

**USING SEDIMENT RECORDS TO DETERMINE SOURCES, DISTRIBUTION,
BIOAVAILABILITY, AND POTENTIAL TOXICITY OF DIOXINS IN THE
HOUSTON SHIP CHANNEL: A MULTI-PROXY APPROACH**

A Thesis

by

SHAYA MARIE SEWARD

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2010

Major Subject: Oceanography

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Approved by:

Chair of Committee,	Patrick Louchouart
Committee Members,	Robin Brinkmeyer
	Peter Santschi
Head of Department,	Piers Chapman

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ABSTRACT

Using Sediment Records to Determine Sources, Distribution, Bioavailability, and Potential Toxicity of Dioxins in the Houston Ship Channel: A Multi-Proxy Approach.

(May 2010)

Shaya Marie Seward, B.S., Texas A&M University at Galveston

Chair of Advisory Committee: Dr. Patrick Louchouart

Urban centers are major sources of contaminants to the surrounding air, water and soils. Above all, combustion-derived carbonaceous aerosols, especially black carbon (BC) and associated polycyclic aromatic hydrocarbons (PAHs), make significant contributions to the pollution in these systems. Here sedimentary records are used to produce a series of historical reconstructions of such contaminants to the Houston Ship Channel (HSC) system and compare these to point source inputs of hydrophobic organic contaminants (HOC). Analytical data on total organic carbon (TOC), BC, PAHs, dioxins and lignin (likely discarded from a pulp and paper mill along the Channel) were determined. This multi-proxy approach revealed that over the last several decades, HOC inputs to the system have been derived from a complex mixture of combustion processes, industrial point-sources, and oil spills. In particular, widespread dioxin contamination was observed throughout the study region with a particular site of the HSC showing total concentrations over 20,000 pg/g and 5000 pg toxic equivalent (TEQ)/g dry weight of sediment. Using two models based on sorption constants of total

OC and BC, porewater concentrations were estimated to be lower than expected, at 20 pg/L and 5 pg TEQ/L. These values, however, are recognized as being extremely high for freely dissolved concentrations in porous media. The pulp and paper waste pit has recently been declared a Superfund site based on dioxin concentrations alone. The relationship between lignin biomarkers and dioxins observed in these sediments confirms that discharges of pulp and paper effluents were responsible for such high dioxin levels. Concentrations of BC, amorphous OC, and TOC were then used to calculate sediment binding of dioxins in sediments of the HSC. Our study found BC to be extremely low in HSC sediments (0.04 to 0.20%) indicating minimal dioxin sorption capacity. This suggests strong potential for fluxes of dioxins from sediments to the water column both through passive diffusion and physical mixing during natural and anthropogenic sediment remobilization events in this shallow system (hurricanes, storms, and dredging). The purposeful addition of BC to these sediments might be promising as a remediation strategy.

DEDICATION

I have a premonition
That soars on silver wings.
It's a dream of your accomplishment
Of many wondrous things.

I do not know beneath which sky
Or where you'll challenge fate.

I only know it will be high!

I only know it will be great!

-Anonymous

For Mom

For Dad

My eternal gratitude and love

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CHAPTER I

INTRODUCTION

BACKGROUND INFORMATION

Today more than half of the world's population lives within 100 miles of a coast (Hinrichsen, 1998) and more than two thirds of all human settlements in coastal zones are urban (Balk, 2005). Urban centers are major sources of pollutants to the environment due to their rapid growth and industrialization. Houston, Texas is no exception. Located near the coast, Houston presently is the nation's sixth most populous metropolitan area (Metropolitan..., 2010). According to the Greater Houston Partnership (2005), if the city of Houston were a state, it would rank 36th in population with its over 2 million residents. With over 5 million inhabitants in its metropolitan area, it would rank 21st if it were a state. Still growing in population, the Houston metropolitan area gained more than 950,000 people between the years 1990 and 2000. The city's population rose by about 27 percent to over 4 million during that period. According to Woods and Poole Economics, the Houston metropolitan area should rank sixth in population growth among the nation's metropolitan areas from 2000 to 2030, with an increase of 2.66 million people.

Due to Houston's proximity to the coast, much of the pollutants caused by human activities in the city have the potential to be focused on the ecologically and economically sensitive coast. These contaminants include, but are not limited to,

This thesis follows the style of Chemosphere.

combustion-derived particulate matter such as black carbon (BC) and associated polycyclic aromatic hydrocarbons (PAHs), as well as volatile organic compounds. These compounds are released into the surrounding air, water, and soils. Due to Houston's size, population, and industrialization level, the total inputs of these pollutants are despite recent decades of environmental regulations.

Contained within the limits of the Houston metropolitan area are several large fossil-fuel electric power plants and one of the world's largest petrochemical complexes (Texas, 2009). Several programs are currently focused on air quality monitoring in the Houston area to determine the importance of combustion on particulate matter emissions (NASA, 2009). Still, however, little is known about the historical evolution of BC emissions in the Houston system over the 20th century. Therefore, due to Houston's size and significance at the national level, it is a system of interest for the study of urban centers in the United States and an ideal candidate for establishing a historical baseline of BC emissions for the southern United States.

The water systems around Houston, especially the Houston Ship Channel (HSC) and its tributaries, also receive contaminants from vascular plants. Since they are basically restricted to land, vascular plants comprise the main source of terrigenous organic matter (TOM) to the ocean (Gough et al., 1993). Rivers transport natural inputs of lignin (a component of vascular plants) in particulate and dissolved forms to watersheds. Additional inputs of TOM to the coastal environments include non-natural or anthropogenic ligneous materials, primarily released through municipal sewages, land

use (agriculture and forest exploitation), and industrial effluents (wastes) (Louchouart et al., 1999).

Pulp mill effluent is considered a coastal contaminant (Macdonald et al., 1992) because it leads to oxygen limitation in the waters and it contains polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) (dioxins), which are persistent environmental contaminants (Santschi et al., 2009). Seventeen dioxin group members cause a variety of immunological, biochemical, and reproductive effects in animals and are suspected carcinogens in humans (Bailar, 1991). Their primary sources, besides pulp and paper mills, include metal smelting, herbicide production, and waste incineration (Buekens et al., 2000; Rappe et al., 1987).

GOALS AND OBJECTIVES

One purpose of this work was to build environmental understanding of historical inputs of contaminants to the Houston Ship Channel (HSC) system by analyzing sediment records. Another purpose was to determine the sources and fate of hydrophobic organic contaminants (HOCs) to the system. Temporal and spatial reconstructions were made of HOC inputs to the HSC using multi-proxy indicators. This approach was used to evaluate the potential redistribution of known point-source inputs throughout the system. The final purpose was to assess the theoretical sorption capacity and potential bioavailability of dioxins present in diverse sedimentary environments of the HSC. This

was done using two different empirical sorption models based on sorbent characteristics and concentrations of organic carbon and black carbon in sedimentary systems.

CHAPTER II

SOURCES AND FATE OF HYDROPHOBIC ORGANIC CONTAMINANTS TO THE HOUSTON SHIP CHANNEL SYSTEM: A MULTI-PROXY APPROACH

INTRODUCTION

Environmental Contaminants

Both the incomplete combustion of biomass and fossil fuels (petroleum, natural gas, and coal) and vegetation fires (Lima et al., 2003; Elmquist et al., 2007) lead to the formation of black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs). BC is neither a single chemical compound nor a homogeneous group (Elmquist et al., 2006). BC has a variety of physical and chemical properties, varying from slightly charred biodegradable material to extremely condensed refractory soot (Elmquist et al., 2006). Masiello (2004), Hammes et al. (2007), and Kuo et al. (2008) improved our understanding of BC by better defining its characteristics and sources. The characteristics included temperature of formation, particle size, sources, reservoirs, and reactivity. Even with these distinctive traits, all BC matter originates from the same process of combustion (Elmquist et al., 2006).

BC has adverse effects that include altering the chemical and physical properties of the atmosphere (Jacobson, 2001) and affecting Earth's radiative heat balance (Elmquist et al., 2006; Ramanathan and Carmichael, 2008). In the atmosphere BC absorbs and scatters solar radiation, contributing to both global warming and changes in cloud formation processes (Jacobson, 2001; Ramanathan and Carmichael, 2008). This

results in BC being the second most important greenhouse substance, after carbon dioxide (Jacobson, 2001; Ramanathan and Carmichael, 2008). BC has also been shown to negatively impact human health by causing respiratory diseases such as bronchitis and cancer and sometimes causing premature death (Highwood and Kinnersley, 2006).

One positive aspect of BC is its ability to sometimes act as a buffer against other contaminants in the system (Cornelissen et al., 2004). In aquatic sediment systems, several hydrophobic organic contaminants sorb to BC 10-1000 times more strongly than to other organic matter (Cornelissen et al., 2004). This changes the solid water partitioning of the hydrophobic contaminants, and thus lowers their bioavailability (Elmqvist et al., 2006). Therefore, despite its negative impact in the atmosphere, the presence of BC in aquatic environments and soils may act as strong geosorbents for organic contaminants and thus reduce their mobility in bioactive reservoirs.

This may be particularly important for compounds such as PAHs and dioxins that are co-generated with BC (Lohmann et al., 2005). As observed in the few studies that have been performed, the presence of BC most likely reduces the bioavailability of PAHs (Burgess and Lohmann, 2004; Cornelissen et al, 2008a). And in the study by Cornelissen et al. (2008a), it was shown that strong sorption to BC ought to be included when making ecotoxicological risk assessments or when modeling the transport of PCDD/Fs in soil to groundwater.

PAHs also have adverse effects. They are suspected carcinogens and mutagens (Lima et al., 2003), meaning they could promote cancer and mutations in organisms. They can be released from petrogenic (oil spill and oil seepage), biogenic (diagenetic

processes), and pyrogenic sources (fossil fuels combustion and wildfire) (Yunker et al., 1996; Lima et al., 2005; Guo et al., 2007). Still, anthropogenic sources such as vehicles, industrial processes, heating and power plants, and refuse and open burning are regarded as the main sources to the environment (Van Metre et al., 2000). Sediment records suggest that anthropogenic activities started introducing PAHs into the environment in the United States of America nearly 100 years ago (Gschwend and Hites, 1981). This caused PAH quantities from that point forward to surpass background levels from natural sources such as natural oil seeps and wildfires.

Even though PAHs only make up about 20% of total hydrocarbons in petroleum (NRC, 1985), they are the main reason for its toxicity (Park et al., 2001). As a result of this toxicity and their constant release to the environment, PAHs are receiving increasing attention (Yunker and Macdonald, 2003). Their concentration and sources are being monitored more closely (Lima et al., 2005).

Although some combustion-derived PAHs are deposited near their source, atmospheric transport can move substantial quantities of these compounds to distant locations (Molina and Molina, 2004), causing them to be ubiquitous in the environment (Lima et al., 2003). Different sources of PAH production result in different molecular distribution patterns (Lima et al., 2005). These patterns can then be used as diagnostic ratios to reconstruct the sources and/or processes responsible for PAH inputs to the environment.

Another marker of contamination to HSC waters comes from vascular plants. These higher plants are made up of a group of relatively recalcitrant molecular organic

compounds. These compounds include cellulose and lignin, the first and second most abundant biomacropolymers on Earth, respectively (de Leeuw and Largeau, 1993). One source of lignin to the HSC system is pulp and paper mills.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) (dioxins) are also produced in pulp and paper mills during the bleaching of pulp with large quantities of chlorine through either chlorination of dibenzo-furan (DBF) and dibenzo-*p*-dioxin (DBD) present in the pulp or through chlorination of non-extractable precursors (Dimmel et al., 1993). DBD/F has several potential sources, with lignin being the most evident given that it already has oxygenated aromatic rings (Dimmel et al., 1993). Paper mill exports contain dioxins and include wastewater sludge, treated wastewater effluent, and bleached pulp (Amendola et al., 1989). These exports have the potential to be released into the environment.

Other sources of dioxins include steel and iron manufacturing, herbicide production, pesticide use, use of leaded gasoline in vehicles, non-ferrous metals production and recycling, wood treatment plants, commercial and residential heating systems, and hazardous and municipal solid waste (MSW) incineration (Buekens et al., 2000; Rappe et al., 1987; Wenning et al., 1992). Other sources to water systems include storm drains, sewer overflows, and atmospheric deposition of particulates (Wenning et al., 1992).

Dioxins are detected as a mixture of 135 polychlorinated dibenzo-furans (PCDFs) and 75 polychlorinated dibenzo-*p*-dioxins (PCDDs) congeners (Industrial..., 2005). The components of such a PCDF and PCDD mixture are frequently called a

dioxin “fingerprint” (Buekens et al., 2000). Fingerprints of dioxins assist in source identification, in atmospheric transport and transformation studies, and in understanding of formation mechanisms (Buekens et al., 2000). Some dioxins have harmful properties. This depends on the amount and position of chlorine atoms in their chemical structure (Executive..., 1998). Seventeen of these, including 2,3,7,8 tetra- to octa-chlorine substituted congeners (see Table 1 for specific compounds of interest), are harmful to the health of animals and humans (Bailar, 1991). Table 1 presents the 17 congeners that were included in this study.

Table 1. General nomenclature for dioxins.

