bay appeared to be inevitable as the city continued to grow and produce more garbage ("Garbage Plans Menace Property, Summer Residents Alarmed by Proposal to Build Disposal Works on Ruffle Bar Island", *Greater New York, Bulletin of the Merchants Association of New York*, Sept.15, 1913, vol.2, no.31, 9). In 1913 it was observed that the plants on Barren Island were so long established that all subsequent development was placed in areas that were not (in theory at least) going to be adversely affected by the presence of the plants. However when plans were announced to build new waste processing plants on Ruffle Bar Island opposition swelled (9).

Ruffle Bar Island was near the center of the bay a short distance from Barren Island and about one mile from the residential section of the Rockaway Peninsula. In the Spring of 1912 the city signed a new waste disposal contract. In order to meet its obligations to the city the contractor needed to build a new plant and selected Ruffle Bar Island as the site ("Garbage Plans Menace Property, Summer Residents Alarmed by Proposal to Build Disposal Works on Ruffle Bar Island", *Greater New York, Bulletin of the Merchants Association of New York*, Sept.15, 1913, vol.2, no.31, 9).

Opposition came from the property owners in Rockaway, Belle Harbor and Neponsit. It was also noted that the new plant was near a stretch of ocean beach which the city had purchased for $2,000,000 (“Garbage Plans Menace Property, Summer Residents Alarmed by Proposal to Build Disposal Works on Ruffle Bar Island”, *Greater New York, Bulletin of the Merchants Association of New York,* Sept.15, 1913, vol.2, no.31, 9).

Opponents to the plan argued that instead of using any site in Jamaica Bay the city could construct artificial islands on the Romer Shoals or in Prince's Bay. They noted that Hoffman and Swinburne Islands off the east shore of Staten Island were created for use as quarantine stations (“Garbage Plans Menace Property, Summer Residents Alarmed by Proposal to Build Disposal Works on Ruffle Bar Island”, *Greater New York, Bulletin of the Merchants Association of New York*, Sept.15, 1913, vol.2, no.31, 9).

A new waste processing site of Rikers Island was considered. The island was already home to a smelly and offensive landfill portions of Queens and the Bronx were downwind of the landfill so there was no shortage of political opposition. The city's Board of Estimate next turned its attention to Staten Island.

A number of things were changing the economics as well as the politics of waste processing. With the outbreak of the First World War the demand for the products of waste reduction might be expected to increase sharply. Glycerine and nitrates could be used to manufacture nitroglycerine. Grease could be used in a number of industries and the worldwide need for fertilizers would increase the value of tankage. Perhaps because the United States was still officially neutral, none of the companies involved in waste reduction came out and declared their intention to become "war industries." It is clear from subsequent events that this was what they became. One of the arguments for moving waste reduction out of Jamaica Bay was that the new operators promised to increase the payments to the city. Politically the negative effects of landfills, waste reduction, and incineration were wearing out the public's patience.

Once plans for a new waste reduction plant on Staten Island were announced, a group of residents promptly sought an injunction against the Board of Estimate. When the courts vacated the injunction the board immediately voted 8 to 3 in favor of building the plant on Staten Island. During the meeting at which the vote was taken, Borough President Calvin Van Name protested strongly but was overruled (“Garbage Disposal Goes to Richmond”, *New York Times*, Apr.11, 1916).

Van Name then began a lengthy speech about the project, an action that made a number of persons at the meeting suspicious. Suddenly, Edward W. Brown, identified only as a "Staten Island taxpayer," burst into the meeting waiving a second injunction. Brown pushed his way to the Mayor Mitchell who was presiding over the meeting. Brown claimed that the injunction forbade the city from proceeding with the plant on Staten Island, Mitchell examined the document and noted that the injunction merely "put a stop to reconsideration of our previous action." With that, he adjourned the meeting. A few minutes later, a contract was signed with the firm of Gaffney, Gahagan, and Van Etten by the Street Cleaning Commissioner. The firm agreed to pay the city $900,000 over a period of five years for the privilege of processing the city's wastes. At the end of the five years the city would have the option to buy the plant. The company posted a $250,000 bond to guarantee that the plant was to be operated without generating odors and be ready for operation by January 1917. The contract was expected to save the city $1,000,000 annually according the mayor(“Garbage Disposal Goes to Richmond”, *New York Times*, Apr.11, 1916).

A request, to study the impacts such a plant might have, came from Dr. Linsly R. Williams, the Deputy State Commissioner of Health, in July of 1916. Hearings on the matter were held in the Staten Island Borough Hall. The stenographic record of the hearings ran to 1694 typewritten pages but the conclusions could be summarized briefly. First, most of Staten Island would be unaffected by the new plant. Secondly, persons living along the shores of the Kill Van Kull and Arthur Kill would be subjected to odors from the barges bringing garbage from Manhattan, Brooklyn, and the Bronx. Thirdly, there would be a limited number of residents at Linoleumville and Fresh Kills who would be exposed to nuisance odors on an intermittent basis. The hearing also concluded that the Cobwell process was the best technology then available for the reduction of garbage. Lastly, "from a sanitary standpoint" there were better sites for the reduction plant, especially Rikers Island and Barren Island (“37th Annual Report of the New York State Dept of Health”, *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751).

The new was built close to the point where the Little Fresh Kill and Great Fresh Kill met.

("Kill" is a Dutch word for creek and the names of many waterways in the New York region include this word.) The site selected was an island in the kills that was about half a mile east of the Arthur Kill that separates New Jersey from Staten Island. The plant was intended to process the garbage from Manhattan, the Bronx, and Brooklyn. Where garbage from Staten Island and Queens would be processed was not mentioned in the press reports (Tuska 1916, 199).

The plant's designers elected to use the Cobwell Process. The process was invented by chemist Raymond Wells ("37th Annual Report of the New York State Dept of Health", *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751). Unlike the processes used at Barren Island the tank where the garbage was reduced was steam-jacketed so that the steam and garbage would not be mixed. A low-boiling point solvent, usually gasoline, was pumped into the tank and heated by the steam. A water, grease, and gasoline mixture evaporated from the tank and condensed. Once the water was allowed to separate out by gravity, the grease was separated from the solvent which was then re-used for another batch of garbage (Tuska 1916, 199).

Waste reduction plants using the Cobwell process were more expensive to build but were more efficient. Recovery of valuable by-products was improved by about 25% compared with plants using only steam extraction. Gasoline was a more effective solvent for grease and glycerine so that less of these materials found their way into the driers (where they could burn and sputter) or into the waste water streams (*American Journal of Public*

Health, Feb. 1918, 176).

Within a year of the Staten Island plant being opened, the Metropolitan By-Products Company recovered enough grease for 70,000,000 cakes of soap, 1,500 tons of nitrogen, 2,000 tons of phosphoric acid and potash. The Cobwell process was credited with recovering enough material to manufacture 700,000 pounds of high explosives, this material would have been lost using less complex reduction technologies streams (*American Journal of Public Health*, Feb. 1918, 176).

Another advantage of this process was that since the water did not actually touch the garbage, there would be no odors produced by the chemical degradation of the garbage. In theory at least, the odor causing compounds would be trapped in the solvent. Any ammonia would be neutralized by acids extracted from the garbage. The tankage would be unloaded only after it was dry and so would not produce unpleasant odors. The odor of the tankage was described as being like the "smell of stale gingerbread" (Tuska 1916 199).

Despite assurances from the plant's designers that the Cobwell process would keep odors under control, they were still a concern that the communities of Fresh Kills and Linoleumville would be exposed to at least an occasional nuisance but that most of Staten Island would not be affected. None the less, others still believed that better sites for the works would be on either Barren Island or Rikers Island (Bachmann 1917, 579).

The plant was housed in a one-story building 200 by 330 feet and housing 250 reducers. Each reduced had a capacity of 8 to 10 tons per 24 hours. Garbage would be brought to the site by barge and unloaded by steam powered cranes. Special canvas shields would prevent loose garbage from dropping into the water or being blown away. A boiler house and buildings to process the solvent and tankage were also part of the plant. Total cost of the project was $3,000,000 and the plant's capacity was $2,000 tons per 24 hours (Tuska 1916, 199). Metropolitan By-Products signed a contract calling for them to process all garbage from Manhattan, the Bronx, and Brooklyn for five years for which they would pay the city $900,000. Garbage was to be delivered to wharves on the Hudson and East Rivers and transported to the plant at night (*American Journal of Public Health*, Feb. 1918, 176).

If certain press reports are to be believed, local opposition to the new plant seems to have abated by July of 1917 when the Metropolitan By-Products Company opened its Staten Island reduction plant. The *New York Times* confidently predicted that the enterprise would be highly profitable since the First World War had created a demand for nitrates and glycerine for munitions manufacture. Opposition to the plant was attributed to deliberate misinformation and the "persistent influence" of those who wanted to see waste reduction continue on Barren Island. Metropolitan By-Products promised to plant trees on the grounds as well as vines and flowers. To avoid the poor living conditions experienced by workers on Barren Island, the company promised to build dormitories and contracted with the Woymar Lumber Company to provide housing. The lumber company was interested in providing housing for the workers at nearby factories (“Model Garbage Plant”, *New York Times*, July 22, 1917).

Within a year of the plant being opened, a Staten Island grand jury declared it a nuisance (“Condemn Garbage Plant”, *New York Times*, June 22, 1918). But with the United States now in the First World War the nitrates, glycerine, and fertilizer were considered vital war materials and the government seriously considered taking over the plant (“Confer on Garbage Plant”, *New York Times* July 26, 1918). The Federal Government never took over the plant.

The plant was closed by the end of the war on the orders of the City's Health Commissioner. The commissioner was accused of closing the plant in response to political pressure from Staten Islanders (“Waste in Garbage Disposal Charged”, *New York Times*, June 27, 1920).

Once the plant on Staten Island was in operation, the plants on Barren Island began to close (“Garbage Plant To Remain”, *New York Times* Aug,30, 1918). While the relief as palatable in Brooklyn, the Staten Island plant was experiencing financial difficulties. It had been taken over by the Metropolitan By-Products Company which had operated on Barren Island (“Garbage Contract Upheld; Court Finds City's Agreement for Refuse Disposal Properly Made”, *New York Times*, July 26, 1919). The Metropolitan By-

Products Company was soon in receivership. This complicated the city's planning process and made the future of both Barren Island and Fresh Kills uncertain ("Hylan Asks Garbage Facts; Also Tells Brooklynites Staten Island Plant Won't Be Used", *New York Times*, Nov.2, 1918).

Without a company to operate the plant, the city turned to the New York Sanitary Utilization Company and the people of Brooklyn feared that the odors from Barren Island would once again be wafting their way ("Garbage Contract Upheld; Court Finds City's Agreement for Refuse Disposal Properly Made", *New York Times*, July 26, 1919).

Despite earlier bad experiences, during the administration of Mayor Hylan the city returned to the practice of ocean dumping. Both waste reduction and incineration had bad reputations that prevented their widespread re-adoption. As a result, by 1925, 80% of the 10,000,000 cubic yards of waste materials generated annually was dumped in the ocean and only 20% percent was being incinerated. At the time the waste consisted of ashes (50%), garbage (10%), and rubbish (40%), the volume of waste was growing at an average rate of 6% a year but with an increase in construction activity the increase was expected to be 12 to 15% ("New Ways are Sought to Keep City Clean; New York Authorities Harassed by Problem Now Met by Dumping Most of Garbage Into Sea, an Unsanitary Method Abandoned Elsewhere" *New York Times*, Feb.1, 1925).

In a statement to the press in the summer of 1924 the Navy Supervisor of New York

Harbor reported that the city's garbage was being dumped at a point 18 miles south of Long Island and 21.5 miles east of New Jersey. The distant dump site, combined with a reduction of volume, reduced the amount of trash reaching the beaches. However an anonymous editorial writer in the New York Times pointed out that this was no time for complacency. Sewage pollution was still a problem and it was hoped that all of the waters around the city would soon be safe for swimming and fishing. The long term solution to ocean dumping pollution was the construction of modern incineration facilities. There was no mention of revitalizing the waste reduction industries ("Cleansing the Waters" *New York Times*, Sep.12, 1924).

In 1925, Frank D. Waterman, a Republican candidate for mayor, reminded members of a Republican club that under Democratic mayor John Frances Hylan the city began dumping its garbage at sea (figure CS1-8). Under previous administrations, especially Mayor Mitchell's the city sold its waste products for a profit. Mitchell was a Fusion candidate, nominated by a coalition of Republicans and progressive reformers. He was in office from 1914 to 1917. Waterman pointed out that disposal at sea was supposed to be a temporary expedient during the First World War, the Tamminy-backed Hylan administration promised to solve the garbage problem in 1917 and 1921 (“Waterman Assails City Garbage Plan”, *New York Times*, Sep.5, 1925).

Waterman went on to say that from 1896 to 1914 the garbage of Manhattan, Brooklyn, and the Bronx was processed on Barren Island for which the city paid an average of

$208,000 a year. When the city signed the contracts with John J. Hart in 1914, the city was not obliged to pay anything to Hart. Instead it would receive $262,500 a year for three years. In 1916 the city signed a contract with the Metropolitan By-Products Company for five years. Metropolitan By-Products agreed to pay the city $900,000 annually and it built a new reduction plant on Staten Island. Between 1917 and the early part of 1918 the company paid the city $182,500 but by October of 1918 Metropolitan By-Products was in receivership. Waterman blamed Mayor Hylan who had taken office in January of 1918. Hylan was opposed to the contract with Metropolitan By-Products and Waterman attributed the company's plight to Hylan's opposition although he did not actually explain what Hylan did or did not do to cause it (“Waterman Assails City Garbage Plan”, *New York Times*, Sep.5, 1925).

Mayor Hylan never made a secret of his opposition to private companies handling the city's waste. In an address to the Engineer's Club of Philadelphia he stated that municipal control of waste collection, street cleaning, and garbage processing operations insured consistent, quality, public service. He feared that contractors would be tempted to cut corners and that their employees were not responsible to the city government. He went on to state that if there were any aspects of waste management not under the city's control he would change them without a day's delay (*The Journal of the Engineers Club of Philadelphia* 1920, 329).

Hylan was a Democratic mayor with ties to the infamous Tammany Hall so it may be that city also placed control of lucrative patronage in the hands of politicians. To determine what extent this may be true is beyond the scope of this work but Fiorello H. La Guardia, who served as Alderman in the Hylan administration and later as New York's most popular mayor and whose integrity has never been questioned, shared Hylan's viewpoint(*The Journal of the Engineers Club of Philadelphia* 1920, 329).

During the hearings on the Staten Island reduction plant conducted by the New York State Department of Health, Dr. G.C. Whipple a professor of sanitary engineering at Harvard and an engineering consultant was the expert retained by the department. In commenting on the advantages of municipal ownership Whipple wrote that a contractor might not keep up with repairs, "to secure the greatest possible profit before the contract expired." Because a city owned plant did not have to generate a profit, it might be kept cleaner, and lastly if combined with an incinerator to burn rubbish, the waste heat might power the reduction plant ("37th Annual Report of the New York State Dept of Health", *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751).

By the beginning of the twentieth century, it became clear that no site in New York City was sufficiently removed from population centers to make it suited for waste disposal. The construction of the waste reduction plant on Staten Island marked a turning point where public opinion and political considerations would play a greater role in waste management decisions. The insistence on municipal control would mean that for Jamaica Bay the city would dictate all future waste management decisions.

After Waste Reduction

For all the problems they created and neighbors they annoyed, the waste reduction plants on Barren Island were a far-sighted solution to the perennial problem faced by all cities, what to do with the garbage. In a marshy environment and at a time when very few people appreciated the ecological services of estuaries, landfills along Jamaica Bay's shorelines seemed like another far-sighted approach to the waste management problem. This was because as populations increased landfills were seen as a good way to create land for housing, industry, and infrastructure.

But putting landfills in a populated area was bound to create problems. In 1900 ex-Fire Marshall Robert E. Rice, who managed the Colonial Hotel at Harway and Surf Avenues, Coney Island, blamed the stench from a landfill on Coney Island Creek for driving guests away from the hotel. Contractor Charles Hart was filling 21 acres of marsh along Coney Island Creek with what he claimed was "street sweepings and ashes." Hart claimed that the fill material was approved by city inspectors. He had twice been brought to court for violating the city Sanitary Code but on both occasions the cases were dismissed. None-the-less accusations persisted, hotel keepers on Surf Avenue sought an injunction to stop the work and several physicians attributed a number of illnesses to odors coming off the landfill ("Odors at Coney Island", *New York Times*, Sep.25, 1900).

Hart blamed the odors on the scows of the Brooklyn Sanitary Company that were loaded at a site at the foot of 21st Street. Not surprisingly, the Brooklyn Sanitary Company denied their scows were the source of the odors (“Odors at Coney Island”, *New York Times*, Sep.25, 1900).

The spread of landfills along the shores of Jamaica Bay began around 1900 and can be traced to two waste streams that defied all attempts at recycling and re-use, street sweepings and ashes. Street sweepings contained dirt, miscellaneous rubbish, discarded food refuse, and horse manure. It was already hard enough to find farmers who wanted manure and the admixture of these other waste streams rendered it completely unfit for fertilizer application. Ashes from coal burning stoves, furnaces, and fireplaces were another waste stream that was both plentiful and hard to dispose of. The practice of combining street sweepings with ashes and using it to fill in marshes was already well established when Dock Commissioner Murray Hulbert announced in 1921 that the main interior channel at Jamaica Bay, between Barren Island and Mill Basin, was selected for filling with material from the Street Cleaning Department. Hulbert went on to say that Rear Admiral Usher, Commandant of the Third Naval District, approved of the idea because it was an alternative to dumping ashes at sea. By filling in the marsh with such material, about 1,100 acres of water front would be created (“11 Improvement Programmes For The Port Of New York, Dock Commissioner Murray Hulbert Outlines a Schedule of Progressive Investment Calling for an Outlay of $20,000,000 Up to the Year 1921”, *Greater New York., Bulletin of the Merchants Association* of *New York*, Nov.4, 1918).

The scale of earlier landfills along the bay's shore pales in comparison to the three modern landfills were operated until the 1980s and 1990s (figures CS1-9 and CS1-10). The Pennsylvania Avenue and Fountain Avenue landfills were located on the northern shore of the bay immediately west of Howard Beach. The Edgemere Landfill was on the eastern end of the Rockaway Peninsula.

The 110-acre Pennsylvania Avenue Landfill was opened in 1956. Originally intended to accept residential and commercial wastes the site has also received sewage sludge and demolition debris. At the time that the landfill was closed in 1979, it was receiving 1000 to 2000 tons of trash each day. Investigators estimate that there are between 6 and 12 million gallons of waste oil buried on the site. Oily leachate has been observed leaking into Jamaica Bay (Goldstein and Izeman n.d., 13). The 287-acre Fountain Avenue landfill operated between 1961 and 1985. It took in commercial and residential trash, asbestos, and incinerator ash. During its last year of operation, the Fountain Avenue Landfill received 8,200 tons of trash per day (13).

The 173-acre Edgemere Landfill forms a peninsula extending northwards into Jamaica Bay. It is located between the Norton Basin and the Somerville Basin. Between its opening in 1938 and closing in June of 1991, the landfill received more than 9 million cubic yards of waste. In 1982 more than 3,000 buried chemical drums were discovered in the landfill (Goldstein and Izeman n.d., 13) (Rhoads n.d., 36).

Even though Jamaica Bay was by this time a city park, there was still pressure on the city's landfills. As one former New York sanitation commissioner observed, garbage has its own imperative, "Unlike polluted air and fouled water, which can be talked about endlessly, garbage must be put somewhere..." (Keating, "The Politics of Garbage," *New York Magazine*, April 13, 1970) Parkland or not, the Department of Sanitation seriously considered filling Jamaica Bay with garbage once Fresh Kills reached capacity. (It should be mentioned that the Department of Sanitation planned to wait until Robert Moses was dead, see chapter 11.) As of 1970, the city was required to dispose of 22,000 tons of refuse daily and waste volumes were growing 4% each year. The non-partisan Citizens Budget Commission urged the city to drop its $1-billion dollar plan to build waste incinerators in favor of increasing the capacity of existing landfills, the development of new landfills on Prall Island (in the Arthur Kill), and consider novel waste processing technologies such as shredding and baling prior to pyrolysis (destruction of refuse under anaerobic conditions), composting, or incineration in a new generation of high temperature incinerators. The new super incinerators would be located in the Brooklyn Navy Yard, Hunts Point, Fresh Kills, and two units at Broad Channel (Kihss, "City Is Urged to Get Rid of Waste in New Ways", *New York Times*, Nov.30, 1970).

Although not nearly as ambitious as the waste reduction industry on Barren Island, proposals to use methane from landfills and the nearby sewage treatment plant to generate electricity for the Starrett City housing project was first advanced in May of 1977 when the city sought a federal grant for a feasibility study and preliminary design (“Starrett City Energy Plan Sought”, *New York Times*, May 28, 1977). Located near Canarsie, Starrett City was established in 1974 and housed 20,000 tenants in 5,881 apartments in 46 high rise buildings (Prial, “Starrett City: 20,000 Tenants, Few Complaints; Starrett City Wins Praise of Residents”, *New York Times*, Dec.10, 1984). The city signed a contract with RSF (Reserve Synthetic Fuels) of Signal Hill, California, in November of 1979. The contract gave RSF gas extraction rights on 400 acres within the 3,000 acres of the Fresh Kills landfill. The gas would be distributed by Brooklyn Union Gas. It was estimated at the time that 7 million cubic feet of gas would be produced at the landfill, enough to heat 16,000 homes. The contract called for RSF to pay the city $1,000,000 annually and the city was to furnish a million tons of refuse a year at Fresh Kills. Brooklyn Union Gas was scheduled to sink four exploratory wells at the Fountain Avenue Landfill from which it was estimated that 12,000 homes could be heated for 15 years. A similar project was considered for a landfill near Pelham Bay that would provide Co-op City with enough gas for about a quarter of its energy needs (Kihss, “City to Get Methane from Refuse”, *New York Times*, Nov.27, 1979).

Eugene H. Luntey, President of Brooklyn Union Gas told the *New York Times* that methane from landfills could ultimately provide 10% of the gas needed in Brooklyn, Queens, and Staten Island. An experimental membrane-filter process was tried at the Fresh Kills and Fountain Avenue landfills (Kihss, “State Studying Use of 38 Landfills for

Getting Power from Garbage; Called Largest Such Landfill to Test Filter Process", *New York Times*, Apr.27, 1981).

By 1982 the National Park Service was in control of Jamaica Bay so that federal approval was required for entering into contracts with private entities for recovering the methane from the landfills. Congress passed the necessary legislation in early August of 1982. The methane recovery plant for the 300-acre Fountain Avenue site was to be a joint venture of the Methane Development Corporation, a subsidiary of Brooklyn Union Gas, and Getty Synthetic Fuel. The Fountain Avenue landfill was producing enough methane to heat 15,000 for a year. The city was required to pay half of its revenues from the site to the federal government. The monies would be used to support the Gateway National Recreation Area ("Congress Passes Methane Gas Plan", *New York Times*, Aug.4, 1982). Although Starrett City was partially powered by methane gas from the sewage plant, it was not clear from later press reports if the landfill also provided gas for the project (Prial, "Starrett City: 20,000 Tenants, Few Complaints; Starrett City Wins Praise Of Residents", *New York Times*, Dec.10, 1984).

Even after these landfills closed, there were occasional proposals to bring waste processing operations back to Jamaica Bay. Community opposition by the South Canarsie Civic Association and Community Board # 18 defeated a proposed Medical Waste Transfer Station. In response to such proposals, legislation was introduced in both houses of the New York legislature that would restrict the placement of waste transfer station within a mile of residential neighborhoods (*Bergen Beach Community Association*, n.d.).

Conclusions

When the first waste management industries were established on Barren Island the city's regulatory umbrella extended only as far as the waterfront. Once the waste products left the city, there was only a contract for disposal but no laws or regulations governed how or where they would be processed. Such an arrangement could last only as long as the city did not grow around Jamaica Bay.

The increase in waste volumes as a result of the sanitary reforms of the mid 1890s showed that waste management sites had become as unwanted as they were necessary. Attempts to expand the industry and to move it onto Staten Island both failed in the face of local opposition.

Little has changed in urban waste management in the last 100 years. The sale of recovered materials was, and still is, necessary to recover the costs of recycling and collection. Local opposition to waste management facilities has always been strong although in recent years tipping fees have sometimes reduced local resistance. While there were no tipping fees paid to communities near Barren Island, the waste industry did finance trash pickup in large portions of New York City. Even this was not enough to protect the industry from public opposition.

With all of its problems, the waste management infrastructure in Jamaica Bay did at least represent a significant attempt to come to grips with a pressing public health problem and find a long-term solution to the problem of waste disposal.

Figures and Tables

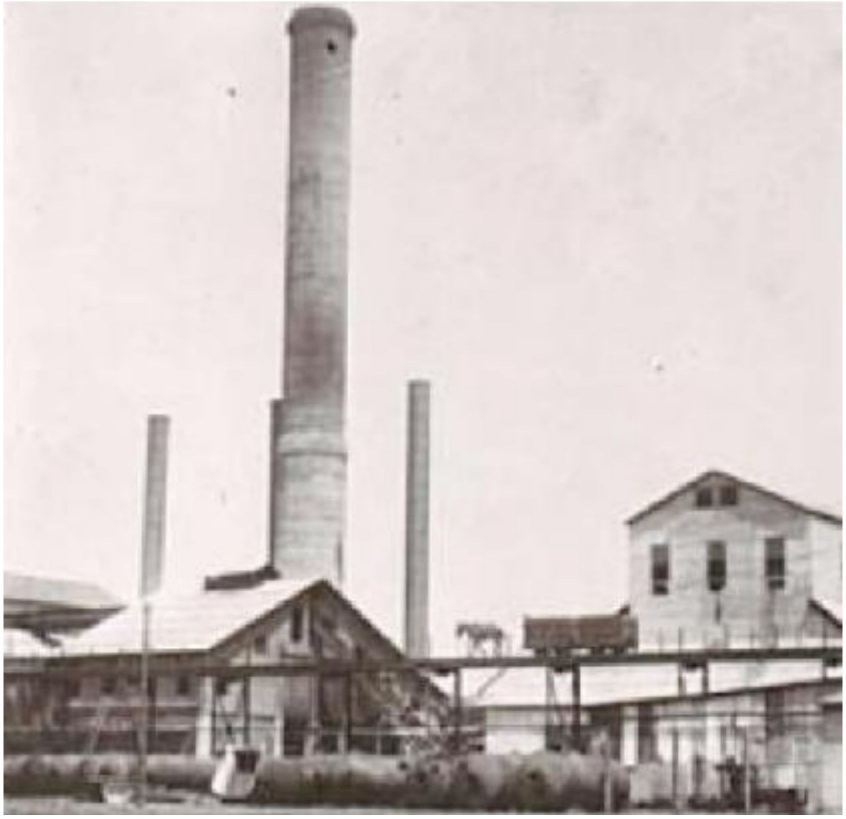


Figure CS1-1. This 1900-era photograph of Barren Island. It illustrates the size of the waste processing plants on Barren Island. (National Park Sevice)

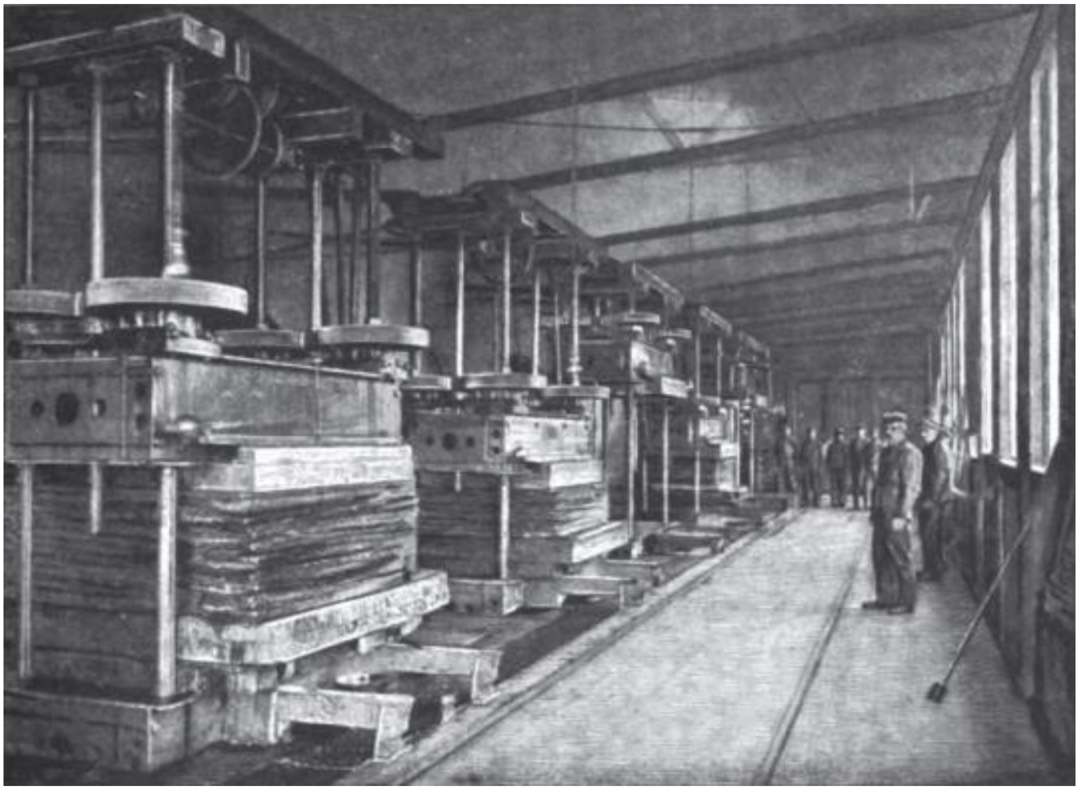


Figure CS1-2. The pressing room at the New York Sanitary Reduction Company. (Google Books)

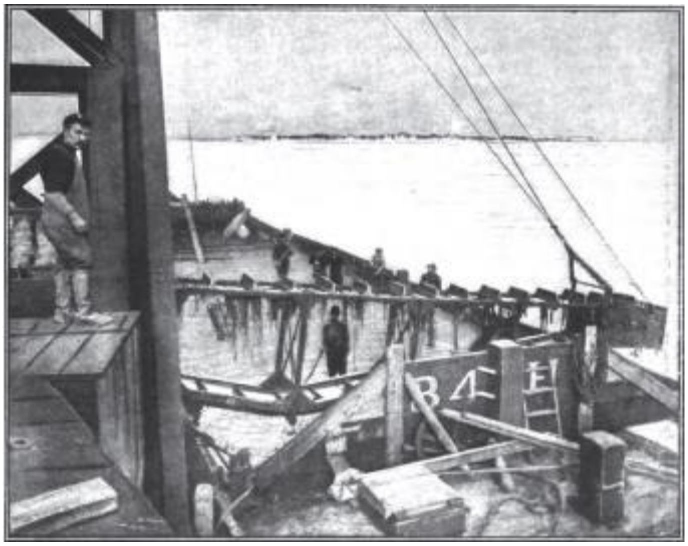


Figure CS1-3. The equipment for unloading barges at Barren Island. This photograph appeared in an 1898 magazine article about the operations on Barren Island. (Google Books)

Figure CS1-4. Workers are shown hand-sorting trash. Photograph from 1915. (Google Books)

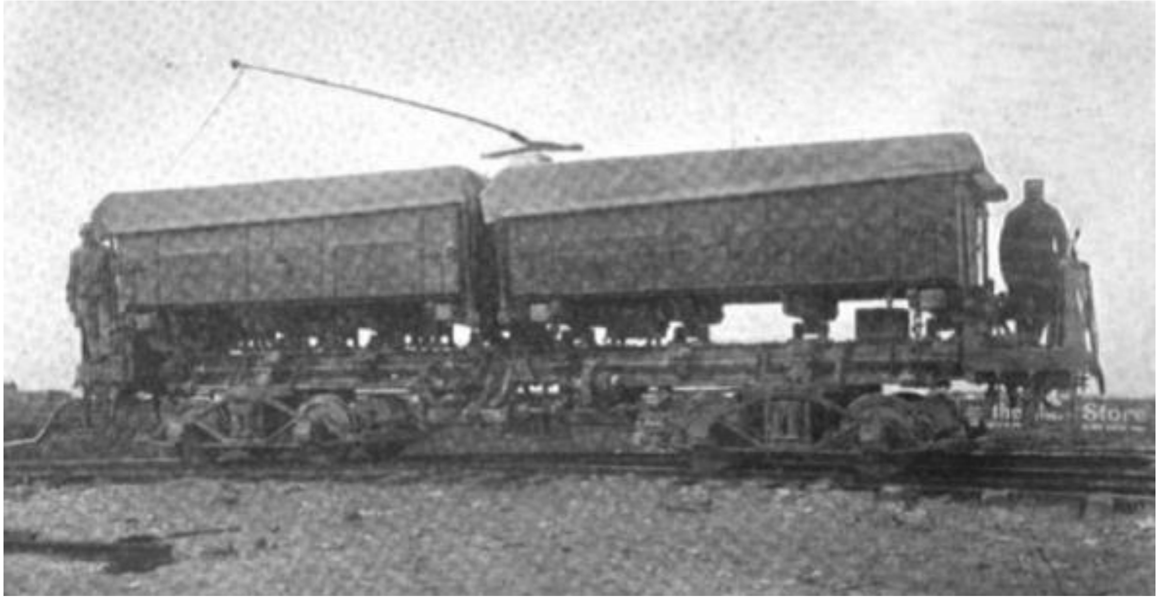
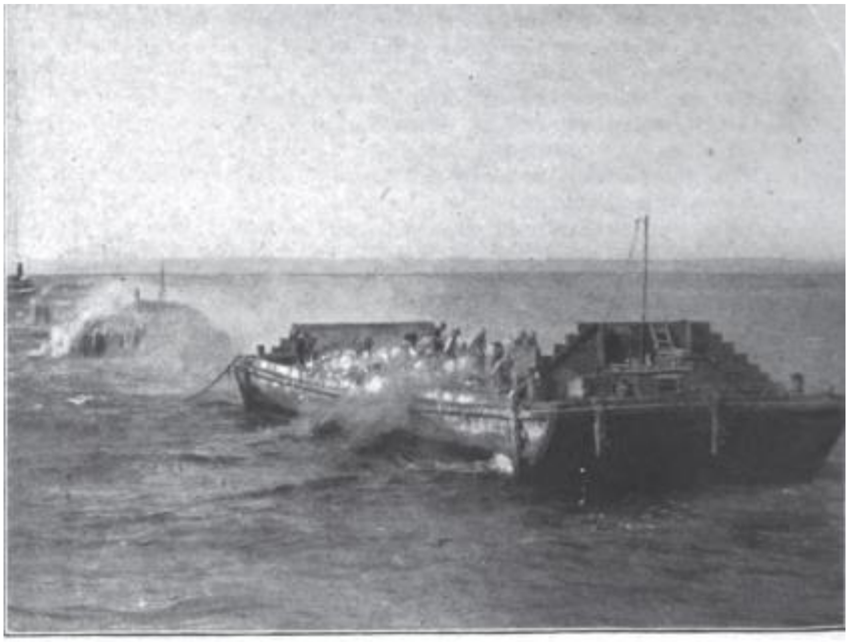


Figure CS1-5. A specialized streetcar for waste collection. The trolley car companies of Brooklyn and Queens used specialized streetcars to collect ashes and bring them to landfills. The lightway cars could run on temporary tracks directly to the dumping sites. (Google Books)

Figure CS1-6. The area where extracted oils were piped into barrels. This photograph dates to 1898. The man on the right is holding what appears to be a cooper’s mallet. Note the exposed electric light bulb. (Google Books)

Figure CS1-7. These houses for workers on Barren Island. These were built over the water like so many other others in and around Jamaica Bay. Note the elevated water tanks. The electrical service suggests a later date for this photograph. (New York Public Library)



UNLOADING A DECK SCOW BY HAND LABOR AT THE "MUD BUOY" THREE MILES FROM CONEY ISLAND.

(The barge in the foreground is of the type usually chartered by the Department when it becomes necessary to hire scows.)

Figure CS1-8. Ocean dumping of wastes. With waste reduction plants no longer operational, New York City reverted to the practice of ocean dumping for the disposal of waste. (Google Books)

Figure CS1-9. The landfills along the shores of Jamaica Bay. These were operational into the 1980s. (NOAA)

Figure CS1-10. 1970s-Era photograph of a New York City Department of Sanitation truck dumping at one of the Jamaica Bay landfills. (NOAA)

Case Study 1, table 1. Twelve reasons why garbage reduction created nuisances ("37th Annual Report of the New York State Dept of Health", *Report of the Division of Sanitary Engineering*, 1917, vol.2, 751).:

1. Garbage is subject to putrefaction and decay resulting in offensive odors and possibly toxic gasses. At the time the science of toxicology was not sufficiently advanced to determine if the odor-causing compounds were in fact harmful to health. Evidence from animal studies and statistical analysis was inconclusive.

2. Garbage may contain bacteria from human feces and saliva. While feces were rarely found in garbage, saliva was much more common although it was though not to play a significant role in disease transmission.

3. Flies bred in household garbage.

4. Piles of garbage would attract flies.

5. Passage of garbage scows would expose persons living near the water or traveling aboard ferryboats to odors.

6. The sight of large garbage scows under tow would be offensive.

7. Odors would be generated at the plant from scows awaiting unloading, filling and emptying digesters, processing the tankage, and general odors around the plant.

8. The odors from the plant would cause loss of appetite and general mental discomfort.

9. Discharge of effluent water might contaminate drinking water supplies.

10. Discharge of effluent water, loose garbage, and wash water would harm fish and other marine life.

11. Discharge of effluent water, loose garbage, and wash water would create offensive sights and smells to persons living on or near the waterways.

12. Under Section 1754 of the Penal Law, the process was noisome and unwholesome and therefore could not be conducted near a public highway.

Case Study 1, table 2. A 1917 analysis of the nutrient, water, and organic materials in a typical load of food and kitchen waste before and after waste processing.

Substance	Percentage
water	73.78
Organic matter	22.63
oil	5.32
ash	3.6
Nitrogen	0.7
Phosphoric acid (P2O5)	0.43
Potash (K2O)	0.27
Total	106.73

(Schroeder, “The Fertilizer Value of City Wastes Part Two, Garbage Tankage, Its Composition; the Availability of its Nitrogen, and its Use as a Fertilizer”, *J. Industrial and Engineering Chemistry,* May 1917, vol.9, no 5, 513)

After processing to remove the water and grease the percentages of the various nutrients become:

Substance	Percentage
water	0.0
Organic matter	81.90
oil	0.0

ash	13.03
Nitrogen	2.5
Phosphoric acid (P_2O_5)	1.56
Potash (K_2O)	0.98
Total	100

(Schroeder, May 1917, 513)

It will be seen that the nutrients are enriched by a factor of 3.6 but in terms of overall percentage they remain fairly low in comparison to many commercial fertilizers. It was recognized at the time that the fertilizer value of garbage tankage was low, containing only 3 to 4% "ammoniacal tankage" which made the product a high volume but low cost material that made an excellent filler. (Terne, Dec.1904, 421).

Case study 2

Jamaica Bay's Fisheries, Their Management and Mismanagement

Abstract

Jamaica Bay is a shallow tidal estuary on the south shore of Long Island and located entirely within the city of New York. Prior to the consolidation of the five boroughs to create modern New York City in 1898, fishng rights in the bay were controlled by the municipalities lining its shores. This control was based on the original patents issued to the towns by the colonial governors. During the 1800s an expanding city of New York increasingly came to rely on Jamaica Bay for recreation. Reliable railroad transportation and a growing infrastructure centered around tourism made the bay popular for swimming, boating, camping, and fishing. By the end of the 1880s the recreational needs of the city focused new attention on the practises of commercial fishermen whose use of sienes and other types of nets was increasingly seen as wasteful. In the interest of preserving game fish as well as protecting the opportunities for recreational fishing, and the tourist dollars it brought in, New York State enacted series of laws that effectively closed the entire bay to commercial fishing that employed any type of net. The first of these laws was the Stadler Bill of 1890. Passage of the bill was in direct opposition to more than two centuries of tradition where the local town governments asserted a right to control Jamaica Bay's resources. The bill also was the first to restrict a specific type of fishing technology at a particular region of New York State. Reaction to the bill was immediate and angry. Commercial fishermen exploited loopholes in the law to continue their traditional net fishing while sportsmen's organizations created private patrols that would enforce the new restrictions. The Stadler Bill was a temporary measure designed to test the principles and after it expired, new laws restricting the use of commercial net

fishing in Jamaica Bay were passed by the New York State legislature in 1896. Problems enforcing the 1896 net ban resulted in another law passed in 1904.