Abbreviation	Compound
2,3,7,8-TeCDD	2,3,7,8-Tetra-chlorinated dibenzo- <i>p</i> -dioxin
1,2,3,7,8-PeCDD	1,2,3,7,8-Penta-chlorinated dibenzo- <i>p</i> -dioxin
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-Hexa-chlorinated dibenzo- <i>p</i> -dioxin
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-Hexa-chlorinated dibenzo- <i>p</i> -dioxin
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-Hexa-chlorinated dibenzo- <i>p</i> -dioxin
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-Hepta-chlorinated dibenzo- <i>p</i> -dioxin
OCDD	Octa-chlorinated dibenzo- <i>p</i> -dioxin
2,3,7,8-TeCDF	2,3,7,8-Tetra-chlorinated dibenzofuran
1,2,3,7,8-PeCDF	1,2,3,7,8-Penta-chlorinated dibenzofuran
2,3,4,7,8-PeCDF	2,3,4,7,8-Penta-chlorinated dibenzofuran
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-Hexa-chlorinated dibenzofuran
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-Hexa-chlorinated dibenzofuran
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-Hexa-chlorinated dibenzofuran
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-Hexa-chlorinated dibenzofuran
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-Hepta-chlorinated dibenzofuran
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-Hepta-chlorinated dibenzofuran
OCDF	Octa-chlorinated dibenzofuran

Houston Ship Channel: History and Economic Growth

Oil was discovered in Texas during the early 20th Century (Sibley, 2008). The early 1900s saw a steady growth in an industrial oil infrastructure in Texas, and its consolidation in Houston. In 1905, Joseph S. Cullinan, who had experience in all phases of oil development and marketing as an employee and manager for Standard Oil and as founder of the Texas Co. (later Texaco), wrote to a colleague in New York that “...Houston seems to me to be the coming center of the oil business in the Southwest” (Houston in 1900..., 2002).

Cullinan then established the criteria for a good Texas refinery location: large acreage, an abundance of fresh water, deepwater shipping, and shelter from storms and floods (Houston in 1900..., 2002). With the Houston Ship Channel (HSC) being the most viable choice, the industrialization of the Houston water front boomed. The HSC had been in use since January 1837 as a link between interior Texas and the Gulf of Mexico (Sibley, 2008). Due in part to the oil industry, it has grown to become one of the busiest waterways in the United States (Sibley, 2008).

By 1930, eight oil refineries operated along the HSC, running 194,000 barrels of crude per day (Houston in 1900..., 2002). By the 1970s, 4,500 ships passed through the Channel every year (Sibley, 2008). This heavy traffic and its potential adverse effects on the system troubled environmentalists. In the 1980s and 1990s the Channel received even more attention as multiple explosions, oil spills, and collisions between freighters, tankers, and barges occurred in the Channel (Sibley, 2008).

Today, the state of Texas leads the United States in both crude oil production and refining capacity. Texas is home to 26 petroleum refineries, with most being located near major ports along the Gulf of Mexico coast (Texas, 2009). These can process up to 4.8 million barrels of crude oil per day and account for more than one-fourth of total U.S. refining capacity. Refineries in the Houston metropolitan area, including the Baytown refinery (the Nation's largest refinery) make up the largest refining center in the United States (Texas, 2009).

The industrial area of Houston located along the Ship Channel produces the highest emissions of fine soot-BC in the Houston-Galveston area (Fraser and Lakshmanan, 2000). These BC emissions are derived from petrochemical operations, fuel oil combustion, and diesel transportation (Fraser et al., 2003). In addition, local sources and onshore breezes (Darby, 2005) frequently push BC plumes northward over the city and its surrounding area (Li et al., 2005).

Another industry that reached the HSC area was the Texas pulp and paper mill industry, which began in 1863 in an attempt to produce enough newsprint and writing papers to relieve the critical shortages that resulted from the Civil War (Burkhart, 2008). The modern era of large pulp and paper mills in Texas began in the 1930s, during the time when Houston became the center of Texas' lumber industry (Houston in 1900..., 2002). On 18 February 1937, the Champion Coated Paper Company of Ohio built a sulfate- and chlorine-bleaching pulp mill along the Houston Ship Channel at Pasadena (Champion Hamilton mill chronology, 1893-2005, 2006). The Champion mill later

expanded to include paper machines, and by the late 1980s it produced 750 tons of bleached coated and uncoated papers every day (Burkart, 2008).

The significant environmental impacts of pulp and paper manufacturing result from the pulping and bleaching processes. In certain processes, nitrogen oxides and sulfur compounds are released into the air, and chlorinated and organic compounds, metals, and nutrients are released into the wastewaters (Pulp and Paper Mills, 1998). The most significant environmental issues are the release of chlorine-based organic compounds (from the applications of chlorine in the bleaching process) and of other toxic organics (Pulp and Paper Mills, 1998).

Solid waste materials such as waste paper and bark produced during the processes can be reused (Pulp and Paper Mills, 1998). However, it was not until the end of 1989 that paper mills in North American began recycling all of their solid papermaking waste (Champion Hamilton..., 2006). Before this, pulp and paper mills released their wastes directly as effluents into water bodies. The market of the pulp industry collapsed in early 1996, causing the pulp and paper mill in Pasadena to close its doors in January 1999 (Jensen et al., 1999). Even with the paper mill no longer in use and no longer producing contaminants, the environment was already damaged from many years of solid waste being released into the surrounding area of the HSC during its operation.

In the 1980s, pulp and paper mills were found to be important sources of dioxins to the environment (Macdonald et al., 1998). Dioxins are toxic and have a tendency to bioaccumulate in fish and benthic invertebrates (Wenning et al., 1992). These

compounds are persistent in the environment due to their very long half-life and increasing number of sources (Wenning et al., 1992). Therefore, the migration of these compounds has been a subject of considerable concern.

Environmental Impacts and Remediation Efforts

Combustion-derived carbonaceous aerosols are well recognized as significant contributors to poor air quality in large urban systems (Molina and Molina, 2004), as explained above. Therefore, understanding the sequential trends of combustion sources and emissions over time is essential to the development of effective environmental policies. Some policies evaluate how exposure to combustion products influences human health. In turn, these policies can help determine how the environment, and hence human health, can be improved in the future.

A complex set of combustion proxies can be used to reveal major changes in the types of atmospheric aerosols produced from certain fuel sources and processes over time (Lima et al., 2005). These changes include oil vs. coal vs. wood and fossil fuel combustion vs. biomass burning, and have been due to climate change and social development. Coal in particular has been a major source of combustion-derived aerosols since the early 20th Century. Biomass and oil combustion have also increased, becoming significant sources of atmospheric contamination.

Despite its importance, little is known about natural or anthropogenic historical emissions of BC and its deposition (McConnell et al., 2007). Because of the potentially wide-ranging impacts on natural and human systems, it is paramount to gain a better

understanding of the influence of combustion processes on climate and its feedback loops. Actual BC values from historical sedimentary records are vital to climate modelers. These records provide datasets against which the large ranges of theoretically modeled estimates of BC emissions can be compared.

In addition, concern over the 17 toxic dioxin congeners (2,3,7,8 tetra- to octa-chlorine substituted congeners) has resulted in the characterization of the quantities and dispersal of these congeners in sediments from water systems across the world (Wenning et al., 1992). It is also important to establish the source and the history of dioxins. Since pulp and paper mills are a major source of dioxins, this information is essential in recognizing the role they play in the environment, in creating and implementing suitable monitoring strategies, and in forecasting the effect of remedial action taken by the mills (Macdonald et al., 1992).

Most industrialized countries have greatly reduced their use of products contaminated by PCDD/Fs and other persistent organic pollutants. One example is polychlorinated biphenyls (PCBs), which were used as heat-resistant coolants or insulators in electrical equipment, as solvents, plasticizers, and degreasers, and in numerous industrial processes. Regarding toxicity, a group of roughly a dozen PCB congeners have similar structures to the highly toxic 2,3,7,8-tetra-chlorinated dibenzo-*p*-dioxin (TeCDD). PCBs also have effects similar to dioxins on immune systems and fetal development. (Industrial..., 2005) Due to their wide range of toxic effects, restrictions on industrial uses of PCBs began around 1971. By 1977, the import, manufacture, and many non-electric uses of PCBs were banned in North America. (Industrial..., 2005)

PCBs have also been phased-out as dielectric fluid in transformers and capacitors in most countries since the 1980s (Rappe et al., 1987).

Another example is 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), which contains high levels of 2,3,7,8-TeCDD. 2,4,5-T used to be a major herbicide in most countries, but now it is only produced and used in New Zealand (Rappe et al., 1987). In addition, new technologies are now available to reduce the emissions from MSW incinerators, reducing the amount of dioxins entering the atmosphere (Rappe et al., 1987). Still, with all these preventative measures to reduce contamination by dioxins, the only true control measure for reducing PCDD/Fs from pulp and paper mills is possibly to lessen or eliminate the quantity of applied chlorine (Dimmel et al., 1993).

Objectives

Use a multi-proxy approach including the analyses of OC and BC, PAHs, and lignin oxidation products (LOPs) to assess the potential source(s) of dioxins to the HSC system. Then evaluate the redistribution of known point-source inputs throughout the entire system.

METHODS

Sampling

A total of 55 sediment cores were previously collected in 2004 from northwest Galveston Bay, the Houston Ship Channel, the lower San Jacinto River, and the lower Trinity River floodplain, Texas (Yeager et al., 2007). Three of these, two subaqueous cores collected by divers using PVC sleeves (11270 and 11193) and one terrestrial core collected from the wetlands adjacent to the Trinity River in an aluminum sleeve (FW1), were used in this study (shown in Figure 1). Seven additional cores were collected by Kevin Yeager and his group by divers using PVC sleeves (Santschi et al., 2009). One such core (SG-6) was included in this study (Figure 1). Each core was sub-sampled at centimeter intervals for the upper 50 cm and at 2 cm intervals thereafter. These subsamples were freeze-dried, ground in a mortar and pestle, homogenized, labeled, and stored for later analyses. Finally, a series of sediment grab samples were collected in 2004 (Figure 1) and analyzed by a research group at the University of Houston (Rifai et al., 2005).

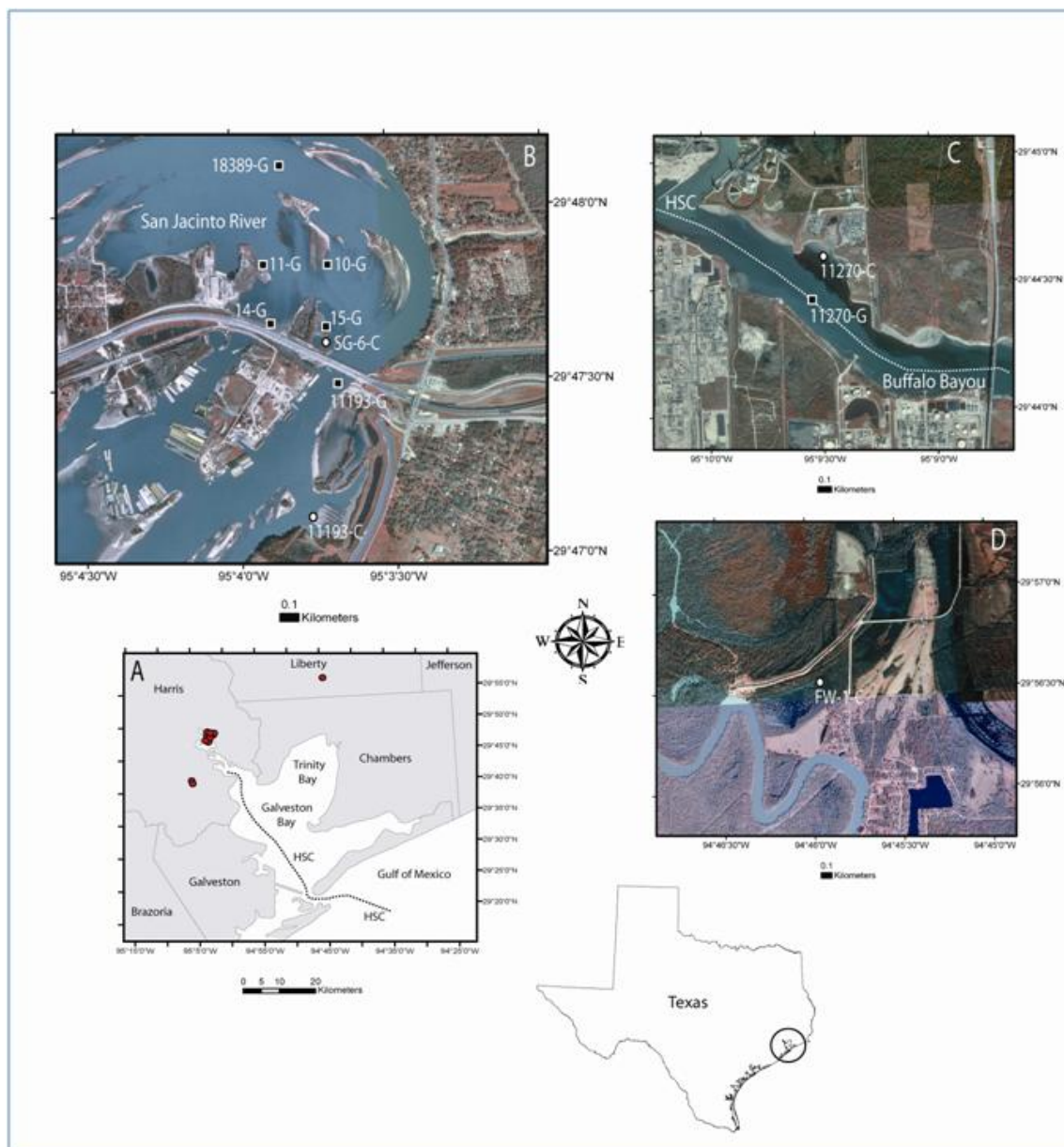


Figure 1. Sampling sites within the HSC and the Trinity River floodplain. The sites with an “S” represent sediment cores (Yeager et al., 2007; Santschi et al., 2009). The sites with a “G” represent grab samples (Rifai et al., 2005).