Jamaica Bay was also home to a large shell fishing industry that was also subject to local control. It faced similar pressures as the city expanded around the bay but in this case the construction of sewers and the discharge of untreated wastes into the bay created a public health crisis among shellfish consumers. The existing laws were inadequate for the protection of this fishery and the pressure of development was relentless. The cases of shellfish poisoning are particularly well documented as scientists and public health officials were establishing the foundations of epidemiology. The bay was closed to all commercial shellfish harvesting in the 1920s.

Introduction

Writers in the 1600s and 1700s often noted the abundance of both fin and shellfish in and around the waters of Long Island. As early as 1660 the area around Canarsie Point was known as Vischers Hook (fishers Hook) after a Dutch fisherman named Hoorn who built a home there (Black 1981, 22).

The earliest recorded efforts to regulate fishing in the bay date to the early 1700s when the town of Jamaica began to assert its title to the bay. In May of 1704 "fishermen of Flatlands" were arrested for fishing with nets and without authorization (Black 1981, 22). Controversies over when and how to regulate net fishing within the bay would continue through the late 1800s.

The *New York Mercury* for January 27, 1754, reported that a period of unseasonably warm weather brought many people in "canoes and pettyaugers" to Jamaica Bay for "oysters, clams, etc. . ." (Black 1981, 22). Among the canoes fishing the bay were some from Newtown. This fact has suggested to historian Frederick Black that the town of Jamaica was unable to "keep non-townsmen off the bay and also revealing that parties from communities not immediately adjacent to the bay fished the bay" (22).

In July of 1763 the Jamaica town government declared that: "Whereas divers persons, without any right or license so to do, have of late, with sloops, boats and other craft, presumed to come into Jamaica Bay and taken, destroyed and carried away quantities of clams, mussels and other fish to the great damage of the said town, this is to give warning to all persons who have no right or liberty that they do forbear to limit any such trespass in the bay for the future. . ." (Black 1981, 22).

Only a month later the town government held a special town meeting to address the problem of continued trespass into "the Bay belonging to this town." Several men were designated to prepare a legal defense of the town's title (Black 1981, 22) Challenges to the title continued and by 1791 the town of Jamaica resolved that: "all persons be precluded from coming with boats and pettiaugers in the bay of this town for the purpose of getting clams or oysters without paying the sum of one shilling for every thousand so taken. . . ." (22).

At the same town meeting the voters decided that "no person or persons other than inhabitants of the township and paying taxes within the same presume to cut any sedge on the marshes in the bay of this township, on the penalty of 40s. for each offence" (*History of Queens County, with illustrations, Portraits& Sketches of Prominent Families and Individuals,* 1882, 193-257).

The township's restrictions on fishing were re-adapted several times over the subsequent years. Voters at the town meeting of 1869 voted to exclude non-residents from fishing in the bay. Two years later the voters instructed the trustees to remove "all stakes or other obstructions illegally standing in the waters of the bay, or in the marshes thereof." Presumably these were the stakes and other obstructions placed by fishermen who were not residents of the town. Stakes were usually driven into the bottom of the bay to hold nets (*History of Queens County, with illustrations, Portraits& Sketches of Prominent Families and Individuals*, 1882, 193-257).

By the 1850s the demand for seafood in New York made oyster raising a manor business. In 1854 it was estimated that some 50,000 persons were engaged in the industry, either directly or indirectly. There was money to be made in oyster saloons, restaurants, and fish markets (Spann n.d., 122).

During 1860s, planting oysters began when in 1863 the trustees of the town granted to

D.H. Waters "the privilege of planting oysters under the waters of Jamaica Bay to the extent of one hundred square yards, under said waters known as Hell Gate Marsh" (*History of Queens County, with illustrations, Portraits& Sketches of Prominent Families and Individuals,* 1882, 193-257). The question of planted oysters soon became part of the long standing disputes over fishing rights.

The position long held by the Township of Jamaica was supported by an act of the legislature in 1871. It authorized the leasing of underwater lands for planting oysters only to persons who were residents of the town. It also permitted penalties for any trespassing on the leased lands. Given the town's longstanding claims to control fishing in the bay, a vote in 1875 on the question of these leases resoundingly was against the practice. Exclusive privileges were supported by only 167 voters while 808 voters rejected them. It is not clear whether the voters were dissatisfied. It might be that they feared the leasing arrangement would have a negative impact on the nascent tourism industry. Another possibility is that they felt the lease arrangements had been mishandled by the community's elected officials. Despite the vote, the leases stood and further debate on the matter was not recorded (*History of Queens County, with illustrations, Portraits& Sketches of Prominent Families and Individuals*, 1882, 193-257).

Despite the abundance of fish, it appears that prior to the middle part of the 1800s the majority of the people living near the bay were primarily engaged in farming or other trades and only fished occasionally for either recreation or to supplement their food supply (Black 1981, 22). Of 221 eighteenth and nineteenth century wills surveyed by historians, there are only three mentions of any possessions connected with fishing. One of the wills was from William Van Dyn of Newtown, who in 1769 bequeathed two canoes, the smaller one with rigging and fishing gear. Two wills dated from the 1770s included fishing nets and in the estate of Abraham Emans, also included a canoe. An examination of wills from Gravesend, Flatlands, Flatbush, New Lots, and Jamaica finds that no person listed their occupation as fishing prior to 1801 (Black 1981, 23).

Some idea of the abundance of fish from the late 1800s and early 1900s comes from the diarist John Baxter of Flatlands: "August 4, 1792--Went for eels had 150 very large. . . . September 9, 1792--I fished along the meadows at the Island got 9 bars and one Drum Fish. Went to Rockaway along with R. Voorhees and Peter Voorhees had 900 eels and 200 large snipes. . . . April 13, 1801--Went out afishing with Peter G. Wyckoff and Joseph White - Garret Wychoff and Elias Hubbard—got 36 shad . . . the same day was caught 613 shads in Lots Creek" (Black 1981, 23).

Net Men and Anlgers, Protecting the Fisheries of Jamaica Bay

As recreational fishing expanded in the second half of the 1800s the traditional fishing methods came increasingly under attack.

There was a large menhadden fishery in the New York region and during the previous decades a number of fish oil processing plants had been established on Barren Island (figure CS2-1). This was seen as an ideal place for them as their odors would not be noticed next to those of the waste processing operations. The menhaden fish oil plants were one the major buyers for the commercial fish catch. To supply these operations, the use of nets by commercial fishermen was increasingly seen as a wasteful practice. The Cromwell Bill that was intended to prevent net fishing in Raritan Bay was in the legislature during the 1888 session, State Senator Hawkins, Brooklyn Tax collector Alden S. Swan, and Henry A. Reeves, an attorney at Greenport, all brought their objections to the state legislature at Albany. Reeves was the spokesman for the trio and in his testimony claimed that during the 1886 fishing season there were eleven fish oil factories operating in Suffolk County. They rendered an estimated 140,300,000 menhaden and produced 10,660 tons of dry fish-scrap fertilizer, 701,500 gallons of oil. As with the Stadler Bill that would later be introduced as a conservation measure in Jamaica Bay, the principle legal objection was that this bill would regulate one type of fishing in only one location. Additionally, according to the state's 1873 constitution and a subsequent 1875 law, local affairs were to be regulated by local officials as far as it were "practical and proper." One provision of the bill specifically allowed county officials to regulate fisheries within their local waters. By this standard, any attempt to regulate fishing in Raritan Bay was the responsibility of Richmond County, and not the state. Reeves pointed out that Suffolk County was one of only a handful of New York Counties that was on the sea coast and that it had, at the suggestion of the legislature, already passed about 30 laws regulating its fisheries. Counting all of the bays and creeks, Suffolk County had about 500 miles of coastline and its county supervisors were in a better position to administer its affairs than the legislature in Albany. ("Menhaden The Fishers' Side of the Mossbunker Case," *Brooklyn Daily Eagle*, May 4, 1888, page 2)

The Honorable George Cromwell was the Republican Congressional Representative from Richmond County although from press reports of the era it appears that his district also included parts of Queens County. It is not clear how a bill before the state legislature had his name attached to it unless he was serving in both bodies or his supporters in Albany named the bill in his honor. In either case in October of 1888 Cromwell made a startling announcement at a meeting of the Republican Committee at Long Island City. With only three weeks before the general election Cromwell admitted that he was not likely to carry Richmond County and in the face of opposition from Reeves, was not likely to have much support in Queens. Many of the accusations that would later dog the Stadler Bill were also made against the Cromwell Bill including the charge that the working people would be deprived on thier livlihoods in favor of affluent recreational anglers ("Cromwell Sure to be Beaten," *Brooklyn Eagle,* Monday, Oct. 22, 1888).

The same year that the Cromwell Bill was introduced, an unlikely conservation hero was serving his first term in the New York State senate. Charles A. Stadler (1848-1928) was born in Bavaria and emigrated to New York with his family. Charles' father operated and engraving and embossing shop on Maiden Lane. Charles started in the brewing business in 1870 and in 1879 entered the malting business. He rose to become president of the American Malting Company. (Harrison, 1902, 319)

Stadler became prominent in the liquor industry. He was appointed by the United States Maltsters' Association to represent the group before Congressional committees on matters related to barley and malt tariffs. Like many successful New Yorkers, he was also active in civic affairs and a member of numerous clubs. He also served as a member of the State Democratic Executive Committee for five years. (Harrison, 1902, 319)

Stadler was elected to the senate from the 9th district. This district was in Manhattan and bounded by the east River, 86th Street, 14th Street, and Third Avenue. It also included Blackwell's Island. Stadler's enemies had no quarrel with his morals or the company he kept but did describe him as a "Tammany Democrat" and were quick to point out that most of his efforts in the legislature were devoted to defeating measures that would have restricted liquor traffic. He served on the committees on Commerce and Navigation, Insurance, Manufactures, and Poor Laws. (Record of the Assembly, 83)

What became known as the Stadler Bill was introduced in March of 1890 and it prohibited fishing anywhere in Jamaica Bay except by "rod, hook, and line." ("Jamaica Bay Netters", *New York Times*, Apr.5, 1890) Nothing in Stadler's background would suggest a strong intetest in fisheries conservation. But he was a member of the Wawayonda Club whose members were drawn from the hospitality industry. He would later serve as president of this club. The Wawayonda clubhouse was located on Captree Island on Great South Bay near Babylon, Long Island. (Great South Bay Clams, *New*

York Times, September 27, 1888) The surviving accounts of the creation of the Stadler Bill do not show any other reasons why Stadler should have concerned himself with conservation issues. The most likely reason he was sympathetic to the hospitality sector as a result of his involvement in the liquor industry.

By April of 1890 the Committee on Game and Fish Laws in the New York State Legislature had drafted a bill that would ban commercial net fishing in Jamaica Bay. Opponents of the bill claimed that the local fish markets would be deprived of an important source of supply. Proponents countered that the three fish markets at Rockaway Beach were being supplied from dealers in Manhattan (“Jamaica Bay Netters”, *New York Times*, Apr.5, 1890).

At that time, one of the preferred methods of net fishing was to wait until predators (sharks and porpoises) chased smaller fish up the side creeks where nets would be stretched across them. Another method of using nets was to wait until low tides forced fish out of the bay's side creeks and into deeper water or "sinks" and then draw nets through the sinks, into the side creeks, and finally up onto land (figure CS2-2). Both of these methods were used during the winter or the spring spawning season. Although laws regulated the size of the mesh of nets, it was reported that these laws were widely ignored. Although the main target of the seine nets was the Menhadden the by-catch included a number of other species (“Jamaica Bay Fishermen”, *New York Times*, Mar.12, 1890).

It must be noted that there was no disagreement as to the conservation science during the debate. The bay's role as a nursery and refuge for breeding fish was fully appreciated. Proponents of the bill seemed willing to accept a compromise position if the commercial netters accepted limited conservation restrictions.("Jamaica Bay Fishermen," *New York Times*, March 12, 1890.) In this respect the parties in this debate were far ahead of the times. Before 1900, only a handful of public officials and scientists saw a linkage between the decline in wetlands ecosystems and a decrease in waterfowl and fish populations. After 1910 and into the 1920s, conclusive evidence of this linkage began appearing in the scientific literature. (Vileisis, 160, 1999) But it was not until early 1960s that there was a sufficient volume of estuarine research to confirm scientifically that two-thirds of all major commercial fisheries depended on tidal marshes as spawning grounds. (219)

By the summer when an estimated 500 to 1,000 recreational anglers arrived at Jamaica Bay every day, seasonal catches of sheepshead, bass, and weakfish were reported to be as small as 100 individuals (“Jamaica Bay Fishermen”, *New York Times*, Mar.12, 1890).

In 1889 it was still possible for fishermen to net eight to ten tons of fish per day with fish prices ranging from 8 to 10 cents per pound. Any fish not sold for human consumption went to the fertilizer manufacturers. However overall catches in Jamaica Bay had been decreasing for the previous five years (“Jamaica Bay Fishermen”, *New York Times*, Mar.12, 1890) (figure CS2-3).

It must be noted that there was no disagreement as to the conservation science during the debate. The bay's role as a nursery and refuge for breeding fish was fully appreciated. Proponents of the bill seemed willing to accept a compromise position where the commercial netters might have been possible if the commercial netters were willing to accept conservation restrictions (“Jamaica Bay Fishermen”, *New York Times,* Mar.12, 1890).

At a hearing on the Stadler Bill in June, opponents would argue that the law that would only help the hoteliers and their privileged guests at the expense of ordinary people. It was also argued that if fishing in one part of New York State was restricted to hook and line, then the restriction had to be applied to the entire state and its $4,000,000 commercial coastal fisheries. The issue of exactly how many persons were working the seine fisheries also arose during the debate. Opponents claimed that 300 men in Flatlands worked in the fishery while supporters claimed that not more than fifty men worked the fishery and the total value of the catch was a mere $3,000 a year (“Net Fishing in Jamaica Bay”, *New York Times*, June 4, 1890). New York Governor David Hill signed the measure on June 7th, 1890. In a memorandum to the Governor attached to the bill when it was signed, the Fish and Game Law Codification Commission noted that the bill did have flaws. In principle the commission was in favor of net fishing in any of New York's tidal waters and that it had no interest in discriminating against net fishermen in favor of recreational anglers. The commissioners however noted the proximity of the bay to population centers and because many of the anglers were poor people in need of recreation, the commissioners were willing to approve the bill for one year ("Jamaica Bay for Anglers", *New York Times*, June 8, 1890).

The bill, signed by the governor on June 7, would only last one year and provide a test of the principle ("Jamaica Bay for Anglers", *New York Times*, June 8, 1890). According to data compiled by Black for his National Park Service cultural resource study, in 1890 there were approximately 130 commercial fishermen in Flatlands, which was down from a peak of approximately 200 in 1870 – 1880. By 1892 there would be fewer than 50 fishermen in Flatlands. Oystermen were also in decline. The numbers of men engaged in that work began climbing after 1870 and peaked at about 75 individuals in 1880. By 1892 there were almost none (Black 1981).

The most vocal opponent of the law was State Senator Hawkins known locally as "Mossbunker" Hawkins because of his connections to the Menhadden fishery. The supporters of the ban noted that the by-catch of the seine netting was destroying the game fish and pointed out that the state had recently created the Adirondack Park to save the northern fish and wildlife. The bill's supporters decried the destruction of Jamaica Bay for the sake of a few tons of fish that would only be ground into fertilizer ("Fighting for the Fish; Jamaica Bay for Anglers Is the Cry. Rockaway Hook - and - Line Fishermen Much Encouraged at the Progress of the Stadler Bill", *New York Times*, Mar.17, 1890).

The law prohibiting the use of seine nets in Jamaica Bay was signed by Governor Hill in place by late June of 1890. The commercial net fishers at first seemed to be following the law but by late July appeared to be ignoring it. They also pointed out that Jamaica Township had a colonial era patent granting them ownership of the bay and had traditionally controlled its waters. Therefore, they argued, the State Legislature had no jurisdiction over the bay. Observers agreed that this argument was not likely to stand up in court and predicted a confrontation between the recreational and commercial anglers before the end of the summer ("It makes the Seine Men Angry", *New York Times*, July 28, 1890).

Meanwhile the organization that had lobbied hardest for the law, the Association for the Protection of Jamaica Bay, was busy documenting violations of the law and appointing three special constables who would enforce the law. The association also announced a reward of $50 for the arrest of the net law violators ("It makes the Seine Men Angry", *New York Times*, July 28, 1890). Immediately after the law was passed the Association for the Protection of Jamaica Bay promised to hire five special constables to monitor compliance and even proposed to fit out a gunboat for patrol duties. One commercial fisherman responded to these announcements by claiming to have a loaded shotgun ready for any persons enforcing the law ("Fishing in Jamaica Bay", *New York Times*, June 23, 1890).

The commercial fishermen struck back at the hoteliers, boat livery operators, and operators of fishing resorts. Noting that selling bottled beers and liquors on Sunday was unlawful, they threatened that the excise laws would be immediately enforced if any one of their number was arrested for using nets ("It makes the Seine Men Angry", *New York Times*, July 28, 1890).

But public opinion had long favored the recreational anglers. The previous summer an unidentified party of "some Rockaway Boys" raided the commercial fishing camps and burned several hundred yards of nets ("Fishing in Jamaica Bay", *New York Times*, June 23, 1890). In March while the bill was first being debated over 15,000 signatures supporting it had been collected from Rockaway Beach and nearby communities. It was estimated that the value of the hotels, boat liveries, tackle shops, and other infrastructure supporting recreational fishing exceeded $200,000 ("Jamaica Bay Fishermen", *New York Times*, Mar.12, 1890). A local banker at Far Rockaway was known as a supporter of the commercial fishermen but changed his views after depositors began withdrawing their funds in protest ("Fishing in Jamaica Bay", *New York Times*, June 23, 1890). Observers noted that the fishing in the bay had improved since the net law went into effect ("It makes the Seine Men Angry", *New York Times*, July 28, 1890).

There are no surviving press accounts of Charles Stadler taking an interest in protecting Jamaica Bay after his bill expired. He returned to private life after serving his one term in the State Senate. The Stadler bill appears to have died quietly after its trial period but another net ban went into effect in 1896. Support for this law was said to come from the boathouse keepers on Jamaica Bay and the act became known as the “Boathouse Keeper’s Anti Netting Law.” A volunteer organization "Protective League of Salt Water Fishermen" was created in 1898 and appears to have assumed they would have the authority to arrest all “violators of the fish and game laws of this vicinity.”(Mullen 1906)

In September of 1891 five fishermen from Canarsie were arrested for using nets. A constable Ward and his party are credited with making the arrest but it is not clear if Ward was the special constable hired by the Association for the Protection of Jamaica Bay and who comprised his party. With the expiration of the one year trial period it is not clear if Ward even had any authorization to make arrests. Ward's full name was not even mentioned in the press reports. As the constables descended on the men's boat, Ward drew his revolver. The captain jumped overboard leaving the rest of the men. The press reported that the commercial netters were growing increasingly bold. They were said to have taken several tons of weakfish and assorted game fish and this was reported to have led to a decline in fish stocks during the summer of 1891 (“Net Men Captures”, *New York Times*, Sept.8, 1891).

Examining the occupations in Flatlands shows that as the numbers of men engaged in fin-fishing would peak in 1870 – 1880 but the number of men working in the shellfish industry would begin to rise in 1870, peak at about 75 individuals in 1880 and then decline to almost none by 1892.(Black, 62)

By October of 1900, the Protective League lobbied the state senate for two new bills. Together the bills called for limits on the size of commercial fish nets and the removal of any fixed nets Saturday at noon and Monday. Taking any type of food fish in tidal waters with purse nets, such as those used for Menhadden, would be prohibited. An exception would be made for fishermen taking fish for their own consumption. The bills also called for a halt to the extraction of oils from food fishes. ("New Fishing Laws," *Brooklyn Daily Eagle*, Oct. 31, 1900) The election of a new governor in the fall of 1900 prompted the league to call for more game and fish protectors. League President Biedenger claimed that commercial fishing interests were coming to share their views. He cited the fact that commercial fishermen working in the Hudson River removed their nets three days each week and that the menhaden industry, “will not fight us.”("Salt Water Fishermen," *Brooklyn Daily Eagle*, Dec. 8, 1900.) At the time the American Fisheries Company had experienced a dramatic decline in Menhaden stocks and was in bankruptcy and voluntary reorganization. ("Discharges in Bankruptcy," *New York Times*, Mar. 8, 1900)

What relationship, if any, existed between Stadler and the league were not recorded. It is clear that the Protective League was going to be at the forefront of efforts to protect Jamaica Bay's fisheries. At its earliest meetings in the spring of 1899, the league’s agenda targeted net and seine fishing in the waters around New York City. The league was also lobbying the state legislature for control of chemical discharges from factories. It promised to organize branches in every assembly district and become a force in the upcoming elections. ("Will Stand by Fishermen," *Brooklyn Daily Eagle,* December 15, 1900.) It is not clear if the league's membership was mostly confined to New York City although later press reports would state that it was trying to increase its membership on Long Island. ("Aim to Protect the Fish," *New York Times,* April 29, 1899.)

Pushback came from Republican state Assemblyman Joseph N. Hallock (1861 - ?) representing the First District of Suffolk, Long Island and member of the Assembly's Fish and Game Committee. Hollock told a reporter for the Brooklyn Daily Eagle that he was opposed to the measures called for in the two bills. Although he confessed to not having had the opportunity to read them, Hollock stated that he would most likely oppose them as he had "learned to view any with suspicion any bill that emanates from the Protective League of Salt Water Fishermen." ("Will Stand by Fishermen," *Brooklyn Daily Eagle*, Dec. 15, 1900) Hollock claimed that when he killed two earlier bills proposed by the Protective League, he was accused of being a lobbyist for the commercial net fishermen. Hollock promised to support the commercial fishermen of his district regardless of the league's wishes. He characterized the league members as being "hook and line fishermen and city sportsmen who fish for pleasure." ("Will Stand by Fishermen," *Brooklyn Daily Eagle,* Dec. 15, 1900)

Finally in May of 1904 the Governor of New York signed a bill formally delineating Jamaica Bay and its adjacent waters. A line drawn between Rockaway Point and Coney Island defined the entrance of the bay. Jamaica, Flatlands, Grassy, Sheepshead, and all other bays and inlets were specifically designated as part of Jamaica Bay. A with the earlier bills, fish could only be taken by angling. Two additional game protectors were appointed for Jamaica Bay with authority to enforce the fishing regulations although their salaries were not actually approved for another two years. (C. J. Mullen, "Will Prosecute Net Fishermen," *Shield's Magazine* 4 (1907)

Shield's Magazine gleefully reported in its February 1907 issue that the new laws were finally having the desired effect. The Brooklyn Branch of the Protective League of Saltwater Fishermen was able to work with the new wardens on enforcement and the magazine credited Gus Christman, president of the league's Brooklyn Branch, with much of the organization's success. The magazine noted that the situation was complicated because the commercial fishermen started working at night. Dick Wanzer, of Canarsie, who had escaped prosecution under the previous law, was arrested and fined $60. (Mullen, 1907.)

The magazine did note that another problem arose, that some of the hoteliers, boat livery operators, and even some fishermen seemed to be afraid of the reprisals from the net fishermen. The Protective League offered to reimburse anyone who suffered a monetary loss as a result of reporting illegal net fishing. (Mullen, 1907)

The Shellfish Industry

At the time that the commercial fin fishing industry was in decline, harvesting shellfish became a major industry along the east coast and Jamaica Bay was a major beneficiary of its growth (figure CS2-4). As before there were conflicts over who should control the resource.

The case of Calvin Huffmire gives a glimpse into how oyster beds were regulated by the individual towns lining the shores of Jamaica Bay. Permits for planting oysters on underwater lands controlled by Flatlands were granted by a Justice of the Peace and the Town Supervisor. The law that authorized them to grant the permit provided that any person who had been an inhabitant of the town for at least six months prior to the application. Huffmire obtained his first permit in December of 1882. There was an annual rent of $10 a year. Each year the permit had to be renewed (Desty, Rich, Farnham and Smith 1915, 422).

James A. Bailey came to control a piece of underwater land measuring 6.4 acres starting in 1898. He obtained the land from Smith Watts, who had leased the land from the Fisheries Commission of the State of New York in 1895. It is not clear if Bailey had obtained control over Watts' lease or had come to own the lands outright. Press reports at the time referred to him as owning the lands but did not explain what happened to the state's lease arrangement (“Sewer Spoiled Oyster Beds”, *Brooklyn Daily Eagle*, Mar.6, 1902).

The shellfish and hospitality industries lead the first attempts to ban sewage disposal in the bay. By 1885 the number of hotels and associated sewers was beginning to trouble local landowners. E.A. Mason, who owned the St. Elmo Villa at Sheepshead Bay, wrote to the State Board of Health in June of that year to complain about the growing amount of waste in the bay and its effect on both his own business and that of the neighboring hotels. An unidentified person who worked for the *New York Herald* newspaper had reservations the St. Elmo but canceled them after seeing the state of Sheepshead Bay. Mason reported that the Manhattan Beach Hotel's artesian well was surrounded by outhouses and kitchen drains. These were also close to the pumping station that supplied both the Manhattan Beach and Orient Hotels. Mason also complained about the local board of health. He stated that the board was powerless to act, they seemed only to consider the construction of sewers within their purview and in the absence of sewers wastes could be discharged into the Sheepshead Bay. Any complaints could be referred to them (Mason 1886).

The complaint was investigated by a R.L. Van Kleek, who is only identified in the reports as a "health officer" but there is no mention of who employed him or what his qualifications were. Van Kleek inspected the wells and noted that all of the cess-pools and privy vaults were in good condition and met all of the health code requirements then in effect. All of the cesspools were more than 100 feet from the wells although one of the water closets was a mere 50 feet from the nearest well head. The wells were designed to provide pure water to the town and the hotels and at a depth of 30 feet; they were thought to be safe from contamination. There was one note of caution in the report, although the area around the hotels' wellheads was undeveloped when the wells were drilled, but 25 buildings were erected in the area during the previous three years. This situation called for careful monitoring and in the future an adequate supply of water would be required to flush wastes out into the bay. As for the allegations that Sheepshead Bay was being filled with human wastes, the sewer outfalls were inspected and while the flows were normal, no solids were being discharged into the bay. A sample of the well water was taken and sent for testing. It was found to be pure, although at the time bacterial tests were unavailable so ammonia, nitrates, and volatile organic content were used as proxy measurements for sewage contamination (Mason 1886).

The State Board of Health was meeting in New York's Everett House to consider sewerage plans in Tarrytown and Kingston. Watkins W. Jones and James Harper, city commissioners from Far Rockaway attended the September 1889 meeting and asked the commissioners if it were possible for the town to run its sewers directly into Jamaica Bay without any disinfection. The commissioners referred the men to a statute intended for the protection of oyster beds that prohibited this action (“Discussing Sewerage”, *New York Times*, Sept.29, 1889).

Harper and Jones apparently did not like that answer because two year later in May of 1891, they would again appear before the State Board of Health at a hearing on sewer plan in which Far Rockaway would discharge its effluent into Norton Creek. The creek connected to Norton Basin and then into Jamaica Bay. A delegation from Far Rockaway testified before the Board of Health that the proposed sewer would contaminate the waters, render Far Rockaway Beach unfit for bathing, affect the sea food in the bay, and reduce property values. Another protest was raised by the "owners" of the oyster beds. A petition against the sewer was signed by eighty-three members of the Oystermen's Association and presented by the president of the association, George H. Schaffer. Another city commissioner, Robert McCafferty was also at the hearing. The three commissioners had developed the plan and were there to defend it. They claimed that the creek was deep and the flow was sufficient to "dispose of the sewage without injury to the health of the locality." The Board of Health rejected the plan on the grounds that the discharge would not be into either deep running water or another system of sewage disposal (“Sewerage Plans Rejected”, *New York Times*, May 28, 1891).

At the same time a similar case was proceeding on the other side of the bay. An 1889 act permitted empowered commissioners at Flatbush to construct a sewer to tidewater. The 15,000 persons of Flatbush were expected to generate 1.5 tons of sewage per day which would be carried through a new, 66-inch diameter, brick-lined sewer to an existing line that discharged into Mill Creek (“Fear a Sewer”, *Brooklyn Daily Eagle*, July 31, 1891).

A petition was circulated in Flatlands and presented to the Board of Health. The petitioners retained the law firm of Evarts, Choate, and Beaman of New York to represent them before the Board of Health. The petition claimed that there was insufficient current at the proposed outlet to carry the wastes out to sea. Mill Creek was only four feet deep.

It ran through coastal marshes and emptied into Garritson's Creek that in turn emptied into Dead Horse Bay between Barren Island and Coney Island. They foresaw sewage piled up on the marshes, endangering the health of their community, and ending up on the beaches of Coney Island. They based their claims on the argument that the 1889 act only allowed for the construction of the sewer and did not grant Flatbush's commissioners the authority to route it any way they chose (“Fear a Sewer”, *Brooklyn Daily Eagle,* July 31, 1891).

The case against the sewer was presented to the State Board of Health in 1894. A sanitary engineer named W.M. Paul Gerhard was asked to prepare a report for the board which was read at the hearing. His report repeated many of the claims made in the original petition and noted that the creek was only four feet deep, had shallow banks, and was bordered on either side by low lying land or salt water marshes covered with thick sea grass. The channel was slow moving, circuitous, and obstructed by sandbars in several places. The report also noted that discharging untreated sewage, a practice called "crude disposal" was common but that in order to be acceptable (i.e. sanitary) the discharge had to be into a large body of water, a running stream, a tidal estuary, or into the ocean. In any case the volume of water had to large enough to "render sewage innocuous by dilution." Alternatively, if the current was rapid and strong, the sewage could be carried off to a large body of water like the ocean. None of these conditions were present at Mill Creek. There was, according to Gerhard, a strong possibility that the sewage would be deposited on the tidal flats, decompose and create noxious gasses. The problem would be especially acute in the hot summer months. The report also claimed that this would "endanger the health of the occupants of summer residences along the shore." Property values would fall and recreational use of the area for boaters and swimmers would be diminished. A small bathing beach at the foot of the long pier would have to be closed. The extensive oyster beds along Mill and Garretson's creeks would be destroyed. The report makes sheds some light on what was believed at the time about fishing and sewage. Fish were though to thrive in "fresh" sewage discharges but could not survive if the discharge was "putrid." The report did not explain why this was the case (New York State Department of Health 1894, 149).

Gerhard believed suitable alternatives included land disposal after suitable purification, position the outfall to carry sewage out to sea, or to construct a reservoir from which sewage could be discharged only during the first hours or the middle third of the outgoing tide. This last option was only practical if the discharge point were located farther downstream where current flows were greater (New York State Department of Health 1894, 149). After all the debate and handwringing, the sewer was built and as its opponents predicted, the oyster beds were damaged.

Calvin Huffmire was one of the first ones affected. Shortly after the sewer was opened Huffmire discovered his oysters were ruined by a coating of tar and "sludge acid." These were by-products of gas manufacturing and were discharged into the sewer (Desty, Rich, Farnham and Smith 1915, 422). Huffmire won his suit in September of 1894. He was awarded $1,000 plus costs. (“Brooklyn”, *New York Times*, Sept.15, 1894).

The decision was appealed and dragged through the courts until reaching the New York Court of Appeals ten years later. Huffmire's essential argument was that while the sewer was legally constructed, dumping a town's sewage on the oysters essential was a government "taking" of private property without compensation. By the time the case came to trial Flatbush had already been absorbed into the City of Brooklyn. The city's attorneys argued that the city was therefore not liable for damages. The Court of Appeals rejected this argument noting that the City of Brooklyn absorbed the tax revenues of Flatbush; they also absorbed its debts and liabilities (Desty, Rich, Farnham and Smith 1915, 422).

The City of Brooklyn also argued that as the sewer was built with the state's authorization there was no fault that could be ascribed to the city. In ruling for Huffmire, the court noted that while legislation that authorized a "public improvement may protect a municipality from liability for consequential injuries, it does not protect it from liability for the direct, actual, and physical taking of property" (Desty, Rich, Farnham and Smith 1915, 422).

Huffmire had legal title to the oysters and while the oyster beds may have been under the town's waters, dumping wastes on them was essentially no different than if he was growing a "crop" on land. He had suffered an "invasion of a private right that had no legislative sanction (Desty, Rich, Farnham and Smith 1915, 422).

In 1894 New York Governor Roswell Flower issued an order directing that the nuisances created by the sewer be abated. The order contained five major points. Firstly, gas house sludge (the tarry by-product of the conversion of coal into gas) and other injurious substances had to be cleaned out of the pipes. Secondly, leaks in the wooden conduit had to be repaired. Thirdly, plans for a new sewage treatment facility had to be submitted to the Board of Health. And lastly, all future sewers from Flatbush, if they discharged into similar locations, would have to be properly treated ("A Nuisance In Flatlands.; Gov. Flower Makes an Order Concerning the Sewage of Flatbush", *New York Times*, July 17, 1894).

It was not clear how Flatbush was supposed to comply with the fourth requirement. This specified that no sewage from Flatbush was to be discharged into Mill Creek that was in "such a condition or in such as manner as will create a nuisance" ("A Nuisance In Flatlands.; Gov. Flower Makes an Order Concerning the Sewage of Flatbush", *New York Times*, July 17, 1894).

Shortly after he took possession of his underwater lands James A. Bailey discovered that the Flatbush sewer had been damaged at a point well above its mouth. Although it was repaired somehow the flow patterns were changed and sewage now flowed over Bailey's oyster beds. He sued the city and in 1902 was awarded $8,676 ("Sewer Spoiled Oyster

Beds", *Brooklyn Daily Eagle*, Mar.6, 1902).

The court ruled that Bailey was entitled to an injunction that restrained the operation of the sewer but that the injunction would be postponed until 1903 because the city is "endeavoring to remove the cause of the damage." to compensate Bailey until the sewer was completely repaired, the city was ordered to pay him $500 ("Sewer Spoiled Oyster Beds", *Brooklyn Daily Eagle*, Mar.6, 1902).

Some people did not seem to care that their oysters were contaminated with sewage. Residents of Rockaway complained to the Board of Health in 1902 that clam diggers working off Rockaway at low tide were harvesting oysters from areas adjacent to sewer outfalls (figure CS2-5). At each low tide up to about a dozen men and boys could be seen digging at the sewer outfalls. It was noted that soft shell clams seemed to thrive in the sewage and it was easy to dig a large quantity in a short period of time. The complaint was not only did this expose consumers, many of whom lived in Rockaway, to contaminated shellfish but that digging in the sewage released noxious gasses ("Want Clam Digging Stopped", *Brooklyn Daily Eagle*, Nov.28, 1902).

Writing for the *New York State Journal of Medicine* in 1913, Dr. Linsly R. Williams noted that the major dangers presented to the public from exposure to polluted harbor waters came from eating shellfish and swimming. Williams noted that in 1910 there were 3,499 cases of typhoid fever of which about half were treated in the homes of the patients. While the sewage coming from an hospital might be disinfected to prevent further spread of disease, there was no such provision for private homes whose sewage would eventually find its way into the harbor (Williams, "Pollution of Harbor Waters of New York, Especially Referring to Bearing on Health", *New York State Journal of Medicine*, Vol.13, no.1, Jan.1913, 19).

Williams cites several disturbing findings. The typhoid bacilli could survive for two weeks in sewage and up to a month in sea water. It was impossible to know how many of the pathogens entered the harbor each year and found their way into shellfish (Williams, "Pollution of Harbor Waters of New York, Especially Referring to Bearing on Health", *New York State Journal of Medicine*, Vol.13, no.1, Jan.1913, 19).

By 1908 it was illegal to place, or allow to be run into waters in the vicinity of oyster beds any sewage, sludge, acid, refuse, or materials injurious to oyster culture. But with the five boroughs of New York City discharging an estimated 500,000,000 gallons of wastewater every twenty four hours, it seems that no oyster taken anywhere in the harbor was going to be safe for human consumption (Williams, "Pollution of Harbor Waters of New York, Especially Referring to Bearing on Health", *New York State Journal of Medicine*, Vol.13, no.1, Jan.1913, 19).

By this time, oyster culture was only permitted at sites approved by the New York State Bureau of Marine Fisheries. Oyster harvesting was prohibited in any part of the inner harbor although the limits of this area seem not to have been clearly defined. Even where clear limits were in place, unlawful harvesting continued to occur. In Jamaica Bay a number of persons dug soft shell clams in contaminated areas but these were primarily for home consumption. During the summer months this was a popular activity with tourists. An outbreak of typhoid at Lawrence was traced back to oysters harvested from the Grass Hassock Channel. The channel was contaminated by sewage from Averne and the oysters from it were sold at Inwood and Lawrence (Williams, "Pollution of Harbor Waters of New York, Especially Referring to Bearing on Health", *New York State Journal of Medicine*, Vol.13, no.1, Jan.1913, 19).

Williams noted that the planned improvements to Jamaica Bay included expanded sewage treatment capacity but he despaired of the waters ever being entirely free of pathogens and predicted that oyster harvesting in the bay would have to be abandoned before long (Williams, "Pollution of Harbor Waters of New York, Especially Referring to Bearing on Health", *New York State Journal of Medicine*, Vol.13, no.1, Jan.1913, 19).

George W. Stiles of the US Department of Agriculture cited three factors causing concerns about gastrointestinal illnesses caused by contaminated oysters. An epidemic of typhoid at Wesleyan University in 1884 was traced to contaminated oysters; there was a similar incident in Lawrence, Nassau County, New York, in 1905; and the passage of the Pure Food and Drug Act of 1906. In the case of the Lawrence, New York, outbreak 21 out of 31 cases were traced to eating oysters and clams that had been floated or grown in the waters of eastern Jamaica Bay near the town of Inwood. In the wake of this incident the George A. Sopor recommended banning the sale in Lawrence of any shellfish taken from locations within Jamaica Bay that were "within the influence of the Averne sewers or from the cove at Inwood, which receives the sewage of Far Rockaway" (Sopor, “Report of a Sporadic Outbreak of Typhoid Fever at Lawrence, NY, due to Oysters”, *Medical News*, Feb.11, 1905, 241-253). Starting in 1908 the Bureau of Chemistry began examining oysters and completed 2,000 bacterial analyses of oysters and clams by 1912 (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances*, 1912, bn. no.156).

The Bureau's attention was focused on Jamaica Bay by an outbreak of 83 cases of typhoid and diarrhea after a banquet at The Music Hall of Goshen, the seat of Orange County, New York, on October 5, 1911. Individual cases were reported at Rochester, and Newburgh, New York. All of the oysters consumed by the victims of these outbreaks were traced to a single oyster dealer on Indian Creek in Canarsie. These outbreaks were not unforeseen, the New York State Board of Health had documented the contamination of Jamaica Bay and the subsequent contamination of shellfish grounds in 1908 (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances*, 1912, bn. no.156).

In 1904, Jamaica Bay were the largest single source of oysters in New York State. The oyster beds of Jamaica Bay were leased by the state. The bay produced between 500,000 and 1,000,000 bushels annually (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances*, 1912, bn. no.156). Although many oyster schooners went directly from Jamaica Bay to New York the principle shipment points were Canarsie (where there were 9 oyster houses as of 1911), Inwood, and Flatbush Bay. (Stiles 1912).

By 1904 public health officials had identified both point and non-point sources of sewage contamination. The latter were principally the summer bungalow colonies at Sand Bay (127 cottages), Old Mill Creek (176 cottages), Ramblersville (220 cottages), Bergen Creek (50 cottages), Bergen Creek (50 cottages), Cornell Creek (53 cottages), and another 200 or more cottages along the line of the New York Woodhaven, and Rockaway Beach Railroad. All of these buildings had privies that discharged into the water or onto marshes subject to tidal overflow (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances*, 1912, bn. no.156).

While there were several sewage plants on the bay that were recognized as point sources of pollution but the huge number of summer visitors stressed their capacity to the point where effective treatment entirely ceased. The Sheepshead Bay Disposal Plant used a method of chemical precipitation and during the winter months treated the sewage of 2,000 persons. On the busiest summer days (most probably race days at the Sheepshead Bay horse racing track) the wastes of between 40,000 and 50,000 people were sent to the overburdened plant. Bergen Beach was visited by between 50,000 and 60,000 persons a week during the summer. The wastes of an estimated 8,000 persons a day was sent into the bay every day during the summer.