Previous Determinations

The samples from the three HSC cores were already analyzed for physical properties (grain size and porosity) and radionuclides (^7Be , ^{137}Cs , and ^{210}Pb) (Yeager et al., 2007). Some dioxin values were already determined for these samples from a previous study using EPA Method 1613B (Yeager et al., 2007), while the rest of the dioxin samples (core SG-6) were analyzed by Dr. Jermiah Shen (National Taiwan University) using the same method. The dioxin fingerprints of the grab samples are also presented as a comparison to the core samples analyzed in the present study. Some SG-6 samples will be analyzed for dioxins in the near future for further work related to this project.

Elemental Analyses

For soot-BC determinations on the samples, the Chemothermal Oxidation method at 375°C in air (CTO-375 method) was used (Louchouart et al., 2007). To start, 30-40 g of each dried sample and National Institute of Standards and Technology (NIST) standard reference material (SRM) 1944 (New York/New Jersey Waterway Sediment) and SRM 1941b (Organics in Marine Sediment) (used for verification of values) were placed in crucibles and the initial weights were recorded. After being oxidized in a furnace for 24 h at 375°C, the final weights were recorded. The difference between the pre-combustion weight and the post-combustion weight is equivalent to mass lost. The mass lost divided by the pre-combustion weight gives the percent lost.

Afterwards, subsamples (~10 mg) of the heat-treated samples were weighed into open silver-foil capsules (5 x 9 mm) and the rest was saved for later analyses.

Carbonates were removed from the samples through acid fumigation (Hedges and Stern, 1984). Specifically, the capsules were inserted into wells of a microtiter plate and the plate was then placed in a desiccator with a beaker of concentrated hydrochloric acid (HCl). The samples and standards were exposed to HCl vapor for 24 h to remove carbonates (Lohmann et al., 2005). After drying the capsules for 24 hours at 60°C, they were removed from the plate and crimped closed (Hedges and Stern, 1984). After correction for mass loss during combustion, the remaining carbon was quantified as BC through combustion at 1000°C on a Perkin-Elmer Series 2400 Elemental Analyzer (CHNS/O) (EA).

To determine total organic carbon content (OC), untreated samples were also acidified with HCl to remove carbonates and analyzed on the elemental analyzer. Replicate analyses of sediments and SRMs were performed to determine accuracy and variability. The EA also gives a reading for the amount of total nitrogen (without acidification) present in the samples (Goñi et al., 2000). This data was used for the calculation of the molar C/N ratios.

PAH Extraction and Analysis

The analytical procedure used for PAH extraction and quantification in this study followed those stated in Park et al. (2001) and Kuo (2009). Included in each analysis were three reference samples (two blanks and SRM 1944) to determine variability and accuracy. Briefly, the dried sediment samples and reference samples were spiked with PAH surrogates (d8-napthalene, d10-acenaphthene, d10-phenanthrene, d10-chrysene, and d12-perylene) and extracted by a Dionex Accelerated Solvent Extractor (ASE) 200 with 100% dichloromethane (CH_2Cl_2) at 1500 psi and 100°C. Activated copper was then added to the extracts to remove elemental sulfur. The extracts were then boiled in a 55°C water bath to reduce their volume and were exchanged into hexane (C_6H_{14}). The concentrated extracts were then eluted through a pre-rinsed aluminum oxide (Al_2O_3) column with 35 mL petroleum ether for cleanup. The resulting extracts were further concentrated and transferred to hexane. PAH internal standards (d10-fluorene and d12-benzo(a)pyrene) were added prior to GC-MS analysis on a GC/MS-MS to determine the recoveries of surrogates in each of the samples.

Lignin Analysis

The terrigenous biomarker analyses were performed using the CuO oxidation method (Louchouart et al., 2010). Two reference samples (a duplicate sediment sample and SRM 1944) were included in each analysis. In short, a sediment amount providing 2–4 mg OC was oxidized under alkaline conditions with copper (II) oxide (CuO) at 155°C for 3 hr in pressurized stainless steel mini-reaction vessels. Upon opening the

reaction vessels, known amounts of recovery standards were added to the solutions (Goñi et al., 2000; Louchouart et al., 2009). The aqueous solutions were then acidified to pH 1 with 6 N HCl and extracted three times with ethyl acetate ($\text{CH}_3\text{CH}_2\text{OC(O)CH}_3$). The extracts were dried with sodium sulfate (Na_2SO_4) and evaporated to dryness using a solvent concentrator. The CuO reaction products were then re-dissolved in 200–500 μL of pyridine and a subsample was derivatized with *bis*-trimethylsilyl trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) (Louchouart et al., 2010). The lignin oxidation products (LOPs) obtained by this method were finally quantified by Gas Chromatography-Mass Spectrometry on a Varian 4000 GC/MS-MS under full scan mode.

Oxidation of lignin by the CuO oxidation method produces 11 main phenolic monomers, which can be divided into four families: cinnamyl (C), syringyl (S), vanillyl (V), and p-hydroxyl (Hedges and Ertel, 1982). Since p-hydroxyl phenols can also be produced by non-lignin components of vascular plants (Wilson et al., 1985), they were excluded from the study.

EXPECTED RESULTS

Even though non-point source inputs are also very important, it has been shown that most pollution to the Houston area will come from the region's "hot spots." These include the industrial areas located along the Houston Ship Channel (Where does Houston's...?, 2003), resulting in an acute pollution problem in some areas of the HSC.

In the work by Yeager et al. (2007), the HSC sediments showed continuous deposition over the last 100 years. The sediments also revealed accumulation rates of radionuclides and dioxins at orders of magnitude higher than atmospheric fallout fluxes measured in the region (FW1), pointing to large inputs from surface runoffs (Yeager et al., 2007). Due to the high predictability of deposition and accumulation rates found in this previous study, the HSC is an ideal location for reconstructing atmospheric deposition of pollutants for the Houston area over the past century.

Historical concentrations of BC and PAHs in the HSC sediments should show peaks between 1908 and 1916. During this period, annual coal production declined as markets were lost to oil and gas produced from several fields discovered in Texas (State Coal..., 2009). There was a movement of major oil companies into Houston, resulting in Texas railroads being powered by first wood, then coal, and later oil, similar to street electric railways, brickyards, breweries, ice factories and cottonseed mills (Houston in 1900..., 2002). The oil industry in Texas centered in on Houston.

High BC and PAH values are also expected around 1930 when industrialization peaked on the waterfront. Peaks are also expected during the late 1950s to early 1960s due to an increase in oil usage after World War II and the introduction of passenger vehicles to the broader public during the 1950s (Elmqvist et al., 2007). Recent values of these contaminants in the Ship Channel area should also be relatively high due to greater inputs of combustion by-products to the air- and watershed from continued growth in industrial activity of the Channel (Folsom Murphy and Allen, 2005) and rampant urban sprawl in the Houston area (Van Metre and Mahler, 2005).

Therefore, high values for BC and PAHs are expected throughout the cores (except at FW1 located in the wetlands) since emissions have almost always been high over the time period of this study. Between the cores, highest values are expected in UH11270 due to its closer proximity to the HSC.

If pulp and paper mills were a significant source of dioxins to the aquatic environment of the HSC, then these contaminants should co-occur with unambiguous markers of pulp mill effluents. Lignin is a known by-product of pulping and is highly enriched in mill effluents discarded into aquatic systems (Louchouart and Lucotte, 1998; Louchouart et al., 1999). Therefore, it is expected that lignin oxidation products will correlate with pulp-derived dioxins in sediments. Or there should at least be some form of relationship between lignin and dioxin concentrations due to their co-generation. Therefore, there is a possibility that lignin could be analyzed as a more cost effective screening method for occurrence of dioxin (an expensive analytical method) in pulp and paper mill impacted systems. The analysis should still show the effects of and the extent of the waste products from the mills.

Between the sediment cores, highest values for lignin are expected in SG-6 since it is a site of pulp and paper waste disposal. In contrast, the surface of FW1 should also show high lignin values but low dioxin values due to the direct deposit of woody litter materials at the surface of sediments and its location in wetland upstream from industrial and urban emissions, respectively.

Between the cores, highest values for dioxins are expected in SG-6 due to its location at the site of a former paper mill's sludge waste ponds. The disposal activity of

this sludge waste was greatest in the early to mid-1960s (Figure 2). Unofficial reports claim that the sinking of a paper mill barge and the dumping of several tons of sludge directly into the HSC occurred during this time (Santschi et al., 2009; TCEQ). Therefore, for SG-6, highest values of lignin and dioxins are expected to be found between 1960 and 1970.

Since the pulp and paper mill has closed, the area where the sludge ponds are located has subsided and the levees around the ponds containing the sludge have eroded (Figure 3). The loss of these levees could thus lead to the redistribution of dioxin contaminated sludge and sediments to a large section of the HSC and Galveston Bay (Santschi et al., 2009; TCEQ).

Because different industrial processes produce PCDD and PCDF in different proportions, congener ratios can be used as first-hand indicators of source fingerprints of dioxins in sedimentary systems. Past studies have shown that total proportion of PCDD tends to be smaller than that of PCDF in thermal industrial processes (Buekens et al., 2000). Also, as shown by Dimmel et al. (1993) in their pulp chlorination work, more tetra-CDF isomers were observed than tetra-CDD isomers, with the 2,3,7,8-substituted congeners being the most prominent.

Therefore, PCDD congeners should be less prevalent than PCDF congeners in the sediments at the pit site, with the majority being 2,3,7,8-substituted and TeCDF having the greatest presence. Levels of 2,3,7,8-TCDD are expected to be between 10 and 400 pg/g based on past work of bleached kraft pulp and paper mill wastewater sludges (Amendola et al., 1989; Clement et al., 1989).



Figure 2. San Jacinto River aerial photo from 1964. (Red circle shows position of the sludge waste emplacement). (San Jacinto..., 2008)



Figure 3. San Jacinto River aerial photo from 2005. These photos show a large increase in human activity along the water front and dramatic changes at the SG-6 site since 1964. (San Jacinto..., 2008)

RESULTS AND DISCUSSION

Historical Inputs to Sediments

FW1

Core FW1 (N29.9425°, W94.7661°) was collected on December 10, 2004 in a wetland adjacent to the Trinity River on the east side of the HSC. Figure 4 to Figure 7 show the vertical profiles of the chemical compounds that were included in this study for this station, and the corresponding values are listed in Table 2. OC decreases rapidly from maximum concentrations in the surface 1-2 cm (11 to 7%, respectively) to near negligible amount below 8 cm depth (< 1%). The greatest amount of OC for all the sediment cores in this study (11%) was found in this surface sediment layer. The same tendency is observed for lignin-derived phenols ($\Sigma 8$, mg/g), which is used as a representation of the lignin present in the samples (Louchouart et al., 1999; 2010), drop ten-fold (from ~3 mg/g to < 0.3 mg/g) over the same depth range (Figure 4). BC was low (~ 0.1-0.2%) and varied greatly throughout the depth of the core (Figure 5). Dioxins (2,3,7,8 TCDD and TCDF), similar to OC and lignin, were highest in the surface layer (1.4 pg/g, or parts per trillion (ppt)) and decreased with depth (Figures 6 and 7). The lowest dioxin values out of all the cores were found at this site (~ 0.4 pg/g).

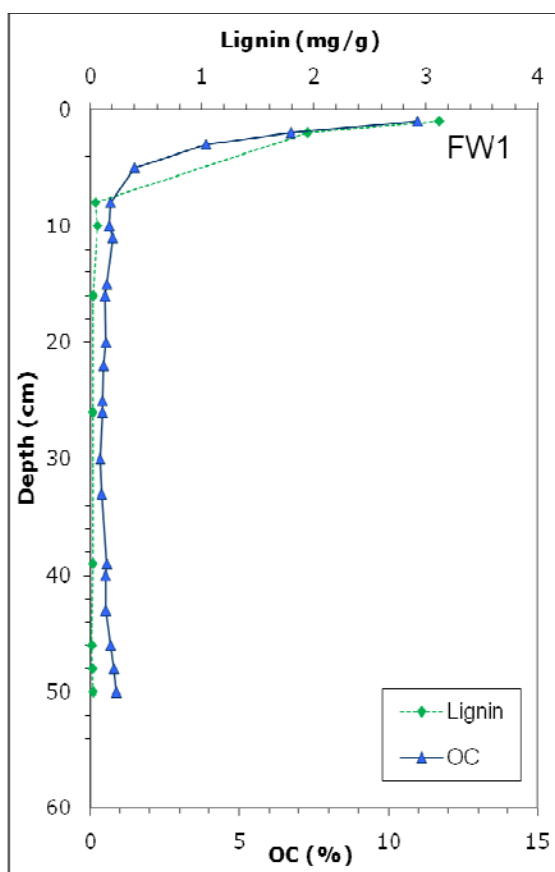


Figure 4. Vertical profile of lignin phenols ($\Sigma 8$; mg/g) and OC (%) for station FW1.