A similar situation existed at Canarsie where 16,000 persons visited the town every day in the summer, the number of visitors rose to about 30,000 on Sundays. "Practically" all of the sewage from these persons was discharged untreated into the bay. A permanent population of 50,000 residents sent their sewage into the New Lotts (or East New York) Disposal Plant. This plant handled 10,000,000 gallons of sewage and storm water every day and a "relief by-pass" was in operation between 11:00 and midnight every day. The sewage that was actually processed received less than 20 minutes of treatment before discharge. The Jamaica disposal plant handled the sewage of 18,000 persons and discharged into Bergen Basin (the total population of Jamaica at the time was 25,000 persons.) This plant also used chemical precipitation but at best, was only capable of reducing bacteria and organic matter by only 50%. In Far Rockaway the permanent population was only 6,500 but rose to 30,000 in the summer. Not surprisingly, the sewer plant was thought to be overloaded during the summer.

The population of Rockaway Beach rose from a winter low of 6,000 to an estimated average daily population of 55,000 to 60,000 persons but the population went up to between 125,000 and 150,000 on the busiest summer days. Twenty nine sewers carried the sewage of these persons into Jamaica Bay. The Hendrix Street disposal plant was built in 1892-93 and was designed to treat 3,000,000 gallons of sewage each day. By

1912 the plant was attempting to treat 10,000,000 gallons every day but the total sewage flow was 18,000,000 on dry days! The sewage plume into Jamaica Bay was said to be 1 mile long. Bacteriological tests at the plant revealed that the sewage was essentially untreated (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances*, 1912, bn. no.156). In the words of the Bureau of Chemistry, "Jamaica Bay is located dangerously near a large city and into it many millions gallons of sewage empty daily" (Stiles 1912).

In reporting on the typhoid outbreak on the Rockaway Peninsula, Dr. George Soper, President of the Metropolitan Sewerage Commission told meeting of the New York Academy of Sciences that "immense quantities" of sewage floated in the East River, the upper Hudson, near bathing establishments, and the Oyster beds of Jamaica Bay. Bacteria counts per milliliter of water were 5,800 compared to only 120 in the open ocean. The worst bacterial contamination was in the Upper Bay at 14,500. Coney Island had counts of 4,500. Speaking specifically about the Rockaway outbreak, Soper said that the oyster dealer had promised the oystermen that their catch would be placed in pure water before being sold but that it was not known if this promise was kept. At the time, Jamaica Bay was supplying New York city with 1,000,000 oysters a year (“Sewage Polluting the Oyster Beds; Dr. Soper Tells of Discoveries of Sewerage Commission in City Waters. New York Behind London. Typhoid and Outbreaks of Other Diseases Traced to Evil Conditions in the Rivers and Harbor”, *New York Times*, Mar.14, 1911).

On September 19, 1912, Soper submitted a paper to the Washington, DC, meeting of the American Public Health Association. Soper was not present and the paper was read by Dr. H.D. Pease of New York. The paper summarized the expert opinions as to the limits that should be set on sewage pollution in New York. Among the recommendations was that the waters of the lower bay might be kept clean enough for shellfish cultivation and bathing but that keeping the waters of the inner harbor equally clean would be impracticable. The opinions from different disciplines were reported; sanitary engineers, hygienists, and health officers all agreed that the value of the oyster industry was not worth the costs of building the sewer plants that would be needed to keep the waters clean. All of the experts consulted agreed that the waters of New York Harbor posed no immediate health risk but that work was needed to prevent further degradation ("Must Clean Waters Around New York; Symposium of Experts Finds the Inner Harbor to be Polluted by Sewage. (No Serious Health Menace: But Report of National Commission Makes Several Important Recommendations for Protection", *New York Times,* Sep.20, 1912).

During the 1910s both the New York State and Federal governments undertook the first systematic surveys of sewage pollution in coastal waters with a view to understanding the impact on the fishing industry.

Nine oyster dealers "floated" their oysters near Indian Creek (figures CS2-6 and CS2-7). The creek was just east of the Paerdegat Sewer where 2,000,000 gallons of sewage were discharged every day and to the west of the Hendrix Street Sewer with its 18,000,000 gallons of daily sewer discharge (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances,* 1912, bn. no.156). A sewage pumping station at that site would not be constructed until the mid-1930s (Rankin 1936).

The practice of "floating" oysters was to place them in the cellar of a bay-side storage building. Sometimes a cellar would be created by enclosing the pilings that supported the building with walls made out of wooden planks. A door in the side of the cellar would allow transfer of oysters directly from boats. At low tide the doors to the storage cellar would be closed and fresh water was allowed to enter from an underground spring. The oysters would plump up from osmosis. Even a 1% drop in salinity would cause the oysters to plump. Observers from the Department of Agriculture noted that the creeks where the oyster houses were located frequently contained visible amounts of floating fecal matter. Observers also noted a three-compartment privy over Indian Creek not far from the dealer that provided the oysters for the banquet at Goshen (Stiles, *Sewage Polluted Oysters as a Cause of Typhoid and Other Gastrointestinal Disturbances*, 1912, bn. no.156).

In response to Dr. Stiles' report, the New York City Health Commissioner, Dr. Ernst Lederle, announced a ban on floating oysters or other shell fish in polluted waters in the City of New York and that no oysters that have been floated or otherwise treated with polluted waters shall be brought into the City of New York or offered for sale in the city

(“Dr. Lederle Denies It”, *New York Times*, Sep.19, 1912).

The New York Times later told its readers that oysters that had been plumped were the most likely to carry typhoid (“Thin Oysters the Safest; Board of Health Goes Into the Theory That They Carry Typhoid”, *New York Times*, Feb.7, 1914).

The American Public Health Association created a scoring method for determining the safety of oysters. The scores were based on the smallest amount of liquid from the inside of the oyster that contained B.coli (Balantidium coli). If for example, 0.1 milliliter of fluid did not test positive for B.coli but 1 milliliter did, then the oysters had a score of 1. If 0.01 milliliters of water did not test positive for the pathogen, but 0.1 did, then the score was 10. This progression continued, a score of 100 meant that 0.01 milliliters tested positive, but 0.001 milliliters tested negative. A "satisfactory" score was 23 or less. Most oysters tested had a score ranging from 3 to 4, but oysters from Jamaica Bay tested from a low around 90 to a high of 250. In other words, the B. coli pathogen could be detected in as little as 0.025 milliliters of water from inside a Jamaica Bay oyster. Between September 28 and December 15, 1911, only three oyster samples had a score of 23 and none scored less. Oysters from other locations on the east coast, from Long Island's Great South Bay to Norfolk, Virginia, averaged 3.31. Bacterial tests on Jamaica Bay water samples confirmed the presence of sewage throughout the bay.

It would not be long before such discoveries would lead city's Board of Health to ban the sale of shellfish that had been raised in Jamaica Bay. Shortly after a ban went into effect, a group of oystermen sued for damages. George A. Carman of Canarsie claimed in a suit against the city that he made $50,000 annually from the oyster beds. The total claims against the city by oystermen amounted to $1,000,000 ("Asks $100,000 For Oysters, Board of Health Closes Bed - Grower Seeks Damages", *New York Times*, Oct.6, 1914).

By December 1924, Dr. Frank J. Monaghan, commissioner of the Department of Health, announced that there were 300 cases of typhoid in New York City. This number of cases was larger than normal but the mortality rate from the disease was lower. According to the Commissioner, there was no danger of an epidemic and no occasion for panic. The water and milk supplies in the city were believed to be pure and attention focused on shellfish. The Health Department Laboratory began examining shellfish but press reports did not include the results of those tests ("Typhoid Increases; Warning is Issued; 300 Cases in City, but Dr. Monaghan Sees No Cause to "Get Excited." Shellfish are Suspected; Health Department Advises All Persons Leaving Here to Have Themselves Inoculated", *New York Times*, Dec.12, 1924). By the 17th of December the number of cases climbed to 331 and intensive investigations failed to detect a link between oysters and the typhoid cases ("31 New Typhoid Cases", *New York Times*, Dec.17, 1924). Commissioner Monaghan issued a ban on shellfish on the 17th. The ban covered Lower New York Bay, Raritan Bay, Sandy Hook Bay, and the entrance to the Shrewsbury River. Other waters near the city were covered by the ban but it was not specifically announced if Jamaica Bay was included in the ban. The public was advised not to eat uncooked shellfish and the Health Department promised that its inspectors would insure that fish dealers would obey the ban (“Ban Put on Oysters from Near-by Waters”, *New York Times*, Dec.17, 1924). The New Jersey Department of Health denied that shellfish from the state posed any danger (“Jersey Denies Any Infection”, *New York Times,* Dec.18, 1924).

Another 23 cases of typhoid were reported by the 21st but the mortality rate remained low (“Typhoid Here Mild, Says Dr. Monaghan”, *New York Times,* Dec.21, 1924). There were 400 people under treatment by the 23rd but the rate of new cases was dropping with only 9 new cases reported (“New Typhoid Cases In City Decrease; Only 9 Reported to the Health Department Sunday and Six Yesterday. 400 Now Under Treatment; Commissioner Monaghan Obtains Federal Aid in Investigating Shellfish Beds Along the Coast”, *New York Times*, Dec.23, 1924). Oyster dealers in Bayport, and West Sayville, Long Island reported their sales fell by 75% since the ban. They cited reports that the Great South Bay at least, had been found free of infection (“New Typhoid Cases Decrease For Week; Long Island Oyster Shippers Complain Against Alleged Discrimination in Embargoes. Product Clean, They Say Point to Health Department Tests to Show Shellfish Are Free From Contamination”, *New York Times,* Dec.28, 1924). Health and conservation officials met at Albany on January 21st, 1925, announced that an extensive survey of shellfish grounds in New York State would soon start and that any polluted areas would be closed to shellfish harvesting (“Oyster Bed Survey To Be Made By State; Conservation and Health Officials at Albany Conference Decide on Action”,.

New York Times, Jan.22, 1925).

The Surgeon General established the National Shellfish Sanitation Program in 1925, one year after a typhoid outbreak was traced to oysters from Raritan Bay. Fifteen hundred illnesses and five hundred deaths resulted. The program would classify shellfish waters on the basis of cleanliness (Steinberg, Suszkowski, Clark and Way 2004).

Even after the implementation of a shell-fishing ban, illegal harvesting would continue. As late as 1932 people were being prosecuted for removing soft clams from Dead Horse Bay without permits and in violation of the statutes (New York Supplement Volume 255 1932, 625).

Shortly after the closure of all commercial shell-fishing in Jamaica Bay the world's second-largest sewage screening plant opened on Queens in 1927. The plant's outfall was to Bergen Creek. It provided primary and secondary treatment with a maximum chlorination capacity of 80 million gallons per day. Capable of processing the sewage from a 24,000 acre area, the new plant was the first unit completed in what was intended to be a group of three. When finished the three plants would have a combined capacity of 240 million gallons per day ("The Jamaica Sewage Plant, the Second Largest Sewage Screening Plant in the World", *American City*, Vol.36, No.3, March 1927, 331-334). Whether these plants would have been sufficient to reverse the tide of sewage pollution washing over the shellfish industry is impossible to say but the answer is probably not.

Sewage pollution would continue to bedevil plans for the bay even to the present day.

Even before the new game wardens were appointed, public health officials were becoming concerned about sewage pollution in Jamaica Bay. The shellfish industries were the first to suffer from pollution and by the mid-1920s all commercial shellfish harvesting in the bay would be banned. Both recreational and commercial fishermen would soon be facing widespread habitat loss as developers filled the marshes along the bay's shore to create new room for housing and industries. They would also face the problems of sewage and industrial pollution.

In one sense the anti-net fishing laws were far-sighted attempts to promote conservation and were enacted at a time when national parks, national forests, and forest preserves were all being created. On the other hand the law did not go far enough to protect fish in that it did nothing to preserve tidal wetlands. Laws against the discharge of sewage and industrial wastes were also passed at this time and were intended to protect the shellfish industry but these laws did not prevent the loss of wetlands either. Both recreational and commercial fishing would ultimately be hampered by this loss and had the two factions joined forces the shape of marine conservation might well have taken a different course. Full protection for the salt marshes along the shoreline would only come with the 1973 passage of the New York Tidal Wetlands Act, Article 25 of the Environmental Conservation Law.

The commercial fishing industry would continue to operate out of Sheepshead Bay and Jamaica Bay would continue to be popular with recreational anglers. The demands of a growing city pitted the two groups against each other but ultimately both would be subsumed under the same urban growth. In 1973 much of the undeveloped shoreline and almost all of the island marshes would come under the control of the National Park Service. Jamaica Bay National Wildlife Refuge and Gateway National Recreation Area would become one of the most-visited national parks in the country but never again would it have the same prominent role in the city's economic and recreational landscape.

Epilog, is the Bay Safe?

As of 2007, six water pollution control plants (WPCP) operate in the Jamaica Bay watershed. These are the Jamaica WPCP (adjacent to Bergen Basin), Rockaway WPCP (Beach Channel Drive in Park), 26th Ward WPCP (Flatlands Ave in the Spring Creek section of Brooklyn), Coney Island WPCP (Adjacent to Shell Bank Creek near Sheepshead Bay), Spring Creek Auxiliary WPCP (located at the head end of Old Mill Creek providing hold overflow for the 26th Ward WPCP), and Cedarhurst WPCP (located at Peninsula Boulevard, Cedarhurst, discharges into Mott Creek). (Watershed Protection Plan, p. 40) New York City's secondary WPCPs are the major source of freshwater for Jamaica Bay, discharging approximately 258 million gallons per day (MGD).

Six smaller, privately operated WPCPs also operate in the watershed. These are the JFK Airport (discharges to Bergen Basin), Lefferts Oil Terminal, Queens (discharges to

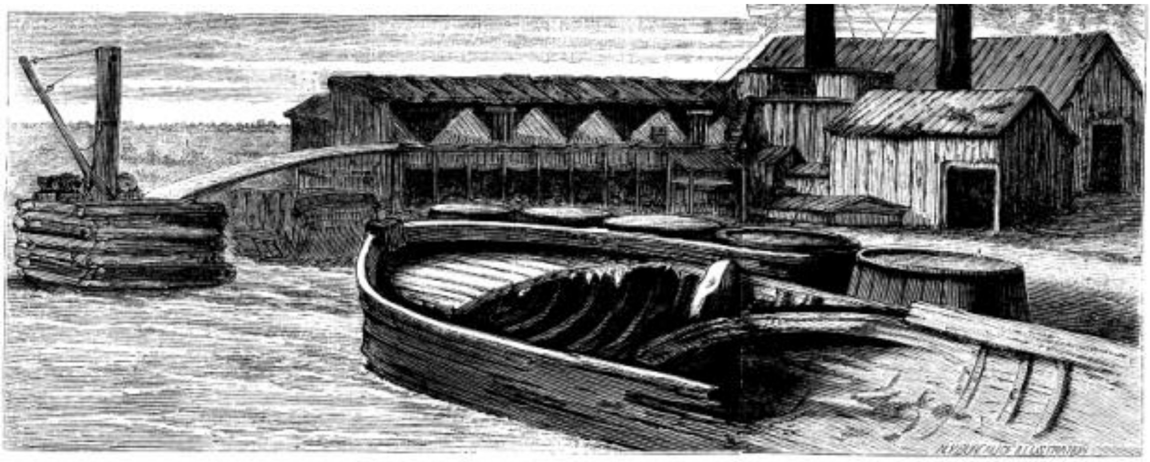
Bergen Basin), Keyspan Generation (Far Rockaway Power Station, discharges to Motts Basin), Carbo Industries (Nassau County, discharges into Jamaica Bay), Exxon Mobile (Inwood, Nassau County, discharges into Head of Bay.) (Watershed Protection Plan, p. 40) Some researchers consider the private WPCPs as only a minor source of wastewater. (Benotti, Abbene and Terracciano 2007) CSO discharge points into Jamaica Bay have floating booms that are supposed to channel wet weather discharges into the bay. Nearby signs instruct people to report dry weather discharges to 311 the city's non-emergency hotline. (Rose George, The Big Necessity page 31) New York City's sewers are designed to handle a maximum of 1.75 inches of rainwater per hour (George 2008, 32).

Conclusions

In retrospect, it would be easy to conclude that the management of Jamaica Bay's fisheries was never adequate to address the fundamental problem, that the growing city was destroying the bay. Viewed from the perspective of the times, the bay's comparative isolation and the small number of surrounding communities must have made human encroachment seem like a distant prospect. The Cromwell and Stadler Bills as well as the decisions to upgrade sewer facilities were all essentially reactive. In the former instance the problem was overfishing and in the latter instance the problem was increasing pollution. The decision makers and stakeholders of the time cannot be said to have been ignorant. All of the decisions made were supported by fundamentally sound science and the value of Jamaica Bay as both a fishery and a source of recreation was never in doubt. Preserving these values, and the tourist dollars that they generated, was a primary motive behind many of the conservation measures.

To modern eyes, the essential management problem appears to have been an absence of coordinated planning informed by the precautionary principle. The fish stocks were saved from the commercial netters only to be lost to the infilling of marshes. In the contest between protecting the oyster beds and providing sewers, the sewers won. If nothing else is learned from this case study it is that the prospect of financial loss created reactive measures but true environmental management requires proactive thinking.

Figures



THE FISH-OIL MANUFACTORY ON BARREN ISLAND.

Figure CS2-1, Fish oil processing works. These were usually very crudely constructed because they were frequently forced to move. This magazine illustration dates to 1871. (Cornell University Making of America Collection)

Figure CS2-2 A fisherman working in a side creek. In what appears to be a bucolic scence a fisherman in a catboat has stretched a net across the entrance of a tidal creek. This practice practically destroyed many fish populations. (Google Books)

Figure CS2-3 Rental boats on Jamaica Bay. Some idea of the number of recreational fishermen who came to Jamaica Bay can be obtained from this photograph showing rowboats for rent at Goose Creek. (Google Books)

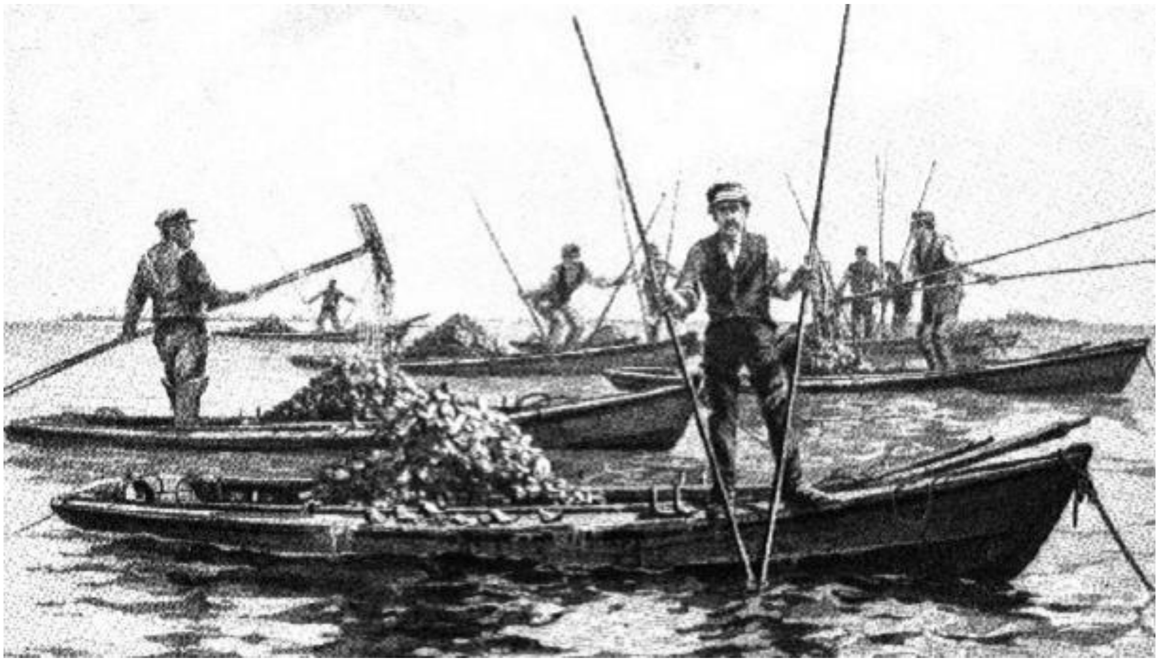


Figure CS2-4 Harvesting shellfish in Jamaica Bay. (Google Books)

Figure CS2-5 Digging clams on the shore of Jamaica Bay. (Google Books)

Bul. 156, Bureau of Chemistry, U. S. Dept. of Agriculture. PLATE IV.

FIG. 1.—VIEW OF INDIAN CREEK, NEAR CANARSIE, LONG ISLAND, WHERE NINE OYSTER DEALERS FLOAT OYSTERS IN THE CELLARS OF THEIR HOUSES.

Figure CS2-6 This 1912 photograph shows a creek near Canarsie where oysters were floated. (Google Books)

Bul. 156, Bureau of Chemistry, U. S. Dept. of Agriculture. PLATE III.

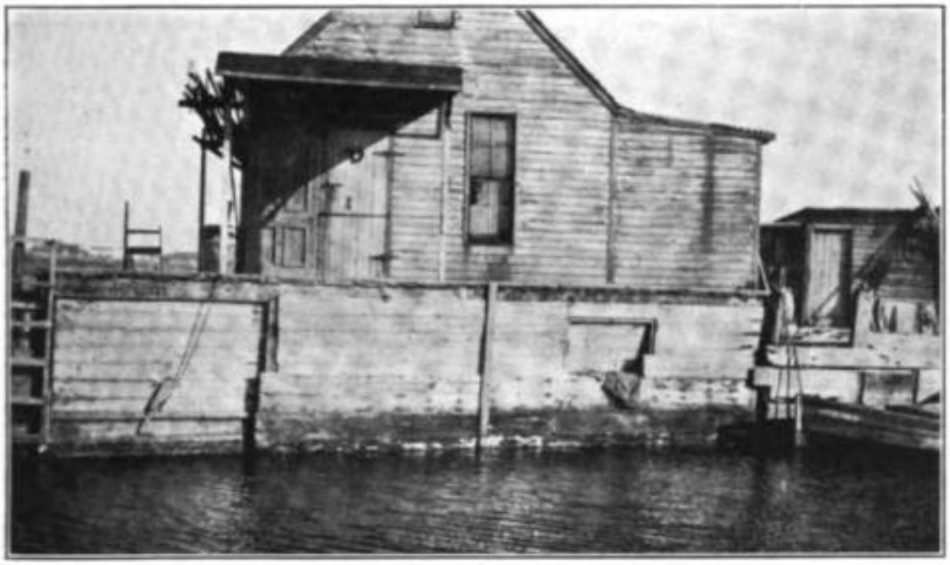


FIG. 1.—OYSTER HOUSE OF DEALER A AT INDIAN CREEK, NEAR CANARSIE, LONG ISLAND, N. Y.

Taken January 25, 1912, with the tide rising. Note the closed trapdoors through which oysters are unloaded from boats. A trapdoor in the floor above permits entrance from the interior of the building.

Figure CS2-7 A 1912 photograph showing an oyster dealer's dock where oysters were floated. Note the lack of visible sanitation facilities. (Google Books)

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Appendices

Appendix 1
What Defines An Urban Sediment?

Introduction

For most people, including scientists, the idea of an urban sediment is a highly contaminated, odiferous muck that was dredged from the bottom of a harbor and best avoided. This is not an unfair definition. In 2004 the USEPA announced that the National Sediment Quality Survey found 8,348 sites where sediment quality would have probable adverse effects on human or ecosystem health (Stern and Peck 2012). Most of these sites are associated with past industrial activities, urban centers, or some combination of the two. Our thinking about urban sediments is dominated by concerns over *legacy contamination*. This broad term encompasses a wide range of contaminants, organic pollutants, nutrient pollution, sewage, and heavy metals. It can also encompass a number of different contamination scenarios ranging from a single polluter discharging a single contaminant such as General Electric discharging PCBs in the Hudson River or the relatively small group of eight paper companies that discharged PCBs into Wisconsin's Fox River. Other legacy contamination sites have multiple contaminants that may have originated with dozens of responsible parties. This is the case in Portland, Oregon, and the Passaic River in New Jersey.

Urban sediments are not just the sediments found in cities. They are an extremely complex aspect of the overall urban environment. They have multiple sources, a wide range of both potential and actual contaminants, and numerous management challenges.

We can list several unique aspects of urban sediments:

1. Most urban sediments are generated by upstream processes but once they reach the urban regions, they act as natural agents in an unnatural setting. A small but highly significant percentage originates within the urban environment.
2. Urban sediments are characterized by legacy contamination
3. Urban sediments are subject to continual recontamination
4. Urban sediments trap pollution
5. The movements of urban sediments are subject to anthropogenic forces especially stream channelization and impervious surfaces.
6. Urban sediments pose unique environmental management challenges.

Sediment in the City

In one sense "urban sediments" is something of a misnomer since sedimentary processes operate on a catchment-wide basis. In coastal cities, much of the sediment loads originate in upland areas and are carried to the cities by rivers. A large proportion of sediments also come from estuarine and marine sources through tidal action (Taylor and Owens 2009). Sediments that actually originate within the urban setting can be broadly divided into two categories, those originating on road surfaces and acted upon by sub-aerial processes, and those transported by aquatic processes from rivers, canals, and docks (Taylor and Owens 2009). In considering this latter category we ignore the question of ultimate origin and simply treat the river, canal, or dock as a source and the remainder of the urban environment as a sink.

In river basins the main "natural" sources of sediments are atmospheric dust deposition and other wind-transported particles, mass movement events such as landslides, soil erosion and re-suspension of channel bed sediments. Significant anthropogenic sources operating outside the urban areas include mining, agriculture, construction, and quarrying

(Taylor and Owens 2009). In many urban estuaries, soils eroded from construction sites are a major source of fine-grained materials. Since construction activities are only disturbing a small fraction of the sediment shed at any one time, the rate of infilling is actually quite slow (Swales et al. 2002).

Although they may be higher is some situations, most urban basins in the developed world have sediment loads between 40 to 500 tons/km^2 - year. This is comparable to agricultural basins but not as high as areas undergoing severe disturbances such as deforestation, wildfires, and earthquakes (Taylor and Owens 2009). This observation has two important implications for environmental management. Accelerated sedimentation is associated with disturbances, including the rapid urbanization that is occurring throughout the world. Secondly, in the absence of disturbance, sediment loads are consistent throughout river basins so that as a management objective, specialized control measures must be applied to sediments that originate within urban environments. These are sediments with greatest potential for contamination. Problems associated with contaminated sediments include a reduced capacity for biological purification and a loss of biodiversity (Ramaroson et al. 2012). Even if sediments are uncontaminated, they still have the capacity to disrupt already fragile ecosystems through accelerated siltation, blocking sunlight in the water column, and damaging wildlife.

In tidal creeks and their associated estuaries sedimentation rates rose during urbanization even when compared to agricultural periods when erosion created by tillage would have been present (Swales et.al. 2002). In the Hudson River watershed the prevailing land cover is forest but the majority of both sediments and organic carbon originate in agricultural, suburban, and urban areas (Howarth et.al. 1991). In England and Wales 75.7% of total river sediment load originates with agriculture, 15.5% originates with channel bank erosion, and point sources account for 3.0%. Only 5.8% comes from diffuse urban sources with sewer discharges being a major source of suspended sediments (Taylor and Owens 2009). As we will soon see, the 5.8% accounts for a disproportionate share of the sediment problems in urban settings.

Urban sediments are also characterized by multiple contamination sources and while much attention is focused on the contamination created in industrial and urban settings, upland areas contribute contamination in the form of agricultural runoff, fertilizers, nutrients, pesticides, and herbicides (Taylor and Owens 2009).

Unfortunately urban sediment contamination occurs over long time periods and harmful effects may not appear until the problem is quite advanced (Swales 2002).

The problem of legacy contamination

Legacy sediment contamination is a ubiquitous problem in urban settings. A classic example of the problem is the River Kymijoki, South-Eastern Finland, and the nearby coastal region of the Gulf of Finland where sediments are contaminated with PCDD/Fs and mercury. The effects of this are widespread and read like a laundry list of problems that are associated with sediment contamination. An extensive survey revealed that in $5x10^6$ m^3 of sediments were severely contaminated with concentrations of PCDD/Fs, and Hg up to 292,000 ng/g, but another 90,000 m^3 of the most highly contaminated sediments were found immediately downstream of the pollution sources. Like many similar sites the problem is legacy pollution from earlier industrial activities. In this instance the sources are the pulp, paper, and by chemical industries. Much of the polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) resulted from the manufacture of a wood preservative known as Ky-5 by companies located along the upper reaches of the river between 1940 and 1984. Much of the mercury originated from chlor-alkali production and the use of mercury as a slimicide by pulp and paper manufacturers. Epidemiological surveys revealed increased cancer risk among farmers living close to the river. The liver concentrations of PCDD/F in the region's fish were orders of magnitude higher than those in reference samples. Not surprisingly, the region's fishermen had somewhat elevated concentrations of these pollutants in their bodies compared with other residents of the region. Benthic assemblages in the impacted area were altered but the connections to the contamination were not clearly established (Verta et al. 2009).

There are many well-known waterways where legacy contamination is significant. Depending on the model used, estimates of the total amount of legacy PCB contamination in Hudson River sediments range from 20 to 440 metric tons. The best estimation as of 2000 was between 150 and 200 metric tons (Mackler 2000). In the Venice Lagoon, legacy PAH contamination is present at concentrations between 0.065

and 0.46 mg/kg and could account for 70 to 80% of the mutagenic effects on marine life (LaRocca et al. 1996). There have been recent announces of newly discovered pesticides in Ukrainian estuaries (Burgess et al. 2011). Persistent organic pollutants (POP) have been recently found in the Bosna River in Bosnia and Herzegovina (Harman et al. 2013), and new research leading to a deeper understanding of legacy metal contamination in Sydney Harbor (Birch 2013).

Cities changed over time. Industrial processes, fuel sources, consumer and industrial chemicals are constantly evolving. Under the right conditions these changes can be reflected in sediment cores. In San Francisco bay the oldest to newest chemicals in sediment cores were PAHs, Hg, Ag, Cu/Pb/Zn, DDT, and PCBs (Van Geen and Luoma 1999). This list reads like a history of the city's industrialization (mercury was used in the mining industry for extracting gold from rocks) and the introduction of novel chemicals into the environment. A similar study in San Francisco's Richardson Bay and San Pablo Bay utilized a combination of molecular fossils (hopanes and steranes) and n-alkanes to study the input of biogenic material. The molecular fossils show an increase in petroleum use beginning 70 to 100 years ago and corresponding to the city's industrial development. Older segments of the core show a predominance of biological input. The cores from San Pablo Bay show the same overall pattern but also reflect slightly different sediment deposition dynamic (Hostettler et al. 1999).

In a surprising discovery, petroleum background contamination in urban sediments has been found to be remarkably consistent. A study of nine urban waterways showed that an unresolved complex mixture (UCM) dominated the contamination with 4 to 6 ring PAHs, mostly pyrene (Py) and fluoranthene (Fl). Although much of the PAH input is pyrogenic in nature, those PAHs originating with petroleum generally had an Fl/Py ratio around 0.9. There was considerable variation both between and within urban settings superimposed on this background (Stout et al. 2004).

The Clean Water Act has been credited with a dramatic improvement in sediment contamination since its passage in the 1970s. In New York Harbor sediments the concentrations of mercury, PCBs, dioxins, and DDT have decreased by an order of magnitude. In New York's Jamaica Bay on the south shore of Long Island, mercury concentrations spiked in the 1960s and were down to 1 mg/kg by 1990s. PCB concentrations were 4 mg/kg in the 1960s and less than 1 mg/kg by the 1980s. DDT concentrations also declined over the same period from 250 ppb in the 1960s to less than 50 ppb by the 1980s (Steinberg et al. 2004).

An example of what could happen if this type material is not properly managed comes from the Savannah Harbor, Georgia. Contaminated river and harbor sediments were stored in upland disposal areas. In the laboratory, the freshwater oligochaete *Lumbriculus variegatus* that were exposed to the dredged sediments showed bioaccumulation of As, Cu, Hg, Se, and Zn. Bioaccumulation of Cd, Hg, Mo and Se was also observed in the livers of birds and raccoons. Clearly, some metals in the dredged sediments were mobile and biologically available. This threatened the habitat quality in the lower Savannah River (Winger et al. 2000).

Contamination from sediments entering the food chain is a well-known threat to fish, wildlife, and human health. But another situation where contaminated sediments can pose a direct threat to human health is when they are present in areas used for recreation. On the east bank of the lower Passaic River High elevated levels of mercury, PCBs and dioxins have been identified in the mid flats at the Riverside Park in Lyndhurst, New Jersey. People wading in the mud or using a nearby boat ramp, are at risk of exposure slightly above levels of concern. Cleanup was scheduled to begin in the spring of 2013 and continue into the summer but another six to eight sites with similar contamination are thought to exist on the lower Passaic. Although these mud flats may not pose an immediate threat for recreational river use, low levels of these contaminants are believed to have been carried into the riverfront parks by floodwaters (Jade Media Partners 2012). This was exactly the scenario on the Gowanus Canal in Brooklyn, New York, during Hurricane Sandy in October of 2012. One of the most polluted waterways in the nation with severely contaminated sediments overtopped its banks and flooded an evacuation zone in the Carroll Gardens neighborhood. The city and the federal EPA announced plans to test the area for residual contamination shortly after the floodwaters receded (Walker 2012).

Ironically in the modern world where pollution control measures have eliminated major pollution point sources, urban sediments themselves have now become a pollution source (Cornelissen et al. 2008). In recognition of this problem the European Union (EU) has proposed to add a specific deleterious substance source/pathway to it Water Framework Directive (WFD), "historical pollution from sediments." Additionally the EU member states may choose to apply environmental quality standards specifically established for sediments (Taylor and Owens 2009).

Continued Recontamination of Urban Sediments (Death by a Thousand Pipes)

All human activities generate some form of chemical signature. As early as 1876 the New Jersey Geological Survey discovered that in increases in chlorine ion concentration in streams correlated with increases in human population. This was regarded as a good proxy measurement for what would later become known as non-point source pollution (Olsen 2011). As urban life becomes more complex; automobiles, massive sewer systems, and the use of consumer chemicals (paints, pesticides, construction materials, etc.); the amount of potential contaminants that will reach the sediments increases.

Urban waterways are not natural systems. Traditionally they have been valued as storm water conduits with the smaller waterways being channelized or confined to pipes. Although their research was conducted in Australia, Davies et. al. 2011, have identified four problems that are common to urban waterways throughout the developed world. Firstly, they are too often seen as storm water conduits; secondly, biodiversity of riparian areas was not understood or appreciated; thirdly, the cumulative effects of development on waterway health were not recognized; and lastly, there was never an adequate definition of "river" under legislation or common law that would have created a legal framework for protection. Instead the typical urban waterway is left to undergo, "death by a thousand pipes" (Davies et al. 2011). The anthropogenic changes to urban systems such as impervious surfaces and channelized waterways have created hydrological and sedimentary processes that are very different than those of natural systems (Taylor and Owens 2009).

Researchers in Norway have recently investigated the sources of brominated flame retardants in urban systems. In an excellent example of the "death by a thousand pipes" phenomena, they found that this contaminant was present in seepage water from a scrapyard and automobile recycling facility, in sewage waste water, in sewage sludge, and as a legacy contaminant on former industrial sites (Nyholm et al. 2013).

Ongoing industrial activities can add new material to existing contamination. In the Norwegian port of Drammen shipyards have traditionally applied antifouling paints that include Tri-butyl Tin (TBT). This type of paint was prized for its durability so it was also used on houses and other structures in the city. In the sediments there is an estimated legacy burden between 300 and 2700 ppb. Freshly deposited to the sediments account for another 360 to 670 ppb while river transport of contaminated sediments from other areas accounts for 60 to 230 ppb of the contaminant loadings. Another 7 to 32 ppb can be attributed to urban runoff and contemporary industrial activity has been estimated to account for another 200 to 11,000 ppb (Cornelissen et al. 2008).

The example of TBT is somewhat unique in that it applies to a single material that has both a contemporary and historic loading. In other instances industrial processes change, companies close or relocate, and waterfront industries evolve. One constant however in urban systems is the presence of impervious surfaces.

The United States Geological Survey (USGS) has determined that different sources of solids in urban waterways contain different amounts of heavy metals and hydrocarbons. The highest toxic potentials were found in sediments from sewers followed by sediments suspended in storm water. Sediments originating in street dirt and urban streambeds had lower toxic potentials (USGS 2013).

Sediments that enter urban waterways from roads (Road Deposited Sediment or RDS) have been documented to contain persistent organic pollutants. These include PAHs, PCBs, pesticides and herbicides, and heavy metals. Many of these contaminants originate with motor vehicles in the form of tire wear, brake wear, and exhaust. Other contamination sources include road salt, paint, and litter. Construction activities can spill sand and cement onto road surfaces. In addition to all of these sources wind can transport additional materials from outside the urban area. A mixture of RDS and sewage can account for up to 40% of urban sediment loads. Unlike more rural areas, urban stream banks are often armored against erosion so that a proportionally greater percentage of sediment loads are washed off the streets (Taylor and Owens 2009). In Great Britain's River Aire and the River Calder, its main tributary, much of the suspended sediment originates outside of the urban areas. In the urban reaches, road dust accounts for between 19 and 22% of the load and sewage treatment solids account for between 14 and 18%. (Carter et al. 2003). The large proportion of ferromagnetic particles in the sediments of Manchester, UK, suggests that the major inputs are roadway derived as opposed to soil-derived materials (Robertson et al. 2003).

RDS are found in all urban rivers and have a range of particle sizes. They also tend to have a short residence time on the streets with 150 to 250 days being typical. Residence times and depositional history will of course vary according to local weather conditions (Taylor and Owens 2009).

Given the importance of RDS in urban waterways there has been a considerable amount of research devoted to finding the best means of removing them from the environment before they can enter the waterways. Mechanical street sweeping, detention basins, and various forms of sediment traps all have their advantages and disadvantages as well varying construction and maintenance costs. Unfortunately the USGS has recently determined that many types of storm water treatment structures are effective at trapping course particles but are not effective for finer materials (USGS 2013).

Among the many types of particles that enter urban sediments from streets and roadways PAHs are among the most toxic (Boxall and Maltby 1997). PAH concentrations in storm water runoff have been found to range between <0.05 and 560 ppb. In Rhode Island's Narragansett Bay the total PAH contribution from urban runoff was 681 kg/year and this represented only 40% of the total PAH input to the 380 km^2 bay (Latimer and Zheng 2003). In a study of wetlands in Virginia's Elizabeth River watershed, total PAH loadings were found to be largest in wetlands near commercial land uses. These materials appear to originate with automobiles and come from exhaust, brake dust, and crank case oil (Kimbrough and Dickhut 2006). In addition to such contaminants washed off roadway surfaces the sealants used on roadways are themselves significant sources of PAH contamination (USGS 2013, Yang et al. 2010).

About 98% of the particles emitted from diesel engines are less than 10 microns in diameter and contain among other contaminants, low molecular weight PAHs, and derivatives of PAHs. In the ports of Los Angeles and Long Beach diesel particulate emissions were 1,760 tons in 2002 alone. Much of this will be transported to coastal sediments as runoff or directly deposited on the water surface. About three-quarters of this material were emitted by ships in coastal waters (defined as 14 to 100 miles offshore) while commercial craft operating in the harbor accounted for 14%. The balance came from cargo handling equipment, trucks, and locomotives (Sharma 2006).

Recent research has also identified pesticides as a significant contaminant in urban sediments. They can originate in urban sediments from upland agricultural sources or be deposited locally from pest control applications in homes, commercial buildings, and landscaping. Organochlorines, chlorpyrifos, and pyrethroids were found in 95, 65, and 95% respectively of urban river sediments in the state of Illinois. This was almost twice as frequent as their occurrence in rural river sediments (Ding et al. 2009). In rapidly-industrializing China, pyrethroid pesticides are recognized as a major contaminant in the urban waterways of the Pearl River Delta (Mehler et al. 2011).

Urban Sediments, Urban Stream Flows, and Contamination - a Complicated Interaction

As will be seen in earlier chapters, the multiplicity of contamination sources and complex sedimentary processes found in urban areas makes precise source apportionment difficult. There is also a mixing of legacy contaminants and materials of recent origin. Multiple contemporary contaminant sources further complicate the situation. The mixing of hydrocarbons in the coastal environment near San Diego serves as an example of this problem. This mixing complicated source tracking but it was possible to determine that lower molecular weight PAHs in the water column originated in wastewater treatment plants and Tijuana River runoff. These appeared to have a petrogenic source. Pyrogenic PAHs were more common in coastal sediments (Zheng and Vista 1997).