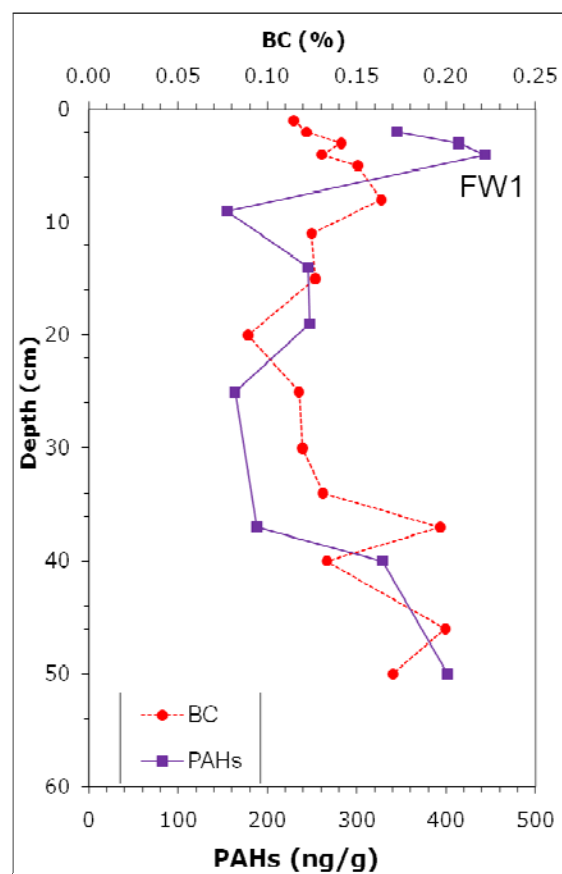


Figure 5. Vertical profile of PAHs (ng/g) and BC (%) for station FW1.

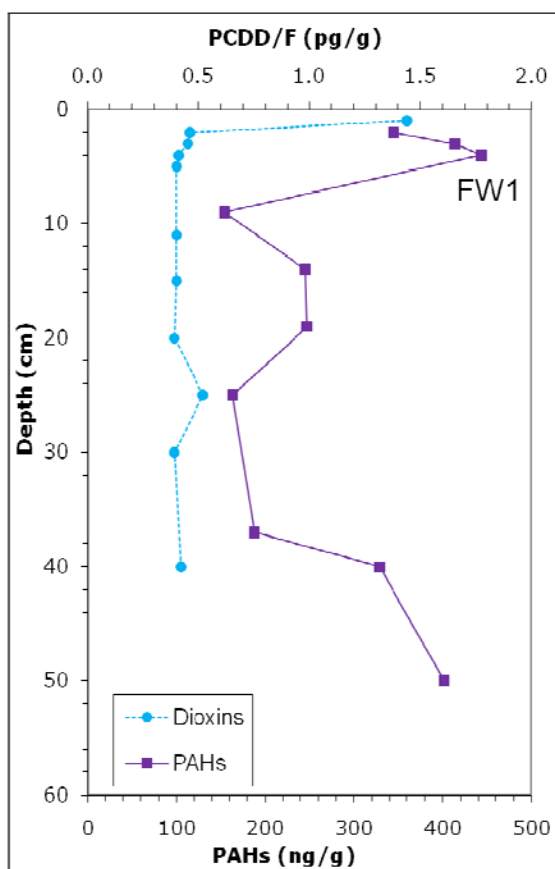


Figure 6. Vertical profile of PAHs (ng/g) and dioxins (pg/g) for station FW1.

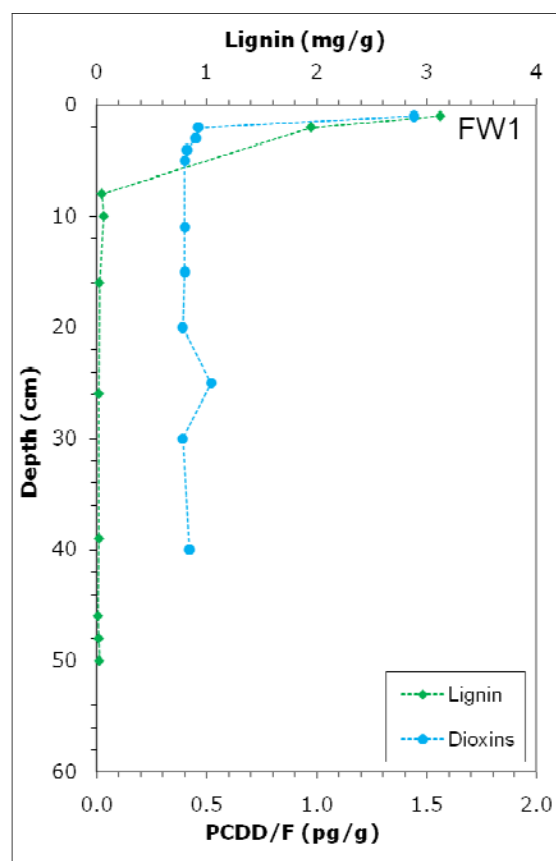


Figure 7. Vertical profile of lignin phenols (Σ8; mg/g) and dioxins (pg/g) for station FW1.

Table 2. Molecular (lignin, dioxins, PAHs) and elemental (OC, BC) concentrations in sediments of core FW1. Approximate dating of sediment horizons is also provided.

Depth (cm)	Age (years)	Year of Deposition	$\Sigma 8^*$ (mg/g)	Dioxins (2,3,7,8 TCDD + TCDF) (pg/g-dry weight)	Total PAH Concentration (ng/g)	BC (%)	OC (%)
1	2.77	2002	3.1180	1.44	-	0.11%	10.98%
2	4.80	2000	1.9457	0.46	344.7724	0.12%	6.73%
3	7.63	1997	-	0.45	413.9451	0.14%	3.90%
4	11.20	1994	-	0.41	443.4395	0.13%	-
5	15.70	1989	-	0.40	-	0.15%	1.50%
8	18.51	1986	0.0478	-	-	0.16%	0.70%
9	20.22	1985	-	-	154.6157	-	-
10	21.38	1984	0.0653	-	-	-	0.66%
11	22.91	1982	-	0.40	-	0.12%	0.77%
14	25.38	1980	-	-	245.5308	-	-
15	26.55	1978	-	0.40	-	0.13%	0.58%
16	27.58	1977	0.0246	-	-	-	0.52%
19	30.36	1975	-	-	247.3352	-	-
20	31.29	1974	-	0.39	-	0.09%	0.55%
22	32.95	1972	-	-	-	-	0.47%
25	35.49	1969	-	0.52	163.4817	0.12%	0.43%
26	36.37	1969	0.0210	-	-	-	0.43%
30	39.90	1965	-	0.39	-	0.12%	0.35%
33	43.42	1962	-	-	-	-	0.40%
34	44.89	1960	-	-	-	0.13%	-
37	49.68	1955	-	-	187.9526	0.20%	-
39	53.54	1951	0.0235	-	-	-	0.58%
40	55.54	1949	-	0.42	328.8367	0.13%	0.54%
43	63.91	1941	-	-	-	-	0.54%
46	74.94	1930	0.0129	-	-	0.20%	0.71%
48	88.03	1917	0.0205	-	-	-	0.82%
50	98.18	1907	0.0250	-	401.6792	0.17%	0.90%

* $\Sigma 8$ is the sum of 8 lignin-derived oxidation products.

Total PAH concentrations showed a slightly different profile. The values dropped by a factor of three from the surface to 8-10 cm depth (~ 400 to 100 ng/g, respectively). However, they increased again back to the surface values (~400 ng/g) in the deep portion of the core.

Diagnostic PAH ratios are used in PAH fingerprinting to determine their main sources. For example, the ratio of methylphenanthrenes to phenanthrene (MP/P) distinguishes between PAHs originating from petrogenic oil spills or seepages (MP/P > 5) and that from pyrogenic combustion (MP/P = 0.4-0.7). In addition, the ratio of 1,7-dimethylphenanthrene (1,7-DMP) to the sum of 1,7- and 2,6-dimethylphenanthrene (2,6-DMP) distinguishes between PAHs originating from softwood combustion (>0.90), coal combustion (0.65-0.68), and combustion of fossil fuels (<0.45) (Elmqvist et al., 2007). Ratios of MP/P found at this site were highly variable and ranged from 1.2 to 4.1. Ratios of 1,7-DMP/(1,7+2,6-DMP) were also variable (0.36 to 0.67). Therefore, the sources of PAHs to these sediments are mixed and include fossil fuel and coal combustion, as well as petrogenic processes (Figures 8-10).

Another way to determine sources of PAH inputs is to look at the compounds present and their proportions. The total pyrogenic PAH concentration is determined by the sum of fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene. Pyrogenic PAHs averaged about 9.4 percent (\pm 3.7%) of the total PAH concentration at FW1, demonstrating the strong inputs from petrogenic sources at this station. This is consistent with the oil spill history in the region.

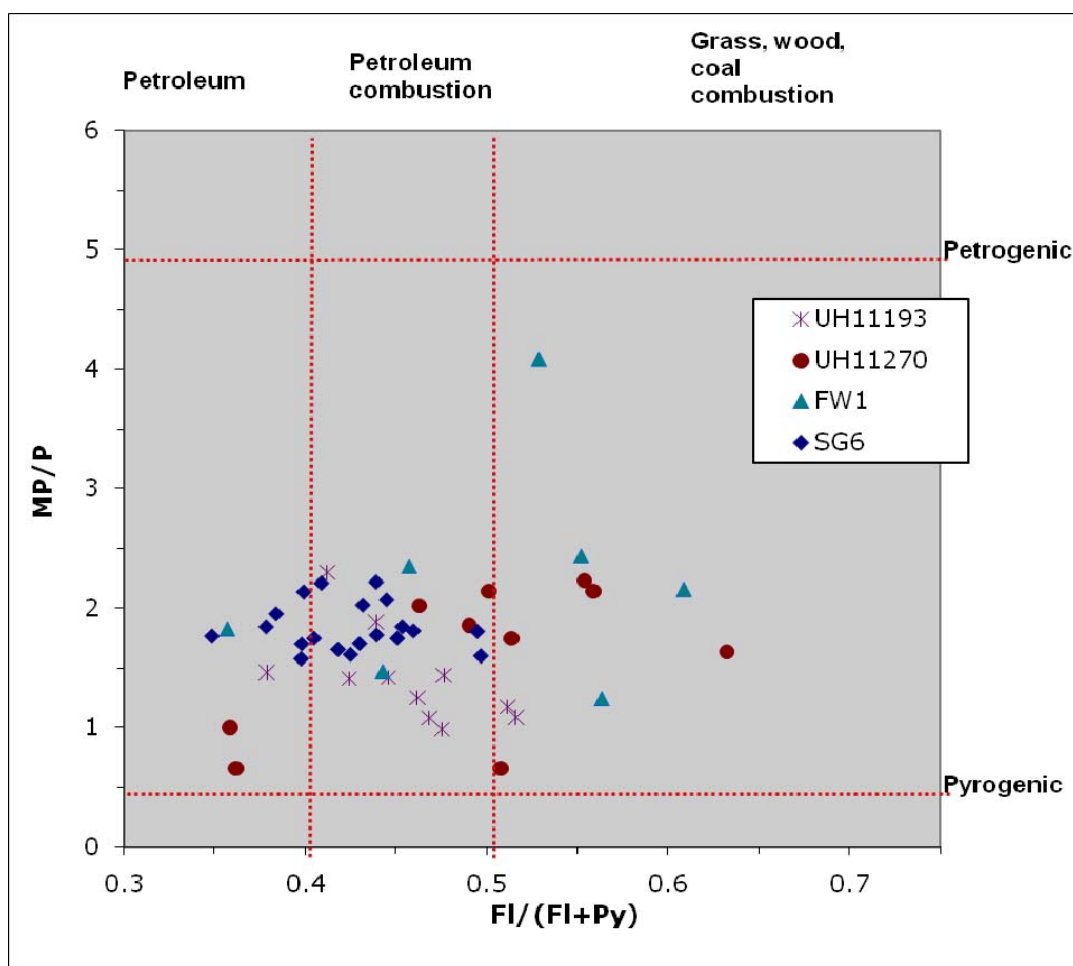


Figure 8. Methylphenanthrenes/Phenanthrene (MP/P) versus Fluoranthene/(Pyrene + Fluoranthene) (FI/(FI+Py)) ratios for HSC stations.

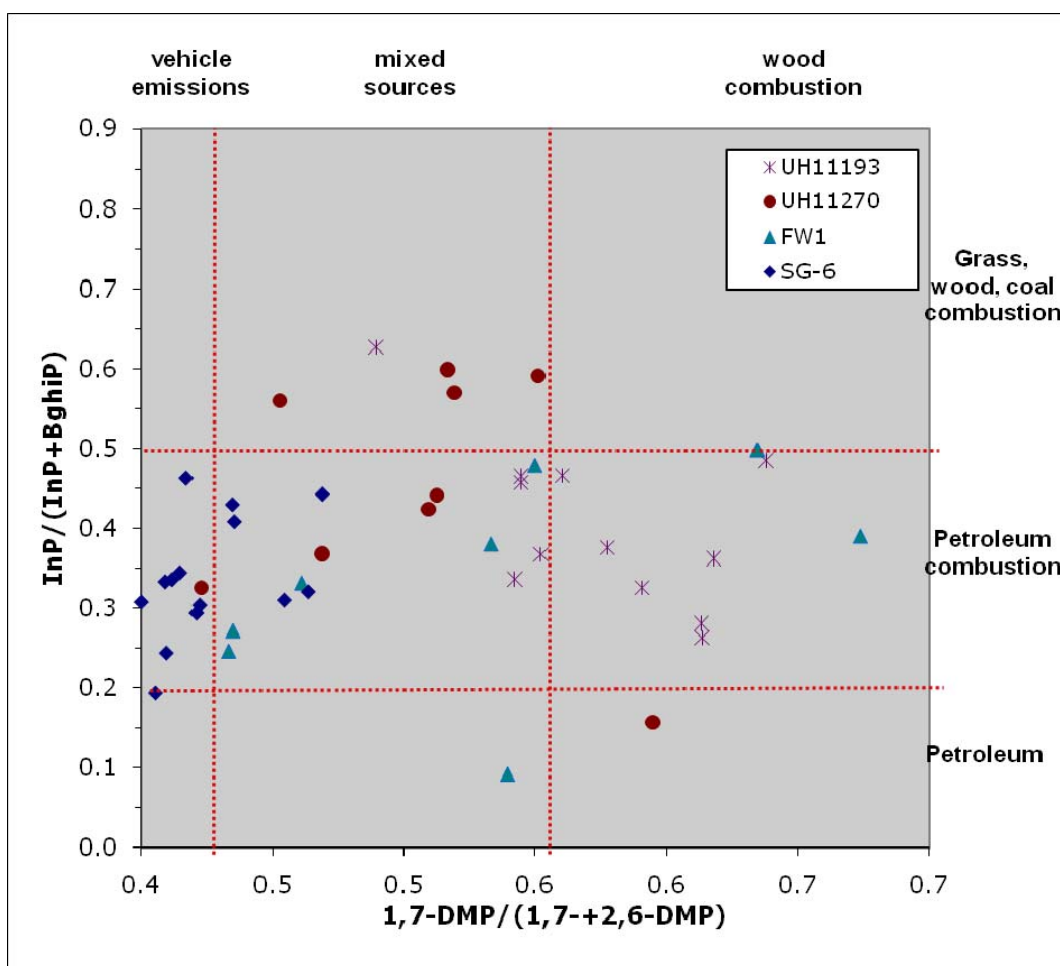


Figure 9. Indeno(1,2,3-c,d)pyrene/(Indeno(1,2,3-c,d)pyrene + Benzo(g,h,i)perylene) ($\text{InP}/(\text{InP}+\text{BghiP})$) versus 1,7-Dimethylphenanthrene/(1,7- + 2,6-Dimethylphenanthrene) ($1,7\text{-DMP}/(1,7\text{-}+2,6\text{-DMP})$) ratios for the HSC stations.

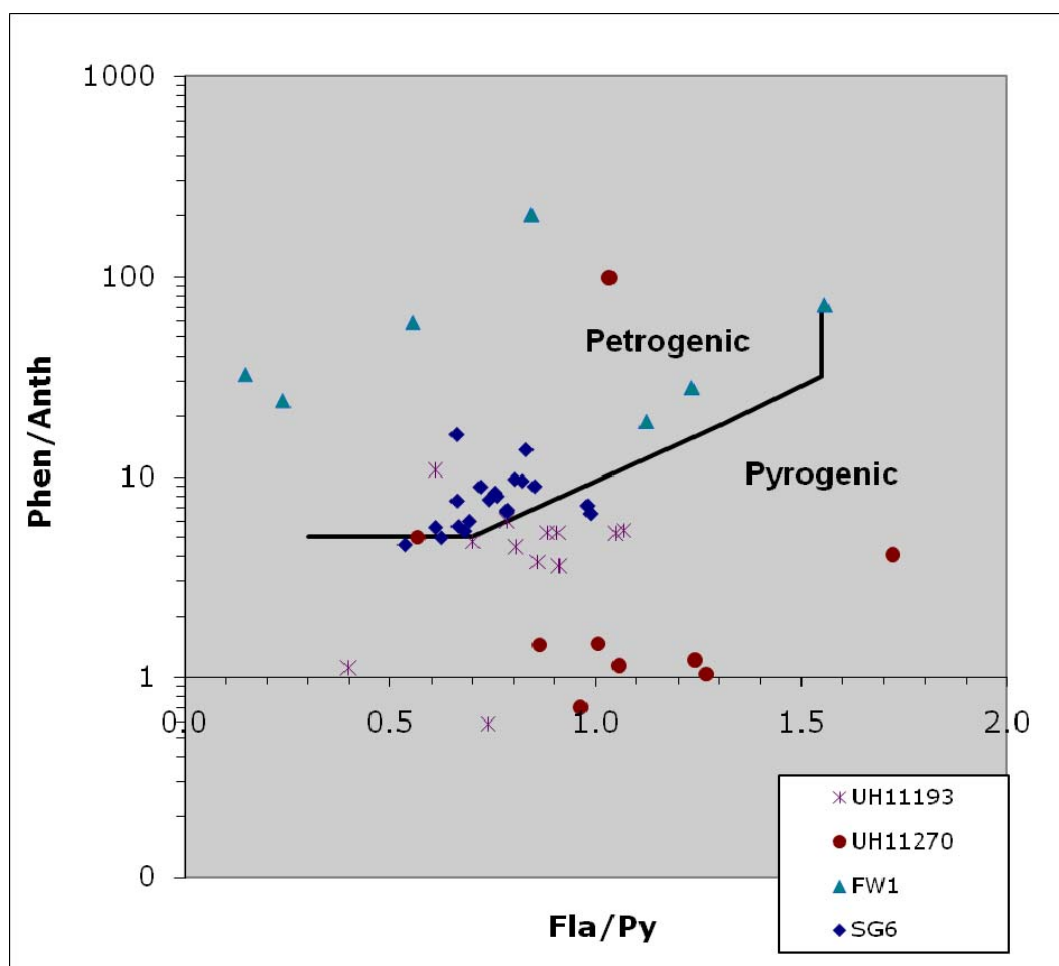


Figure 10. Phenanthrene/Anthracene (Phen/Anth) versus Fluoranthene/Pyrene (Fla/Py) ratios for the HSC stations, indicating a large proportion of PAHs from petrogenic sources (oil spills).

UH11193

Core UH11193 (N29.7856°, W95.0625°) was collected on August 30, 2004 at a location north of the HSC. As shown graphically in Figure 11 (listed in Table 3), OC was low and highly variable throughout the depth of the core with values ranging from ~ 0.2-0.7%. The highest value for OC occurred in the surface sediment layer, with other major peaks occurring at 8 and 50 cm depth. Lignin concentrations also varied greatly,

with the highest and lowest values (0.70 and 0.05 mg/g, respectively) being found in the deepest sections of the core (≥ 40 cm) (Figure 11). BC for core UH11193 also varied greatly (Figure 12) and was 14-31% of OC, with an average of 21%. Dioxins were found to be highest in the surface sediments (56 pg/g) and to decrease with depth (Figures 13 and 14). Total PAHs for this site were found to be highly variable, with values ranging from ~ 200 to > 2000 ng/g (Figure 13).

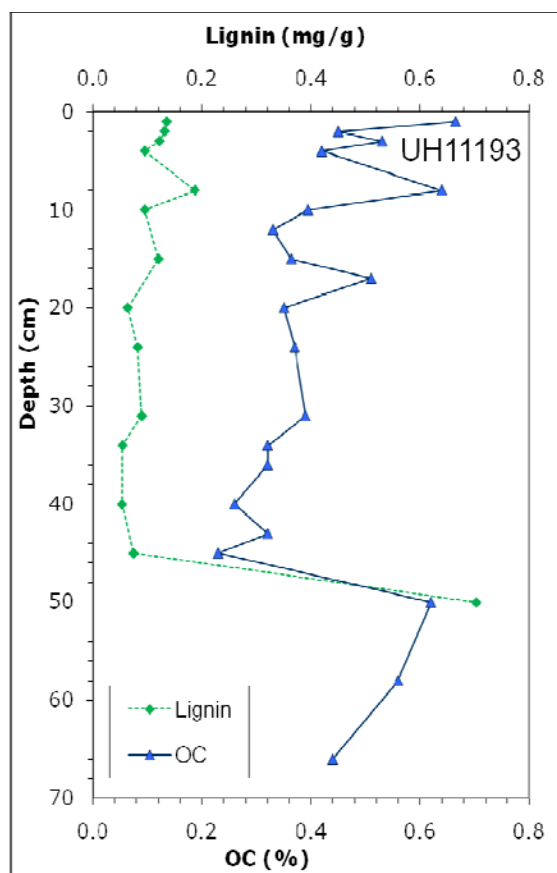


Figure 11. Vertical profile of lignin phenols ($\Sigma 8$; mg/g) and OC (%) for station UH11193.

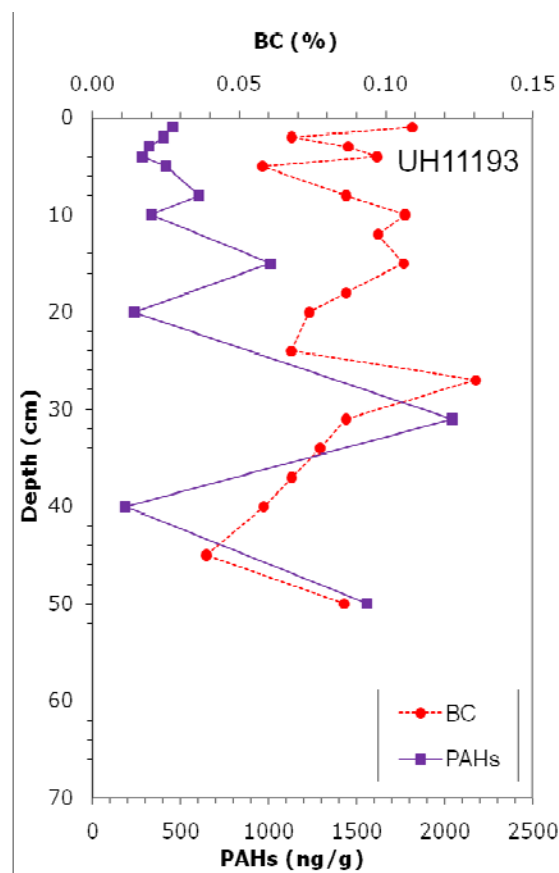


Figure 12. Vertical profile of PAHs (ng/g) and BC (%) for station UH11193.

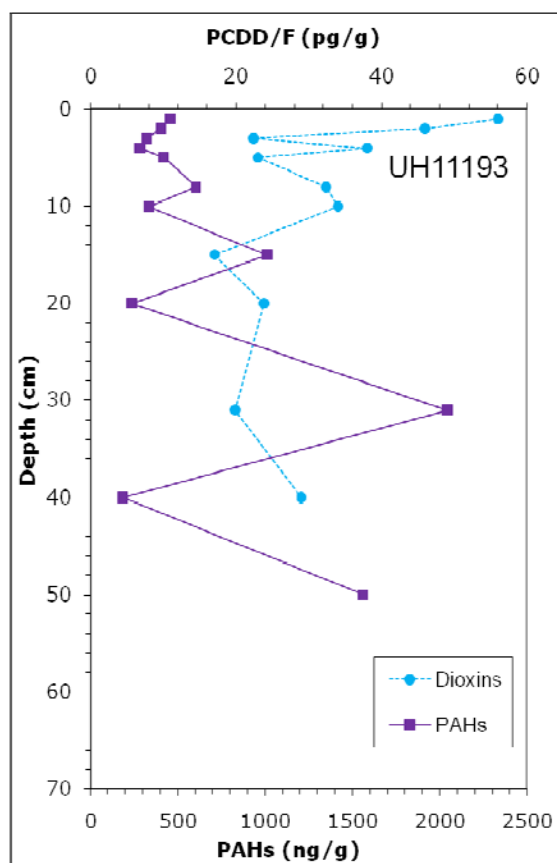


Figure 13. Vertical profile of PAHs (ng/g) and dioxins (pg/g) for station UH11193.

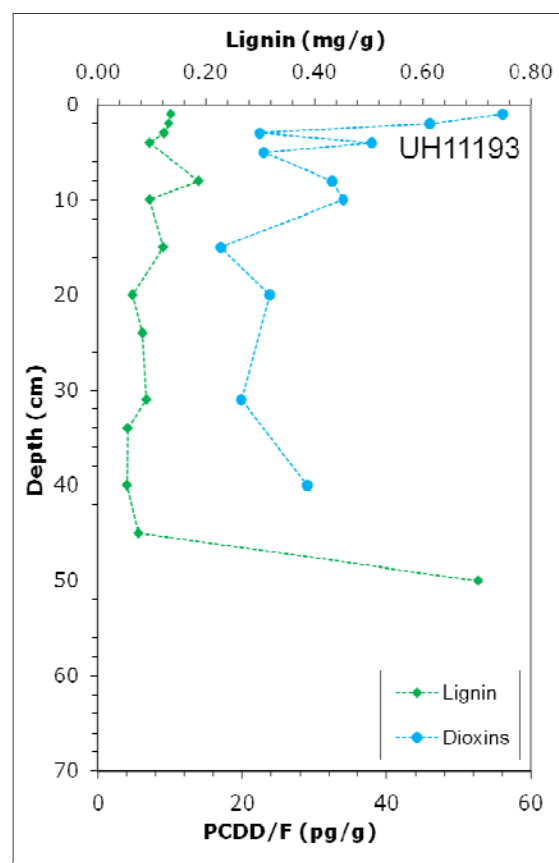


Figure 14. Vertical profile of lignin phenols ($\Sigma 8$; mg/g) and dioxins (pg/g) for station UH11193.