A similar example can be found off the coast of Tunisia where sediments were studied by Pyrolysis-GC/MS. (Py-GC/MS) N-Alkanes and fatty acids were found to have originated in primary production but these were mixed with "ubiquitous" petroleum contamination that originated with offshore oil exploration, river discharges, shipping activities, and atmospheric deposition (Amorri et al. 2011).

The affinity of contaminants for sediment particles is one reason pollution tends to accumulate in urban waterways instead of being carried out of the region by water currents. For example, fecal steroids in wastewater rapidly partition to the solid phase and thus their subsequent distribution is governed by sediment dynamics (Vane et al. 2010). In Puget Sound vertical flux was found to be the dominant transport mechanism for hydrocarbons sorbed to fine-grained particles. The residence times were far too brief for significant horizontal transport. Horizontal movement was mainly through re-suspension and redistribution of the nephaloid layer (Bates et al. 1987).

Another process that is common to sedimentary dynamics in urban areas is flocculation. The generally higher concentrations organic matter in urban waters enhances flocculation with consequent acceleration of settling rates (Taylor and Owens 2009).

Contaminants sorbed to sediment particles exhibit another unique characteristic in urban systems. While it is generally true that contaminants will preferentially sorb to smaller particles, this is not always the case. Pollutants may be found on larger particles if those are what are dominant in areas where contaminants originate (Taylor and Owens 2009).

The combination of impervious surfaces, combined sewer overflows (CSOs) and channelized river systems, radically alters flow regimes. During storm events there can be a rapid rise in river levels, accelerated flows, and increased sediment transport. In the city of Atlanta, Georgia, more than 94% of sediment transport occurred during storm events. In the town of Bradford Beck, United Kingdom, 40% of the annual sediment transport occurred in less than 1% of the year (Taylor and Owens 2009).

This rapid sediment transport phenomena can be used to help predict the impacts storm water runoff will water quality. Total Suspended Solids (TSS) measurements have been shown to be reliable predictors of riverbed siltations of the riverbed, elevated oxygen demand resulting from organic matter degradation, and the transport of contaminants to river sediments. An important advantage of TSS as a predictor of environmental impacts is that it is routinely measured (Rossi et al. 2012).

Learning to Live With Urban Sediments

One of the major imitative that can be used to improve urban waterways and keep sediments cleaner, is to reduce the amount of storm water runoff. This can be done by restoring waterways and improve their ability to deliver ecosystem services. Reducing storm water runoff is widely seen as a critical step for improving water quality. The USEPA has permitting authority for storm water runoff in selected states, federal territories, and Indian lands. States are authorized to implement the Storm water NPDES (National Pollution Discharge Elimination System) permitting program. The EPA's regulations are divided into three categories, municipal separate storm sewer systems, construction activities, and industrial activities (USEPA 2012).

The other significant issue related to urban sediments is maintenance and remediation dredging in rivers and harbors. These topics are explored in chapter four.

Appendix Two

Detailed Examination of Materials and Methods

Introduction

At its most basic, pyrolysis is defined as a chemical transformation that occurs at temperatures above ambient (Şerban and Victord 2002). Pyrolysis as an analytical technique was first described in 1862. In analytical chemistry, pyrolysis experiments monitor the changes to sample mass as pyrolysis products are released as gases and/or capture these gases and subject them to additional characterization. Even a cursory glance at the literature reveals that there is little standardization over the terminology used to describe different types of pyrolysis processes used in analytical chemistry. Variations exist in the choice of pyrolysis temperatures, the rate of sample heating, the use of matrix additions to catalyze decomposition reactions, or matrix additions to prevent decomposition. Different procedures vary the atmosphere under which the sample is pyrolysed, or use catalysts to enhance product decomposition after heating and before analysis. There are other chemical transformations, most commonly oxidation, that can alter also be used to alter pyrolysis products prior to analysis. As a practical matter however, pyrolysis usually describes rapid heating in the absence of oxygen (Vercammen et al. 2012).

Types of Pyrolysis

The author prefers the term “analytical pyrolysis” to describe his protocols although it might also be confused with “flash pyrolysis.” In flash pyrolysis sample heating can be as fast as 10,000 K / sec (Şerban and Victord 2002, IUPAC 1993). There are two methods used to reach such temperatures quickly, resistance heating and Curie point pyrolysis.   The latter use dedicated ferromagnetic alloys that are exposed to a radiofrequency (RF) field.   Heating is extremely rapid until the material reaches its Curie point temperature, when it becomes paramagnetic. The advantage of this is that temperature control can be very precise but not variable. Resistance heating provides much more control over heating rates and final temperatures. Early versions of resistance heating pyrolyzers placed the sample directly on a hot wire. While this was a very simple approach, it increased the risk of unwanted catalytic decomposition (Vercammen et. al. 2012).   The CDS Model 1500 used in this study employs a coiled heating element fabricated from platinum wrapping around a small quartz tube that holds the sample. This instrument is capable of rapid heating and can utilize a temperature program.

The IUPAC defines several variations of pyrolysis where temperatures, the number of pyrolysis steps, or both, are varied. In “Sequential Pyrolysis” a single sample repeatedly is subjected to identical pyrolysis conditions for several. This varies from “Stepwise Pyrolysis” where the sample is subjected to pyrolysis temperatures that are increased stepwise. The pyrolysis products are analyzed between each step. Some confusion may result because the phrase "sequential flash pyrolysis” often appears in the literature to describe either of these processes. Finally, “Temperature-Programmed Pyrolysis” refers to a process where the sample is heated at a controlled rate. The temperature range is selected so that pyrolysis products are formed throughout this range. (IUPAC 1993)

A variation of flash pyrolysis is non-discriminating flash pyrolysis where rapid heating is achieved using a Silcosteel capillary (Poerschmann et al. 2008). In a typical system, the sample is placed directly in a disposable capillary and held in place using two plugs of glass wool. The GC carrier gas flows directly through the capillary and into a column interface. This approach dramatically reduces discrimination against high molecular weight compounds as there are no cold spots for them to condense between the pyrolysis site and the GC column (Parsi et al. 2007). Some systems of this type are configured so that a gas that is different from the GC carrier gas can be used for the pyrolysis step. The system used in this research is similar to non-discriminating flash pyrolysis in that there is a very short tubing run (less than 7 cm) from the pyrolysis chamber to the GC injector. This tubing run is heated both ends and is insulated to prevent condensation of pyrolysis products.

Thermodesorption

Pyrolysis is usually thought of as involving thermal decomposition. But many non-polymeric organic compounds that are somewhat volatile at elevated temperatures do not necessarily fragment upon pyrolysis. Pyrolysis technology provides an effective way of removing them from complex sample matrices and sometimes this is referred to as flash evaporation pyrolysis or EV-Py (Wampler 2007).

Flash evaporation pyrolysis combined with GC/MS can be used to detect sedimentary contaminants at low concentrations. It has been used to screen complex matrices for

PAHs, halogenated organics, aliphatic hydrocarbons, heteroaromatics, elemental sulfur, and cyanides. In one demonstration, five-milligram samples of lake sediments were spiked with PCBs and heated to 1000 ^{o}c. Even with the mass spectrometer operating in full scan mode, detection at the 10 µg/kg level was achieved. However with an electron capture detector (ECD), the signal from the PCBs was obscured by the many other electron-capturing compounds released by the sample (Wampler 2007). In contrast to flash evaporation pyrolysis, thermal distillation pyrolysis (TD-Py) uses a slow temperature rise to separate low boiling point intact compounds (generally from 100 ^{o}C to 200 ^{o}C) and thermal decomposition products created in the 350-600 ^{o}C range (Wampler 2007).

EV-Py and TD-Py overlap somewhat with Thermal Extraction in which heating is used to release organic molecules from sample matrices. An official USEPA analytical method, Method 8275a, uses thermal extraction and capillary GC/MS procedure for rapid quantitative determination of selected PCBs and PAHs in soils, sludge and solid wastes. This method however stresses the release of compounds and not their destruction. Therefore the sample is only heated to a maximum of 340 ^{o}C. (USEPA 8275a, 1996) Temperature is not the only variable. Clay matrices can have sorptive and/or catalytic effects that reduce the yield during the pyrolysis process as reported by Sauer at al (1988) who performed organic polymer analysis of drilling muds that were rich in bentonite and barite (Sauer 1988).

Thermochemolysis

Although many pyrolysis processes are carried out under inert atmospheres but it is possible to create additional reactions with a reactive atmosphere, the additions of another materials to the sample matrix, or to incorporate catalysts in the pyrolysis system. The most common added reactants are oxygen, hydrogen, water, and quaternary N-alkyl ammonium hydroxides (tetramethylammonium hydroxide or TMAH) (Șerban and Victord 2002). When molecular hydrogen is used, it can act like an inert gas and it is necessary to add a metal catalyst such as nickel or platinum. An advantage is that the number of pyrolysis products is reduced. For example two or more molecules with the same length carbon chains can have multiple double bonds in varying positions. Hydrogenation would eliminate the double bond in this situation and produce identical alkanes (Șerban and Victord 2002). The presence of water can create different pyrolysis products and for this reason samples are usually dried before analysis. However water can sometimes be added deliberately to create hydrolysis reactions. Chain scission through hydrolysis can be achieved in cellulose and starch (Șerban and Victord, 2002).

TMAH is a widely used pyrolysis reagent. It is strongly basic and when added to a sample prior to pyrolysis, it can cause methylation of amides, esters, and ethers. These methylated products are often more volatile than the original molecules and have improved GC separation. When these reactions occur at low temperatures (250-300^{o}C) the process is usually described as TMAH Thermochemolysis. Cleavage of the C-C bonds in macromolecules requires higher temperatures and is described as TMAH

Pyrolysis (Lehtonen et al. 2004).

The methylation occurring with TMAH it does not occur identically for all analytes. Lignin being somewhat acidic is very susceptible to TMAH methylation and acts predictably. Cellulose does not behave this way despite having many potentially reactive hydrogens (Șerban and Victord 2002).

Copper oxide (CuO) or alkaline copper oxide (CuO-NaOH) treatments are widely used to help break C-O bonds that hold phenols and aliphatic acids to humic matter. However breaking C-C bonds requires more energy and as a result the CuO pyrolysis products may only represent the more loosely held structural elements (Lehtonen et al. 2004).

The combination of bond cleavage and improved chromatographic separation makes TMAH or CuO treatments a powerful tool for characterizing organic macromolecules found in humic substances. But using too much of these materials may destroy the desired analytes. There are other disadvantages such as the difficulty of distinguishing between pyrolysis products that are “naturally” occurring substances and those created with the chemical treatments. There may be a number of unwanted oxidative products if the TMAH treatment is not carried out under inert atmospheres. Another example of this phenomena is when CuO treatment causes aromatic rings to break apart and create low molecular weight aliphatic acids. The products of these chemical treatments may differ significantly from the original molecules (Lehtonen et al. 2004).

Detection Systems

Many of these approaches can be combined to create the optimal analytical system for a given analyte. There are also numerous possibilities for analyte detection and identification. Historically, most pyrolysis systems use a mass spectrometer or flame ionization detector (FID) for peak detection. In recent years two-dimensional GC Pyrolysis and two-dimensional GC (GC X GC) systems such as py-GC X GC/MS and py-GC X GC have been shown to have several advantages despite their complexity and costs. Rather than a point on a one-dimensional line (retention time), each compound is placed at an unique location on the separation plane. Distinct bands on the separation plane are often the result of compounds belonging to the same chemical class. This facilitates the identification of unknown compounds. This improved separating power is very useful when confronted with complex mixtures of pyrolysis products (Parsi et al. 2005).

Historical Background

Analytical pyrolysis combined with GC (py-GC) first became a common analytical technique in the mid 1950s for the study of polymers and related compounds. Although pyrolysis/mass spectrometry (py-MS) had been developed a few years earlier, GC offered the advantages of lower cost and less complicated equipment. There was an upsurge in interest in the technique during the early 1960s when it was seen as an effective way for space probes to detect biological molecules. This particular idea was not implemented for some years but it did lead to widespread use of py-GC and py-MS for the characterization of organic polymers, microbial materials, and other types of biological samples (Henk et al. 1982).

Analytical pyrolysis was first used for characterizing organic matter in sediments beginning in the late 1970s and early 1980s. One of the first publications on the topic was by Boon and Haverkamp (1979) who used it in a study of sedimentary organic matter digestion by the lugworm (*Arenicola marina*). This was followed shortly by van de Meent et al. (1980) using pyrolysis to characterize non-volatile organics in the suspended matter and sediments of the Rhine River Delta.

An early example of py-GC/MS for the detection of phenolic and lignin pyrolysis products as a means of determining the origins of organic matter in estuary sediments was reported by Whelan et al. in 1986. In the same year automated py-GC/MS analysis combined with factor-discriminant analysis was used to map the geographical position and organic matter sources of the organic matter in the Rhine estuary and a nearby dredge-spoil disposal site. Among the findings were at that time at least, sewage sludge was a major source of particulate organic matter in densely populated regions of The Netherlands. (Boon et al. 1986) It should be noted that these two publications were the first time that pyrolysis as a means of sediment analysis appeared in *Chemical Abstracts*. Additional pyrolysis studies of the Rhine river sediments were published by van de Meent et al. in 1985.

The characterization of humic substances originating from the decay of aquatic plants was reported by Gadel and Bruchet (1987). Fogel et al. (1989) reported that organic matter preserved in sediments of St. Catherine's Island, Georgia, salt marshes originated in bacteria, plankton, and *Spartina alterniflora*. They used a combination of techniques including stable C and N isotopes and py-GC to examine muds up to 1400 years old. Isotopic mass balance allowed the tracing of how planktonic and higher plant debris inputs shifted over time and how microbial action resulted in the diagenesis of the organic material. The odd-to-even ratio of higher-plant derived n-hydrocarbons becomes less pronounced with age, as determined by depth (Fogel et al. 1989).

At the time of this writing the National Atmospheric and Space Administration (NASA) and the European Space Agency (ESA) plans to employ the Mars Organic Molecule Analyzer MOMA on its Mars rover ExoMars scheduled for launch in 2018. The MOMA is a Py-GC/MS system that will be used to explore the Martian soil and has been calibrated with samples taken from the Norwegian arctic (Steininger and Goetz 2012)

Whether on Mars or New York Harbor, among the advantages of Py-GC/MS are that it requires minimal sample pre-treatment thus saving on the time and costs associated with solvent extraction. This allows more samples to be processed and studies conducted over larger geographical areas (Poerschmann et al. 2008). Pyrolysis of whole sediment also avoids any analytical bias that may result from different extraction techniques used to separate analytes from sediment matrices (Payeur et al. 2011).

The USEPA has published seven sample preparation methods for soils and sediments (3540, 3541, 3545, 3546, 3550, 3560, and 3561). Method 3546 is a microwave extraction procedure that replaces the more time-consuming Soxhlet extraction. EPA method 3540 is a Soxhlet extraction method using two solvent systems, an extraction solvent system to remove the analytes from the sample matrix and an exchange solvent that it used for sample cleanup. At the end of the extraction procedure the solvents must be boiled to concentrate the sample prior to GC/MS injection. Method 3541 is automated Soxhlet procedure. Method 3550 makes use of ultrasonic extraction. Methods 3560 and 3561 employ supercritical fluid extraction. All of these methods are time consuming and require specialized equipment and / or glassware.

Procedures used in this Project

Initial Sample Preparation and Overview of Chromatographic Procedures

After sampling, the sediments were oven-dried overnight at 40 ^{o}C. The next step in the analysis was to hand-grind the dried sediments using a mortar and pestle. Small pebbles, shells, and macroscopic plant materials such as blades of grass or leaves were removed at this time. Milligram quantities of the dried sediments were used for the analysis. Approximately 4 to 5 milligrams of fine, organic rich sediments were loaded into a quartz pyrolysis tube, but if the sediments were sandier, approximately 8 to 10 milligrams were used (Figure 1). The USEPA thermal desorption method calls for sample grinding until it can pass through a 60-mesh (0.25 mm) screen. (USEPA 8275a, 1996) EPA solvent extraction methods generally call for reducing particle sizes to less than 1 mm (USEPA 3454 1996, USEPA 3561, 1996). In this research particle sizes were judged by eye and were estimated to be less than 1 mm.

The dried sediments were spiked with 5 µL of an internal standard solution containing deuterated PAHs from Cambridge Isotopes, Andover, Ma.. The solution contained naphthalene (D-naphthalene, cat. DLM-365-1), deuterated anthracene (D-anthracene, cat. DLM-102-1), and deuterated pyrene (D-pyrene, cat. DLM-155) in hexane. The spike concentration was manipulated such that each injection introduced 24.50 ng of D-naphthalene and 27.00 ng of D-anthracene into the chromatographic system. D-Pyrene was the only compound used for quantization.

The chromatographic system used for the study was a Thermo Electron Focus GC and Thermo Electron DSQ quadrapole type mass spectrometer. A CDS model 1500 pyrolysis system was used to heat the samples at 610 ^{o}C for 20 seconds under a helium atmosphere. The extracted molecules and pyrolysis products are swept onto the GC column by a stream of helium gas. The GC column used for organic geochemical determinations was a 30m J&W Scientific DB-1MS column, with a 0.25 mm i.d. and 0.25µm film thickness. The PAH determinations were performed using a 60m J&W Scientific DB-1MS column, with a 0.25mm i.d. and 0.25µm film thickness. All GC temperature programs began at 50 ^{o}C for 5 minutes and rose at a rate of 5 ^{o}C per minute until reaching 300 ^{o}C and holding for 25 minutes. Gas pressure at the column head was 228 kPa with a split ratio of 1 to 25. When operated in the full scan mode the mass spectrometer was set to 50-550 Da, 1.08 scans/sec., 70eV ionization voltage. In the SIM mode the MS was also set to 70 eV ionization voltage and identification was based on a combination of molecular weight and retention time window.

Compound identification was through a combination of retention time window and at least one characteristic ion. Concentrations of analyte molecules were estimated using the following formulas:

$$\text{ng analyte} = (\text{ng internal std} / \text{area counts internal standard peak})\ (\text{area counts analyte peak})$$

$$\text{ng} / \text{mg} = \text{ng analyte} / \text{mg dried sample}$$

A correction factor was applied to each result. This factor was based on the ratio between the peak area obtained in the total ion chromatogram and the peak area obtained from integrating only the ion used for quantitation.

The PAH analysis described in this chapter was conducted in the selected ion monitoring (SIM) mode. Compound identification was again based on a combination of molecular weight and retention time window. A correction factor was not applied for this class of compounds because both the internal standard and analytes were chemically very similar.

Details of Drying, Grinding, and Culling

Samples must be dried at the start of the pyrolysis process because as has already been discussed, water may introduce unwanted chemical reactions. At one time the author attempted to take wet samples directly from the field and dry them in the pyrolysis system before high-temperature heating. This did little more than create a hard crust on the exterior of the sample that could have trapped pyrolysis products. Grinding sediments prior to analysis creates homogenous samples where all particles have comparable surface areas. But the possibility that the heat and pressure even from hand-grinding might destroy low molecular weight compounds or allow them to volatilize is something that deserves additional investigation. There is little in the literature on this topic but Maley (1997) states that when extracting metals from organic-rich sediments there is little effect from grinding on “extractability.” Craswell and Waring (1972) note that there was an absence of evidence that increases in the rate of organic matter decomposition could be attributed to the physical disruption of the sample matrix. They do go on to state that when soils were ground to a particle size between 0.18 and 0.05 mm, aerobic mineralization of nitrogen increased. This was observed in seven of ten soils in their study.

Removing macroscopic biomass such as insects, seeds, leaves, grass fragments, and other plant materials is necessary to insure that large quantities of these materials do not skew the results. Measuring the effects of any macroscopic biomass missed during culling is a potential area for future research.

Use of Deuterated Internal Standards

Deuterated internal standards are particularly useful in situations where it is necessary to mimic the behavior of analytes during clean up and extraction processes. They are also useful in situations where there may be significant matrix interferences. There is one critical caveat. The degree of deuteration must be high so that there can be no confusion between the standard and an analyte. According to Hübschmann (2008), deuterated compounds will generally elute slightly earlier than the original materials although no explanation of this phenomena was provided. These standards can also be readily identified through a combination of molecular weight and retention times. Deuterated standards also have an advantage in complex matrices, if added in excess, they can occupy potential sorption sites and enhance analyte recovery.

In this research the author has observed that the best results for internal standard quantitation are obtained when the deuterated internal standard and the analyte are of the same chemical class, PAH and D-PAH for example. This method of quantitation should not be confused with the use of deuterated standards as surrogates to measure analyte recovery during extraction and clean up procedures.

There are many examples of the quantitation using this approach. The use of deuterated *n*-alkane internal standards for py-GC/MS analysis of kerogen was reported by Eglinton, et. al. 1991. The standards were only used to quantify compounds most like themselves, i.e. alkanes. Wagener et. al. (2010) used deuterated internal standards for PAH quantitation in addition to conventional calibration. The extraction efficiency for fecal and plant sterols was measured by Benfenati et a. (1994) was quantified through the use of internal standards. The characterization of organotin compounds in natural waters and sediments by Arnold et al. (1998) used accelerated solvent extraction and perdeuterated organitins as internal standards. They achieved method detection limits between 0.4 to 2 ng/g for the sediment samples.

Deuterated PAH internal standards were used to quantify the PAH concentrations in the Gulf of Trieste, Northern Adriatic Sea (Notar et al. 2001) The performance of ion-trap MS for PAH detection was optimized using a strategy of selected ion storage (SIS) and deuterated internal standards. Method sensitivity reached 0.02–11.0 ng/g with 77% recovery was achieved on a reference sediment sample from Lake Ontario (Leite et al. 2008).

Selection of a Pyrolysis Temperature

Selection of a pyrolysis temperature is often a balance between maximum desorption of intact molecules and the desired degree of thermal degradation in the macromolecules. Generally speaking, as pyrolysis temperature increases, the chromatogram becomes dominated by smaller fragments with less diagnostic value. (Şerban and Victord 2002)

Temperatures in the range 300 to 350 ^{o}C are widely used to desorb lighter materials without creating breakdown products (Medina-Vera 1996, Faure and Lanadais 2000). A temperature of 300 ^{o}C was found adequate to thermally desorb saturated hydrocarbons greater than C_{27} (Faure and Lanadais 2001).

Pyrolysis is particularly useful for large biological molecules that are not well suited for chromatographic analysis. While the pyrolysis products of these materials are often well-suited for GC analysis they are not all created at the same temperature.

In "typical" dry weight biomass, cellulose is the most abundant material 40-60%, hemicellulose concentrations are slightly lower at 20-40%, and lignin only comprises 10-25%. Of these, hemicellulose being amorphous and easily hydrolyzed is the most prone to decomposition. Cellulose is harder to decompose but lignin as it is made from benzene-propane units and heavily cross-linked is most resistant to decomposition (Yang 2006).

Because there is little or no interaction between hemicellulose, cellulose, and lignin, the pyrolysis process can be considered a simple superimposition of temperature profiles. Yang et al. (2006) measured pyrolysis temperatures for synthetic biomass. Below 230 ^{o}C moisture was evolved, hemicellulose decomposed from 230-315^{o}C, and cellulose decomposed from 315-400 ^{o}C. Lignin decomposed above 400 ^{o}C. However these were not rigid boundaries as there was some overlap. And while there was little chemical interaction between these three materials particle formation and interjection into the sample matrix could physically interfere with the process. There are also examples of particular types of lignins that decompose at low temperatures. Of particular relevance to complex sample matrices is that metals salts (NaOH, Na_2CO_3, NaCl, $NiCl_2$, $CuSO_4$) lower the temperature of cellulose pyrolysis (Yang 2006).

One of the more common thermal degradation products encountered in pyrolysis is PAHs, which can be formed at temperatures between 300 and 600^{o}C (Del Rio and Philip 1992). The most common chemical reaction during pyrolysis is the ß elimination in which two adjacent atoms lose attached groups and form a double bond. Six membered rings can be formed as an intermediate in this situation (Şerban and Victord 2002). In the author's experience naphthalene is readily formed and for this reason will not be reported in subsequent discussions.

Pyrolysis temperatures in the range of 600 to 750 ^{o}C have been used for sediment studies. Higher temperatures will also be required to desorb those heavier molecules that will not undergo pyrolysis (Faure and Lanadais 2001, Poerschmann 2008). Studies of sewage sludge pyrolysis have shown that most biodegradable organic matter volatilizes in the temperature range 150 to 400 ^{o}C and non-biodegradable organic matter volatilizes between 400 to 550 ^{o}C (Barneto et al. 2009).

Use of Correction Factors

Every GC detector requires the use of a response factor for quantitation. The area of a

GC peak is proportional to the amount of analyte that reached the GC detector. But no detector responds equally to different compounds and so the peak area is a combination of the amount of analyte and the response of the detector to that particular type of molecule (response factor). An FID will not produce a large signal for a compound that does not burn. An ECD will not produce a strong signal from a non-halogenated compound.

This problem is especially acute in mass spectrometry. The size of the peak is proportional to the number of ions that are generated by the molecule when it is fragmented in the ion source. Consider a group of benzene molecules and an equal number of hexane molecules. The benzene will only generate one major ion because it does not fragment readily. The hexane will fragment into C_5, C_4, and C_3 chain-length ions in addition to C_6 ions. The resulting hexane peak will have a much greater area than the benzene peak even though the number of molecules was the same. The correction factors used in this research were developed by Michael Kruge at Montclair State and builds on the principle of the response factor. A deuterated PAH will generate a mass spectrum dominated by a single molecular ion because aromatic molecules tend not to fragment. There will of course be smaller fragments but there are only a comparatively small number of them. Most of the other analytes will generate a larger number of fragments.

The large number of fragments can be used to advantage in a complex sample matrix.

For example, two compounds may co-elute but they may also have characteristic fragments. Using the GC/MS software we can isolate these unique fragments thus de-convolute the peaks. To quantitate the peak, one ion is selected and the area under the GC trace for that ion is integrated. The advantage of this approach is that only the ions from a particular compound are used to quantify that compound but the disadvantage is that this one ion represents only a small fraction of the total peak area. Thus the correction factor compensates for this difference.

An example of a similar approach comes from biomedical science. Isotopic metabolic tracer studies employ labeled variants (isotopomers) of the desired analytes. Raw GC/MS data must be corrected using three conversions. The background must be corrected for. Ion abundances in the isotopomers will be different than those from the original molecule, and the resulting "skew" is corrected. Lastly, any overlapping spectra must be deconvoluted (Rosenblatt et al. 1992).

Method Performance Measurements

Sediments obtained for other research projects were also analyzed by Py-GC/MS. Samples from both the north and south banks of the Toms River were taken in the summers of 2011 and 2012. The objective of this project was to determine if materials originating in sewage were reaching the tidal portion of the river from upland portions of the watershed. The sediments were analyzed using the same procedures as described above except that to improve sensitivity the mass range was restricted to 190 to 300 amu.

Almost all of the biomarkers characteristic of sewage inputs have diagnostic ions in this range (Kruge, et al. 2010).

The analytes were quantitated by comparison with an internal standard. Allopregnane was selected for this purpose because it is rare in the environment yet chemically very similar to the compounds of interest. The internal standard concentration was manipulated such that each injection introduced 20.00 ng of allopregnane. Because of the chemical similarity of the internal standard and compounds of interest, no correction factors were applied.

Among the principle pyrolysis products of sewage are cholestenes, methylcholestenes, and ethylcholestenes. There are four common species for each of these compounds and they appear as a distinctive cluster of four peaks. All three types of cholestenes were integrated as if they were single peaks so that three, not twelve, concentration values will be reported.

Eight replicate injections were made of a sample obtained from Cedar Point in Berkeley Township, New Jersey on the south bank of the Toms River. Sample sizes ranged from 10.4 to 15.9 mg. The results are shown in table one.

A generic method of finding a method’s lower limit of detection (LLD) is to calculate the standard deviation of the results of seven replicate determinations. This value is then multiplied by three. On table one it will be seen that the detection limits for common steranes fall between 0.05 and 0.09 mg/kg or approximately 50% to 80% of the analyte's mean concentration. This is far from an ideal situation but consistent with the low concentration of the sewage markers in the samples. This compares favorably with USEPA method 8270D (GC/MS analysis of semi-volatile organic compounds) that includes an estimated lower quantitation limit of 660 μg/kg (0.660 mg/kg) for compounds in soils and sediments. (USEPA 2007) The quantitation limit (SQL) is defined as the detection limit after correction for sample dilution or other preparation steps.

The coefficients of variation (CV) expressed as percentages were somewhat high and it would be instructive to determine the source of the variation. It was possible to divide the area counts of the analytes by the mg of sample and compare these to the area counts of the allopregnane standards. The percent CVs of the analyte area counts were 14.1 for cholestenes, 25.3 for methylcholestenes, and 14.7 for ethylcholestenes. The standards only had a %CV of 8.5. This means that a greater proportion of the variation in the results come from the sample's response to the pyrolysis process and not inconsistency in the standards.

Adding a known quantity of analyte to a sample and measuring its recovery is a common practice. It can determine if interfering substances are present in a sample matrix. Two sandy samples from the Toms River with low concentrations of sewage markers was mixed with a small amount of a fine-grained organic-rich sediment sample taken from

Brooklyn's Gowanus Canal. The Gowanus Canal is an industrial waterway and is well known for sewage contamination that stretches back more than a century. Spike recoveries are reported in table 2-1.

As might be expected in the Toms River Sample 1, the more abundant compounds had more consistent recoveries.

Comparison of Py-GC/MS running in the SIM mode with Conventional Solvent Extraction

An invitation to Montclair State University from the USEPA to participate in sediment survey of the Gowanus Canal in Brooklyn, New York, provided an excellent opportunity to compare Py-GC/MS analysis of PAH contamination with conventional solvent extraction. The Gowanus Canal is a 2.9 kilometer long waterway extending inland from the Gowanus Bay. It was created from the Gowanus Creek in 1853 – 54 and completed until 1874. The peak years of the canal use were between 1900 and 1932 when 50 to 60 businesses used the canal. It provided a major impetus to the industrial growth of Brooklyn and its banks were eventually lined with paint factories, tanneries, coal yards, sulfur works, petroleum storage, chemical manufacturers, manufactured gas plants (MGP), and waste disposal facilities (Gowanus CDC).

The majority of the PAH contamination can be attributed to three manufactured gas plants operated on the banks of the canal, Citizen Works (now referred to as the Public

Place) on Smith Street, Fulton Municipal Gas Company on the south bank between Douglass and Sackett streets, and the Metropolitan Gas Light Company along Second Avenue (Gowanus CDC). Of the three sites the Citizen Works deserves special mention. Gas manufacturing operations were carried out from the 1860s to the late 1950s. This 5.8 acre site has been identified as the most promising for redevelopment because of its large size, long frontage on the canal, and ownership by the city. It is also the most severely contaminated. BTEX (benzene, toluene, ethylbenzene, and xylene), PAHs, and volatile organics have all been detected on the site. The contamination has been detected as deep as 50 meters below grade (Gowanus CDC).

The ten samples used in the present study were collected by the USEPA and the US Army Corps of Engineers in 2006 as part of an ongoing study of the waterway contamination. The samples were split in the field with one portion going to the EPA's Edison, New Jersey, laboratory for analysis and another portion going to Montclair State University. This has provided an unique opportunity for side by side comparison of polyaromatic hydrocarbon (PAH) analysis GC/MS analysis by EPA method 8270 (a conventional solvent extraction method) and high temperature (610 ^{o}C) pyrolysis.

The Py-GC/MS sediment samples were dried overnight at 40 ^{o}C and the finely ground with a mortar and pestle. Milligram quantities of the samples were placed in a quartz tube. A plug of quartz wool held the sample in place. The sample was spiked with 5 µL of an internal standard cocktail. The spike solution was not actually mixed with the sediment, rather it was placed on the quartz wool. This was done to prevent absorption of the internal standard on the sediment grains.

The spike solution contained deuterated naphthalene (D-naphthalene), deuterated anthracene (D-anthracene), and deuterated pyrene (D-pyrene). The spike concentration was manipulated such that each injection introduced 24.50 ng of D-naphthalene and 27.00 ng of D-Anthracene into the chromatographic system. D-pyrene was used for quantization. All PAH concentrations were determined by comparison to the internal standard.

The GC column was a Restek 30 meter, Dimethylpolysiloxane stationary phase, 0.25 mm ID. The GC temperature program began at 50^{o}C for 5 minutes and rose at a rate of 5^{o}C per minute until reaching 30oc and holding for 25 minutes. Gas pressure at the column head was 33 psi with a split ratio of 1 to 25. The MS was also set to 70eV ionization voltage and identification was based on a combination of molecular weight and retention time window for each of the PAHs.

Generally speaking the canal bottom is composed of black silt with degrees of hardness from "very soupy" to "stiff." Sediment characteristics are listed in table 2-2. The data in table 2-2 shows that the percentage of "Fines" (defined as clay and silt particles) is high and thus we might expect a large concentration of organic matter because small particles have a high relative surface area to volume and provide many binding sites (Lauenstein and Kimbrough 2007).

The Py-GC/MS results were consistently higher than those achieved with solvent extraction. The PAH concentrations are listed in table three and the sample points in table 2-4. Thirteen individual PAH's measured at each of the ten sample points provided for 130 direct comparisons between the two approaches. The pyrolysis result was larger in 119 instances or 92% of the time.

The results obtained by Py-GC/MS was divided the concentration obtained by solvent extraction. The results of this simple calculation ranged from a low of 0.4 (pyrolysis result only 40% of the solvent extraction) to a high of 16.3. Dividing the range into quartiles reveals that the about half of the samples (64) fall into the first quartile (0 to 400% increase) and of these about one third (28) show an increase of less than 200%. The number of comparisons in the second, third, fourth quartiles decrease almost exponentially, 34 in the second (400 to 800% increase), 3 in the 3rd (800 to 1200%), and only 1 in the fourth quartile (1200 to 1600%).

These results however are not at all well correlated with either molecular weight ($r = -0.22$) or the number of rings in the molecule ($r = -0.10$). The location within the canal also seems to have little effect. The average increase of all PAH concentrations with the Py-GC/MS method was approximately 350% in six out the ten sample points. There are multiple explanations for this phenomena and these include the generation of PAH compounds by the pyrolysis process, the potential for better recoveries by pyrolysis, the different approaches to quantitation, (internal as opposed to external standards). How these factors interact and produce this result is a question deserving additional research.

Regardless of their cause, percent increases of the magnitudes reported in this dissertation only seem excessive. But when measuring concentrations in the ppb or mg/kg range, most of the reported differences between pyrolysis and solvent extraction are actually quite small.

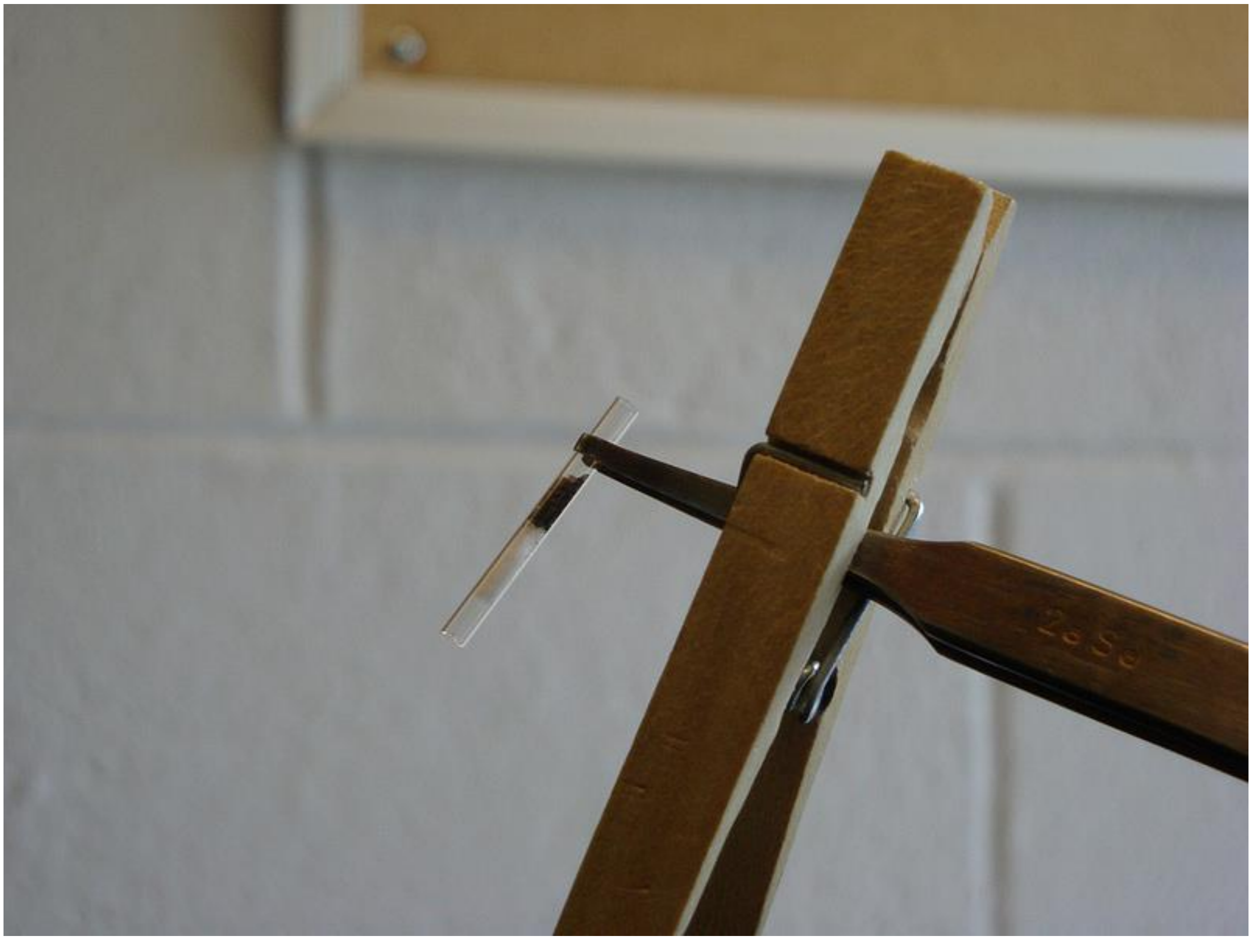
A more relevant question is whether the Py-GC/MS shows the same overall pattern of PAH distributions within the canal as the solvent extraction method? Both methods rank the eight of the ten sample points in the same order based on total PAH concentration. From the least to the most contaminated, these sample points are: 27A, 26A, 20A, 28A, 16A, 19A, 29A and 15A. Py-GC/MS placed sample point 21a as being the least contaminated and 31a as the second least contaminated. The solvent extraction method reversed the order of these two points.

Conclusions

The essential challenge of any GC/MS analysis is to separate the compounds of interest from the sample matrix and place them on the GC column. The usual method of doing this is solvent extraction and concentration. In theory, pyrolysis represents a superior methodology because it is suitable to a much wider range of compounds, is not solventselective, and requires minimal sample pre-treatment. The greatest advantage is that it will work on anything that burns and the analytes recovered are not dependent on either the extraction solvent or extraction conditions.

At least when applied to sediment samples, in actual practice, Py-GC/MS has some limitations. While the creation of novel compounds by pyrolysis is very reproducible, the process is heavily dependent on temperature and sample composition. This can be anticipated and compensated for during data analysis. However the greatest limitations are the lack of reproducibility and erratic sample recovery. For these reasons Py-GC/MS should be regarded, at least at this time, as only providing approximate quantitation data.

Figures and Tables



Appendix 2 - Figure 1. The quartz tube is loaded for pyrolysis. The sediment sample rests against a plug of glass wool. The internal standard solution is loaded onto the glass wool.