Table 3. Molecular (lignin, dioxins, PAHs) and elemental (OC, BC) concentrations in sediments of core UH11193. Approximate dating of sediment horizons is also provided.

Depth (cm)	Age (years)	Year of Deposition	Σ8 (mg/g)	Dioxins (2,3,7,8 TCDD + TCDF) (pg/g-dry weight)	Total PAH Concentration (ng/g)	BC (%)	OC (%)
1	0.10	2004	0.1351	56.0	456.5851	0.11%	0.67%
2	0.25	2004	0.1314	46.0	402.4648	0.07%	0.45%
3	0.50	2004	0.1218	22.4	321.7786	0.09%	0.53%
4	0.74	2004	0.0954	38.0	282.6724	0.10%	0.42%
5	0.99	2004	-	23.0	417.8495	0.06%	-
8	1.74	2003	0.1871	32.4	604.3778	0.09%	0.64%
10	2.23	2002	0.0955	34.0	334.3833	0.11%	0.40%
12	2.73	2002	-	-	-	0.10%	0.33%
15	3.47	2001	0.1202	17.1	1010.9812	0.11%	0.36%
17	3.98	2001	-	-	-	-	0.51%
18	5.47	1999	-	-	-	0.09%	-
20	8.45	1996	0.0641	23.8	236.9762	0.07%	0.35%
24	14.41	1990	0.0825	-	-	0.07%	0.37%
27	18.88	1986	-	-	-	0.13%	-
31	24.84	1980	0.0898	19.9	2042.5726	0.09%	0.39%
34	29.31	1975	0.0550	-	-	0.08%	0.32%
36	32.29	1972	-	-	-	-	0.32%
37	33.78	1971	-	-	-	0.07%	-
40	38.25	1966	0.0539	29.0	185.7532	0.06%	0.26%
43	42.72	1962	-	-	-	-	0.32%
45	45.70	1959	0.0750	-	-	0.04%	0.23%
50	53.15	1952	0.7023	-	1559.3094	0.09%	0.62%
58	55.14	1950	-	-	-	-	0.56%
66	57.12	1948	-	-	-	-	0.44%

With regards to PAHs in these sediments, MP/P ratios were found to range from 1.0 to 2.3 and 1,7-DMP/(1,7-+2,6-DMP) ratios ranged from 0.50 to 0.64. This also confirms the substantial inputs from both petrogenic and pyrogenic in PAHs, and that the pyrogenic sources include both fossil fuel and coal combustion. In contrast to FW1,

where the majority of PAHs were petrogenic, close to 50% ($56 \pm 14\%$) of all PAHs in core UH11193 are of pyrogenic origin, showing the influence of combustion-derived constituents in this area of the HSC.

UH11270

Core UH11270 (N29.74361°, W95.15827°) was collected on October 18, 2004 in the Buffalo Bayou section of the HSC. Various percentages of OC were found in the core (0.08-1.5%), with lowest amounts occurring in the deepest sections of the core (≥ 39 cm). Amounts of lignin also fluctuated throughout the core, following the same general trend as OC (Figure 15). BC values ranged from 0.05 to 0.15% (Figure 16). OC was 6 to 76 percent BC, with an average of 22%. Dioxin concentrations were high from 8 to 40 cm depth (up to more than 600 pg/g), but were very low at the surface and below 40 cm (Figures 17 and 18). Total PAH concentrations followed the trends of lignin and OC, with lowest values being found at depths greater than 40 cm (< 100 ng/g) (Figure 17).

Contrary to the expected, lowest values of lignin-derived phenols (0.003 mg/g), dioxins (5 pg/g), total PAH concentration (45 ng/g), BC (0.05%), and OC (0.08%) all occurred in 1957. These lignin and PAH concentrations were the lowest in the entire study and can be seen in Table 4. On the other hand, none of the highest values for these compounds in UH11270 occurred in the same year.

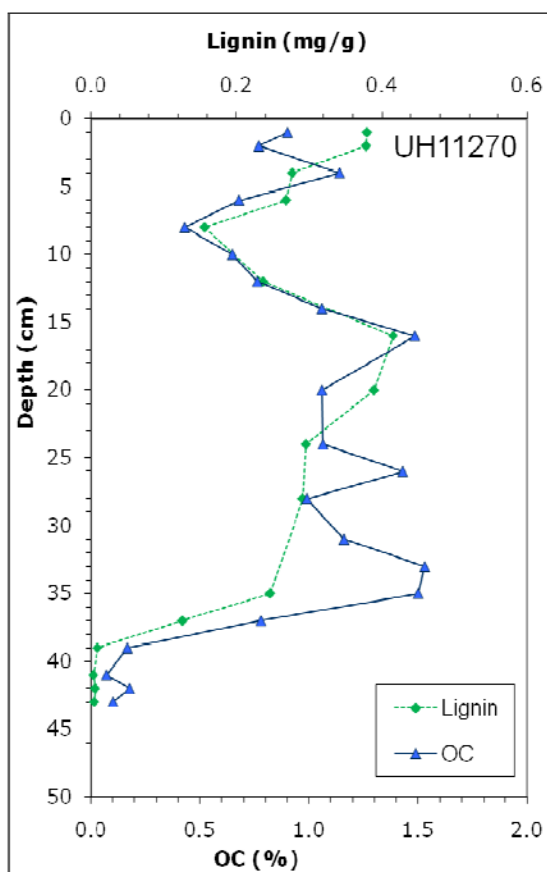


Figure 15. Vertical profile of lignin phenols ($\Sigma 8$; mg/g) and OC (%) for station UH11270.

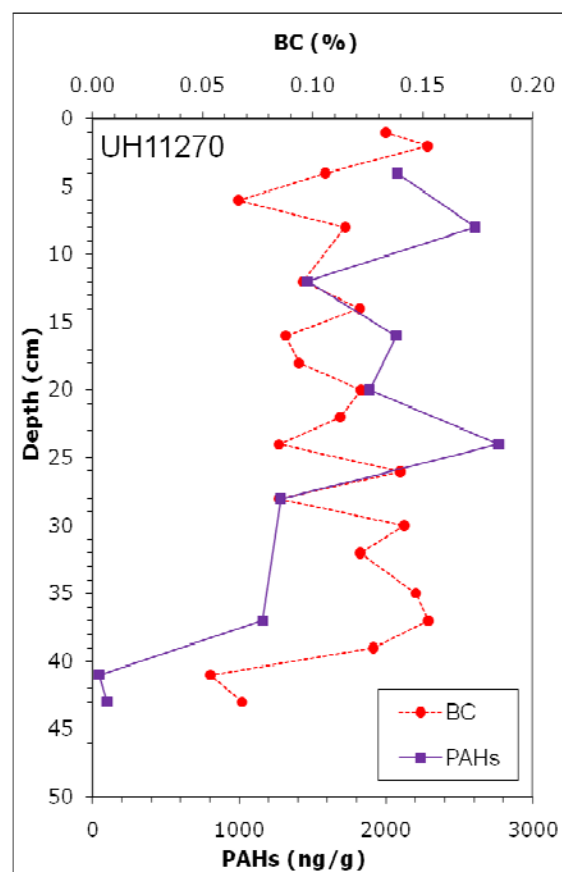


Figure 16. Vertical profile of PAHs (ng/g) and BC (%) for station UH11270.

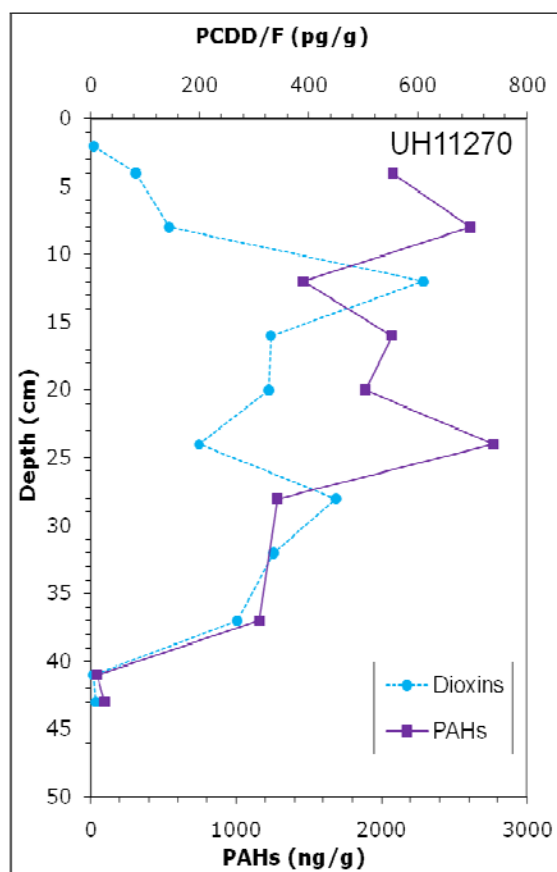


Figure 17. Vertical profile of PAHs (ng/g) and dioxins (pg/g) for station UH11270.

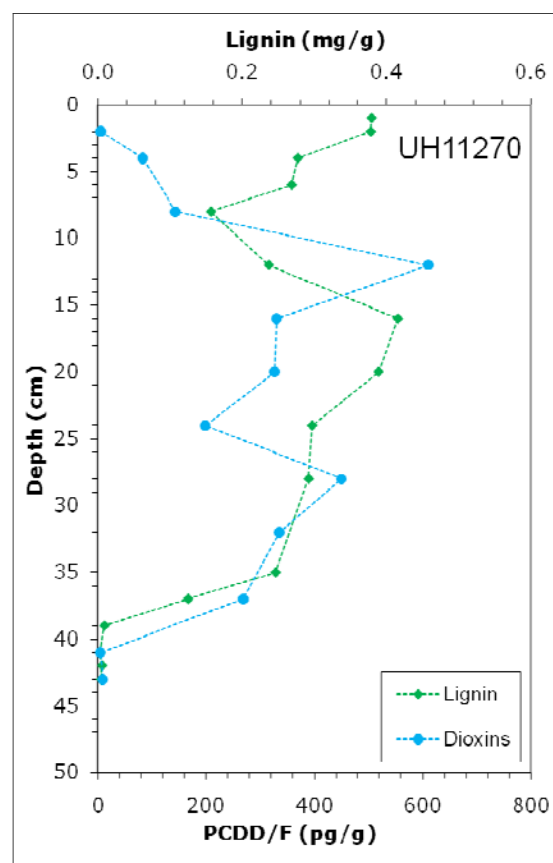


Figure 18. Vertical profile of lignin phenols (Σ8; mg/g) and dioxins (pg/g) for station UH11270.

Table 4. Molecular (lignin, dioxins, PAHs) and elemental (OC, BC) concentrations in sediments of core UH11270. Approximate dating of sediment horizons is also provided.

Depth (cm)	Age (years)	Year of Deposition	$\Sigma 8$ (mg/g)	Dioxins (2,3,7,8 TCDD + TCDF) (pg/g-dry weight)	Total PAH Concentration (ng/g)	BC (%)	OC (%)
1	1.16	2004	0.3792	-	-	0.13	0.90
2	2.32	2003	0.3781	5.5	-	0.15	0.77
4	4.64	2000	0.2765	83.0	2077.7489	0.11	1.14
6	6.96	1998	0.2680	-	-	0.07	0.68
8	9.28	1996	0.1569	144.0	2608.1790	0.11	0.43
10	11.60	1993	-	-	-	-	0.65
12	13.92	1991	0.2366	610.0	1464.2505	0.10	0.76
14	16.24	1989	-	-	-	0.12	1.06
16	18.56	1986	0.4156	330.0	2068.7138	0.09	1.49
18	20.88	1984	-	-	-	0.09	-
20	23.20	1982	0.3888	326.0	1887.5421	0.12	1.06
22	25.52	1979	-	-	-	0.11	-
24	27.84	1977	0.2961	199.0	2768.0043	0.08	1.07
26	30.16	1975	-	-	-	0.14	1.43
28	32.48	1972	0.2915	450.0	1281.6391	0.08	0.99
30	34.80	1970	-	-	-	0.14	-
31	35.96	1969	-	-	-	-	1.16
32	37.12	1968	-	335.0	-	0.12	-
33	38.28	1967	-	-	-	-	1.53
35	40.60	1964	0.2460	-	-	0.15	1.50
37	42.92	1962	0.1255	269.0	1160.4745	0.15	0.78
39	45.24	1960	0.0089	-	-	0.13	0.17
41	47.56	1957	0.0034	5.0	45.2417	0.05	0.08
42	48.72	1956	0.0058	-	-	-	0.18
43	49.88	1955	0.0044	9.2	99.1788	0.07	0.11

PAH concentrations in these sediments had MP/P ratios ranging from 0.7 to 2.2. Their 1,7-DMP/(1,7-+2,6-DMP) ratios spanned from 0.32 to 0.59. These values reveal that the inputs of PAHs to this area over the time span of this study have also been from both petrogenic and pyrogenic processes, including fossil fuel combustion and some coal combustion. At this station, and similarly to UH11193, the majority of PAHs ($58 \pm 21\%$) are derived from pyrogenic sources, confirming the impact of combustion on the inputs of HOCs to the HSC. Again, this shows that most inputs to these sediments are and have been from pyrogenic sources.