Figure 2

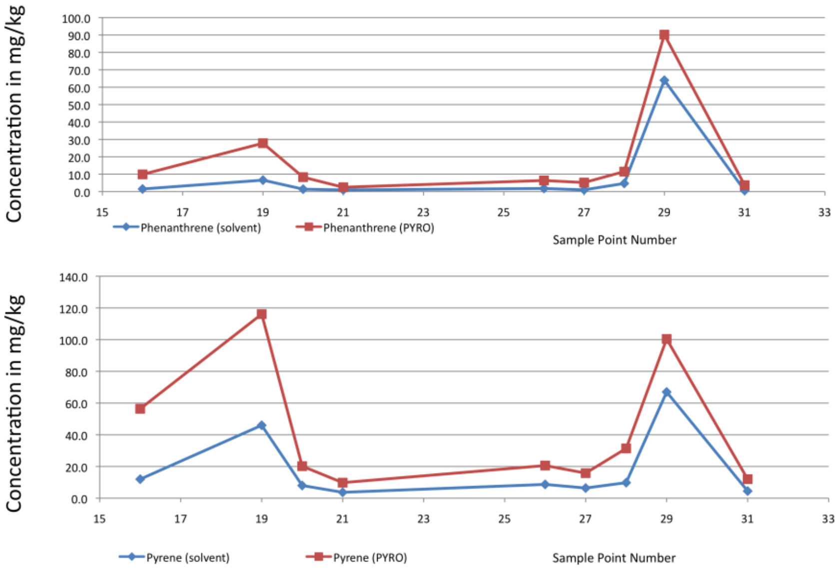
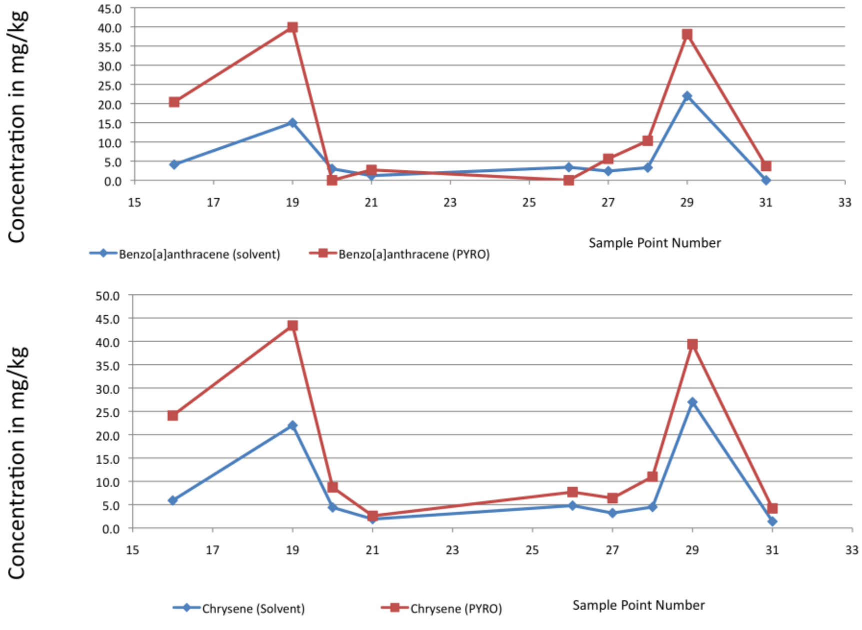


Figure 2a



Appendix 2 - Figure 2 The plots of selected PAH molecules showing how each analysis system quantified them at each sample point.

Appendix 2 -Table 1. Reproducibility of the PyGC/MS operating in full scan mode. All results in ng/mg (mg/kg). No correction factor was applied.

Cholestenes	0.14	0.14	0.14	0.13	0.12	0.14	0.18	0.14
Methylchlestenes	0.07	0.11	0.13	0.08	0.11	0.08	0.14	0.09
Ethylcholestenes	0.13	0.15	0.16	0.18	0.15	0.19	0.22	0.13

Analyte	Mean	Std dev	3x std dev	% CV
Cholestenes	0.14	0.02	0.05	12.23
Methylchlestenes	0.10	0.03	0.08	25.01
Ethylcholestenes	0.16	0.03	0.09	19.02

Spike sample recovery (all results reported as percent)

Analyte	Toms Rvr spl 1	Toms Rvr spl 1	Toms Rvr spl 4
Cholestenes	86.9	88.1	61.5
Methylchlestenes	84.2	152.7	101.7
Ethylcholestenes	100.3	122.1	75.2

Table 2-2, Percent Composition of Gowanus Canal Sediments (courtesy USACE)

	Gravel	Sand	Silt	Clay
Mean	3.59	25.53	58.64	12.23
Median	0.9	25.65	60.05	12
Max	15.4	64.6	79.4	15.5
Min	0	5.8	27.3	7.5

Appendix 2 -Table 3. Comparing results for priority PAH compounds as determined by solvent extraction (USEPA method number 8270) and Py-GC/MS operating on the SIM mode.

Name		Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo[a]anthracene	Chrysene	Benzo[b+j]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	indeno(1,2,3-cd) pyrene	Dibenzo[a,h]anthracene	∑PAH
EPA	15A	150.0	110.0	270.0	100.0	720.0	290.0	270.0	800.0	170.0	260.0	130.0	37.0	180.0	78.0	34.0	3599
EPA	16A	0.6	1.4	1.0	0.5	1.5	1.4	5.9	12.0	4.1	5.9	3.9	1.3	3.6	0.0	0.0	43
EPA	19A	1.4	5.6	16.0	1.7	6.6	20.0	23.0	46.0	15.0	22.0	9.7	3.6	7.3	3.8	24.0	206
EPA	20A	0.0	0.9	1.0	0.0	1.4	1.4	4.8	8.0	3.0	4.4	2.6	1.4	2.3	0.0	0.0	31
EPA	21A	0.0	0.4	0.0	0.0	1.0	0.6	1.9	3.7	1.2	1.9	0.0	0.0	0.0	0.0	0.0	11
EPA	26A	0.0	1.0	0.0	0.0	1.8	1.2	4.1	8.7	3.4	4.8	2.7	0.9	0.0	0.0	0.0	29
EPA	27A	0.0	0.7	0.0	0.0	1.0	1.1	3.0	6.4	2.4	3.2	0.0	0.0	0.0	0.0	0.0	18
EPA	28A	0.0	1.0	0.8	0.5	4.7	2.0	4.1	9.8	3.3	4.5	0.0	0.0	0.0	0.0	0.0	31

342	9	80					4188	249	547
31.0	0.0	6.1					0	0	0
4.5	0.0	0.9					0	0	18.4
15.0	0.0	3.1					236.2	15.6	45.1
4.4	0.0	1.3					65.1	5	11.4
14.0	0.0	3.7					353.9	38.1	58.2
27.0	1.4	8.3					316	24.1	43.4
22.0	0.0	6.0					290.1	20.4	39.9
67.0	4.5	18.5					762.2	56.4	116.1
32.0	1.8	9.0					129.1	35.2	74.5
31.0	0.6	6.6					431	14.2	50.5
64.0	0.6	9.2					969.8	9.9	27.8
8.3	0.0	1.2					91.1	1.3	2
4.6	0.0	2.6					106.7	2.8	10.5
7.5	0.5	2.1					281	15.9	37.9
9.8	0.0	1.3					155.8	9.8	11
29A	31A	MEAN					15a	16a	19a
EPA	EPA						MSU	MSU	MSU

96	42	80	78	102	556	58	201
0	0	0	0	0	0	0	0.0
0	0	0	0	0	0	0	2.0
7	0.5	4.3	3.6	0.5	37.8	3.6	13.1
2.3	0.6	1.1	1.2	0.2	9.5	1.3	3.6
12.6	5.5	5.6	7.8	2.3	56.4	9.7	21.8
8.7	2.6	7.7	6.4	11	39.4	4.2	16.4
0	2.7	0	5.6	10.3	38.1	3.7	13.4
20.2	9.8	20.6	15.8	31.4	100.4	12	42.5
15.5	6.8	14.3	13.8	20.7	64.8	5.5	27.9
6	2.5	5.3	4.6	8.6	36.1	3.5	14.6
8.3	2.5	6.4	5.2	11.5	90.2	3.7	18.4
1.9	0.6	1.2	0	0	5.2	0.9	1.5
2.2	0.4	0.8	1.2	0.6	4.3	0.7	2.6
4.8	2.8	6.6	4.5	4	35	2.8	12.7
6.5	4.2	6.4	8.1	0.8	39.1	6.2	10.2
20a	21a	26a	27a	28a	29a	31a	MEAN
MSU	MSU	MSU	MSU	MSU	MSU	MSU	

Appendix 2 -4. Sample points for the Gowanus Canal study. The Gowanus Expressway crosses the canal near its entrance and thus provides a useful method of measuring distance. Sample point 31A is outside the canal.

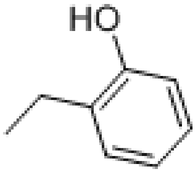
Sample Point	Long. °	Lat. °	Distance from the Gowanus Expressway Bridge in meters
15A	-73.99588178	40.67477411	433
16A	-73.99497783	40.67483169	465
19A	-73.99389275	40.67554899	589
20A	-73.99331692	40.67605837	695
21A	-73.99166907	40.67585664	753
26A	-73.98955684	40.67693014	1068
27A	-73.98921699	40.67774284	1219
28A	-73.98881191	40.67886533	1312
29A	-73.98792833	40.68012167	1463
31A	-74.00066425	40.66869058	

Appendix 3: Chemical Structures of significant biomarkers

Unless otherwise indicated, all images courtesy of Chemical Book, http://www.chemicalbook.com

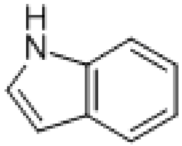
Ethylguaiacol

Molecular Formula: C8H10O
Formula Weight: 122.16
CAS number 90-00-6



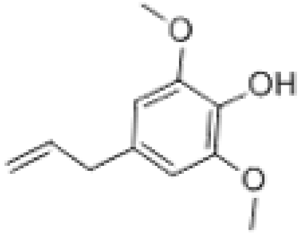
Indole

Molecular Formula: C8H7N
Formula Weight: 117.15
CAS number 120-72-9



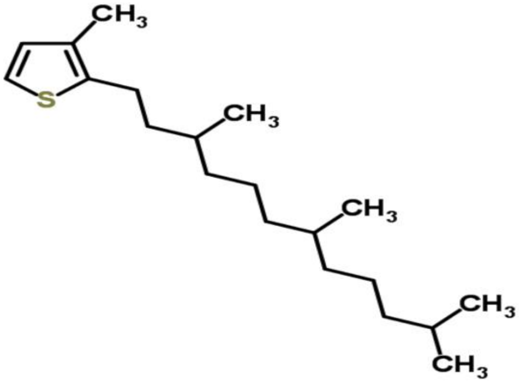
Isoeugenol

Molecular Formula: C10H12O2
Formula Weight: 164.2
CAS number 97-54-1



3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene

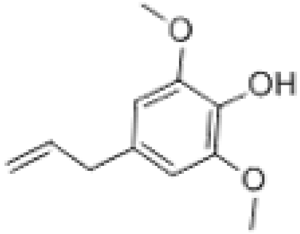
Molecular Formula: C20H36S
Average mass: 308.56



(Chemspider)

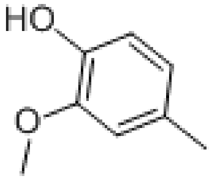
Methoxyeugenol

Molecular Formula: C11H14O3
Formula Weight: 194.23
CAS number 6627-88-9



Methylguaiacol

Molecular Formula: C8H10O2
Formula Weight: 138.16
CAS number 93-51-6



Methylphenol
Molecular Formula: C7H8O
Formula Weight: 108.14

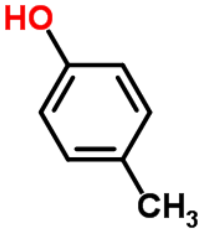
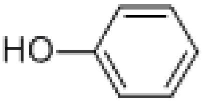


Image courtesy of Chemspider, http://www.chemspider.com

Phenol

Molecular Formula: C6H6O
Formula Weight: 94.11
CAS number 108-95-2



Steranes (C27)

Formula: C27H48
Formula Weight: 372.6700

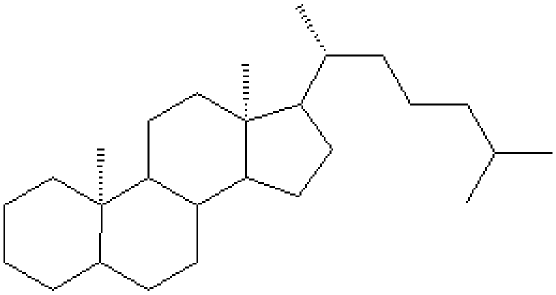
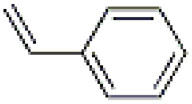


Image courtesy National Institute of Standards and Technology (NIST)

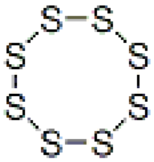
Styrene

Molecular Formula: C8H8
Formula Weight: 104.15
CAS No.: 79637-11-9



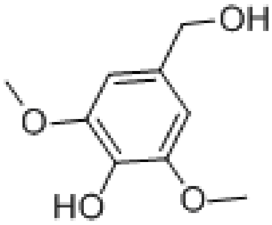
Sulfur

Molecular Formula: S8
Formula Weight: 256.52
CAS number 7704-34-9



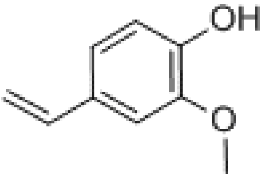
Syringol

Molecular Formula C9H12O4
Molecular Weight: 184.19
CAS number 530-56-3



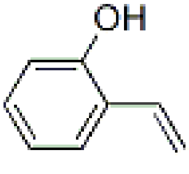
Vinylguaiacol

Molecular Formula: C9H10O2
Molecular Weight: 150.17
CAS number 7786-61-0



Vinylphenol

Molecular Formula: C8H8O
Formula Weight: 120.14852
CAS Number 31257-96-2



Appendix 4,

Raw Data from the Gateway National Recreation Area Samples

Compound number	Target Compound	Gateway 1	Gateway 3	Gateway 4	Gateway 5
		mg/kg	mg/kg	mg/kg	mg/kg
2	C11 n-alk-1-ene	0.51	3.16	0.94	0.06
3	C12 n-alk-1-ene	0.44	2.79	0.73	0.04
4	C13 n-alk-1-ene	0.18	2.63	0.80	0.04
5	C14 n-alk-1-ene	0.50	2.48	0.77	0.05
6	C15 n-alk-1-ene	0.53	1.90	0.57	0.04
7	C16 n-alk-1-ene	0.32	1.65	0.51	0.04
8	C17 n-alk-1-ene	0.28	1.45	0.44	0.02
9	C18 n-alk-1-ene	0.30	1.45	0.45	0.01
10	C19 n-alk-1-ene	0.20	1.17	0.23	0.01
11	C20 n-alk-1-ene	0.22	1.11	0.32	0.01
12	C21 n-alk-1-ene	0.14	0.78	0.22	0.01
13	C22 n-alk-1-ene	0.17	0.95	0.19	0.00
14	C23 n-alk-1-ene	0.19	0.94	0.14	0.01
15	C24 n-alk-1-ene	0.12	1.05	0.16	0.00
16	C25 n-alk-1-ene	0.13	0.76	0.07	0.00
17	prist-1-ene	0.09	2.08	0.24	0.01
18	prist-2-ene	0.09	2.08	0.24	0.01
19	C10 n-alkane	1.00	5.07	0.77	0.03
20	C11 n-alkane	0.70	0.72	0.89	0.03
21	C12 n-alkane	0.72	4.23	0.97	0.03
22	C13 n-alkane	0.71	4.84	1.13	0.10
23	C14 n-alkane	0.64	3.70	0.94	0.05
24	C15 n-alkane	0.12	4.17	1.14	0.05
25	C16 n-alkane	0.57	3.04	0.90	0.03
26	C17 n-alkane	0.59	2.94	0.78	0.03
27	C18 n-alkane	0.43	2.97	0.69	0.02
28	C19 n-alkane	0.46	2.50	0.64	0.03
29	C20 n-alkane	0.37	2.06	0.50	0.02
30	C21 n-alkane	0.47	2.09	0.51	0.02
31	C22 n-alkane	0.54	2.44	0.54	0.01
32	C23 n-alkane	0.60	2.66	0.47	0.01
33	C24 n-alkane	0.34	1.62	0.33	0.01
34	C25 n-alkane	0.74	1.94	0.32	0.02
35	C26 n-alkane	0.33	1.51	0.33	0.01
36	C27 n-alkane	0.61	1.94	0.27	0.01
37	C28 n-alkane	0.34	1.33	0.19	0.01
38	C29 n-alkane	1.16	3.36	0.44	N.D.
39	C30 n-alkane	0.26	1.31	0.10	N.D.
40	C31 n-alkane	0.82	3.46	0.28	0.01
41	ethylbenzene	2.69	20.0	6.43	0.23
42	styrene	4.56	13.4	9.17	0.42
43	n-propylbenzene	0.86	5.42	1.65	N.D.
44	n-butylbenzene	0.75	5.29	1.28	0.07

45	n-pentylbenzene	0.70	3.75	1.13	0.06
46	n-hexylbenzene	0.44	2.85	0.94	0.02
47	n-heptylbenzene	0.19	3.69	0.76	0.04
48	n-octylbenzene	0.45	2.65	0.95	0.05
49	n-nonylbenzene	0.39	2.00	0.67	N.D.
50	n-decylbenzene	0.72	4.62	0.81	0.04
51	n-undecylbenzene	0.31	1.98	0.47	0.03
52	n-dodecylbenzene	0.46	2.33	0.82	N.D.
53	n-tridecylbenzene	0.25	1.26	N.D.	0.01
54	n-tetradecylbenzene	0.37	2.00	0.67	0.03
55	n-pentadecylbenzene	0.23	1.18	N.D.	0.01
56	n-hexadecylbenzene	0.44	1.52	N.D.	N.D.
57	6-phenylundecane	0.16	4.31	N.D.	N.D.
58	5-phenylundecane	0.15	1.21	N.D.	N.D.
59	4-phenylundecane	0.13	1.23	N.D.	N.D.
60	6-phenyldodecane	0.37	N.D.	N.D.	N.D.
61	5-phenyldodecane	0.61	1.05	N.D.	N.D.
62	4-phenyldodecane	0.36	1.00	0.47	0.04
63	6-phenyltridecane	0.19	N.D.	N.D.	N.D.
64	Phytane	0.10	1.66	0.40	N.D.
65	5-phenyltridecane	0.18	N.D.	N.D.	N.D.
66	4-phenyltridecane	0.22	N.D.	N.D.	N.D.
67	naphthalene	1.52	10.6	2.92	0.15
68	2-methylnaphthalene	0.55	2.99	0.96	0.04
69	1-methylnaphthalene	0.41	2.70	0.80	0.03
70	dimethylnaphthalenes	0.74	5.70	1.68	0.07
71	trimethylnaphthalenes	0.43	3.12	0.79	0.05
72	tetramethylnaphthalenes	0.43	2.53	0.85	0.04
73	fluorene	0.46	2.83	0.65	0.01
74	methylfluorenes	0.92	5.82	1.41	0.07
75	phenanthrene	0.35	2.86	0.78	0.03
76	anthracene	0.20	2.23	0.23	0.03
77	3-methylphenanthrene	0.15	0.72	0.19	0.01
78	2-methylphenanthrene	0.11	0.95	0.32	0.01
79	methylanthracene	0.53	4.59	1.63	0.08
80	9-methylphenanthrene	0.10	0.67	0.18	0.01
81	1-methylphenanthrene	0.08	0.99	0.30	0.02
82	dimethylphenanthrenes	0.31	3.34	0.92	0.04
83	retene	0.02	0.18	0.10	N.D.
84	fluoranthene	0.30	3.88	0.38	0.02
85	pyrene	0.24	2.97	0.71	0.03
86	methylpyrene isomers	1.02	7.73	1.67	0.06
87	dimethylpyrene isomers	0.37	3.45	0.98	0.02
88	benzo[a]anthracene	0.22	1.70	N.D.	N.D.
89	chrysene	0.19	2.39	0.28	0.00
90	methylchrysene isomers	0.21	2.35	0.66	0.01

91	benzo[b]fluoranthene	0.02	0.99	0.06	N.D.
92	benzo[j]fluoranthene	0.03	0.63	0.12	N.D.
93	benzo[k]fluoranthene	0.01	0.58	0.04	N.D.
94	benzo[e]pyrene	0.01	0.09	0.03	N.D.
95	benzo[a]pyrene	0.01	0.35	0.09	N.D.
96	perylene	0.01	0.11	N.D.	N.D.
97	indenol[1,2,3-cd]pyrene	0.01	N.D.	N.D.	N.D.
98	benzo[ghi]perylene	N.D.	N.D.	N.D.	N.D.
99	dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
100	dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
101	C29 hopane (17a, 21b)	0.03	0.31	N.D.	N.D.
102	C30 hopane (17a,21b)	0.00	0.32	0.09	N.D.
103	cholestene	0.01	0.03	0.01	0.00
104	ethylcholestene	0.01	0.05	0.01	N.D.
105	C27 sterane	N.D.	N.D.	N.D.	N.D.
106	C28 sterane	N.D.	N.D.	N.D.	N.D.
107	C29 sterane	N.D.	N.D.	N.D.	N.D.
108	naphthalene-d8	0.02	0.06	0.02	0.00
109	anthracene-d10	1.06	4.29	2.55	0.68
110	pyrene-d10	2.06	8.25	6.82	1.76
111	chrysene-d12	1.03	7.39	4.22	0.25
112	C2-alkylpyrrole	0.75	4.54	1.35	0.03
113	phenol	28.0	213	21.0	0.78
114	2-methylphenol	1.40	9.23	1.28	0.06
115	4&3-methylphenols	15.6	114	10.3	0.25
116	4-ethylphenol	15.0	124	5.66	0.08
117	vinylphenol	58.8	510	9.26	0.05
118	guaiacol	2.49	21.3	0.26	0.01
119	methylguaiacol	1.16	17.5	0.22	0.00
120	ethylguaiacol	1.13	13.9	0.15	N.D.
121	vinylguaiacol	15.7	141	1.21	N.D.
122	vanillin	0.96	6.96	0.40	0.01
123	eugenol	0.28	3.43	0.07	0.00
124	cis iso-eugenol	0.33	0.00	0.07	N.D.
125	trans iso-eugenol	2.11	0.00	0.35	0.00
126	acetovanillone	0.04	3.27	0.06	0.00
127	syringol	0.76	6.90	0.03	N.D.
128	methylsyringol	0.35	7.97	N.D.	N.D.
129	ethylsyringol	0.18	1.95	N.D.	N.D.
130	vinylsyringol	1.37	12.9	0.05	N.D.
131	syringaldehyde	0.24	2.04	N.D.	N.D.
132	prop-1-enyl syringol	0.49	7.07	0.02	N.D.
133	cis-prop-2-enyl syringol	0.40	8.15	N.D.	N.D.
134	trans-prop-2-enyl syringol	2.50	42.1	0.06	N.D.
135	benzaldehyde	0.38	2.00	0.87	0.05

136	benzaldehyde methyl	0.77	5.98	2.90	0.17
137	methylfurfural	8.39	41.5	6.79	0.17
138	methylfuranone	3.18	17.7	1.26	N.D.
139	2-methylcyclopentenone	0.76	3.71	1.07	0.01
140	3-methylcyclopentenone	1.11	3.82	1.46	N.D.
141	benzonitrile	0.69	2.06	1.25	0.11
142	benzoacetonitrile	1.79	7.42	2.30	0.21
143	benzenepropanitrile	3.60	12.0	4.06	0.36
144	quinoline	0.60	1.50	1.04	0.03
145	isoquinoline	1.45	6.67	2.53	0.14
146	indole	11.0	39.23	9.79	0.62
147	methylindole	2.88	10.95	2.90	0.14
148	phenylpyridine	0.32	1.35	0.35	0.01
149	carbazole	0.59	2.09	0.31	N.D.
150	diketodipyrrole	2.14	8.86	2.42	0.04
151	cyclo-Pro-Pro-diketopi...	0.29	6.88	1.09	0.02
152	n-tetradecanitrile	0.02	N.D.	0.03	0.00
153	n-hexadecanitrile	0.06	0.17	0.09	0.00
154	n-octadecanitrile	0.02	0.18	0.09	0.00
155	tetradecylamide	0.50	1.23	0.21	N.D.
156	hexadecylamide	2.49	8.12	0.77	0.01
157	octadecylamide	0.45	1.67	0.19	N.D.
158	benzothiophene	0.09	2.16	0.28	N.D.
159	4-methyldibenzothiophene	N.D.	0.41	0.11	N.D.
160	1-methyldibenzothiophene	0.04	0.50	N.D.	N.D.
161	3-&2-methyldibenzothiophenes	N.D.	0.34	0.10	N.D.
162	benzonaphthothiophene isomer	0.04	0.50	N.D.	N.D.
163	C13-alk-2one	0.54	1.95	0.53	0.03
164	C14-alk-2-one	0.23	0.69	0.27	0.01
165	C15-alk-2-one	0.32	1.16	0.47	0.02
166	C16-alk-2-one	0.23	1.02	0.27	0.01
167	C17-alk-2-one	0.38	1.11	0.56	0.03
168	C18-alk-2-one	0.18	0.50	0.31	N.D.
169	C19-alk-2-one	0.12	0.47	0.31	0.00
170	n-tetradecanoic acid	0.05	0.18	0.00	0.00
171	Pristane	0.41	2.09	0.04	0.00
172	pentadecanoic acid isomer	0.04	0.18	N.D.	0.00
173	pentadecanoic acid isomer	0.02	0.19	0.03	N.D.
174	n-pentadecanoic acid	0.07	0.31	0.04	0.00
175	n-hexadecanoic acid	0.11	0.51	0.08	0.00

176	n-heptadecanoic acid	0.01	0.08	0.03	N.D.
177	n-octadecanoic acid	0.03	0.10	0.03	0.00
178	n-eicosanoic acid	0.02	0.08	0.01	N.D.
179	n-docosanoic acid	0.01	0.07	0.01	0.00
180	n-tetracosanoic acid	0.01	0.08	N.D.	0.00
181	elemental sulfur	0.84	1.77	22.08	1.03
182	phyta-1,3(4)-diene	1.69	4.41	0.51	N.D.
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	4.16	16.9	5.54	0.08
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	15.9	48.4	22.3	0.19
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	21.0	58.1	26.0	0.13
186	hexadecanamine,N,N-dimethyl	4.36	3.84	41.67	N.D.
187	octadecanamine,N,N-dimethyl	14.1	7.01	62.7	N.D.
n/a	Percent Loss On Ignition	N.D.	N.D.	4.41	0.38
n/a	Percent Silt & Clay	N.D.	N.D.	74.0	3.81

Compound number	Target Compound	Gateway 6	Gateway 8	Gateway 9	Gateway 10 M
		mg/kg	mg/kg	mg/kg	mg/kg
2	C11 n-alk-1-ene	0.20	1.01	0.80	0.95
3	C12 n-alk-1-ene	0.17	0.81	0.65	0.79
4	C13 n-alk-1-ene	0.14	0.86	0.58	0.75
5	C14 n-alk-1-ene	0.25	0.83	0.86	0.84
6	C15 n-alk-1-ene	0.14	0.70	0.76	0.57
7	C16 n-alk-1-ene	0.12	0.63	0.48	0.46
8	C17 n-alk-1-ene	0.09	0.59	0.42	0.42
9	C18 n-alk-1-ene	0.11	0.47	0.51	0.49
10	C19 n-alk-1-ene	0.06	0.39	0.26	0.25
11	C20 n-alk-1-ene	0.06	0.38	0.32	0.27
12	C21 n-alk-1-ene	0.04	0.30	0.17	0.21
13	C22 n-alk-1-ene	0.04	0.31	0.27	0.21
14	C23 n-alk-1-ene	0.02	0.29	0.10	0.16
15	C24 n-alk-1-ene	0.03	0.36	0.17	0.15
16	C25 n-alk-1-ene	0.01	0.12	0.10	0.10
17	prist-1-ene	0.13	0.41	0.20	0.21
18	prist-2-ene	0.13	0.41	0.20	0.21
19	C10 n-alkane	0.17	1.12	0.62	0.84
20	C11 n-alkane	0.18	1.03	0.65	0.96
21	C12 n-alkane	0.21	1.04	0.68	1.08
22	C13 n-alkane	0.32	1.56	1.07	1.32
23	C14 n-alkane	0.23	1.07	0.92	1.03
24	C15 n-alkane	0.32	1.19	1.08	1.33
25	C16 n-alkane	0.20	0.98	0.82	0.91
26	C17 n-alkane	0.17	0.88	0.75	0.80
27	C18 n-alkane	0.19	0.80	0.78	0.97
28	C19 n-alkane	0.17	0.86	0.71	0.72
29	C20 n-alkane	0.11	0.65	0.50	0.49
30	C21 n-alkane	0.11	0.71	0.54	0.48
31	C22 n-alkane	0.11	0.76	0.55	0.43
32	C23 n-alkane	0.08	0.94	0.46	0.48
33	C24 n-alkane	0.06	0.59	0.28	0.31
34	C25 n-alkane	0.05	0.57	0.56	0.38
35	C26 n-alkane	0.04	0.42	0.20	0.21
36	C27 n-alkane	0.04	0.49	0.24	0.23
37	C28 n-alkane	0.03	0.31	0.17	0.17
38	C29 n-alkane	0.07	0.94	0.40	0.39
39	C30 n-alkane	0.02	0.24	0.12	0.27
40	C31 n-alkane	0.04	0.71	0.25	0.28
41	ethylbenzene	1.14	4.37	4.50	5.96
42	styrene	2.65	3.96	16.4	8.39
43	n-propylbenzene	0.32	2.21	1.20	1.74
44	n-butylbenzene	0.29	2.05	1.14	0.49

45	n-pentylbenzene	0.22	1.88	0.66	1.08
46	n-hexylbenzene	0.17	1.27	0.66	0.90
47	n-heptylbenzene	0.18	1.22	0.55	0.97
48	n-octylbenzene	0.19	1.34	0.82	0.85
49	n-nonylbenzene	0.19	0.87	0.58	0.73
50	n-decylbenzene	0.27	1.75	0.83	0.93
51	n-undecylbenzene	0.15	0.88	0.44	0.75
52	n-dodecylbenzene	0.29	1.08	0.77	0.93
53	n-tridecylbenzene	0.09	0.75	0.58	0.49
54	n-tetradecylbenzene	0.13	0.95	0.41	0.56
55	n-pentadecylbenzene	0.09	0.73	N.D.	0.44
56	n-hexadecylbenzene	0.09	0.76	N.D.	0.56
57	6-phenylundecane	0.08	N.D.	0.79	0.29
58	5-phenylundecane	0.07	N.D.	0.65	0.30
59	4-phenylundecane	N.D.	N.D.	0.50	N.D.
60	6-phenyldodecane	0.23	N.D.	0.55	0.51
61	5-phenyldodecane	0.25	N.D.	0.36	0.52
62	4-phenyldodecane	0.23	N.D.	0.56	0.46
63	6-phenyltridecane	N.D.	N.D.	N.D.	N.D.
64	Phytane	0.02	0.09	0.14	0.12
65	5-phenyltridecane	N.D.	N.D.	N.D.	N.D.
66	4-phenyltridecane	N.D.	N.D.	N.D.	N.D.
67	naphthalene	0.54	4.63	2.05	3.18
68	2-methylnaphthalene	0.18	1.02	0.85	1.01
69	1-methylnaphthalene	0.15	1.00	0.65	0.85
70	dimethylnaphthalenes	0.40	1.58	1.39	2.04
71	trimethylnaphthalenes	0.30	1.10	0.79	1.05
72	tetramethylnaphthalenes	0.24	0.36	0.91	0.85
73	fluorene	0.21	1.45	0.70	0.78
74	methylfluorenes	0.35	1.81	1.16	1.29
75	phenanthrene	0.17	1.06	0.71	0.93
76	anthracene	0.09	0.36	0.35	0.30
77	3-methylphenanthrene	0.04	0.64	0.17	0.38
78	2-methylphenanthrene	0.08	0.72	0.21	0.36
79	methylanthracene	0.57	1.96	1.18	2.49
80	9-methylphenanthrene	0.07	0.35	0.18	0.34
81	1-methylphenanthrene	0.08	0.22	0.26	0.34
82	dimethylphenanthrenes	0.23	0.69	0.86	0.91
83	retene	0.03	0.07	0.07	0.08
84	fluoranthene	0.08	0.25	0.53	0.92
85	pyrene	0.10	0.57	0.65	0.82
86	methylpyrene isomers	0.42	1.41	1.61	1.76
87	dimethylpyrene isomers	0.22	0.58	0.86	1.10
88	benzo[a]anthracene	0.04	0.11	0.22	0.53
89	chrysene	0.05	0.16	0.15	0.53
90	methylchrysene isomers	0.11	0.24	0.27	0.50

91	benzo[b]fluoranthene	0.01	0.02	0.01	0.10
92	benzo[j]fluoranthene	0.00	0.02	0.05	0.12
93	benzo[k]fluoranthene	0.01	0.01	N.D.	0.04
94	benzo[e]pyrene	N.D.	N.D.	N.D.	0.08
95	benzo[a]pyrene	N.D.	N.D.	N.D.	0.03
96	perylene	N.D.	N.D.	N.D.	N.D.
97	indenol[1,2,3-cd]pyrene	N.D.	N.D.	N.D.	N.D.
98	benzo[ghi]perylene	0.01	N.D.	N.D.	N.D.
99	dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
100	dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	0.03
101	C29 hopane (17a, 21b)	0.01	N.D.	N.D.	N.D.
102	C30 hopane (17a,21b)	N.D.	N.D.	N.D.	0.05
103	cholestene	0.01	0.01	0.01	0.02
104	ethylcholestene	<0.01	<0.01	<0.01	0.01
105	C27 sterane	<0.01	N.D.	N.D.	N.D.
106	C28 sterane	<0.01	N.D.	N.D.	N.D.
107	C29 sterane	N.D.	N.D.	N.D.	N.D.
108	naphthalene-d8	0.00	0.03	0.05	0.03
109	anthracene-d10	1.25	2.81	4.71	3.64
110	pyrene-d10	2.21	7.00	10.2	6.95
111	chrysene-d12	1.06	3.16	3.83	2.94
112	C2-alkylpyrrole	0.38	0.72	1.00	1.83
113	phenol	7.22	43.24	19.75	31.98
114	2-methylphenol	0.35	1.74	1.14	1.56
115	4&3-methylphenols	5.17	19.0	13.4	19.0
116	4-ethylphenol	2.46	28.2	7.33	11.90
117	vinylphenol	4.22	102	14.7	24.0
118	guaiacol	0.16	3.04	0.36	0.60
119	methylguaiacol	0.06	2.26	0.31	0.31
120	ethylguaiacol	0.06	2.61	0.31	0.41
121	vinylguaiacol	0.78	20.4	2.37	3.23
122	vanillin	0.10	1.16	0.44	0.37
123	eugenol	0.02	0.32	0.10	0.11
124	cis iso-eugenol	0.02	0.46	0.13	0.17
125	trans iso-eugenol	0.14	2.76	0.74	0.83
126	acetovanillone	0.01	0.41	0.12	0.20
127	syringol	0.02	0.76	0.05	0.06
128	methylsyringol	0.01	1.00	0.08	0.05
129	ethylsyringol	0.01	0.24	N.D.	N.D.
130	vinylsyringol	0.04	1.36	0.11	0.16
131	syringaldehyde	0.03	0.23	0.03	0.11
132	prop-1-enyl syringol	0.03	0.86	0.12	0.16
133	cis-prop-2-enyl syringol	N.D.	1.22	0.12	0.09
134	trans-prop-2-enyl syringol	0.11	5.81	0.69	0.46
135	benzaldehyde	0.19	0.87	0.62	0.73

136	benzaldehyde methyl	0.66	4.33	2.02	2.06
137	methylfurfural	1.10	14.09	4.30	6.15
138	methylfuranone	0.21	2.00	N.D.	0.90
139	2-methylcyclopentenone	0.29	0.76	1.00	1.08
140	3-methylcyclopentenone	0.28	0.83	1.06	1.53
141	benzonitrile	0.43	0.79	0.97	1.64
142	benzoacetonitrile	1.01	1.78	2.73	3.76
143	benzenepropanitrile	1.95	2.59	4.27	6.73
144	quinoline	0.22	0.59	0.69	1.06
145	isoquinoline	0.78	1.43	2.08	3.20
146	indole	6.74	5.27	12.7	15.7
147	methylindole	1.97	1.51	4.38	4.51
148	phenylpyridine	0.13	0.47	0.30	0.43
149	carbazole	0.17	0.22	0.44	0.68
150	diketodipyrrole	0.84	2.66	1.98	3.27
151	cyclo-Pro-Pro-diketopi...	0.62	1.26	1.39	1.30
152	n-tetradecanitrile	N.D.	N.D.	0.03	0.04
153	n-hexadecanitrile	0.04	0.10	0.18	0.15
154	n-octadecanitrile	0.02	0.04	0.07	0.05
155	tetradecylamide	0.14	0.16	0.23	0.35
156	hexadecylamide	0.66	0.23	1.58	2.28
157	octadecylamide	0.07	0.04	0.14	0.22
158	benzothiophene	0.12	0.51	0.30	0.39
159	4-methyldibenzothiophene	N.D.	N.D.	0.07	N.D.
160	1-methyldibenzothiophene	N.D.	0.29	N.D.	0.25
161	3-&2-methyldibenzothiophenes	0.04	N.D.	0.12	N.D.
162	benzonaphthothiophene isomer	0.02	N.D.	N.D.	N.D.
163	C13-alk-2one	0.20	0.63	0.63	0.79
164	C14-alk-2-one	0.09	0.29	0.21	0.23
165	C15-alk-2-one	0.18	0.46	0.50	0.66
166	C16-alk-2-one	0.10	0.30	0.31	0.33
167	C17-alk-2-one	0.26	0.49	0.61	0.63
168	C18-alk-2-one	0.08	0.18	0.26	0.28
169	C19-alk-2-one	0.08	0.26	0.29	0.23
170	n-tetradecanoic acid	0.02	0.07	0.05	0.00
171	Pristane	0.00	N.D.	0.53	0.03
172	pentadecanoic acid isomer	0.01	0.04	0.07	0.04
173	pentadecanoic acid isomer	0.01	0.06	0.05	0.01
174	n-pentadecanoic acid	0.01	0.05	0.04	0.03
175	n-hexadecanoic acid	0.05	0.22	0.12	0.14

176	n-heptadecanoic acid	0.01	N.D.	0.01	0.02
177	n-octadecanoic acid	0.00	0.05	0.04	0.02
178	n-eicosanoic acid	<0.01	0.06	0.01	0.01
179	n-docosanoic acid	<0.01	0.02	0.01	0.01
180	n-tetracosanoic acid	<0.01	0.02	0.01	0.01
181	elemental sulfur	7.03	39.11	11.08	21.52
182	phyta-1,3(4)-diene	0.32	0.07	1.13	1.77
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	2.82	3.04	9.17	11.55
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	14.4	14.6	43.4	82.0
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	13.8	9.00	49.1	78.5
186	hexadecanamine,N,N-dimethyl	8.82	N.D.	39.7	35.85
187	octadecanamine,N,N-dimethyl	14.4	N.D.	60.1	47.9
n/a	Percent Loss On Ignition	1.77	5.45	6.03	6.73
n/a	Percent Silt & Clay	22.2	57.1	66.7	13.0

Compound number	Target Compound	Gateway 11	Gateway 12	Gateway 13A	Gateway 16
		mg/kg	mg/kg	mg/kg	mg/kg
2	C11 n-alk-1-ene	0.16	2.96	1.33	0.12
3	C12 n-alk-1-ene	0.16	2.11	1.11	0.09
4	C13 n-alk-1-ene	0.13	2.26	1.11	0.11
5	C14 n-alk-1-ene	0.22	2.77	1.04	0.18
6	C15 n-alk-1-ene	0.11	4.31	1.14	0.07
7	C16 n-alk-1-ene	0.11	2.14	0.69	0.05
8	C17 n-alk-1-ene	0.09	1.64	0.70	0.05
9	C18 n-alk-1-ene	0.08	1.74	0.80	0.05
10	C19 n-alk-1-ene	0.05	1.38	0.35	0.03
11	C20 n-alk-1-ene	0.06	1.36	0.36	0.05
12	C21 n-alk-1-ene	0.04	0.93	0.27	0.02
13	C22 n-alk-1-ene	0.04	1.16	0.26	0.02
14	C23 n-alk-1-ene	0.03	1.10	0.27	0.02
15	C24 n-alk-1-ene	0.03	1.00	0.30	0.02
16	C25 n-alk-1-ene	0.01	0.79	0.20	0.01
17	prist-1-ene	0.12	0.28	0.23	0.04
18	prist-2-ene	0.12	0.28	0.23	0.05
19	C10 n-alkane	0.15	4.33	1.28	0.14
20	C11 n-alkane	0.14	2.65	1.14	0.10
21	C12 n-alkane	0.17	4.29	1.30	0.10
22	C13 n-alkane	0.21	4.03	1.66	0.16
23	C14 n-alkane	0.17	3.34	1.13	0.11
24	C15 n-alkane	0.24	4.58	1.34	0.16
25	C16 n-alkane	0.13	2.81	1.19	0.09
26	C17 n-alkane	0.11	2.77	1.07	0.10
27	C18 n-alkane	0.11	2.38	1.09	0.07
28	C19 n-alkane	0.13	3.04	0.95	0.08
29	C20 n-alkane	0.08	2.31	0.70	0.05
30	C21 n-alkane	0.09	2.52	0.66	0.07
31	C22 n-alkane	0.10	3.03	0.68	0.06
32	C23 n-alkane	0.09	3.33	0.76	0.04
33	C24 n-alkane	0.05	1.94	0.52	0.03
34	C25 n-alkane	0.08	5.06	0.60	0.02
35	C26 n-alkane	0.03	0.22	0.50	0.02
36	C27 n-alkane	0.06	3.36	0.44	0.04
37	C28 n-alkane	0.04	2.27	0.31	0.02
38	C29 n-alkane	0.07	6.58	0.78	0.04
39	C30 n-alkane	0.03	2.15	0.52	0.02
40	C31 n-alkane	0.10	5.49	0.70	0.04
41	ethylbenzene	0.97	20.6	8.42	0.63
42	styrene	1.16	68.4	13.4	0.90

43	n-propylbenzene	0.32	3.87	1.88	0.03
44	n-butylbenzene	0.23	3.32	1.81	0.18
45	n-pentylbenzene	0.17	2.87	1.33	0.12
46	n-hexylbenzene	0.11	1.61	1.06	0.08
47	n-heptylbenzene	0.08	2.14	0.81	0.10
48	n-octylbenzene	0.14	1.64	1.02	0.09
49	n-nonylbenzene	0.07	1.49	0.84	0.09
50	n-decylbenzene	0.22	3.73	1.42	0.12
51	n-undecylbenzene	0.06	1.34	0.77	0.06
52	n-dodecylbenzene	0.11	1.70	1.03	0.10
53	n-tridecylbenzene	0.04	0.83	0.45	0.05
54	n-tetradecylbenzene	0.08	1.06	0.55	0.03
55	n-pentadecylbenzene	0.04	0.92	0.35	0.03
56	n-hexadecylbenzene	0.03	1.95	0.40	0.02
57	6-phenylundecane	N.D.	3.97	0.32	N.D.
58	5-phenylundecane	N.D.	4.09	0.18	N.D.
59	4-phenylundecane	N.D.	0.61	N.D.	N.D.
60	6-phenyldodecane	0.24	0.62	N.D.	0.20
61	5-phenyldodecane	0.24	0.71	N.D.	0.19
62	4-phenyldodecane	0.22	0.64	N.D.	0.19
63	6-phenyltridecane	N.D.	1.25	N.D.	N.D.
64	Phytane	0.02	0.38	0.12	0.03
65	5-phenyltridecane	N.D.	0.99	N.D.	N.D.
66	4-phenyltridecane	N.D.	1.02	N.D.	N.D.
67	naphthalene	0.33	7.12	2.79	0.27
68	2-methylnaphthalene	0.14	2.67	1.13	0.09
69	1-methylnaphthalene	0.06	2.18	1.01	0.07
70	dimethylnaphthalenes	0.29	5.13	2.08	0.18
71	trimethylnaphthalenes	0.16	2.82	1.52	0.11
72	tetramethylnaphthalenes	0.16	2.16	1.07	0.11
73	fluorene	0.07	1.98	1.03	0.06
74	methylfluorenes	N.D.	0.97	0.01	N.D.
75	phenanthrene	0.08	1.66	0.75	0.06
76	anthracene	0.04	1.08	0.74	0.04
77	3-methylphenanthrene	0.03	0.58	0.19	0.05
78	2-methylphenanthrene	0.04	0.73	0.40	0.04
79	methylanthracene	0.03	0.55	0.22	0.02
80	9-methylphenanthrene	0.03	0.49	0.17	0.05
81	1-methylphenanthrene	0.03	0.55	0.31	0.05
82	dimethylphenanthrenes	0.17	1.65	0.99	0.12
83	retene	0.01	0.10	0.13	N.D.
84	fluoranthene	0.08	3.15	0.83	0.01
85	pyrene	0.08	3.27	1.42	0.02
86	methylpyrene isomers	0.24	5.75	2.16	0.18
87	dimethylpyrene isomers	0.16	2.16	1.48	0.10
88	benzo[a]anthracene	0.04	1.26	0.51	N.D.

89	chrysene	0.08	1.70	0.95	0.02
90	methylchrysene isomers	0.07	2.77	0.95	0.05
91	benzo[b]fluoranthene	0.01	0.50	0.25	N.D.
92	benzo[j]fluoranthene	0.01	0.34	0.23	N.D.
93	benzo[k]fluoranthene	0.01	0.21	0.09	N.D.
94	benzo[e]pyrene	<0.01	0.11	0.03	N.D.
95	benzo[a]pyrene	N.D.	0.07	0.03	N.D.
96	perylene	N.D.	0.03	N.D.	N.D.
97	indenol[1,2,3-cd]pyrene	0.01	N.D.	N.D.	N.D.
98	benzo[ghi]perylene	N.D.	N.D.	0.03	N.D.
99	dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
100	dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
101	C29 hopane (17a, 21b)	<0.01	0.33	0.17	N.D.
102	C30 hopane (17a,21b)	0.01	0.22	0.19	N.D.
103	cholestene	<0.01	0.05	0.01	<0.01
104	ethylcholestene	<0.01	0.05	0.01	<0.01
105	C27 sterane	<0.01	0.03	N.D.	<0.01
106	C28 sterane	<0.01	N.D.	N.D.	N.D.
107	C29 sterane	N.D.	0.01	N.D.	N.D.
108	naphthalene-d8	<0.01	0.05	0.02	<0.01
109	anthracene-d10	1.20	6.36	4.72	0.78
110	pyrene-d10	3.14	13.21	11.93	1.70
111	chrysene-d12	1.39	6.31	7.28	0.86
112	C2-alkylpyrrole	0.26	2.93	1.47	0.31
113	phenol	4.40	133	30.2	6.17
114	2-methylphenol	0.23	8.87	1.64	0.23
115	4&3-methylphenols	2.71	92.66	17.4	2.76
116	4-ethylphenol	1.80	95.26	13.2	1.85
117	vinylphenol	5.27	509	39.7	5.16
118	guaiacol	0.10	19.60	1.35	0.06
119	methylguaiacol	0.05	14.26	1.16	0.02
120	ethylguaiacol	0.06	0.97	0.67	0.04
121	vinylguaiacol	0.68	124	7.80	0.53
122	vanillin	0.11	5.47	0.87	0.06
123	eugenol	0.02	3.33	0.27	0.01
124	cis iso-eugenol	0.02	4.71	0.37	0.01
125	trans iso-eugenol	0.11	30.4	2.13	0.06
126	acetovanillone	0.02	0.20	0.31	0.02
127	syringol	0.01	7.67	0.18	0.01
128	methylsyringol	N.D.	8.01	0.16	0.01
129	ethylsyringol	0.01	2.30	0.03	0.01
130	vinylsyringol	0.03	17.8	0.52	0.03
131	syringaldehyde	0.02	1.53	0.06	0.01
132	prop-1-enyl syringol	0.03	9.13	0.31	0.01
133	cis-prop-2-enyl syringol	0.02	10.66	0.33	<0.01
134	trans-prop-2-enyl	0.12	56.4	1.44	0.09

	syringol				
135	benzaldehyde	0.13	1.41	0.96	0.13
136	benzaldehyde methyl	0.47	2.07	2.40	0.34
137	methylfurfural	1.10	0.58	8.71	1.19
138	methylfuranone	0.35	12.9	2.23	0.41
139	2-methylcyclopentenone	0.22	2.78	1.45	0.19
140	3-methylcyclopentenone	0.25	3.72	1.27	0.15
141	benzonitrile	0.22	2.62	0.83	0.11
142	benzoacetonitrile	0.71	7.52	3.06	0.68
143	benzenepropanitrile	1.20	9.69	4.32	1.76
144	quinoline	0.15	1.30	1.15	0.13
145	isoquinoline	0.47	5.13	2.96	0.48
146	indole	2.94	36.6	13.4	3.74
147	methylindole	0.82	10.4	3.78	0.76
148	phenylpyridine	0.07	0.16	0.38	0.07
149	carbazole	0.08	1.87	0.48	0.13
150	diketodipyrrole	0.36	8.17	2.48	0.45
151	cyclo-Pro-Pro-diketopi...	0.50	3.04	2.36	0.58
152	n-tetradecanitrile	<0.01	0.07	N.D.	<0.01
153	n-hexadecanitrile	0.03	0.10	0.11	0.02
154	n-octadecanitrile	0.01	0.10	0.08	0.01
155	tetradecylamide	0.10	1.50	0.30	0.18
156	hexadecylamide	0.61	7.01	2.25	0.77
157	octadecylamide	0.05	1.71	0.43	0.11
158	benzothiophene	0.03	0.75	0.31	0.02
159	4-methyldibenzothiophene	N.D.	0.52	0.19	N.D.
160	1-methyldibenzothiophene	N.D.	0.76	0.09	N.D.
161	3-&2-methyldibenzothiophenes	N.D.	N.D.	0.11	N.D.
162	benzonaphthothiophene isomer	N.D.	N.D.	0.13	N.D.
163	C13-alk-2one	0.07	1.65	0.67	0.09
164	C14-alk-2-one	0.03	0.49	0.30	0.04
165	C15-alk-2-one	0.11	1.02	0.70	0.05
166	C16-alk-2-one	0.05	1.07	0.24	0.07
167	C17-alk-2-one	0.12	1.28	0.63	0.12
168	C18-alk-2-one	0.04	0.76	0.30	0.05
169	C19-alk-2-one	0.04	0.51	1.95	0.02
170	n-tetradecanoic acid	0.02	<0.01	0.05	0.01
171	Pristane	<0.01	0.66	0.03	<0.01
172	pentadecanoic acid isomer	0.01	0.09	0.02	0.01
173	pentadecanoic acid isomer	0.01	0.13	0.06	0.01

174	n-pentadecanoic acid	0.01	0.26	0.04	0.01
175	n-hexadecanoic acid	0.04	0.43	0.12	0.02
176	n-heptadecanoic acid	<0.01	0.08	<0.01	0.01
177	n-octadecanoic acid	0.01	0.11	0.01	<0.01
178	n-eicosanoic acid	<0.01	0.07	0.01	<0.01
179	n-docosanoic acid	<0.01	0.05	0.02	<0.01
180	n-tetracosanoic acid	<0.01	0.06	0.01	<0.01
181	elemental sulfur	0.09	0.09	6.53	3.05
182	phyta-1,3(4)-diene	0.65	9.03	4.18	0.62
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	0.87	13.1	12.3	2.51
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	6.29	123	61.1	13.2
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	6.99	92.5	59.5	11.3
186	hexadecanamine,N,N-dimethyl	6.02	96.4	124.94	4.47
187	octadecanamine,N,N-dimethyl	7.66	202	258	10.8
n/a	Percent Loss On Ignition	1.46	34.8	7.82	1.47
n/a	Percent Silt & Clay	29.0	>95	76.9	15.8

Compound number	Target Compound	Gateway 18	Gateway 22	Gateway 23M	Gateway 23S
		mg/kg	mg/kg	mg/kg	mg/kg
2	C11 n-alk-1-ene	0.22	0.98	0.43	0.08
3	C12 n-alk-1-ene	0.18	0.73	0.33	0.07
4	C13 n-alk-1-ene	0.19	0.70	0.26	0.05
5	C14 n-alk-1-ene	0.29	0.97	0.38	0.12
6	C15 n-alk-1-ene	0.16	0.60	0.24	0.06
7	C16 n-alk-1-ene	0.14	0.55	0.23	0.07
8	C17 n-alk-1-ene	0.12	0.50	0.12	0.05
9	C18 n-alk-1-ene	0.12	0.40	0.19	0.04
10	C19 n-alk-1-ene	0.08	0.30	0.10	0.02
11	C20 n-alk-1-ene	0.09	0.32	0.09	0.02
12	C21 n-alk-1-ene	0.06	0.23	0.10	0.03
13	C22 n-alk-1-ene	0.06	0.24	0.12	0.02
14	C23 n-alk-1-ene	0.05	0.19	0.06	0.02
15	C24 n-alk-1-ene	0.06	0.24	0.06	0.01
16	C25 n-alk-1-ene	0.04	0.11	0.02	<0.01
17	prist-1-ene	0.23	0.33	0.17	0.06
18	prist-2-ene	0.05	0.20	0.07	0.02
19	C10 n-alkane	0.23	0.58	0.29	0.04
20	C11 n-alkane	0.21	0.72	0.33	0.08
21	C12 n-alkane	0.20	0.92	0.31	0.07
22	C13 n-alkane	0.27	1.27	0.56	0.13
23	C14 n-alkane	0.18	0.90	0.31	0.08
24	C15 n-alkane	0.27	1.47	0.44	0.09
25	C16 n-alkane	0.19	0.75	0.30	0.09
26	C17 n-alkane	0.21	0.81	0.29	0.08
27	C18 n-alkane	0.16	0.56	0.27	0.07
28	C19 n-alkane	0.19	0.68	0.30	0.08
29	C20 n-alkane	0.13	0.57	0.22	0.07
30	C21 n-alkane	0.15	0.61	0.21	0.06
31	C22 n-alkane	0.20	0.64	0.20	0.08
32	C23 n-alkane	0.18	0.56	0.18	0.05
33	C24 n-alkane	0.08	0.43	0.12	0.03
34	C25 n-alkane	0.20	0.49	0.12	0.12
35	C26 n-alkane	0.08	0.23	0.07	0.02
36	C27 n-alkane	0.07	0.28	0.09	0.01
37	C28 n-alkane	0.06	0.18	0.06	0.02
38	C29 n-alkane	0.16	0.31	0.05	0.01
39	C30 n-alkane	0.06	0.20	0.19	<0.01
40	C31 n-alkane	0.06	0.33	0.23	<0.01
41	ethylbenzene	0.98	3.46	1.88	0.33
42	styrene	1.54	4.68	2.07	0.80
43	n-propylbenzene	0.28	1.30	0.62	0.01

44	n-butylbenzene	0.29	2.06	0.48	0.11
45	n-pentylbenzene	0.23	1.18	0.38	0.11
46	n-hexylbenzene	0.14	0.64	0.33	0.05
47	n-heptylbenzene	0.16	0.63	0.28	0.06
48	n-octylbenzene	0.20	0.81	0.32	0.07
49	n-nonylbenzene	0.10	0.67	0.23	0.05
50	n-decylbenzene	0.21	0.64	0.31	0.08
51	n-undecylbenzene	0.07	0.52	0.17	0.03
52	n-dodecylbenzene	0.23	0.65	0.31	0.08
53	n-tridecylbenzene	0.08	0.51	0.10	0.04
54	n-tetradecylbenzene	0.10	0.52	0.09	0.03
55	n-pentadecylbenzene	0.09	0.29	0.08	0.02
56	n-hexadecylbenzene	N.D.	0.21	0.06	0.06
57	6-phenylundecane	N.D.	N.D.	N.D.	N.D.
58	5-phenylundecane	N.D.	N.D.	N.D.	N.D.
59	4-phenylundecane	N.D.	N.D.	0.02	N.D.
60	6-phenyldodecane	N.D.	N.D.	N.D.	N.D.
61	5-phenyldodecane	0.10	0.42	N.D.	N.D.
62	4-phenyldodecane	N.D.	0.44	0.23	0.08
63	6-phenyltridecane	N.D.	N.D.	N.D.	N.D.
64	Phytane	0.04	0.03	0.03	0.01
65	5-phenyltridecane	N.D.	N.D.	N.D.	N.D.
66	4-phenyltridecane	N.D.	N.D.	N.D.	N.D.
67	naphthalene	0.51	2.69	1.16	0.22
68	2-methylnaphthalene	0.22	0.80	0.39	0.09
69	1-methylnaphthalene	0.17	0.59	0.29	0.06
70	dimethylnaphthalenes	0.31	1.18	0.66	0.16
71	trimethylnaphthalenes	0.21	0.76	0.43	0.11
72	tetramethylnaphthalenes	N.D.	0.59	0.35	0.11
73	fluorene	0.13	0.75	0.25	0.05
74	methylfluorenes	N.D.	N.D.	N.D.	N.D.
75	phenanthrene	0.17	0.74	0.28	0.08
76	anthracene	0.08	0.15	0.19	0.04
77	3-methylphenanthrene	0.02	0.08	0.07	0.04
78	2-methylphenanthrene	0.05	0.09	0.07	0.04
79	methylanthracene	0.04	0.23	0.06	0.01
80	9-methylphenanthrene	0.03	0.19	0.05	0.02
81	1-methylphenanthrene	0.04	0.12	0.08	0.03
82	dimethylphenanthrenes	0.22	0.59	0.40	0.12
83	retene	0.01	0.05	0.06	<0.01
84	fluoranthene	0.31	0.21	0.32	0.02
85	pyrene	0.28	0.43	0.46	0.08
86	methylpyrene isomers	0.48	1.12	0.82	0.15
87	dimethylpyrene isomers	0.23	0.60	0.50	0.08
88	benzo[a]anthracene	0.12	0.05	0.09	0.01
89	chrysene	0.19	0.26	0.23	0.01

90	methylchrysene isomers	0.14	0.36	0.33	0.04
91	benzo[b]fluoranthene	N.D.	N.D.	N.D.	N.D.
92	benzo[j]fluoranthene	N.D.	N.D.	N.D.	N.D.
93	benzo[k]fluoranthene	N.D.	N.D.	N.D.	N.D.
94	benzo[e]pyrene	N.D.	N.D.	N.D.	N.D.
95	benzo[a]pyrene	N.D.	N.D.	N.D.	N.D.
96	perylene	N.D.	N.D.	N.D.	N.D.
97	indenol[1,2,3-cd]pyrene	N.D.	N.D.	N.D.	N.D.
98	benzo[ghi]perylene	N.D.	N.D.	N.D.	N.D.
99	dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
100	dibenzo[a,h]anthracene	N.D.	0.06	N.D.	N.D.
101	C29 hopane (17a, 21b)	0.01	N.D.	N.D.	N.D.
102	C30 hopane (17a,21b)	N.D.	N.D.	0.07	N.D.
103	cholestene	<0.01	N.D.	0.01	<0.01
104	ethylcholestene	<0.01	N.D.	<0.01	N.D.
105	C27 sterane	N.D.	N.D.	0.01	N.D.
106	C28 sterane	N.D.	N.D.	N.D.	N.D.
107	C29 sterane	N.D.	N.D.	N.D.	N.D.
108	naphthalene-d8	0.03	0.01	0.03	0.01
109	anthracene-d10	1.45	3.65	2.42	0.87
110	pyrene-d10	3.08	9.81	5.58	2.25
111	chrysene-d12	1.61	7.84	2.84	0.71
112	C2-alkylpyrrole	0.27	0.55	0.40	0.10
113	phenol	6.06	25.59	8.36	1.94
114	2-methylphenol	0.32	1.51	0.50	0.12
115	4&3-methylphenols	3.50	14.4	5.06	1.25
116	4-ethylphenol	2.24	14.9	2.97	0.44
117	vinylphenol	7.57	61.9	4.14	0.92
118	guaiacol	0.19	1.29	0.15	0.03
119	methylguaiacol	0.08	0.84	0.12	0.01
120	ethylguaiacol	0.07	0.79	0.07	0.01
121	vinylguaiacol	1.12	8.06	0.44	0.08
122	vanillin	0.11	0.82	0.13	0.04
123	eugenol	0.02	0.19	0.04	<0.01
124	cis iso-eugenol	0.03	0.29	0.03	0.01
125	trans iso-eugenol	0.15	1.43	0.11	0.03
126	acetovanillone	0.02	0.09	0.01	0.01
127	syringol	0.02	0.19	0.01	N.D.
128	methylsyringol	0.03	0.21	0.01	<0.01
129	ethylsyringol	0.01	0.06	<0.01	<0.01
130	vinylsyringol	0.04	0.47	0.02	<0.01
131	syringaldehyde	0.02	0.17	0.03	0.01
132	prop-1-enyl syringol	0.03	0.24	N.D.	0.01
133	cis-prop-2-enyl syringol	0.04	0.27	N.D.	0.01
134	trans-prop-2-enyl syringol	0.18	1.51	0.01	<0.01

135	benzaldehyde	0.15	0.71	0.33	0.05
136	benzaldehyde methyl	0.57	1.85	1.03	0.31
137	methylfurfural	1.56	5.11	1.88	0.61
138	methylfuranone	0.37	0.65	N.D.	0.04
139	2-methylcyclopentenone	0.25	0.68	0.32	0.02
140	3-methylcyclopentenone	0.22	0.64	0.31	0.04
141	benzonitrile	0.21	0.72	0.54	0.19
142	benzoacetonitrile	0.83	2.66	1.34	0.41
143	benzenepropanitrile	1.40	3.26	2.28	0.67
144	quinoline	0.19	0.59	0.27	0.06
145	isoquinoline	0.65	2.17	1.05	0.45
146	indole	3.34	7.82	4.19	2.49
147	methylindole	0.95	2.16	1.71	0.55
148	phenylpyridine	0.09	0.28	0.11	0.04
149	carbazole	0.10	0.44	0.19	0.06
150	diketodipyrrole	0.49	1.83	0.76	0.22
151	cyclo-Pro-Pro-diketopi...	0.51	0.16	0.27	0.19
152	n-tetradecanitrile	N.D.	0.03	0.02	<0.01
153	n-hexadecanitrile	0.03	0.09	0.04	0.02
154	n-octadecanitrile	0.01	0.05	0.03	0.01
155	tetradecylamide	0.10	0.14	0.10	0.04
156	hexadecylamide	0.37	0.57	0.23	0.08
157	octadecylamide	0.05	0.07	0.12	<0.01
158	benzothiophene	0.03	0.15	0.08	0.03
159	4-methyldibenzothiophene	N.D.	0.09	N.D.	N.D.
160	1-methyldibenzothiophene	0.02	N.D.	0.09	0.02
161	3-&2-methyldibenzothiophenes	N.D.	N.D.	0.03	N.D.
162	benzonaphthothiophene isomer	N.D.	N.D.	0.07	N.D.
163	C13-alk-2one	0.16	0.40	0.20	0.06
164	C14-alk-2-one	0.07	0.22	0.07	0.01
165	C15-alk-2-one	0.13	0.47	0.20	0.06
166	C16-alk-2-one	0.07	0.19	0.20	0.03
167	C17-alk-2-one	0.16	0.44	0.24	0.05
168	C18-alk-2-one	0.05	0.18	0.08	0.03
169	C19-alk-2-one	0.05	0.11	0.08	0.03
170	n-tetradecanoic acid	<0.01	0.08	0.02	0.01
171	Pristane	0.01	N.D.	0.02	<0.01
172	pentadecanoic acid isomer	0.01	0.07	0.03	<0.01
173	pentadecanoic acid isomer	0.01	0.07	0.03	0.01
174	n-pentadecanoic acid	0.01	0.04	0.02	0.01

175	n-hexadecanoic acid	0.02	0.21	0.10	0.03
176	n-heptadecanoic acid	0.01	0.03	N.D.	N.D.
177	n-octadecanoic acid	0.01	0.04	0.01	0.01
178	n-eicosanoic acid	<0.01	0.04	0.01	<0.01
179	n-docosanoic acid	<0.01	0.01	<0.01	<0.01
180	n-tetracosanoic acid	N.D.	0.01	<0.01	<0.01
181	elemental sulfur	0.55	4.69	1.00	0.96
182	phyta-1,3(4)-diene	0.33	0.27	0.04	NO DATA
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	1.77	0.78	0.69	NO DATA
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	7.13	7.73	3.07	NO DATA
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	7.45	7.83	3.37	NO DATA
186	hexadecanamine,N,N-dimethyl	6.40	N.D.	1.67	NO DATA
187	octadecanamine,N,N-dimethyl	9.20	N.D.	2.94	NO DATA
n/a	Percent Loss On Ignition	1.31	2.77	1.09	1.09
n/a	Percent Silt & Clay	35.0	61.5	9.09	9.09

Compound number	Target Compound	Gateway 24	Gateway 26	Gateway 27	Gateway 28
		mg/kg	mg/kg	mg/kg	mg/kg
2	C11 n-alk-1-ene	2.12	2.71	3.34	2.58
3	C12 n-alk-1-ene	1.87	2.30	2.54	2.16
4	C13 n-alk-1-ene	1.52	1.96	2.93	1.81
5	C14 n-alk-1-ene	1.86	2.16	3.05	2.42
6	C15 n-alk-1-ene	1.20	1.49	2.31	1.51
7	C16 n-alk-1-ene	1.18	1.50	1.90	1.63
8	C17 n-alk-1-ene	0.99	1.33	1.86	1.58
9	C18 n-alk-1-ene	1.36	1.49	2.78	1.30
10	C19 n-alk-1-ene	0.58	0.77	1.08	0.95
11	C20 n-alk-1-ene	0.62	0.83	1.21	1.03
12	C21 n-alk-1-ene	0.40	0.70	0.76	0.66
13	C22 n-alk-1-ene	0.42	0.62	1.17	0.87
14	C23 n-alk-1-ene	0.34	0.62	0.76	0.79
15	C24 n-alk-1-ene	0.40	0.65	0.58	0.82
16	C25 n-alk-1-ene	0.31	0.26	0.59	0.56
17	prist-1-ene	1.65	1.86	3.06	1.60
18	prist-2-ene	0.55	0.31	0.38	0.18
19	C10 n-alkane	1.96	2.40	3.68	4.23
20	C11 n-alkane	2.23	2.54	4.05	2.89
21	C12 n-alkane	2.46	3.15	4.13	3.70
22	C13 n-alkane	2.86	3.66	4.51	3.67
23	C14 n-alkane	2.41	2.87	3.81	3.16
24	C15 n-alkane	2.92	3.48	5.07	4.17
25	C16 n-alkane	2.13	2.72	3.65	2.78
26	C17 n-alkane	1.99	2.50	3.59	2.49
27	C18 n-alkane	2.19	2.78	3.91	2.11
28	C19 n-alkane	1.77	1.96	3.14	2.68
29	C20 n-alkane	1.20	1.51	2.11	1.63
30	C21 n-alkane	1.26	1.71	2.53	1.98
31	C22 n-alkane	1.29	1.66	2.06	2.30
32	C23 n-alkane	1.15	1.68	2.16	2.45
33	C24 n-alkane	0.75	1.20	1.54	1.64
34	C25 n-alkane	0.84	1.83	4.64	2.07
35	C26 n-alkane	0.59	0.82	1.18	1.47
36	C27 n-alkane	0.99	1.31	1.38	2.28
37	C28 n-alkane	0.59	1.14	1.59	1.59
38	C29 n-alkane	1.62	2.23	2.35	2.88
39	C30 n-alkane	0.37	0.85	1.48	0.84
40	C31 n-alkane	0.99	1.36	1.06	2.81
41	ethylbenzene	10.7	14.4	29.1	16.6
42	styrene	19.9	20.8	78.9	15.8

43	n-propylbenzene	3.09	3.89	0.63	4.37
44	n-butylbenzene	3.31	3.80	7.11	3.71
45	n-pentylbenzene	2.16	2.93	4.97	3.01
46	n-hexylbenzene	1.53	2.19	3.27	2.02
47	n-heptylbenzene	1.86	2.54	4.17	2.06
48	n-octylbenzene	1.54	2.08	2.75	1.86
49	n-nonylbenzene	1.18	1.62	2.47	1.57
50	n-decylbenzene	1.84	2.38	3.23	3.47
51	n-undecylbenzene	1.00	1.61	1.55	1.43
52	n-dodecylbenzene	1.63	2.42	2.99	1.44
53	n-tridecylbenzene	0.75	1.07	1.21	1.10
54	n-tetradecylbenzene	1.34	1.59	2.02	1.23
55	n-pentadecylbenzene	0.81	1.02	1.56	0.83
56	n-hexadecylbenzene	0.84	1.68	1.39	0.91
57	6-phenylundecane	0.81	0.80	4.58	1.23
58	5-phenylundecane	0.34	0.78	3.54	0.77
59	4-phenylundecane	0.27	N.D.	1.64	0.29
60	6-phenyldodecane	0.72	1.36	4.61	1.08
61	5-phenyldodecane	1.05	1.24	3.44	0.47
62	4-phenyldodecane	0.75	1.29	2.40	0.45
63	6-phenyltridecane	N.D.	N.D.	4.56	0.98
64	Phytane	0.60	0.37	1.45	0.33
65	5-phenyltridecane	N.D.	N.D.	2.01	1.00
66	4-phenyltridecane	N.D.	N.D.	1.32	0.88
67	naphthalene	4.78	6.27	9.01	7.27
68	2-methylnaphthalene	1.51	2.79	3.12	2.45
69	1-methylnaphthalene	1.49	2.12	2.50	2.03
70	dimethylnaphthalenes	3.41	3.83	5.08	4.37
71	trimethylnaphthalenes	1.82	2.86	1.53	2.50
72	tetramethylnaphthalenes	1.70	1.42	1.72	1.52
73	fluorene	1.13	1.84	2.14	1.90
74	methylfluorenes	0.19	N.D.	0.18	0.56
75	phenanthrene	1.30	1.62	2.38	1.80
76	anthracene	0.57	0.84	1.15	0.63
77	3-methylphenanthrene	0.33	0.44	0.71	0.36
78	2-methylphenanthrene	0.52	0.59	0.96	0.55
79	methylanthracene	0.24	0.36	0.51	0.37
80	9-methylphenanthrene	0.37	0.47	0.76	0.38
81	1-methylphenanthrene	0.57	0.60	0.81	0.43
82	dimethylphenanthrenes	1.43	1.61	2.18	1.62
83	retene	0.18	0.22	0.67	0.15
84	fluoranthene	1.58	1.67	3.73	1.35
85	pyrene	1.43	1.60	3.30	1.22
86	methylpyrene isomers	3.06	3.17	5.65	3.44
87	dimethylpyrene isomers	1.84	2.08	3.73	1.60
88	benzo[a]anthracene	0.60	0.60	1.61	0.47

89	chrysene	0.71	1.05	2.58	1.00
90	methylchrysene isomers	0.76	0.98	2.23	0.91
91	benzo[b]fluoranthene	0.11	0.15	0.83	0.17
92	benzo[j]fluoranthene	0.09	0.18	0.54	0.14
93	benzo[k]fluoranthene	0.02	0.02	0.20	0.15
94	benzo[e]pyrene	0.06	N.D.	0.24	N.D.
95	benzo[a]pyrene	N.D.	N.D.	0.12	N.D.
96	perylene	N.D.	N.D.	0.08	N.D.
97	indenol[1,2,3-cd]pyrene	N.D.	N.D.	0.11	0.07
98	benzo[ghi]perylene	0.02	N.D.	0.04	N.D.
99	dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
100	dibenzo[a,h]anthracene	N.D.	0.03	N.D.	N.D.
101	C29 hopane (17a, 21b)	0.49	0.55	1.08	0.39
102	C30 hopane (17a,21b)	0.33	0.33	0.83	0.48
103	cholestene	0.05	0.04	0.51	0.04
104	ethylcholestene	0.07	0.02	0.22	0.08
105	C27 sterane	0.04	N.D.	0.22	0.04
106	C28 sterane	N.D.	N.D.	0.07	N.D.
107	C29 sterane	0.02	N.D.	0.06	0.03
108	naphthalene-d8	0.06	<0.01	0.04	0.05
109	anthracene-d10	4.76	3.54	5.83	4.42
110	pyrene-d10	8.97	8.17	8.75	8.17
111	chrysene-d12	4.87	4.76	4.66	4.34
112	C2-alkylpyrrole	3.04	3.23	3.61	3.20
113	phenol	49.0	63.6	87.0	210
114	2-methylphenol	2.69	3.57	4.52	8.49
115	4&3-methylphenols	30.2	36.0	41.9	80.7
116	4-ethylphenol	22.9	23.2	21.8	95.7
117	vinylphenol	50.6	59.7	82.9	388
118	guaiacol	1.23	1.80	3.23	14.3
119	methylguaiacol	0.76	0.93	2.25	8.36
120	ethylguaiacol	0.73	0.96	1.77	0.71
121	vinylguaiacol	7.08	10.4	24.1	93.8
122	vanillin	0.88	0.67	1.12	4.04
123	eugenol	0.24	0.32	0.74	1.84
124	cis iso-eugenol	0.27	0.41	1.09	2.36
125	trans iso-eugenol	1.64	1.91	5.41	15.5
126	acetovanillone	0.39	0.54	1.14	2.78
127	syringol	0.19	0.27	0.87	4.34
128	methylsyringol	0.17	0.30	0.78	3.56
129	ethylsyringol	0.04	0.08	0.23	1.03
130	vinylsyringol	0.49	0.68	2.34	9.02
131	syringaldehyde	0.07	0.04	0.12	0.35
132	prop-1-enyl syringol	0.36	0.57	1.32	4.08
133	cis-prop-2-enyl syringol	0.36	0.46	1.33	4.78
134	trans-prop-2-enyl	1.44	2.01	6.96	26.14

	syringol				
135	benzaldehyde	1.08	1.42	1.64	1.96
136	benzaldehyde methyl	2.53	2.50	3.00	2.47
137	methylfurfural	11.01	17.87	20.36	0.63
138	methylfuranone	3.00	4.98	8.14	11.86
139	2-methylcyclopentenone	2.56	2.70	3.96	3.03
140	3-methylcyclopentenone	2.91	3.06	3.94	4.13
141	benzonitrile	1.51	1.83	5.26	2.64
142	benzoacetonitrile	5.46	6.03	7.13	6.53
143	benzenepropanitrile	10.03	9.76	13.67	9.84
144	quinoline	1.77	2.15	2.30	1.14
145	isoquinoline	5.33	2.68	2.84	5.02
146	indole	25.8	29.9	48.4	30.0
147	methylindole	8.55	7.68	11.94	7.55
148	phenylpyridine	0.74	0.91	0.15	0.15
149	carbazole	1.18	1.21	2.12	1.46
150	diketodipyrrole	4.67	5.78	6.95	8.84
151	cyclo-Pro-Pro-diketopi...	1.83	4.77	3.03	1.75
152	n-tetradecanitrile	0.06	0.05	0.08	0.08
153	n-hexadecanitrile	0.20	0.22	0.32	0.14
154	n-octadecanitrile	0.13	0.20	0.17	0.08
155	tetradecylamide	0.97	0.98	1.73	1.16
156	hexadecylamide	6.68	8.20	11.7	5.83
157	octadecylamide	1.48	1.96	4.87	1.64
158	benzothiophene	0.46	1.20	0.70	0.66
159	4-methyldibenzothiophene	0.25	0.41	1.04	0.40
160	1-methyldibenzothiophene	0.21	0.64	0.65	0.22
161	3-&2-methyldibenzothiophenes	0.18	0.22	0.26	0.18
162	benzonaphthothiophene isomer	N.D.	0.17	0.52	0.18
163	C13-alk-2one	1.28	1.81	0.39	1.32
164	C14-alk-2-one	0.63	0.73	0.87	0.53
165	C15-alk-2-one	1.03	1.36	1.59	1.13
166	C16-alk-2-one	0.73	0.64	1.36	0.66
167	C17-alk-2-one	1.22	1.52	1.70	1.33
168	C18-alk-2-one	0.54	0.60	0.75	0.59
169	C19-alk-2-one	0.31	0.66	N.D.	0.38
170	n-tetradecanoic acid	0.03	0.13	0.16	<0.01
171	Pristane	0.34	0.09	1.24	0.25
172	pentadecanoic acid isomer	0.06	0.05	0.09	0.10
173	pentadecanoic acid isomer	0.03	0.06	0.17	0.10

174	n-pentadecanoic acid	0.06	0.08	0.10	0.18
175	n-hexadecanoic acid	0.19	0.23	0.44	0.39
176	n-heptadecanoic acid	0.02	0.05	0.03	0.04
177	n-octadecanoic acid	0.05	0.08	0.13	0.08
178	n-eicosanoic acid	0.03	0.03	0.06	0.10
179	n-docosanoic acid	0.03	0.04	0.09	0.05
180	n-tetracosanoic acid	0.02	0.01	0.03	0.04
181	elemental sulfur	9.61	31.00	14.80	1.84
182	phyta-1,3(4)-diene	5.25	5.31	4.72	4.94
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	33.61	33.41	5.65	5.43
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	206.8	136.8	137	40.7
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	156	139	110.1	40.0
186	hexadecanamine,N,N-dimethyl	346	298	2532	80.9
187	octadecanamine,N,N-dimethyl	725.7	644	4907	171
n/a	Percent Loss On Ignition	15.74	15.15	21.86	28.04
n/a	Percent Silt & Clay	>95	94.7	95.0	88.9

Compound number	Target Compound	Gateway 29	Gateway 100	Gateway 101	Gateway 102
		mg/kg	mg/kg	mg/kg	mg/kg
2	C11 n-alk-1-ene	2.70	0.37	1.54	1.59
3	C12 n-alk-1-ene	2.68	0.31	1.24	1.36
4	C13 n-alk-1-ene	2.66	0.22	1.10	1.11
5	C14 n-alk-1-ene	2.51	0.40	1.43	1.35
6	C15 n-alk-1-ene	1.91	0.20	0.94	0.94
7	C16 n-alk-1-ene	1.67	0.19	0.92	0.89
8	C17 n-alk-1-ene	1.52	0.19	0.76	0.73
9	C18 n-alk-1-ene	2.08	0.15	0.83	0.77
10	C19 n-alk-1-ene	0.86	0.11	0.47	0.60
11	C20 n-alk-1-ene	1.02	0.13	0.65	0.59
12	C21 n-alk-1-ene	0.72	0.07	0.35	0.43
13	C22 n-alk-1-ene	0.84	0.12	0.50	0.59
14	C23 n-alk-1-ene	0.72	0.05	0.35	0.39
15	C24 n-alk-1-ene	0.91	0.08	0.47	0.46
16	C25 n-alk-1-ene	0.28	0.04	0.22	0.29
17	prist-1-ene	1.81	0.23	1.14	0.92
18	prist-2-ene	0.88	0.12	0.47	0.36
19	C10 n-alkane	3.11	0.36	1.64	1.20
20	C11 n-alkane	3.01	0.40	1.80	1.33
21	C12 n-alkane	3.43	0.38	1.48	1.62
22	C13 n-alkane	4.11	0.52	1.89	1.86
23	C14 n-alkane	3.44	0.39	1.70	1.45
24	C15 n-alkane	4.03	0.50	1.75	1.91
25	C16 n-alkane	3.22	0.34	1.47	1.47
26	C17 n-alkane	2.88	0.29	1.38	1.23
27	C18 n-alkane	2.91	0.28	1.21	1.16
28	C19 n-alkane	2.51	0.26	1.32	1.48
29	C20 n-alkane	1.85	0.21	0.97	1.01
30	C21 n-alkane	1.94	0.20	0.98	1.04
31	C22 n-alkane	2.03	0.24	1.18	1.14
32	C23 n-alkane	1.67	0.18	1.04	0.99
33	C24 n-alkane	1.19	0.14	0.76	0.79
34	C25 n-alkane	2.63	0.18	0.88	0.89
35	C26 n-alkane	1.00	0.13	0.67	0.55
36	C27 n-alkane	1.11	0.16	1.06	0.78
37	C28 n-alkane	0.69	0.10	0.59	0.50
38	C29 n-alkane	1.82	0.19	1.62	1.02
39	C30 n-alkane	0.75	0.02	0.48	0.35
40	C31 n-alkane	1.55	0.08	1.40	1.09
41	ethylbenzene	15.0	0.03	8.96	0.68
42	styrene	42.5	3.36	12.9	12.6
43	n-propylbenzene	4.38	0.80	2.49	2.82