SG-6

Core SG-6 (N29.79402°, W95.06218°) was collected on April 14, 2007 at the site of a paper mill sludge waste pit located where the San Jacinto River and the upper HSC meet (Santschi et al., 2009). OC values fluctuated throughout SG-6, with high values being found between 31 and 37 cm depth ($\sim 4-7\%$). Lignin values followed this same trend, with highest values ranging from ~ 3 to 10 mg/g (Figure 19). Values for BC fluctuated throughout the core, with two large peaks in percentage at 32 and 80 cm depth (0.3 and 0.4%, respectively) (Figure 20). BC comprised 2 to 12 percent of the OC, with an average value of 7 percent. The highest C/N ratios (up to 61) were also found at this site, implying added terrestrial carbon from the pulp mill (Macdonald et al., 1992).

The highest dioxin values out of all the cores were found at this site. The combined total PCDDs and PCDFs ranged from ~ 7000 to > 18000 pg/g (Figures 21 and 22). Total PAH concentrations followed the same trend as BC, with a large peak at 32

cm and in increase in concentration at depth (Figure 21). Regarding lignin, PAHs, BC and OC, all the lowest values occurred between 23 and 25 cm depth (1991-1992). The highest lignin and PAH values between all the cores were found at this site (Table 5).

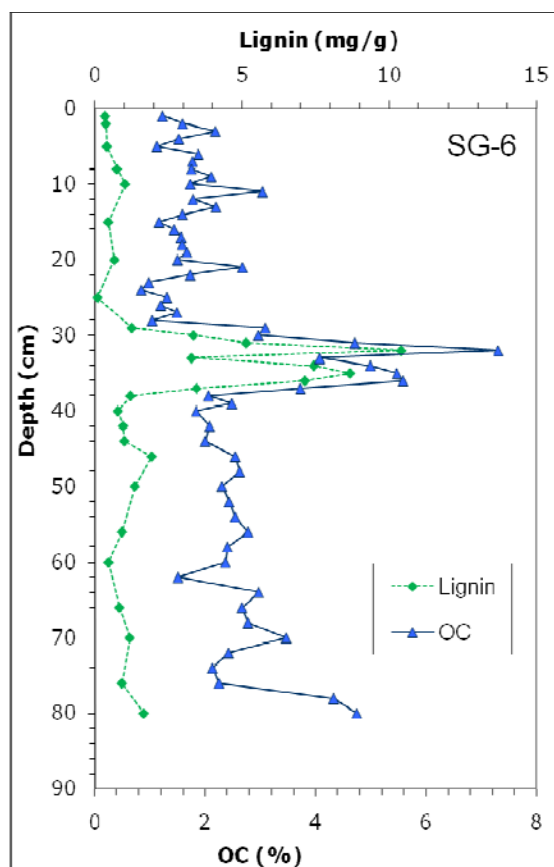


Figure 19. Vertical profile of lignin phenols ($\Sigma 8$; mg/g) and OC (%) for station SG-6.

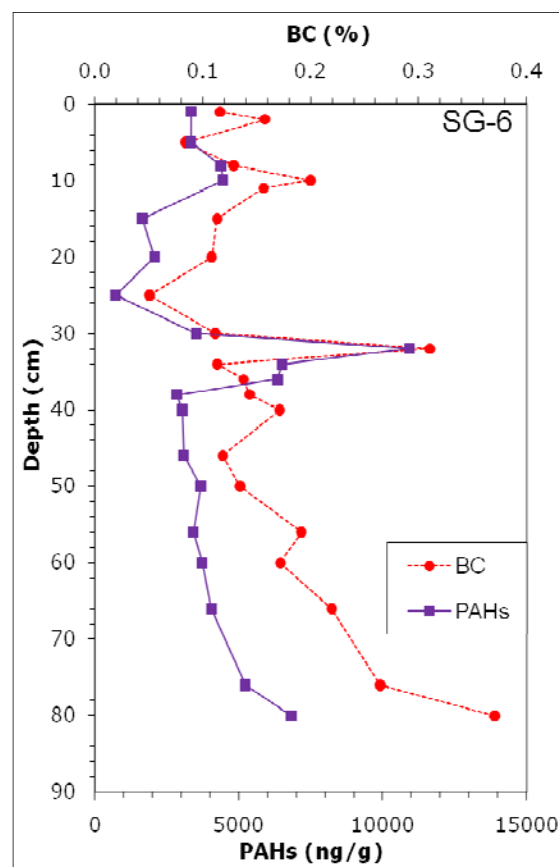


Figure 20. Vertical profile of PAHs (ng/g) and BC (%) for station SG-6.

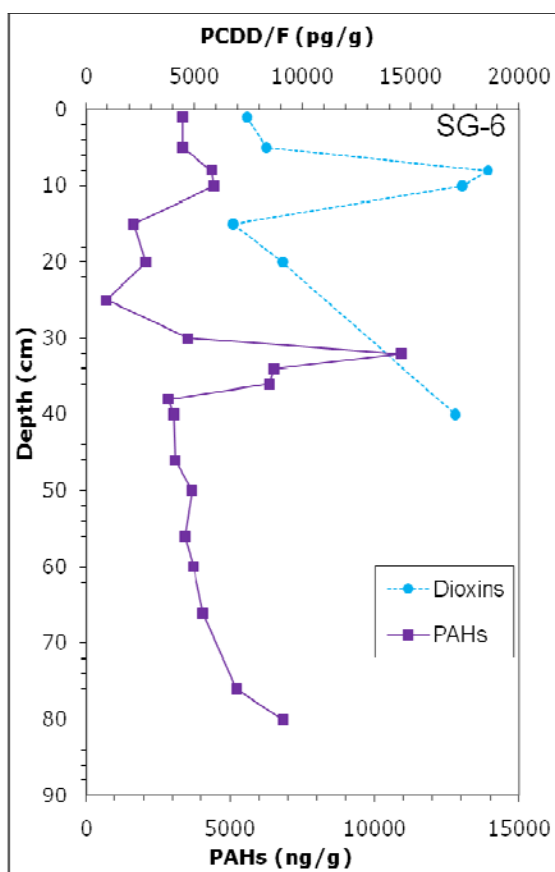


Figure 21. Vertical profile of PAHs (ng/g) and dioxins (pg/g) for station SG-6.

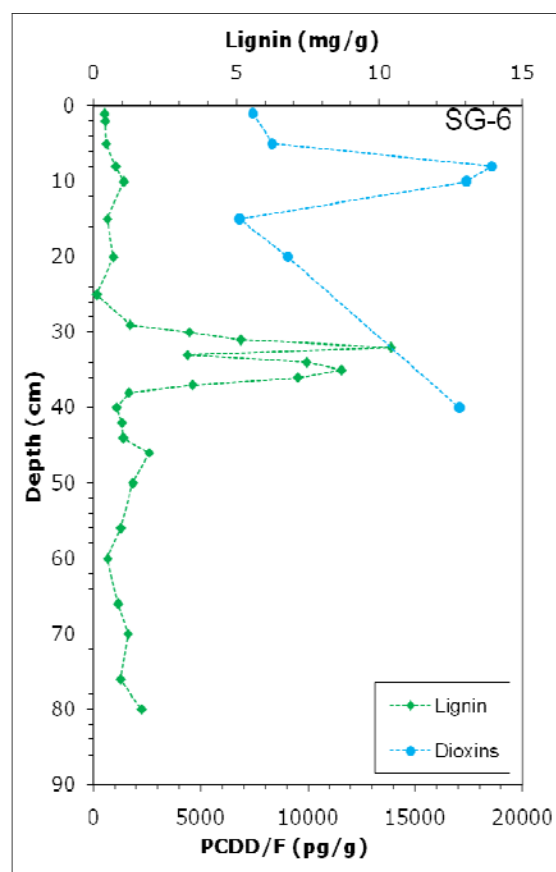


Figure 22. Vertical profile of lignin phenols ($\Sigma 8$; mg/g) and dioxins (pg/g) for station SG-6.

Table 5. Molecular (lignin, dioxins, PAHs) and elemental (OC, BC) concentrations in sediments of core SG-6. Approximate dating of sediment horizons is also provided.

Depth (cm)	Age (years)	Year of Deposition	$\Sigma 8$ (mg/g)	Dioxins (TCDD + TCDF) (ng/kg)	Total PAH Concentration (ng/g)	BC (%)	OC (%)
1	0.33	2007	0.3681	7441.61	3349.2304	0.12%	1.23
2	1.02	2006	0.3958	-	-	0.16%	1.59
3	1.71	2006	-	-	-	-	2.19
4	2.40	2005	-	-	-	-	1.52
5	3.08	2004	0.4313	8338.72	3339.3177	0.08%	1.13
6	3.77	2004	-	-	-	-	1.88
7	4.45	2003	-	-	-	-	1.77
8	5.14	2002	0.7691	18570.19	4374.5529	0.13%	1.75
9	5.82	2001	-	-	-	-	2.12
10	6.51	2001	1.0446	17382.41	4449.1602	0.20%	1.73
11	7.19	2000	-	-	-	0.16%	3.04
12	7.88	1999	-	-	-	-	1.78
13	8.56	1999	-	-	-	-	2.21
14	9.25	1998	-	-	-	-	1.59
15	9.93	1997	0.4765	6812.95	1654.3302	0.11%	1.17
16	10.62	1997	-	-	-	-	1.44
17	11.30	1996	-	-	-	-	1.57
18	11.99	1995	-	-	-	-	1.59
19	12.67	1995	-	-	-	-	1.67
20	13.36	1994	0.6874	9073.10	2075.7333	0.11%	1.50
21	14.04	1993	-	-	-	-	2.68
22	14.73	1993	-	-	-	-	1.73
23	15.41	1992	-	-	-	-	0.99
24	16.10	1991	-	-	-	-	0.85
25	16.78	1991	0.1080	-	717.6185	0.05%	1.31
26	17.47	1990	-	-	-	-	1.20
27	18.15	1989	-	-	-	-	1.49
28	18.84	1988	-	-	-	-	1.05
29	19.52	1988	1.2720	-	-	-	3.09
30	20.21	1987	3.3487	-	3523.6454	0.11%	2.97
31	20.89	1986	5.1482	-	-	-	4.71
32	21.58	1986	10.4228	-	10933.3397	0.31%	7.31
33	22.26	1985	3.2822	-	-	-	4.08

Table 5. Continued...

Depth (cm)	Age (years)	Year of Deposition	$\Sigma 8$ (mg/g)	Dioxins (TCDD + TCDF) (ng/kg)	Total PAH Concentration (ng/g)	BC (%)	OC (%)
34	22.95	1984	7.4576	-	6503.7533	0.11%	4.99
35	23.63	1984	8.6754	-	-	-	5.48
36	24.32	1983	7.1541	-	6350.5192	0.14%	5.59
37	25.00	1982	3.4660	-	-	-	3.73
38	25.68	1982	1.2273	-	2850.8446	0.14%	2.07
39	26.37	1981	-	-	-	-	2.49
40	27.05	1980	0.8005	17064.50	3038.2511	0.17%	1.84
42	28.42	1979	0.9812	-	-	-	2.09
44	29.79	1977	1.0240	-	-	-	2.01
46	31.16	1976	1.9415	-	3088.2201	0.12%	2.55
48	32.53	1975	-	-	-	-	2.63
50	33.90	1973	1.3712	-	3680.6469	0.13%	2.31
52	35.62	1972	-	-	-	-	2.44
54	36.99	1970	-	-	-	-	2.55
56	38.36	1969	0.9411	-	3422.6110	0.19%	2.78
58	39.73	1968	-	-	-	-	2.41
60	41.10	1966	0.4876	-	3726.1303	0.17%	2.38
62	42.47	1965	-	-	-	-	1.51
64	43.84	1963	-	-	-	-	2.97
66	45.21	1962	0.8534	-	4053.9372	0.22%	2.67
68	46.58	1961	-	-	-	-	2.78
70	47.95	1959	1.2001	-	-	-	3.47
72	49.32	1958	-	-	-	-	2.43
74	50.69	1957	-	-	-	-	2.14
76	52.06	1955	0.9360	-	5227.9243	0.26%	2.26
78	53.43	1954	-	-	-	-	4.33
80	54.80	1952	1.6707	-	6821.3572	0.37%	4.75

Nevertheless, only 7 of the sediment intervals of SG-6 have been analyzed for dioxins. Therefore, the trend of how dioxins have changed over time in this location is yet incomplete. Still, it can be determined that large amounts of dioxins have constantly been released at this location over the time span of this study (1952-2007) as the

sediments are characterized by dioxin concentrations that are 1-3 orders of magnitude above those of the other cores discussed previously.

Ratios of MP/P ranged from 1.6 to 2.2 and ratios of 1,7-DMP/(1,7-+2,6-DMP) ranged from 0.38 to 0.47. This shows that PAHs to this area of the system were also derived from both petrogenic and pyrogenic processes, and that almost all the pyrogenic PAHs originated from fossil fuel combustion. Still, as was shown at station FW1, only a small fraction of the PAHs (24.0 ± 7.3 % on average) were high molecular pyrogenic PAH. This demonstrates the strong inputs from petrogenic sources.

Discussion on Historical Data

Surface mixing and bioturbation should be considered during data analysis. These are important when relating depth to age in a core. Bioturbation redistributes contaminants as it forces them deeper into sediments while at the same time slowing the natural rate of sediment recovery (burial of contaminated horizons) by mixing new inputs of cleaner sediments with older more contaminated sediments prolonging the contact between the contaminants and biota at the surface. This is important when trying to determine how long the sediments will take to recover from contamination. (Macdonald et al., 1992; Brandenberger et al., 2008)

It was generally found that the depths or dates of maximum concentration in the cores were different for each core and each compound. This suggests that more than one source may have been operating for each of these compounds. In addition, these sources changed in time and location.