44	n-butylbenzene	4.26	0.57	0.65	2.79
45	n-pentylbenzene	2.88	0.46	1.96	1.61
46	n-hexylbenzene	1.94	0.31	1.09	1.29
47	n-heptylbenzene	1.72	0.33	1.51	1.85
48	n-octylbenzene	1.95	0.31	1.15	1.10
49	n-nonylbenzene	1.95	0.22	1.10	1.02
50	n-decylbenzene	1.85	0.37	1.21	1.09
51	n-undecylbenzene	1.32	0.28	0.76	0.88
52	n-dodecylbenzene	1.99	0.34	1.14	1.58
53	n-tridecylbenzene	1.15	0.21	0.60	0.79
54	n-tetradecylbenzene	1.59	0.19	0.72	0.90
55	n-pentadecylbenzene	0.82	0.18	0.59	0.71
56	n-hexadecylbenzene	1.54	0.16	0.57	1.11
57	6-phenylundecane	2.48	0.16	0.38	0.15
58	5-phenylundecane	1.05	0.14	N.D.	0.10
59	4-phenylundecane	1.57	N.D.	N.D.	N.D.
60	6-phenyldodecane	1.43	0.05	1.05	N.D.
61	5-phenyldodecane	1.83	0.18	1.24	0.33
62	4-phenyldodecane	1.03	0.11	0.68	0.69
63	6-phenyltridecane	0.58	N.D.	N.D.	N.D.
64	Phytane	0.61	0.06	0.33	0.12
65	5-phenyltridecane	0.60	N.D.	N.D.	N.D.
66	4-phenyltridecane	0.58	N.D.	N.D.	N.D.
67	naphthalene	7.19	1.21	5.13	6.66
68	2-methylnaphthalene	3.19	0.38	1.49	1.73
69	1-methylnaphthalene	2.18	0.33	1.03	1.39
70	dimethylnaphthalenes	4.64	0.68	2.71	2.87
71	trimethylnaphthalenes	2.58	0.48	1.80	1.47
72	tetramethylnaphthalenes	1.68	0.29	0.96	1.09
73	fluorene	1.56	0.35	1.45	1.53
74	methylfluorenes	0.32	0.05	N.D.	0.16
75	phenanthrene	1.70	0.41	1.38	1.58
76	anthracene	0.90	0.15	0.85	1.00
77	3-methylphenanthrene	0.47	0.08	1.02	0.31
78	2-methylphenanthrene	0.62	0.17	0.54	0.48
79	methylanthracene	0.50	0.08	0.52	0.28
80	9-methylphenanthrene	0.56	0.17	0.50	0.40
81	1-methylphenanthrene	0.85	0.23	0.50	0.53
82	dimethylphenanthrenes	2.17	0.35	1.42	1.12
83	retene	0.46	0.06	0.10	0.17
84	fluoranthene	3.37	0.73	2.23	1.47
85	pyrene	3.32	0.59	1.71	2.08
86	methylpyrene isomers	5.00	0.75	2.59	3.00
87	dimethylpyrene isomers	2.60	0.39	1.45	1.81
88	benzo[a]anthracene	1.47	0.27	0.81	0.47
89	chrysene	2.08	0.41	1.34	1.15

90	methylchrysene isomers	2.46	0.28	1.00	2.07
91	benzo[b]fluoranthene	1.24	0.08	0.34	0.14
92	benzo[j]fluoranthene	0.54	0.07	0.18	0.11
93	benzo[k]fluoranthene	0.31	0.05	0.05	0.13
94	benzo[e]pyrene	0.32	0.06	0.15	0.15
95	benzo[a]pyrene	0.06	0.01	0.03	0.03
96	perylene	0.09	0.01	0.04	N.D.
97	indenol[1,2,3-cd]pyrene	N.D.	0.01	0.04	N.D.
98	benzo[ghi]perylene	N.D.	N.D.	0.02	N.D.
99	dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
100	dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	0.04
101	C29 hopane (17a, 21b)	0.91	0.03	0.32	0.33
102	C30 hopane (17a,21b)	0.67	0.02	0.26	0.39
103	cholestene	0.08	<0.01	0.03	0.01
104	ethylcholestene	0.07	<0.01	0.02	<0.01
105	C27 sterane	0.09	<0.01	0.02	N.D.
106	C28 sterane	N.D.	N.D.	0.01	N.D.
107	C29 sterane	0.06	<0.01	0.01	0.02
108	naphthalene-d8	0.08	0.02	0.03	0.08
109	anthracene-d10	6.47	0.58	3.68	2.68
110	pyrene-d10	12.9	1.72	8.39	8.45
111	chrysene-d12	5.89	1.22	4.46	5.65
112	C2-alkylpyrrole	2.72	0.09	1.45	0.87
113	phenol	48.6	13.1	51.8	68.9
114	2-methylphenol	3.32	0.70	2.61	3.06
115	4&3-methylphenols	32.1	6.26	24.6	21.6
116	4-ethylphenol	23.6	3.64	15.2	15.8
117	vinylphenol	55.0	8.68	42.2	63.8
118	guaiacol	1.60	0.35	1.97	2.69
119	methylguaiacol	1.16	0.18	1.00	1.21
120	ethylguaiacol	1.10	0.17	0.77	1.06
121	vinylguaiacol	10.41	1.47	8.59	12.72
122	vanillin	1.40	0.26	1.73	2.34
123	eugenol	0.40	0.05	0.31	0.33
124	cis iso-eugenol	0.48	0.09	0.52	0.36
125	trans iso-eugenol	2.75	0.33	2.34	2.14
126	acetovanillone	0.63	0.12	0.67	0.70
127	syringol	0.36	0.04	0.26	0.52
128	methylsyringol	0.29	0.03	0.21	0.33
129	ethylsyringol	0.06	0.01	N.D.	0.05
130	vinylsyringol	0.94	0.10	0.84	1.04
131	syringaldehyde	0.23	0.03	0.35	0.60
132	prop-1-enyl syringol	0.73	0.09	0.50	0.51
133	cis-prop-2-enyl syringol	0.57	0.07	0.43	0.56
134	trans-prop-2-enyl syringol	3.03	0.27	1.87	1.98

135	benzaldehyde	1.64	0.24	1.08	0.96
136	benzaldehyde methyl	2.57	1.27	3.09	4.50
137	methylfurfural	13.3	2.19	8.66	8.80
138	methylfuranone	3.73	0.02	3.75	2.19
139	2-methylcyclopentenone	2.73	0.11	1.25	0.10
140	3-methylcyclopentenone	2.32	0.31	1.75	1.20
141	benzonitrile	2.39	0.73	2.07	2.03
142	benzoacetonitrile	5.28	1.47	4.00	3.50
143	benzenepropanitrile	9.41	2.62	7.23	5.10
144	quinoline	2.06	0.33	1.30	1.31
145	isoquinoline	6.34	1.23	3.88	3.63
146	indole	27.6	6.20	16.9	12.9
147	methylindole	9.08	1.59	4.09	3.11
148	phenylpyridine	0.71	0.17	0.58	0.44
149	carbazole	0.98	0.21	0.86	0.49
150	diketodipyrrole	5.26	1.06	3.54	3.54
151	cyclo-Pro-Pro-diketopi...	5.26	0.71	2.50	1.63
152	n-tetradecanitrile	0.15	0.01	0.07	0.02
153	n-hexadecanitrile	0.16	0.05	0.12	0.09
154	n-octadecanitrile	0.16	0.02	0.06	0.04
155	tetradecylamide	0.90	0.16	0.91	0.46
156	hexadecylamide	7.54	0.78	3.49	1.51
157	octadecylamide	2.18	0.09	0.65	0.28
158	benzothiophene	0.84	0.11	0.74	0.31
159	4-methyldibenzothiophene	0.83	0.07	0.31	0.18
160	1-methyldibenzothiophene	0.44	0.07	0.41	0.37
161	3-&2-methyldibenzothiophenes	0.44	0.04	0.21	0.13
162	benzonaphthothiophene isomer	0.43	0.08	0.20	0.19
163	C13-alk-2one	1.75	0.24	1.23	1.10
164	C14-alk-2-one	0.63	0.08	0.39	0.18
165	C15-alk-2-one	1.40	0.19	0.86	0.52
166	C16-alk-2-one	0.70	0.08	0.50	0.36
167	C17-alk-2-one	1.61	0.30	0.86	0.72
168	C18-alk-2-one	0.68	0.09	0.31	0.21
169	C19-alk-2-one	12.07	0.08	0.24	0.48
170	n-tetradecanoic acid	0.10	<0.01	0.12	0.08
171	Pristane	0.51	0.01	0.25	0.65
172	pentadecanoic acid isomer	0.07	0.02	0.03	0.07
173	pentadecanoic acid isomer	0.05	0.02	0.04	0.06
174	n-pentadecanoic acid	0.07	0.02	0.11	0.10

175	n-hexadecanoic acid	0.34	0.07	0.23	0.41
176	n-heptadecanoic acid	0.03	0.01	0.02	0.02
177	n-octadecanoic acid	0.07	0.02	0.04	0.06
178	n-eicosanoic acid	0.03	0.01	0.04	0.10
179	n-docosanoic acid	0.05	<0.01	0.02	0.03
180	n-tetracosanoic acid	0.01	<0.01	0.01	0.02
181	elemental sulfur	6.86	8.48	25.7	13.9
182	phyta-1,3(4)-diene	5.47	0.13	1.90	0.37
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	13.9	1.47	8.53	2.48
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	159.1	4.14	57.0	14.3
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	124	8.22	59.1	14.7
186	hexadecanamine,N,N-dimethyl	699	5.98	52.1	69.2
187	octadecanamine,N,N-dimethyl	1446	7.47	87.3	111
n/a	Percent Loss On Ignition	19.47	2.00	12.10	5.43
n/a	Percent Silt & Clay	>95	37.5	>95	75.0

Compound number	Target Compound	Gateway NB	Sandy Hook W1		
		mg/kg	mg/kg		
2	C11 n-alk-1-ene	1.94	3.80		
3	C12 n-alk-1-ene	1.37	2.59		
4	C13 n-alk-1-ene	1.25	2.51		
5	C14 n-alk-1-ene	1.41	2.82		
6	C15 n-alk-1-ene	1.24	1.77		
7	C16 n-alk-1-ene	0.97	1.55		
8	C17 n-alk-1-ene	0.89	1.59		
9	C18 n-alk-1-ene	1.00	1.36		
10	C19 n-alk-1-ene	0.55	1.13		
11	C20 n-alk-1-ene	0.62	1.04		
12	C21 n-alk-1-ene	0.32	0.74		
13	C22 n-alk-1-ene	0.51	1.05		
14	C23 n-alk-1-ene	0.36	0.91		
15	C24 n-alk-1-ene	0.41	1.18		
16	C25 n-alk-1-ene	0.20	0.69		
17	prist-1-ene	0.15	1.27		
18	prist-2-ene	0.39	0.96		
19	C10 n-alkane	1.94	4.31		
20	C11 n-alkane	1.90	2.98		
21	C12 n-alkane	1.94	2.99		
22	C13 n-alkane	2.37	3.29		
23	C14 n-alkane	1.64	2.94		
24	C15 n-alkane	2.37	3.52		
25	C16 n-alkane	1.60	2.72		
26	C17 n-alkane	1.56	2.53		
27	C18 n-alkane	1.69	2.48		
28	C19 n-alkane	1.49	2.40		
29	C20 n-alkane	1.07	1.66		
30	C21 n-alkane	1.21	1.90		
31	C22 n-alkane	1.25	2.14		
32	C23 n-alkane	1.04	2.57		
33	C24 n-alkane	0.74	1.62		
34	C25 n-alkane	0.76	2.02		
35	C26 n-alkane	0.58	1.35		
36	C27 n-alkane	0.78	1.36		
37	C28 n-alkane	0.59	1.31		
38	C29 n-alkane	1.40	2.96		
39	C30 n-alkane	0.38	0.98		
40	C31 n-alkane	0.83	2.58		
41	ethylbenzene	11.5	17.9		
42	styrene	12.3	11.5		

43	n-propylbenzene	2.93	4.46		
44	n-butylbenzene	2.81	4.13		
45	n-pentylbenzene	2.06	3.35		
46	n-hexylbenzene	1.50	2.08		
47	n-heptylbenzene	1.34	2.24		
48	n-octylbenzene	1.78	2.20		
49	n-nonylbenzene	1.30	1.71		
50	n-decylbenzene	1.84	4.52		
51	n-undecylbenzene	0.92	1.36		
52	n-dodecylbenzene	1.39	2.25		
53	n-tridecylbenzene	0.74	0.73		
54	n-tetradecylbenzene	1.05	1.14		
55	n-pentadecylbenzene	0.84	0.89		
56	n-hexadecylbenzene	0.82	0.80		
57	6-phenylundecane	N.D.	5.24		
58	5-phenylundecane	N.D.	1.41		
59	4-phenylundecane	N.D.	1.11		
60	6-phenyldodecane	0.67	0.05		
61	5-phenyldodecane	0.72	1.68		
62	4-phenyldodecane	0.67	1.51		
63	6-phenyltridecane	N.D.	N.D.		
64	Phytane	0.20	0.32		
65	5-phenyltridecane	N.D.	N.D.		
66	4-phenyltridecane	N.D.	N.D.		
67	naphthalene	4.74	10.5		
68	2-methylnaphthalene	1.97	2.98		
69	1-methylnaphthalene	1.14	1.91		
70	dimethylnaphthalenes	2.67	5.22		
71	trimethylnaphthalenes	1.69	3.45		
72	tetramethylnaphthalenes	0.96	2.05		
73	fluorene	1.37	2.30		
74	methylfluorenes	N.D.	N.D.		
75	phenanthrene	1.01	2.52		
76	anthracene	0.51	2.53		
77	3-methylphenanthrene	0.37	1.63		
78	2-methylphenanthrene	0.53	0.91		
79	methylanthracene	0.38	0.78		
80	9-methylphenanthrene	0.40	0.73		
81	1-methylphenanthrene	0.34	0.94		
82	dimethylphenanthrenes	1.03	2.68		
83	retene	0.08	0.33		
84	fluoranthene	1.14	3.93		
85	pyrene	1.04	7.04		
86	methylpyrene isomers	2.69	8.97		
87	dimethylpyrene isomers	1.24	4.05		
88	benzo[a]anthracene	0.48	3.84		

89	chrysene	0.46	5.04		
90	methylchrysene isomers	0.65	3.04		
91	benzo[b]fluoranthene	0.18	1.93		
92	benzo[j]fluoranthene	0.10	0.60		
93	benzo[k]fluoranthene	0.02	0.26		
94	benzo[e]pyrene	0.03	0.29		
95	benzo[a]pyrene	0.04	0.21		
96	perylene	N.D.	N.D.		
97	indenol[1,2,3-cd]pyrene	N.D.	N.D.		
98	benzo[ghi]perylene	0.03	N.D.		
99	dibenzoanthacene isomer	N.D.	N.D.		
100	dibenzo[a,h]anthracene	N.D.	N.D.		
101	C29 hopane (17a, 21b)	0.23	0.23		
102	C30 hopane (17a,21b)	0.12	0.20		
103	cholestene	0.03	0.02		
104	ethylcholestene	0.01	0.01		
105	C27 sterane	N.D.	N.D.		
106	C28 sterane	N.D.	N.D.		
107	C29 sterane	0.02	N.D.		
108	naphthalene-d8	0.03	0.13		
109	anthracene-d10	5.96	7.98		
110	pyrene-d10	11.1	18.9		
111	chrysene-d12	6.38	15.4		
112	C2-alkylpyrrole	2.14	2.96		
113	phenol	50.9	190		
114	2-methylphenol	2.62	9.69		
115	4&3-methylphenols	28.5	108		
116	4-ethylphenol	19.7	121		
117	vinylphenol	56.0	677		
118	guaiacol	1.66	19.9		
119	methylguaiacol	1.35	16.9		
120	ethylguaiacol	1.05	13.1		
121	vinylguaiacol	10.4	143		
122	vanillin	1.28	7.78		
123	eugenol	0.44	2.89		
124	cis iso-eugenol	0.69	4.14		
125	trans iso-eugenol	3.23	24.1		
126	acetovanillone	0.57	2.31		
127	syringol	0.31	7.71		
128	methylsyringol	0.33	8.41		
129	ethylsyringol	0.07	1.79		
130	vinylsyringol	0.74	17.0		
131	syringaldehyde	0.16	4.19		
132	prop-1-enyl syringol	0.57	9.07		
133	cis-prop-2-enyl syringol	0.61	10.9		
134	trans-prop-2-enyl	2.87	55.3		

	syringol				
135	benzaldehyde	1.28	1.88		
136	benzaldehyde methyl	2.63	7.41		
137	methylfurfural	12.7	50.3		
138	methylfuranone	3.50	23.4		
139	2-methylcyclopentenone	2.03	2.79		
140	3-methylcyclopentenone	1.89	4.81		
141	benzonitrile	1.20	1.14		
142	benzoacetonitrile	5.46	6.67		
143	benzenepropanitrile	8.36	8.55		
144	quinoline	1.53	1.61		
145	isoquinoline	4.42	5.64		
146	indole	22.5	31.5		
147	methylindole	6.31	7.81		
148	phenylpyridine	0.57	1.07		
149	carbazole	0.80	2.11		
150	diketodipyrrole	4.06	5.84		
151	cyclo-Pro-Pro-diketopi...	2.76	7.39		
152	n-tetradecanitrile	0.04	0.06		
153	n-hexadecanitrile	0.15	0.24		
154	n-octadecanitrile	0.08	0.07		
155	tetradecylamide	0.82	1.15		
156	hexadecylamide	5.27	7.78		
157	octadecylamide	1.15	1.73		
158	benzothiophene	0.56	1.28		
159	4-methyldibenzothiophene	0.21	0.27		
160	1-methyldibenzothiophene	0.22	0.48		
161	3-&2-methyldibenzothiophenes	2.57	N.D.		
162	benzonaphthothiophene isomer	N.D.	1.02		
163	C13-alk-2one	1.33	1.12		
164	C14-alk-2-one	0.55	0.75		
165	C15-alk-2-one	1.17	0.94		
166	C16-alk-2-one	0.62	0.77		
167	C17-alk-2-one	1.13	0.97		
168	C18-alk-2-one	0.39	0.46		
169	C19-alk-2-one	0.36	0.53		
170	n-tetradecanoic acid	0.11	0.23		
171	Pristane	0.11	0.41		
172	pentadecanoic acid isomer	0.05	0.31		
173	pentadecanoic acid isomer	0.06	0.06		

174	n-pentadecanoic acid	0.04	0.12		
175	n-hexadecanoic acid	0.21	0.51		
176	n-heptadecanoic acid	0.04	0.15		
177	n-octadecanoic acid	0.03	0.15		
178	n-eicosanoic acid	0.05	0.14		
179	n-docosanoic acid	0.03	0.08		
180	n-tetracosanoic acid	0.01	0.04		
181	elemental sulfur	41.4	1.27		
182	phyta-1,3(4)-diene	4.39	6.20		
183	thiophene, 3,4-dimethyl-2-(2,6,10-trimethylundecyl)-	16.9	10.3		
184	thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-	167	59.1		
185	thiophene, 3-(4,8,12-trimethyltridecyl)-	142	46.5		
186	hexadecanamine,N,N-dimethyl	114	N.D.		
187	octadecanamine,N,N-dimethyl	157	N.D.		
n/a	Percent Loss On Ignition	12.0	17.8		
n/a	Percent Silt & Clay	83.3	95.0		

Appendix 5

Raw Data from the Dundee Lake Core.

Average Depth (cm)	4.5	10.5	16.5	22.5
Target Compounds	mg/kg	mg/kg	mg/kg	mg/kg
C11 n-alk-1-ene	32.6	50.4	23.8	52.5
C12 n-alk-1-ene	27.1	43.9	19.6	42.2
C13 n-alk-1-ene	22.0	39.0	15.3	18.7
C14 n-alk-1-ene	30.0	41.6	21.2	43.9
C15 n-alk-1-ene	27.8	40.2	13.6	30.4
C16 n-alk-1-ene	19.3	30.3	14.6	33.0
C17 n-alk-1-ene	21.4	24.7	12.9	31.5
C18 n-alk-1-ene	18.8	24.6	15.0	28.9
C19 n-alk-1-ene	10.0	17.2	8.13	13.8
C20 n-alk-1-ene	17.3	23.3	12.8	20.8
C21 n-alk-1-ene	13.5	16.3	5.66	13.7
C22 n-alk-1-ene	17.7	23.1	2.72	16.5
C23 n-alk-1-ene	13.1	11.1	5.45	12.0
C24 n-alk-1-ene	14.5	21.1	4.79	12.1
C25 n-alk-1-ene	4.14	6.83	4.18	4.56
prist-1-ene	31.5	25.7	13.4	25.4
prist-2-ene	16.3	42.7	17.5	30.8
C10 n-alkane	24.6	37.0	18.3	34.6
C11 n-alkane	34.2	48.1	25.6	50.7
C12 n-alkane	32.5	48.3	23.9	51.0
C13 n-alkane	38.1	58.7	23.0	54.6
C14 n-alkane	34.9	48.2	22.9	48.6
C15 n-alkane	42.3	62.6	26.8	62.7
C16 n-alkane	29.2	49.9	14.7	46.8
C17 n-alkane	33.5	44.9	30.7	43.0
C18 n-alkane	26.1	39.3	15.7	39.9
C19 n-alkane	35.5	54.3	30.1	56.7
C20 n-alkane	24.8	40.2	16.3	35.3
C21 n-alkane	25.8	43.9	14.5	39.0
C22 n-alkane	40.0	50.2	16.3	47.2
C23 n-alkane	31.7	40.3	16.4	41.5
C24 n-alkane	21.1	23.8	12.9	25.1
C25 n-alkane	112	62.0	43.5	110
C26 n-alkane	17.4	22.9	11.6	20.5
C27 n-alkane	19.2	25.0	15.9	21.4
C28 n-alkane	7.80	19.3	13.0	21.9
C29 n-alkane	12.0	31.3	22.95	18.2
C30 n-alkane	9.48	4.51	8.41	7.65
C31 n-alkane	11.9	4.21	17.3	8.66
ethylbenzene	127	178	91.0	161
styrene	129	240	183	237
n-propylbenzene	40.7	60.3	N.D.	60.7
n-butylbenzene	28.6	49.8	35.3	55.7
n-pentylbenzene	25.3	47.2	26.5	50.9

n-hexylbenzene	14.9	34.2	19.5	39.5
n-heptylbenzene	16.4	30.8	12.4	40.0
n-octylbenzene	17.6	40.9	19.3	40.6
n-nonylbenzene	11.4	36.9	15.6	33.3
n-decylbenzene	18.6	32.0	20.9	37.1
n-undecylbenzene	13.2	26.8	13.4	29.9
n-dodecylbenzene	12.7	37.0	16.0	34.0
n-tridecylbenzene	7.87	23.5	10.7	22.7
n-tetradecylbenzene	7.84	24.1	12.4	26.5
n-pentadecylbenzene	15.3	N.D.	N.D.	19.3
n-hexadecylbenzene	N.D.	N.D.	9.24	N.D.
6-phenylundecane	N.D.	N.D.	N.D.	N.D.
5-phenylundecane	N.D.	N.D.	N.D.	N.D.
4-phenylundecane	N.D.	N.D.	N.D.	N.D.
6-phenyldodecane	N.D.	N.D.	N.D.	N.D.
5-phenyldodecane	N.D.	N.D.	N.D.	N.D.
4-phenyldodecane	N.D.	15.3	N.D.	N.D.
6-phenyltridecane	N.D.	13.0	N.D.	N.D.
Phytane	11.5	14.7	16.4	21.9
5-phenyltridecane	N.D.	13.7	N.D.	N.D.
4-phenyltridecane	N.D.	N.D.	N.D.	N.D.
naphthalene	474	459	323	426
2-methylnaphthalene	156	139.7	83.6	140
1-methylnaphthalene	93.5	93.7	63.7	96.0
dimethylnaphthalenes	191	178	96.5	185
trimethylnaphthalenes	118	138	59.8	133
tetramethylnaphthalenes	3.23	64.7	36.0	80.0
fluorene	118	117	69.8	139
methylfluorenes	26.7	24.8	13.4	25.2
phenanthrene	581	639	537	643
anthracene	375	261	217	372
3-methylphenanthrene	153	115	93.3	116
2-methylphenanthrene	171	142	116	149
methylanthracene	92.5	49.0	45.9	83.5
9-methylphenanthrene	166	102	90.1	109
1-methylphenanthrene	239	138	123	179
dimethylphenanthrenes	350	179	87.0	285
retene	11.2	11.6	11.4	22.3
fluoranthene	978	955	1222	1329
pyrene	1053	844	1061	1150
methylpyrene isomers	868	575	573	805
dimethylpyrene isomers	2267	177	154	271
benzo[a]anthracene	111	192	182	231
chrysene	279	367	382	649
methylchrysene isomers	340	192	226	538
benzo[b]fluoranthene	56.7	81.4	69.9	85.8

benzo[j]fluoranthene	78.0	56.9	50.8	101
benzo[k]fluoranthene	22.8	7.74	2.67	2.44
benzo[e]pyrene	33.5	17.0	19.2	28.1
benzo[a]pyrene	16.9	28.6	20.2	34.9
perylene	N.D.	4.35	4.01	N.D.
indenol[1,2,3-cd]pyrene	N.D.	N.D.	N.D.	N.D.
benzo[ghi]perylene	N.D.	N.D.	N.D.	N.D.
dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
C29 hopane (17a, 21B)	7.90	17.0	12.9	16.4
C30 hopane (17a,21B)	9.70	16.0	14.5	15.3
cholestene	N.D.	N.D.	0.21	N.D.
ethylcholestene	N.D.	N.D.	N.D.	0.27
C27 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C28 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C29 sterane 5a, 14a, 1...	0.78	N.D.	0.24	1.08
C2-alkylpyrrole	5.57	24.6	3.65	20.1
phenol	505	940	312	714
2-methylphenol	43.7	67.3	18.5	52.3
4&3-methylphenols	259	467	142	343
4-ethylphenol	104	248	78.9	138
vinylphenol	153	397	44.2	166
guaiacol	20.4	44.0	11.8	28.1
methylguaiacol	17.6	27.6	5.84	12.9
ethylguaiacol	9.63	12.1	2.69	4.30
vinylguaiacol	50.5	97.3	11.9	31.6
vanillin	15.0	24.5	5.08	10.9
eugenol	3.02	5.99	1.55	4.42
cis iso-eugenol	2.82	7.08	N.D.	3.46
trans iso-eugenol	16.1	34.7	4.18	14.8
acetovanillone	N.D.	N.D.	N.D.	N.D.
syringol	1.12	3.86	0.45	0.67
methylsyringol	N.D.	N.D.	N.D.	N.D.
ethylsyringol	N.D.	N.D.	0.85	2.23
vinylsyringol	1.57	12.53	N.D.	N.D.
syringaldehyde	N.D.	N.D.	10.29	N.D.
prop-1-enyl syringol	0.76	4.98	N.D.	N.D.
prop-2-enyl syringol cis	N.D.	3.21	N.D.	N.D.
prop-2-enyl syringol t...	N.D.	16.9	N.D.	N.D.
benzaldehyde	17.4	30.9	9.13	34.2
benzaldehyde, methyl	61.6	169	70.0	79.7
methylfurfural	54.6	217	124	162
methylfuranone	N.D.	N.D.	N.D.	N.D.
2-methylcyclopentenone	N.D.	22.1	5.66	N.D.
3-methylcyclopentenone	8.53	N.D.	5.61	22.5
benzonitrile	47.2	97.4	37.2	113

benzoacetonitrile	44.0	118	47.4	110
benzenepropanitrile	45.1	108	30.9	83.3
quinoline	16.4	14.4	5.36	26.5
isoquinoline	59.3	105	29.7	78.6
indole	109	359	55.6	242
methylindole	37.6	99.2	18.1	61.9
phenylpyridine	2.32	11.6	4.90	3.57
carbazole	4.70	26.3	9.56	19.1
diketodipyrrole	51.0	167	47.8	178
cyclo-Pro-Pro-diketopi...	14.8	42.3	N.D.	23.5
n-tetradecanitrile	N.D.	0.84	N.D.	N.D.
n-hexadecanitrile	2.13	5.68	1.50	6.82
n-octadecanitrile	1.82	2.54	1.39	2.73
tetradecylamide	N.D.	3.79	2.01	5.50
hexadecylamide	3.89	14.8	7.15	2.91
octadecylamide	1.00	1.42	0.63	0.95
benzothiophene	55.3	66.8	36.5	58.6
4-methyldibenzothiophene	64.2	45.0	35.1	47.2
1-methyldibenzothiophene	19.6	20.5	12.0	36.2
3-&2-methyldibenzothio...	44.0	26.1	20.9	32.0
benzonaphthothiophene ...	71.7	47.1	43.1	65.2
C13-alk-2one	10.9	20.2	16.5	21.7
C14-alk-2-one	4.64	7.12	5.24	9.56
C15-alk-2-one	12.4	31.3	13.0	21.9
C16-alk-2-one	5.82	11.8	3.51	8.30
C17-alk-2-one	11.5	24.7	12.3	19.8
C18-alk-2-one	3.35	7.59	3.14	4.10
C19-alk-2-one	8.15	6.66	5.69	7.49
n-tetradecanoic acid, ...	3.52	6.98	2.56	6.89
Pristane	17.6	15.9	19.9	27.5
pentadecanoic acid iso...	2.15	4.95	2.45	3.83
pentadecanoic acid iso...	2.95	3.68	1.42	3.09
n-pentadecanoic acid, ME	1.57	3.16	1.18	2.03
n-hexadecanoic acid, m...	11.4	34.8	6.64	22.3
n-heptadecanoic acid, ...	4.05	2.84	4.40	4.69
n-octadecanoic acid, m...	3.09	6.48	1.03	4.27
n-eicosanoic acid, met...	0.77	1.51	N.D.	0.83
n-docosanoic acid, met...	1.02	1.28	0.37	1.48
n-tetracosanoic acid, ...	0.44	0.88	0.30	0.58
elemental sulfur	N.D.	N.D.	N.D.	N.D.

Average Depth (cm)	28.5	34.5	51.5	61.5
Target Compounds	mg/kg	mg/kg	mg/kg	mg/kg
C11 n-alk-1-ene	55.4	54.5	57.4	18.2
C12 n-alk-1-ene	47.7	49.3	48.4	13.4
C13 n-alk-1-ene	37.6	17.1	39.1	12.6
C14 n-alk-1-ene	43.2	40.6	46.1	14.7
C15 n-alk-1-ene	31.8	25.6	32.3	12.3
C16 n-alk-1-ene	43.7	23.0	37.7	12.4
C17 n-alk-1-ene	29.1	21.1	24.5	12.4
C18 n-alk-1-ene	26.9	28.4	24.4	11.7
C19 n-alk-1-ene	19.4	17.6	18.2	8.28
C20 n-alk-1-ene	26.0	18.8	20.1	10.7
C21 n-alk-1-ene	16.1	11.7	16.0	9.89
C22 n-alk-1-ene	32.5	16.8	19.5	10.5
C23 n-alk-1-ene	15.4	11.9	11.8	5.20
C24 n-alk-1-ene	18.0	15.6	18.9	8.27
C25 n-alk-1-ene	10.0	8.49	20.9	5.26
prist-1-ene	22.7	29.8	32.0	15.4
prist-2-ene	30.8	32.9	25.8	16.4
C10 n-alkane	40.0	49.1	48.6	15.8
C11 n-alkane	51.4	58.8	65.6	12.5
C12 n-alkane	58.5	61.9	66.5	16.1
C13 n-alkane	62.3	65.6	73.7	20.3
C14 n-alkane	56.4	54.3	62.0	17.4
C15 n-alkane	67.3	58.8	72.5	26.9
C16 n-alkane	53.3	42.8	48.6	20.0
C17 n-alkane	49.5	45.5	61.6	35.5
C18 n-alkane	45.7	39.0	45.5	20.8
C19 n-alkane	60.0	50.6	68.7	24.4
C20 n-alkane	47.1	35.4	45.1	21.8
C21 n-alkane	45.3	4.76	47.6	23.1
C22 n-alkane	58.0	41.3	61.6	31.9
C23 n-alkane	60.3	39.0	49.3	31.1
C24 n-alkane	41.9	27.8	42.1	15.9
C25 n-alkane	144	47.0	75.5	45.2
C26 n-alkane	48.2	16.8	31.4	1.15
C27 n-alkane	11.2	45.2	51.0	15.9
C28 n-alkane	75.8	44.1	35.4	22.5
C29 n-alkane	97.9	65.8	98.0	19.1
C30 n-alkane	31.7	17.3	2.47	7.85
C31 n-alkane	61.2	11.0	52.6	18.7
ethylbenzene	19.8	358	253	74.3
styrene	208	248	165	86.7
n-propylbenzene	85.1	103	N.D.	16.2
n-butylbenzene	77.5	83.7	71.3	16.4

n-pentylbenzene	67.2	68.6	47.2	10.8
n-hexylbenzene	36.7	36.0	34.1	10.5
n-heptylbenzene	41.9	38.4	29.4	8.37
n-octylbenzene	41.7	39.0	29.9	7.68
n-nonylbenzene	46.9	28.8	31.3	7.41
n-decylbenzene	44.6	33.7	34.9	11.8
n-undecylbenzene	35.9	28.0	25.1	7.10
n-dodecylbenzene	38.6	25.5	21.7	9.96
n-tridecylbenzene	30.5	14.2	18.5	6.29
n-tetradecylbenzene	30.2	21.2	17.6	6.86
n-pentadecylbenzene	30.8	16.8	19.6	N.D.
n-hexadecylbenzene	N.D.	21.2	N.D.	N.D.
6-phenylundecane	N.D.	N.D.	N.D.	N.D.
5-phenylundecane	N.D.	N.D.	N.D.	N.D.
4-phenylundecane	N.D.	N.D.	N.D.	N.D.
6-phenyldodecane	N.D.	N.D.	N.D.	N.D.
5-phenyldodecane	N.D.	N.D.	N.D.	N.D.
4-phenyldodecane	N.D.	N.D.	N.D.	6.63
6-phenyltridecane	N.D.	N.D.	N.D.	N.D.
Phytane	20.0	21.8	26.0	12.8
5-phenyltridecane	N.D.	N.D.	N.D.	N.D.
4-phenyltridecane	N.D.	N.D.	N.D.	N.D.
naphthalene	405	564	659	400
2-methylnaphthalene	142	226	216	130
1-methylnaphthalene	104	125	147	85.1
dimethylnaphthalenes	160	282	295	190
trimethylnaphthalenes	143	178	173	186
tetramethylnaphthalenes	84.9	112	85.3	92.0
fluorene	136	155	141	142
methylfluorenes	23.9	33.9	23.8	37.9
phenanthrene	711	681	540	1119
anthracene	275	380	244	334
3-methylphenanthrene	133	210	137	301
2-methylphenanthrene	175	222	139	368
methylanthracene	68.6	91.9	51.7	97.7
9-methylphenanthrene	125	166	141	251
1-methylphenanthrene	181	248	132	344
dimethylphenanthrenes	330	371	233	456
retene	34.3	32.3	29.7	18.8
fluoranthene	1574	1451	932	1337
pyrene	1381	1377	911	1349
methylpyrene isomers	1020	1083	820	1117
dimethylpyrene isomers	385	379	295	300
benzo[a]anthracene	492	596	414	372
chrysene	985	1054	829	547
methylchrysene isomers	697	710	465	519

benzo[b]fluoranthene	358	818	169	120
benzo[j]fluoranthene	252	797	137	118
benzo[k]fluoranthene	49.9	795	24.1	5.98
benzo[e]pyrene	117	187	31.4	18.7
benzo[a]pyrene	137	77.2	34.3	19.5
perylene	N.D.	17.2	N.D.	N.D.
indenol[1,2,3-cd]pyrene	N.D.	N.D.	N.D.	N.D.
benzo[ghi]perylene	N.D.	N.D.	N.D.	N.D.
dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
C29 hopane (17a, 21B)	44.6	29.6	28.	5.67
C30 hopane (17a,21B)	59.2	29.8	35.2	9.30
cholestene	1.31	0.44	N.D.	N.D.
ethylcholestene	1.81	0.27	0.69	0.26
C27 sterane 5a, 14a, 1...	4.27	1.70	N.D.	N.D.
C28 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C29 sterane 5a, 14a, 1...	5.20	1.50	N.D.	1.11
C2-alkylpyrrole	N.D.	44.1	N.D.	N.D.
phenol	767	1360	981	312
2-methylphenol	60.5	109	82.0	30.6
4&3-methylphenols	375	655	460	185
4-ethylphenol	145	289	215	75.3
vinylphenol	133	358	242	87.9
guaiacol	12.7	45.6	32.6	12.7
methylguaiacol	8.84	23.6	19.4	7.84
ethylguaiacol	2.76	14.1	9.49	2.96
vinylguaiacol	24.9	81.7	46.8	21.0
vanillin	12.4	16.8	11.6	5.22
eugenol	2.30	5.51	3.87	1.94
cis iso-eugenol	1.96	6.53	5.13	2.35
trans iso-eugenol	9.27	27.9	16.1	7.74
acetovanillone	N.D.	3.64	4.45	N.D.
syringol	N.D.	3.29	1.81	0.92
methylsyringol	N.D.	N.D.	N.D.	N.D.
ethylsyringol	2.69	2.58	2.51	N.D.
vinylsyringol	N.D.	5.91	N.D.	N.D.
syringaldehyde	N.D.	N.D.	16.3	N.D.
prop-1-enyl syringol	N.D.	2.00	N.D.	N.D.
prop-2-enyl syringol cis	N.D.	N.D.	N.D.	N.D.
prop-2-enyl syringol t...	3.54	7.54	N.D.	N.D.
benzaldehyde	N.D.	35.8	24.7	11.9
benzaldehyde, methyl	28.7	N.D.	115	30.0
methylfurfural	80.2	206	124	59.1
methylfuranone	N.D.	N.D.	N.D.	N.D.
2-methylcyclopentenone	N.D.	N.D.	N.D.	N.D.
3-methylcyclopentenone	N.D.	37.33	N.D.	N.D.

benzonitrile	125	157	106	39.7
benzoacetonitrile	76.5	96.8	84.7	47.4
benzenepropanitrile	91.1	118	84.3	33.6
quinoline	47.6	52.9	51.0	18.3
isoquinoline	74.7	144	64.5	38.4
indole	280	351	246	132
methylindole	74.2	110	107	37.8
phenylpyridine	14.9	5.88	17.5	5.97
carbazole	46.6	45.8	44.0	20.7
diketodipyrrole	188	167	112	42.3
cyclo-Pro-Pro-diketopi...	50.9	57.2	57.8	16.6
n-tetradecanitrile	1.72	1.17	1.46	0.36
n-hexadecanitrile	11.4	5.61	4.88	2.50
n-octadecanitrile	5.95	4.77	4.77	3.08
tetradecylamide	3.82	5.43	2.48	0.77
hexadecylamide	19.6	21.5	5.87	2.28
octadecylamide	3.68	5.92	2.22	0.82
benzothiophene	67.1	30.1	52.6	77.5
4-methyldibenzothiophene	59.2	53.7	40.7	97.8
1-methyldibenzothiophene	36.3	29.0	22.8	32.4
3-&2-methyldibenzothio...	36.0	32.0	28.2	63.4
benzonaphthothiophene ...	157	104	106	81.4
C13-alk-2one	23.0	18.5	22.4	11.2
C14-alk-2-one	5.34	7.41	7.66	4.39
C15-alk-2-one	18.9	16.5	19.3	13.2
C16-alk-2-one	9.51	7.51	12.7	5.90
C17-alk-2-one	22.9	18.4	30.1	18.1
C18-alk-2-one	5.49	3.61	8.59	2.80
C19-alk-2-one	11.8	6.47	10.2	6.15
n-tetradecanoic acid, ...	5.28	5.66	7.30	1.34
Pristane	25.7	27.8	29.2	20.2
pentadecanoic acid iso...	5.77	5.09	5.73	3.70
pentadecanoic acid iso...	5.10	4.44	3.78	2.14
n-pentadecanoic acid, ME	2.06	3.53	2.35	2.32
n-hexadecanoic acid, m...	20.6	27.3	24.7	5.37
n-heptadecanoic acid, ...	5.17	1.52	4.68	4.15
n-octadecanoic acid, m...	4.89	4.82	6.54	1.69
n-eicosanoic acid, met...	1.38	0.97	1.16	0.85
n-docosanoic acid, met...	1.64	1.22	1.95	0.41
n-tetracosanoic acid, ...	0.91	1.13	1.32	0.30
elemental sulfur	25.8	N.D.	N.D.	N.D.

Average Depth (cm)	71.5	81.5	91.5	101.5
Target Compounds	mg/kg	mg/kg	mg/kg	mg/kg
C11 n-alk-1-ene	59.2	54.1	25.1	17.4
C12 n-alk-1-ene	47.7	48.5	22.0	16.2
C13 n-alk-1-ene	38.5	39.3	20.4	12.8
C14 n-alk-1-ene	40.5	57.7	27.2	22.7
C15 n-alk-1-ene	31.7	34.3	19.0	23.3
C16 n-alk-1-ene	27.7	33.2	13.2	11.5
C17 n-alk-1-ene	31.0	29.1	11.3	12.8
C18 n-alk-1-ene	28.8	31.9	19.5	19.4
C19 n-alk-1-ene	18.5	15.6	10.5	7.78
C20 n-alk-1-ene	20.5	12.5	9.87	6.12
C21 n-alk-1-ene	17.8	14.1	7.45	6.77
C22 n-alk-1-ene	19.6	13.4	10.3	3.32
C23 n-alk-1-ene	21.2	14.4	8.50	8.66
C24 n-alk-1-ene	15.3	9.96	5.75	5.94
C25 n-alk-1-ene	11.4	13.4	5.84	4.45
prist-1-ene	41.5	47.2	31.1	38.1
prist-2-ene	42.0	52.1	32.3	43.1
C10 n-alkane	50.7	43.7	26.3	14.1
C11 n-alkane	71.4	55.7	33.2	20.0
C12 n-alkane	69.6	58.1	35.4	22.8
C13 n-alkane	73.8	87.0	48.7	36.9
C14 n-alkane	66.6	63.5	32.9	24.9
C15 n-alkane	74.9	92.7	49.3	45.9
C16 n-alkane	55.0	70.9	33.0	32.5
C17 n-alkane	60.1	256	126	301
C18 n-alkane	78.4	179	89.8	191
C19 n-alkane	78.3	67.0	38.0	46.1
C20 n-alkane	54.2	68.4	38.6	49.8
C21 n-alkane	50.2	63.3	32.7	19.1
C22 n-alkane	56.9	74.2	11.5	51.2
C23 n-alkane	51.8	69.2	42.1	49.3
C24 n-alkane	34.7	53.0	24.7	31.0
C25 n-alkane	114	160	90.2	44.2
C26 n-alkane	42.8	56.0	34.3	32.6
C27 n-alkane	42.4	67.9	15.1	39.1
C28 n-alkane	41.2	70.6	32.5	48.7
C29 n-alkane	63.5	96.2	51.8	50.9
C30 n-alkane	14.4	22.1	4.65	10.3
C31 n-alkane	19.3	36.2	5.05	28.0
ethylbenzene	315	276	107	98.3
styrene	209	274	130	143
n-propylbenzene	85.8	73.8	30.6	24.3
n-butylbenzene	66.6	71.2	33.6	41.6

n-pentylbenzene	59.6	62.6	32.7	29.4
n-hexylbenzene	39.2	40.9	27.8	25.9
n-heptylbenzene	39.6	43.1	28.3	28.1
n-octylbenzene	34.5	44.8	23.4	26.5
n-nonylbenzene	24.0	34.1	20.2	23.6
n-decylbenzene	29.9	43.7	25.0	28.2
n-undecylbenzene	25.2	28.8	16.8	19.9
n-dodecylbenzene	23.0	38.4	20.5	17.7
n-tridecylbenzene	18.9	12.7	7.82	9.62
n-tetradecylbenzene	13.2	16.0	13.1	10.2
n-pentadecylbenzene	15.9	12.2	8.79	9.66
n-hexadecylbenzene	15.7	N.D.	10.36	N.D.
6-phenylundecane	N.D.	N.D.	N.D.	N.D.
5-phenylundecane	N.D.	N.D.	N.D.	N.D.
4-phenylundecane	N.D.	N.D.	N.D.	N.D.
6-phenyldodecane	N.D.	14.9	4.86	N.D.
5-phenyldodecane	N.D.	14.8	N.D.	N.D.
4-phenyldodecane	N.D.	N.D.	4.23	N.D.
6-phenyltridecane	N.D.	N.D.	N.D.	N.D.
Phytane	38.1	99.2	43.5	121
5-phenyltridecane	N.D.	N.D.	N.D.	N.D.
4-phenyltridecane	N.D.	N.D.	N.D.	N.D.
naphthalene	1748	1746	983	717
2-methylnaphthalene	895	1732	537	563
1-methylnaphthalene	514	1076	413	689
dimethylnaphthalenes	977	271	816	1053
trimethylnaphthalenes	485	1075	522	852
tetramethylnaphthalenes	142	454	177	311
fluorene	447	1473	525	833
methylfluorenes	78.4	546	118	304
phenanthrene	2342	8431	3494	6845
anthracene	547	2726	1039	1907
3-methylphenanthrene	492	2426	975	1622
2-methylphenanthrene	573	2728	1092	1814
methylanthracene	163	987	368	635
9-methylphenanthrene	388	1907	841	1358
1-methylphenanthrene	537	2675	1071	1767
dimethylphenanthrenes	655	2736	1382	2284
retene	37.7	9.66	53.0	60.0
fluoranthene	2055	5528	308	5050
pyrene	2120	6785	377	6944
methylpyrene isomers	1686	6733	3266	5336
dimethylpyrene isomers	556	1918	1042	1528
benzo[a]anthracene	801	2964	1650	2748
chrysene	1351	4055	234	3623
methylchrysene isomers	956	3438	1653	2803

benzo[b]fluoranthene	297	1036	833	1505
benzo[j]fluoranthene	234	547	810	1459
benzo[k]fluoranthene	40.5	1356	778	1481
benzo[e]pyrene	118	275	153	327
benzo[a]pyrene	39.1	233	119	314
perylene	4.57	N.D.	7.56	57.7
indenol[1,2,3-cd]pyrene	4.05	N.D.	N.D.	11.4
benzo[ghi]perylene	N.D.	N.D.	N.D.	40.7
dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
C29 hopane (17a, 21B)	14.9	24.7	9.70	7.49
C30 hopane (17a,21B)	18.1	18.1	11.8	5.91
cholestene	N.D.	2.99	1.81	1.85
ethylcholestene	0.60	3.11	1.20	1.48
C27 sterane 5a, 14a, 1...	0.80	1.69	N.D.	N.D.
C28 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C29 sterane 5a, 14a, 1...	1.08	1.12	N.D.	N.D.
C2-alkylpyrrole	45.9	47.8	29.6	22.3
phenol	1105	1122	632	491
2-methylphenol	109	93.6	48.3	26.5
4&3-methylphenols	648	741	429	351
4-ethylphenol	294	305	214	210
vinylphenol	369	445	546	367
guaiacol	39.9	44.7	59.1	35.5
methylguaiacol	32.0	40.4	53.8	27.1
ethylguaiacol	12.5	15.5	20.6	15.4
vinylguaiacol	90.2	134	187	112
vanillin	16.1	94.1	26.3	57.8
eugenol	8.09	12.3	13.0	6.57
cis iso-eugenol	8.46	11.4	14.4	7.29
trans iso-eugenol	41.2	69.4	71.4	44.3
acetovanillone	4.16	N.D.	N.D.	N.D.
syringol	2.40	1.79	7.54	2.69
methylsyringol	N.D.	N.D.	N.D.	N.D.
ethylsyringol	5.15	13.47	4.40	8.70
vinylsyringol	N.D.	N.D.	23.18	14.9
syringaldehyde	N.D.	4.93	N.D.	N.D.
prop-1-enyl syringol	3.73	8.48	11.1	6.76
prop-2-enyl syringol cis	N.D.	4.43	11.3	N.D.
prop-2-enyl syringol t...	N.D.	35.6	56.4	26.8
benzaldehyde	27.0	28.1	17.4	15.0
benzaldehyde, methyl	N.D.	53.8	59.1	96.8
methylfurfural	230	224	188	169
methylfuranone	N.D.	N.D.	49.5	N.D.
2-methylcyclopentenone	N.D.	N.D.	N.D.	N.D.
3-methylcyclopentenone	N.D.	N.D.	N.D.	13.9

benzonitrile	120	124	39.6	31.3
benzoacetonitrile	100	157	83.1	80.0
benzenepropanitrile	128	191	115	126
quinoline	73.7	98.4	51.2	41.8
isoquinoline	100	181	91.0	86.9
indole	369	608	423	406
methylindole	134	230	136	133
phenylpyridine	28.6	73.5	26.1	34.8
carbazole	66.1	75.4	44.2	44.8
diketodipyrrole	112	146	119	117
cyclo-Pro-Pro-diketopi...	70.2	154	108	91.3
n-tetradecanitrile	0.73	N.D.	N.D.	N.D.
n-hexadecanitrile	4.52	3.34	3.16	3.93
n-octadecanitrile	2.61	3.10	3.21	2.73
tetradecylamide	8.42	14.1	12.5	5.54
hexadecylamide	46.2	86.3	70.8	69.3
octadecylamide	8.11	14.3	16.4	20.6
benzothiophene	130	893	419	581
4-methyldibenzothiophene	148	881	414	526
1-methyldibenzothiophene	44.0	216	243	309
3-&2-methyldibenzothio...	98.2	645	295	384
benzonaphthothiophene ...	177	821	514	661
C13-alk-2one	27.9	27.2	17.4	17.0
C14-alk-2-one	9.31	8.63	5.26	5.61
C15-alk-2-one	21.6	26.9	17.2	18.4
C16-alk-2-one	8.71	12.7	6.72	0.83
C17-alk-2-one	26.3	25.6	19.4	18.8
C18-alk-2-one	5.55	7.17	3.23	5.60
C19-alk-2-one	9.41	17.6	6.93	10.3
n-tetradecanoic acid, ...	4.83	N.D.	1.17	2.16
Pristane	55.0	191	80.7	244
pentadecanoic acid iso...	3.66	3.37	3.36	4.01
pentadecanoic acid iso...	3.27	2.76	2.50	2.01
n-pentadecanoic acid, ME	2.43	10.3	2.31	1.73
n-hexadecanoic acid, m...	18.2	16.1	11.4	11.1
n-heptadecanoic acid, ...	8.70	23.5	11.4	20.2
n-octadecanoic acid, m...	4.90	5.00	3.48	3.51
n-eicosanoic acid, met...	1.45	0.91	1.30	0.67
n-docosanoic acid, met...	1.09	1.21	1.01	1.04
n-tetracosanoic acid, ...	1.07	0.74	0.57	0.74
elemental sulfur	71.1	138	115	176

Average Depth (cm)	111.5	121.5	131.5	141.5
Target Compounds	mg/kg	mg/kg	mg/kg	mg/kg
C11 n-alk-1-ene	14.8	15.8	15.4	16.7
C12 n-alk-1-ene	11.6	12.2	17.0	15.5
C13 n-alk-1-ene	12.3	11.5	12.5	14.5
C14 n-alk-1-ene	20.9	21.5	22.8	20.6
C15 n-alk-1-ene	12.1	12.5	14.7	13.2
C16 n-alk-1-ene	11.4	13.9	17.2	11.1
C17 n-alk-1-ene	10.8	10.8	10.7	10.2
C18 n-alk-1-ene	16.3	16.2	14.9	13.5
C19 n-alk-1-ene	8.37	3.69	8.41	8.06
C20 n-alk-1-ene	7.41	5.86	11.0	8.82
C21 n-alk-1-ene	8.15	6.25	7.21	5.19
C22 n-alk-1-ene	5.26	7.23	8.87	7.92
C23 n-alk-1-ene	9.92	4.29	8.38	8.22
C24 n-alk-1-ene	3.61	2.42	7.41	6.00
C25 n-alk-1-ene	43.3	19.1	12.2	4.13
prist-1-ene	<0.01	26.25	33.51	<0.01
prist-2-ene	<0.01	11.2	15.5	<0.01
C10 n-alkane	10.9	12.3	18.0	18.6
C11 n-alkane	10.4	2.87	19.3	20.7
C12 n-alkane	15.7	16.5	18.7	20.5
C13 n-alkane	25.0	24.9	27.7	29.3
C14 n-alkane	20.7	19.4	21.3	23.1
C15 n-alkane	41.3	29.8	38.3	31.9
C16 n-alkane	25.3	19.7	26.2	23.5
C17 n-alkane	38.7	33.0	35.2	39.3
C18 n-alkane	26.1	24.4	25.3	25.7
C19 n-alkane	98.3	65.6	66.8	41.7
C20 n-alkane	56.4	43.9	35.2	31.0
C21 n-alkane	50.7	51.5	41.5	31.9
C22 n-alkane	9.72	89.3	54.5	41.2
C23 n-alkane	92.3	8.19	65.3	47.0
C24 n-alkane	39.6	21.6	45.7	32.9
C25 n-alkane	186	151	88.8	34.7
C26 n-alkane	16.1	10.3	46.6	35.2
C27 n-alkane	86.4	106	74.4	64.8
C28 n-alkane	69.6	92.9	46.7	44.0
C29 n-alkane	90.6	127	79.6	93.5
C30 n-alkane	23.6	32.5	17.4	16.1
C31 n-alkane	27.9	41.1	48.7	72.8
ethylbenzene	136	60.5	97.0	125
styrene	85.6	65.4	117	131
n-propylbenzene	27.3	10.2	28.0	33.
n-butylbenzene	48.5	29.0	41.7	37.5

n-pentylbenzene	37.1	32.9	26.7	27.5
n-hexylbenzene	29.0	25.1	21.4	17.0
n-heptylbenzene	28.7	19.7	23.0	27.2
n-octylbenzene	31.2	27.9	23.5	24.4
n-nonylbenzene	26.3	16.5	15.7	22.2
n-decylbenzene	33.6	27.2	27.4	31.0
n-undecylbenzene	30.1	26.3	14.7	19.5
n-dodecylbenzene	27.8	25.3	26.2	21.7
n-tridecylbenzene	13.7	8.29	12.4	11.1
n-tetradecylbenzene	11.6	15.4	12.7	14.0
n-pentadecylbenzene	12.8	9.53	13.8	13.8
n-hexadecylbenzene	24.0	14.5	N.D.	16.9
6-phenylundecane	N.D.	N.D.	N.D.	N.D.
5-phenylundecane	N.D.	N.D.	N.D.	N.D.
4-phenylundecane	N.D.	N.D.	N.D.	N.D.
6-phenyldodecane	17.3	N.D.	N.D.	N.D.
5-phenyldodecane	13.7	N.D.	N.D.	5.14
4-phenyldodecane	15.7	14.8	N.D.	15.0
6-phenyltridecane	N.D.	N.D.	N.D.	5.68
Phytane	107	71.9	39.8	39.6
5-phenyltridecane	N.D.	14.3	N.D.	5.68
4-phenyltridecane	N.D.	N.D.	N.D.	5.68
naphthalene	714	605	631	689
2-methylnaphthalene	574	280	297	252
1-methylnaphthalene	385	167	163	148
dimethylnaphthalenes	1032	384	384	387
trimethylnaphthalenes	722	294	246	275
tetramethylnaphthalenes	367	90.0	125	108
fluorene	737	290	244	227
methylfluorenes	270	116	121	109
phenanthrene	5977	3413	2859	2433
anthracene	1567	832	826	563
3-methylphenanthrene	1415	788	669	570
2-methylphenanthrene	1578	895	816	638
methylanthracene	461	253	245	184
9-methylphenanthrene	1186	650	599	453
1-methylphenanthrene	1215	834	753	590
dimethylphenanthrenes	1840	1007	1003	730
retene	150	143	109	110
fluoranthene	4776	2958	2748	1793
pyrene	6675	3862	3852	2619
methylpyrene isomers	4367	2555	2818	1787
dimethylpyrene isomers	1097	651	685	510
benzo[a]anthracene	2051	1266	1430	899
chrysene	2881	1831	2117	1310
methylchrysene isomers	1794	1459	1433	858

benzo[b]fluoranthene	440	229	322	150
benzo[j]fluoranthene	37	267	251	193
benzo[k]fluoranthene	182	147	58.3	101
benzo[e]pyrene	167	194	104	129
benzo[a]pyrene	233	201	144	157
perylene	9.95	24.1	N.D.	18.6
indenol[1,2,3-cd]pyrene	N.D.	8.47	N.D.	10.5
benzo[ghi]perylene	N.D.	N.D.	N.D.	2.47
dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
C29 hopane (17a, 21B)	14.2	9.42	8.81	1.98
C30 hopane (17a,21B)	11.6	6.97	10.0	4.03
cholestene	2.45	1.77	0.34	0.61
ethylcholestene	1.20	3.15	1.36	3.31
C27 sterane 5a, 14a, 1...	1.04	N.D.	N.D.	1.09
C28 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C29 sterane 5a, 14a, 1...	0.63	N.D.	N.D.	1.01
C2-alkylpyrrole	7.48	N.D.	11.2	26.3
phenol	319	254	467	729
2-methylphenol	14.3	14.0	24.8	36.6
4&3-methylphenols	194	156	265	428
4-ethylphenol	164	99.5	206	334
vinylphenol	357	265	497	832
guaiacol	34.5	28.5	59.5	105
methylguaiacol	22.7	19.6	39.9	77.5
ethylguaiacol	10.9	8.47	16.8	39.1
vinylguaiacol	104	92.4	161	338
vanillin	17.8	14.5	46.6	45.2
eugenol	6.41	5.13	9.20	19.1
cis iso-eugenol	8.98	6.46	9.67	17.8
trans iso-eugenol	51.5	38.0	50.7	120
acetovanillone	7.55	6.43	11.9	18.0
syringol	3.40	2.27	7.73	16.3
methylsyringol	4.33	N.D.	8.26	24.1
ethylsyringol	9.72	2.53	N.D.	5.75
vinylsyringol	12.4	8.58	26.7	61.6
syringaldehyde	23.4	15.3	9.27	10.3
prop-1-enyl syringol	5.58	5.19	9.14	21.7
prop-2-enyl syringol cis	5.80	N.D.	7.81	20.0
prop-2-enyl syringol t...	27.5	22.6	43.94	91.8
benzaldehyde	20.3	15.7	21.6	24.7
benzaldehyde, methyl	73.6	83.9	97.7	102
methylfurfural	274	227	241	312
methylfuranone	35.2	13.8	18.2	63.1
2-methylcyclopentenone	5.44	N.D.	12.7	22.7
3-methylcyclopentenone	13.3	7.59	6.65	15.0

benzonitrile	24.8	19.4	29.1	37.8
benzoacetonitrile	74.9	65.7	76.7	90.7
benzenepropanitrile	93.3	62.4	92.4	118
quinoline	37.5	26.1	34.1	43.0
isoquinoline	78.3	45.2	82.7	86.5
indole	335	208	313	399
methylindole	84.3	49.9	89.2	113
phenylpyridine	65.9	26.0	22.6	13.9
carbazole	32.38	26.95	24.91	21.41
diketodipyrrole	113	79.1	146	169
cyclo-Pro-Pro-diketopi...	12.9	10.8	78.5	10.3
n-tetradecanitrile	N.D.	0.89	1.07	N.D.
n-hexadecanitrile	5.57	3.68	4.25	3.54
n-octadecanitrile	1.39	2.64	1.99	2.38
tetradecylamide	6.27	6.80	10.5	11.9
hexadecylamide	59.6	34.4	51.6	80.8
octadecylamide	9.68	6.28	11.8	15.9
benzothiophene	576	267	214	190
4-methyldibenzothiophene	500	246	207	161
1-methyldibenzothiophene	151	58.7	55.9	41.7
3-&2-methyldibenzothio...	377	185	151	116
benzonaphthothiophene ...	531	325	331	190
C13-alk-2one	25.8	24.2	15.6	16.6
C14-alk-2-one	5.75	6.02	5.42	6.39
C15-alk-2-one	30.1	25.4	24.1	16.8
C16-alk-2-one	9.43	9.49	7.67	7.55
C17-alk-2-one	23.1	20.8	19.4	20.3
C18-alk-2-one	5.95	3.50	5.47	5.56
C19-alk-2-one	6.80	4.69	4.52	5.97
n-tetradecanoic acid, ...	3.06	2.83	3.36	1.98
Pristane	27.4	132	71.0	61.2
pentadecanoic acid iso...	4.18	2.86	2.66	3.20
pentadecanoic acid iso...	3.12	2.58	1.84	2.85
n-pentadecanoic acid, ME	3.85	2.60	2.79	2.58
n-hexadecanoic acid, m...	22.3	14.4	22.2	15.1
n-heptadecanoic acid, ...	17.6	11.1	9.91	6.77
n-octadecanoic acid, m...	5.66	3.80	5.44	4.11
n-eicosanoic acid, met...	0.99	0.56	1.04	0.63
n-docosanoic acid, met...	1.35	0.89	1.45	1.50
n-tetracosanoic acid, ...	0.82	0.59	1.12	0.98
elemental sulfur	384	400	43.8	39.9

Average Depth (cm)	151.5	161.5	171.5	181.5
Target Compounds	mg/kg	mg/kg	mg/kg	mg/kg
C11 n-alk-1-ene	42.0	28.1	22.5	6.42
C12 n-alk-1-ene	36.0	22.7	18.8	3.28
C13 n-alk-1-ene	36.2	22.6	17.1	3.74
C14 n-alk-1-ene	34.3	29.1	24.9	6.26
C15 n-alk-1-ene	22.9	17.8	16.9	3.54
C16 n-alk-1-ene	22.6	20.8	15.0	8.76
C17 n-alk-1-ene	23.2	18.6	13.6	3.69
C18 n-alk-1-ene	24.4	25.9	21.0	4.38
C19 n-alk-1-ene	15.0	10.3	11.5	1.74
C20 n-alk-1-ene	17.2	7.69	14.6	2.23
C21 n-alk-1-ene	13.3	11.9	9.30	4.71
C22 n-alk-1-ene	14.0	15.8	15.3	2.97
C23 n-alk-1-ene	10.4	10.9	9.51	3.76
C24 n-alk-1-ene	15.4	11.6	11.2	3.30
C25 n-alk-1-ene	10.4	6.02	6.85	4.62
prist-1-ene	48.9	59.2	49.9	8.78
prist-2-ene	27.4	62.4	52.0	1.94
C10 n-alkane	36.7	26.9	20.0	3.68
C11 n-alkane	41.9	34.0	24.4	4.88
C12 n-alkane	45.8	34.8	28.9	4.08
C13 n-alkane	51.1	44.5	39.2	13.2
C14 n-alkane	45.5	42.3	30.8	4.23
C15 n-alkane	53.8	62.5	44.5	9.31
C16 n-alkane	44.5	38.6	26.7	6.90
C17 n-alkane	45.0	55.5	49.9	14.4
C18 n-alkane	35.1	39.1	33.8	12.6
C19 n-alkane	54.5	46.7	47.5	18.3
C20 n-alkane	40.7	42.9	36.9	13.1
C21 n-alkane	38.6	42.5	36.3	11.3
C22 n-alkane	48.1	50.9	45.7	10.2
C23 n-alkane	52.4	52.1	45.8	13.6
C24 n-alkane	28.5	30.1	30.6	6.85
C25 n-alkane	74.6	45.1	57.5	30.7
C26 n-alkane	5.42	11.7	27.9	6.14
C27 n-alkane	40.7	51.1	45.6	10.2
C28 n-alkane	31.0	19.1	16.9	8.76
C29 n-alkane	60.4	82.2	13.1	35.8
C30 n-alkane	16.00	23.67	22.13	2.94
C31 n-alkane	66.9	117	130	37.8
ethylbenzene	221	140	110	27.5
styrene	209	191	139	5.94
n-propylbenzene	76.0	44.2	10.9	N.D.
n-butylbenzene	67.2	57.9	33.9	4.17

n-pentylbenzene	45.5	46.4	33.8	5.92
n-hexylbenzene	35.3	N.D.	17.8	4.82
n-heptylbenzene	42.8	33.8	17.7	3.54
n-octylbenzene	33.6	26.3	24.8	3.46
n-nonylbenzene	27.8	22.9	17.2	2.32
n-decylbenzene	31.0	25.8	19.8	4.41
n-undecylbenzene	24.8	21.4	16.4	2.27
n-dodecylbenzene	22.3	22.0	23.1	5.00
n-tridecylbenzene	13.7	12.2	12.1	N.D.
n-tetradecylbenzene	26.1	13.2	10.2	3.33
n-pentadecylbenzene	13.5	15.1	12.1	2.33
n-hexadecylbenzene	50.9	N.D.	N.D.	N.D.
6-phenylundecane	N.D.	N.D.	N.D.	N.D.
5-phenylundecane	N.D.	N.D.	N.D.	N.D.
4-phenylundecane	N.D.	N.D.	N.D.	N.D.
6-phenyldodecane	N.D.	N.D.	N.D.	N.D.
5-phenyldodecane	N.D.	N.D.	N.D.	N.D.
4-phenyldodecane	N.D.	N.D.	N.D.	10.2
6-phenyltridecane	N.D.	N.D.	N.D.	N.D.
Phytane	21.2	23.2	17.4	9.34
5-phenyltridecane	N.D.	N.D.	N.D.	N.D.
4-phenyltridecane	N.D.	N.D.	N.D.	N.D.
naphthalene	1523	1476	1193	446
2-methylnaphthalene	416	463	563	154
1-methylnaphthalene	186	309	316	91.7
dimethylnaphthalenes	302	N.D.	N.D.	N.D.
trimethylnaphthalenes	165	N.D.	N.D.	N.D.
tetramethylnaphthalenes	68.2	N.D.	N.D.	N.D.
fluorene	171	506	473	155
methylfluorenes	69.8	139.9	95.9	21.2
phenanthrene	1515	401	5010	3244
anthracene	411	834	1023	799
3-methylphenanthrene	354	950	932	419
2-methylphenanthrene	402	1061	1073	468
methylanthracene	109	223	237	129
9-methylphenanthrene	287	647	697	334
1-methylphenanthrene	361	877	888	428
dimethylphenanthrenes	411	N.D.	N.D.	N.D.
retene	115	134	146	79.5
fluoranthene	1133	257	3249	2893
pyrene	1456	350	4377	3703
methylpyrene isomers	1030	N.D.	N.D.	N.D.
dimethylpyrene isomers	269	N.D.	N.D.	N.D.
benzo[a]anthracene	425	1197	1384	785
chrysene	683	1707	1929	1416
methylchrysene isomers	419	N.D.	N.D.	N.D.

benzo[b]fluoranthene	71.5	368	227	145
benzo[j]fluoranthene	71.3	194	286	105
benzo[k]fluoranthene	7.03	32.7	38.8	37.7
benzo[e]pyrene	31.5	85	150	147
benzo[a]pyrene	11.8	32.8	23.6	29.3
perylene	N.D.	4.81	N.D.	4.55
indenol[1,2,3-cd]pyrene	N.D.	N.D.	N.D.	N.D.
benzo[ghi]perylene	N.D.	N.D.	N.D.	N.D.
dibenzoanthacene isomer	N.D.	N.D.	N.D.	N.D.
dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	N.D.
C29 hopane (17a, 21B)	2.85	N.D.	N.D.	N.D.
C30 hopane (17a,21B)	N.D.	N.D.	N.D.	N.D.
cholestene	0.24	0.92	0.28	N.D.
ethylcholestene	0.46	2.47	1.75	N.D.
C27 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C28 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	N.D.
C29 sterane 5a, 14a, 1...	N.D.	0.69	N.D.	N.D.
C2-alkylpyrrole	41.7	N.D.	N.D.	N.D.
phenol	1312	1123	936	105
2-methylphenol	81.9	608	43.8	2.71
4&3-methylphenols	703	647	495	35.1
4-ethylphenol	384	420	285	16.7
vinylphenol	832	768	696	119
guaiacol	113	93.6	102	20.7
methylguaiacol	70.6	56.2	54.6	7.14
ethylguaiacol	33.6	29.6	28.5	4.04
vinylguaiacol	299	245	249	55.2
vanillin	56.0	31.2	34.7	9.76
eugenol	12.5	14.7	12.7	2.08
cis iso-eugenol	11.5	14.4	15.0	2.22
trans iso-eugenol	72.1	89.8	82.2	16.2
acetovanillone	17.5	14.8	10.8	N.D.
syringol	17.2	9.35	9.90	1.29
methylsyringol	21.3	7.13	12.8	0.69
ethylsyringol	3.65	2.80	3.35	N.D.
vinylsyringol	49.4	N.D.	41.3	4.58
syringaldehyde	14.6	N.D.	18.5	5.56
prop-1-enyl syringol	14.4	8.99	13.4	2.15
prop-2-enyl syringol cis	10.9	4.41	N.D.	1.82
prop-2-enyl syringol t...	59.4	41.9	62.4	12.2
benzaldehyde	33.1	24.2	23.8	5.12
benzaldehyde, methyl	119	73.7	129	9.69
methylfurfural	335	355	329	93.5
methylfuranone	63.3	51.2	N.D.	N.D.
2-methylcyclopentenone	39.1	22.4	N.D.	N.D.
3-methylcyclopentenone	39.8	28.5	12.6	N.D.

benzonitrile	83.1	60.0	30.4	6.94
benzoacetonitrile	141	144	123	16.0
benzenepropanitrile	155	169	144	15.8
quinoline	59.4	69.1	51.3	7.42
isoquinoline	135	131	96.9	5.22
indole	494	567	486	47.9
methylindole	149	155	110	8.62
phenylpyridine	18.9	62.0	49.4	5.18
carbazole	25.7	26.9	17.4	3.24
diketodipyrrole	211	238	222	18.2
cyclo-Pro-Pro-diketopi...	115	127	98.4	11.3
n-tetradecanitrile	0.74	N.D.	N.D.	N.D.
n-hexadecanitrile	4.73	5.18	4.96	1.00
n-octadecanitrile	2.14	3.19	1.16	0.85
tetradecylamide	11.4	13.7	14.5	1.62
hexadecylamide	59.7	95.0	68.1	2.75
octadecylamide	6.98	20.4	16.7	1.01
benzothiophene	128	128	156	129
4-methyldibenzothiophene	79.4	133	139	77.4
1-methyldibenzothiophene	24.9	44.6	41.3	14.8
3-&2-methyldibenzothio...	58.7	91.0	97.9	55.3
benzonaphthothiophene ...	82.6	98.7	166	167
C13-alk-2one	19.7	21.3	23.2	7.67
C14-alk-2-one	6.56	6.07	5.74	2.99
C15-alk-2-one	20.6	23.5	22.9	9.35
C16-alk-2-one	9.93	9.80	8.17	5.19
C17-alk-2-one	26.4	30.7	28.2	11.8
C18-alk-2-one	5.14	7.01	4.97	1.85
C19-alk-2-one	6.59	10.97	6.85	0.83
n-tetradecanoic acid, ...	4.45	N.D.	2.45	1.88
Pristane	46.1	52.1	36.2	13.4
pentadecanoic acid iso...	4.45	3.74	3.85	1.27
pentadecanoic acid iso...	2.71	3.46	2.06	1.96
n-pentadecanoic acid, ME	3.12	2.56	3.56	2.23
n-hexadecanoic acid, m...	24.7	20.3	17.4	9.14
n-heptadecanoic acid, ...	4.69	12.1	12.8	10.1
n-octadecanoic acid, m...	6.63	5.59	6.52	2.24
n-eicosanoic acid, met...	1.39	1.30	1.39	0.39
n-docosanoic acid, met...	2.49	1.61	1.62	0.80
n-tetracosanoic acid, ...	1.71	1.42	1.46	0.21
elemental sulfur	N.D.	30.94	27.2	N.D.

Average Depth (cm)	191.5	201.5	215	
Target Compounds	mg/kg	mg/kg	mg/kg	
C11 n-alk-1-ene	9.88	41.4	46.8	
C12 n-alk-1-ene	7.85	36.1	44.1	
C13 n-alk-1-ene	9.18	31.9	33.3	
C14 n-alk-1-ene	14.8	47.4	43.8	
C15 n-alk-1-ene	12.5	29.1	39.2	
C16 n-alk-1-ene	11.4	30.6	34.7	
C17 n-alk-1-ene	8.58	26.0	31.3	
C18 n-alk-1-ene	12.0	36.6	33.8	
C19 n-alk-1-ene	3.81	20.1	22.5	
C20 n-alk-1-ene	2.16	29.3	29.1	
C21 n-alk-1-ene	10.2	24.8	17.2	
C22 n-alk-1-ene	8.29	23.6	23.4	
C23 n-alk-1-ene	4.40	15.1	17.3	
C24 n-alk-1-ene	7.79	18.1	29.3	
C25 n-alk-1-ene	7.89	14.1	13.0	
prist-1-ene	28.8	43.0	72.2	
prist-2-ene	28.8	42.8	79.5	
C10 n-alkane	6.16	28.5	42.0	
C11 n-alkane	12.4	45.2	54.1	
C12 n-alkane	9.85	42.4	55.6	
C13 n-alkane	20.6	60.3	73.4	
C14 n-alkane	13.0	50.6	52.2	
C15 n-alkane	18.2	79.1	72.3	
C16 n-alkane	14.0	58.2	62.5	
C17 n-alkane	20.9	62.9	63.0	
C18 n-alkane	17.0	54.4	57.3	
C19 n-alkane	28.0	68.7	60.3	
C20 n-alkane	16.1	54.9	55.1	
C21 n-alkane	23.6	59.5	55.3	
C22 n-alkane	28.6	68.3	70.5	
C23 n-alkane	29.2	62.5	62.6	
C24 n-alkane	17.3	40.0	46.4	
C25 n-alkane	32.3	97.7	51.5	
C26 n-alkane	20.0	35.1	43.5	
C27 n-alkane	22.3	19.0	67.5	
C28 n-alkane	15.7	39.7	37.5	
C29 n-alkane	71.3	100	126	
C30 n-alkane	11.8	31.7	32.1	
C31 n-alkane	76.3	121	102	
ethylbenzene	17.9	138	206	
styrene	13.8	217	227	
n-propylbenzene	6.71	38.8	50.9	

n-butylbenzene	22.6	46.5	64.5	
n-pentylbenzene	18.8	52.8	42.7	
n-hexylbenzene	N.D.	37.4	38.6	
n-heptylbenzene	7.08	35.1	35.8	
n-octylbenzene	10.2	40.7	33.2	
n-nonylbenzene	7.03	30.9	33.7	
n-decylbenzene	10.4	48.0	32.0	
n-undecylbenzene	8.18	30.9	23.1	
n-dodecylbenzene	13.5	44.5	32.1	
n-tridecylbenzene	5.74	25.1	25.6	
n-tetradecylbenzene	6.86	28.1	24.5	
n-pentadecylbenzene	7.15	20.6	18.8	
n-hexadecylbenzene	N.D.	N.D.	N.D.	
6-phenylundecane	N.D.	3.39	N.D.	
5-phenylundecane	N.D.	N.D.	N.D.	
4-phenylundecane	N.D.	N.D.	N.D.	
6-phenyldodecane	N.D.	N.D.	N.D.	
5-phenyldodecane	N.D.	N.D.	N.D.	
4-phenyldodecane	N.D.	7.79	22.0	
6-phenyltridecane	N.D.	N.D.	N.D.	
Phytane	13.1	23.3	12.6	
5-phenyltridecane	N.D.	N.D.	N.D.	
4-phenyltridecane	N.D.	N.D.	N.D.	
naphthalene	708	849	581	
2-methylnaphthalene	189	285	242	
1-methylnaphthalene	96.1	123	111	
dimethylnaphthalenes	N.D.	N.D.	N.D.	
trimethylnaphthalenes	N.D.	N.D.	N.D.	
tetramethylnaphthalenes	N.D.	N.D.	N.D.	
fluorene	159	220	258	
methylfluorenes	10.9	36.1	43.9	
phenanthrene	2750	3505	3601	
anthracene	682	1114	1320	
3-methylphenanthrene	315	787	626	
2-methylphenanthrene	343	786	626.	
methylanthracene	91.4	243	244	
9-methylphenanthrene	209	575	535	
1-methylphenanthrene	272	574	551	
dimethylphenanthrenes	N.D.	N.D.	523	
retene	33.9	49.5	33.7	
fluoranthene	2631	3096	4512	
pyrene	3384	3692	5498	
methylpyrene isomers	N.D.	N.D.	N.D.	
dimethylpyrene isomers	N.D.	N.D.	N.D.	
benzo[a]anthracene	903	928	1883	
chrysene	923	1524	2641	

methylchrysene isomers	N.D.	N.D.	N.D.	
benzo[b]fluoranthene	18.6	228	755	
benzo[j]fluoranthene	52.9	157	581	
benzo[k]fluoranthene	15.6	27.6	171	
benzo[e]pyrene	13.4	122	618	
benzo[a]pyrene	3.94	77.9	264	
perylene	N.D.	N.D.	N.D.	
indenol[1,2,3-cd]pyrene	N.D.	N.D.	N.D.	
benzo[ghi]perylene	N.D.	N.D.	25.1	
dibenzoanthacene isomer	N.D.	N.D.	N.D.	
dibenzo[a,h]anthracene	N.D.	N.D.	N.D.	
C29 hopane (17a, 21B)	N.D.	N.D.	N.D.	
C30 hopane (17a,21B)	N.D.	N.D.	N.D.	
cholestene	0.13	N.D.	N.D.	
ethylcholestene	0.32	N.D.	0.47	
C27 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	
C28 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	
C29 sterane 5a, 14a, 1...	N.D.	N.D.	N.D.	
C2-alkylpyrrole	N.D.	36.5	39.4	
phenol	368	1511	1909	
2-methylphenol	15.0	66.3	107	
4&3-methylphenols	175	692	1000	
4-ethylphenol	140	381	549	
vinylphenol	392	970	1252	
guaiacol	64.9	139	151	
methylguaiacol	30.6	60.6	87.2	
ethylguaiacol	17.3	25.9	49.8	
vinylguaiacol	131	291	457	
vanillin	22.4	52.6	108	
eugenol	6.76	13.2	20.2	
cis iso-eugenol	6.88	12.3	18.8	
trans iso-eugenol	40.5	66.8	113	
acetovanillone	N.D.	N.D.	N.D.	
syringol	5.97	11.5	24.0	
methylsyringol	N.D.	N.D.	N.D.	
ethylsyringol	N.D.	3.56	8.64	
vinylsyringol	14.6	43.8	89.8	
syringaldehyde	N.D.	N.D.	21.4	
prop-1-enyl syringol	6.29	14.9	19.5	
prop-2-enyl syringol cis	N.D.	9.62	18.1	
prop-2-enyl syringol t...	22.9	51.4	94.5	
benzaldehyde	17.9	46.5	46.0	
benzaldehyde, methyl	85.6	233	260	
methylfurfural	213	494	405	
methylfuranone	N.D.	N.D.	N.D.	
2-methylcyclopentenone	N.D.	N.D.	31.0	

3-methylcyclopentenone	8.52	N.D.	61.5	
benzonitrile	20.8	86.8	84.8	
benzoacetonitrile	68.8	228	210	
benzenepropanitrile	72.2	207	240	
quinoline	10.1	45.2	68.4	
isoquinoline	32.7	124	126	
indole	203	654	732	
methylindole	44.6	149	217	
phenylpyridine	9.82	25.4	27.2	
carbazole	8.02	24.3	33.1	
diketodipyrrole	123	389	340	
cyclo-Pro-Pro-diketopi...	36.3	111	149	
n-tetradecanitrile	0.64	1.37	N.D.	
n-hexadecanitrile	4.00	8.25	0.94	
n-octadecanitrile	1.60	4.46	4.28	
tetradecylamide	3.83	7.25	12.2	
hexadecylamide	12.2	58.2	69.6	
octadecylamide	3.49	10.4	22.3	
benzothiophene	92.4	153	140	
4-methyldibenzothiophene	52.3	129	112	
1-methyldibenzothiophene	14.3	24.6	28.0	
3-&2-methyldibenzothio...	36.5	91.6	78.1	
benzonaphthothiophene ...	127	190	323	
C13-alk-2one	16.2	35.2	36.3	
C14-alk-2-one	4.52	17.3	11.8	
C15-alk-2-one	19.7	34.2	40.1	
C16-alk-2-one	7.64	15.8	19.1	
C17-alk-2-one	21.0	41.5	48.0	
C18-alk-2-one	2.62	10.4	8.01	
C19-alk-2-one	4.47	12.5	14.3	
n-tetradecanoic acid, ...	6.04	9.14	6.92	
Pristane	24.0	41.6	17.3	
pentadecanoic acid iso...	4.04	8.86	5.40	
pentadecanoic acid iso...	2.82	5.74	4.80	
n-pentadecanoic acid, ME	2.51	5.36	2.70	
n-hexadecanoic acid, m...	25.6	46.3	25.0	
n-heptadecanoic acid, ...	10.9	2.08	3.55	
n-octadecanoic acid, m...	7.77	13.7	6.84	
n-eicosanoic acid, met...	1.81	3.00	1.90	
n-docosanoic acid, met...	1.69	2.54	2.50	
n-tetracosanoic acid, ...	0.90	1.56	1.63	
elemental sulfur	49.7	13.7	N.D.	

Cesium -137	
Depth in cm	pCi/g
4.5	0.044
10.5	0.051
13.5	0.019
16.5	0.027
19.5	0.004
22.5	0.078
26.5	0.065
31.5	0.045
36.5	0.049
41.5	0.077
51.5	0.02
61.5	0.069
66.5	0.032
71.5	0.017
76.5	0.016
81.5	0.03

Depth in cm	Percent Loss on Ignition
4.5	16.06
7.5	13.92
11.5	16.27
16.5	14.29
19.5	20.32
22.5	16.68
26.5	15.84
36.5	14.97
36.5	16.53
41.5	21.71
61.5	17.68
66.5	17.99
71.5	17.72
76.5	21.92
86.5	16.78
91.5	16.90
91.5	19.45