It was predicted that BC and PAHs would show peaks between 1908 and 1916 (State Coal..., 2009; Houston in 1900..., 2002), around 1930, between 1956 and 1964 (Elmqvist et al., 2007), and in recent years (Folsom Murphy and Allen, 2005; Van Metre and Mahler, 2005). Only the FW1 samples included the years 1908-1916 and 1930, and did show higher values during these times than at other times. This was probably due to an increase in oil usage and industrialization. The years from 1956 to 1964 did not show high values for these constituents, nor did recent years. Highest values for BC and PAHs were expected in UH11270, but were actually found to occur in SG-6 at the sludge pit site.

BC values were variable and low throughout the entire system (0.04-0.37%). The values were not consistent on a regional scale, suggesting more localized inputs. Station UH11270 had the highest proportions of BC with respect to OC (6-76%), showing the importance of combustion processes on inputs to the sediments. PAH concentrations were also variable, with the pit (SG-6) usually showing the highest values. Sources were found to be a mixture of pyrogenic and petrogenic inputs with the proportion changing dependent on location. This shows that inputs of PAHs to the environment are not exclusively from combustion processes. This is to be expected in a ship channel since PAHs could also be added through oil spills.

Based on all the data, lignin concentrations were highly variable across all depths and locations. Values were predicted to be highest in FW1, but actually tended to be highest in the sludge waste pit (SG-6). The highest values of lignin for SG-6 were expected between 1960 and 1970. This was not the case, with these years actually

corresponding to some of the lowest lignin phenol concentrations for this site. Low cinnamyl:vanillyl (C/V) and high syringyl:vanillyl (S/V) phenol ratios for these sediments suggest woody angiosperms as the sources of the lignin (Goñi and Hedges, 1992).

Throughout the HSC, dioxins showed very large differences in concentrations. As expected, the sludge waste pit had the highest values, confirming the high contamination of this area. Highest values are expected between 1960 and 1970. However, since dioxin data for these years have yet to be obtained, this has not been confirmed.

It was also found that hardly any relationship exists between dioxins and lignin oxidation products in the system, with the highest correlation occurring at SG-6 (Figure 23). Therefore, the analysis of lignin cannot be used as a potential surrogate screening test for the expensive analysis of dioxins. Similarly, hardly any relationship existed between dioxins and PAHs in the sediments. Again, the highest correlation for this relationship was found at SG-6 (Figure 24). Except for at the waste pit site, dioxins are not related to pyrogenic PAHs. Thus, they are not predominantly derived from combustion processes. This lack of relationship away from the waste pit, suggests that the dioxins in sediments at the waste pit are from the pulp and paper mill, and those away from the mill have a different source other than the mill.

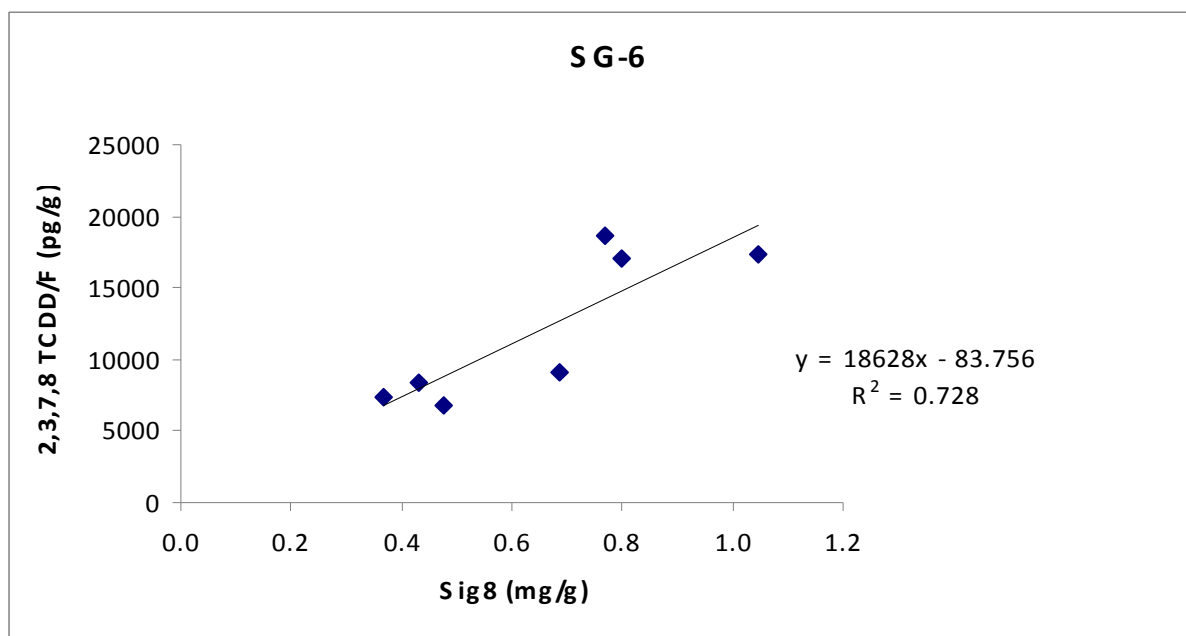


Figure 23. Correlation between dioxins and lignin phenols found in the paper mill sludge waste pit (SG-6).

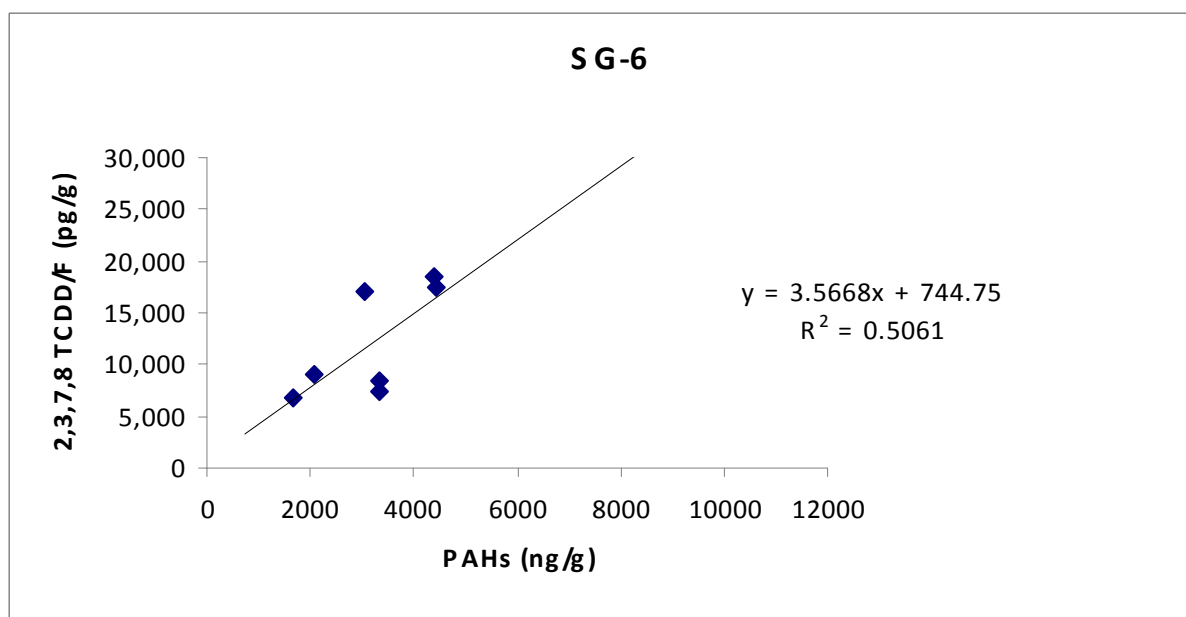


Figure 24. Correlation between dioxins and PAHs found at the site of the waste pit.

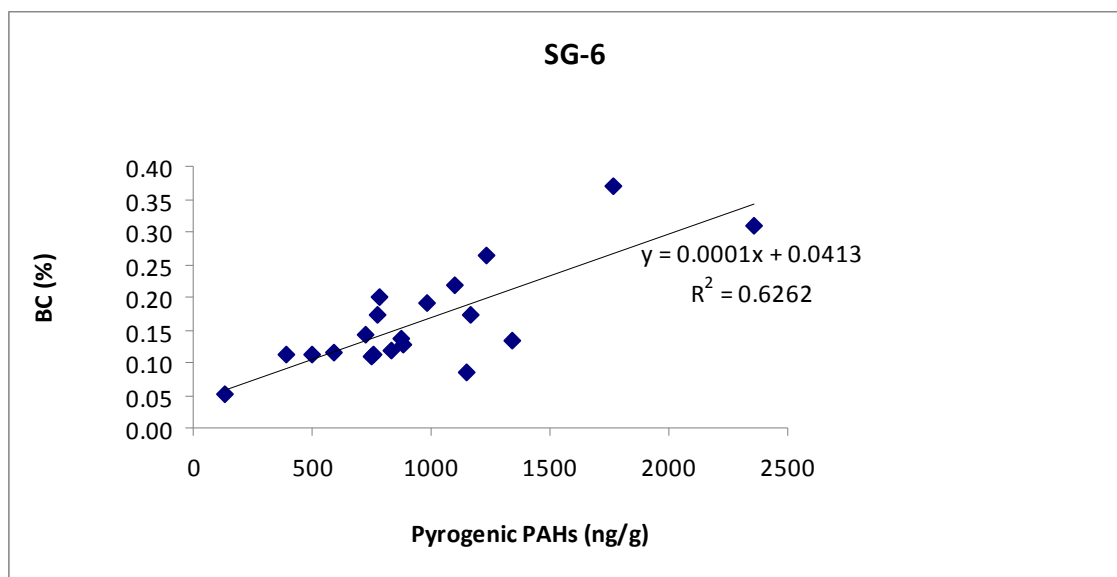


Figure 25. Correlation between BC and pyrogenic PAHs found at the site of the waste pit.

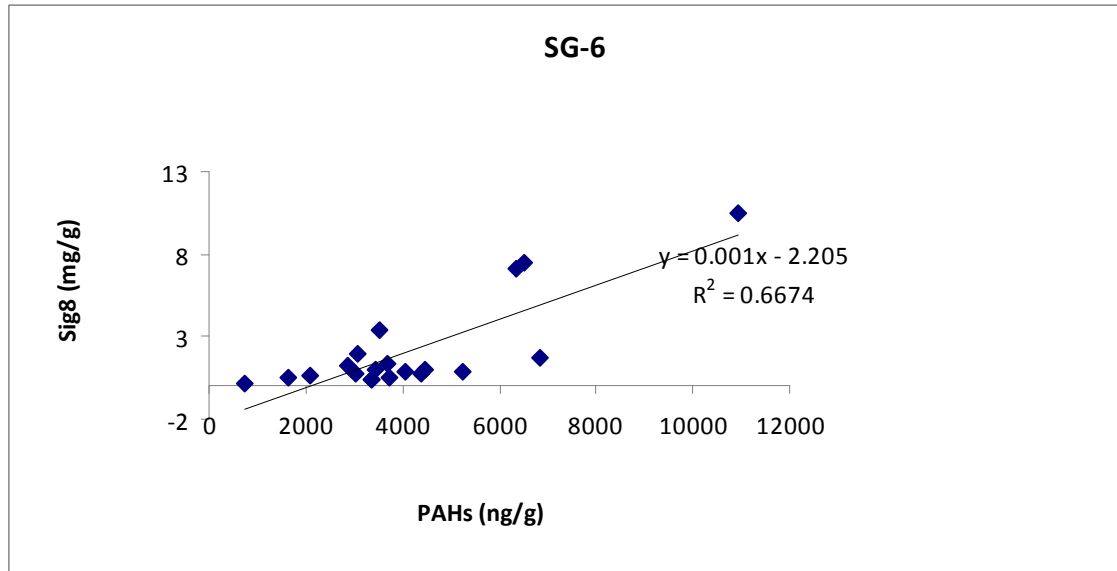


Figure 26. Correlation between lignin and total PAHs found at the site of the waste pit.

At the waste pit site, BC is related to pyrogenic PAHs (Figure 25) confirming the common combustion sources for these constituents. The lignin and total PAHs found at this site were also related, showing again that the sludge that was dumped in the SG-6 waste pit is heavily contaminated with a variety of HOCs and combustion by-products (Figure 26).

The only significant relationships for these comparisons occurred at SG-6. At this site, the relationship between dioxins and lignin was shown by an r^2 value (regression coefficient squared) of 0.73 (Figure 23). Dioxins probably have a relationship to lignin at this location due to both of them being present in pulp and paper effluents. The relationship between dioxins and PAHs was shown by an r^2 value of 0.51 (Figure 24). The relationship between BC and pyrogenic PAHs was shown by an r^2 value of 0.63 (Figure 25). And lignin and total PAHs at the waste pit site have an r^2 value of 0.67 (Figure 26).

Sources and Fate of Dioxins

Values for total PCDF were expected to be higher in the pit site sediments than values for total PCDD based on past studies. This was found to be true. However, at all other locations in the HSC, total PCDDs were larger than total PCDFs in the sediments. In addition, it has been shown that since dibenzodioxins (DBD) has higher reactivity with respect to chlorine than dibenzofurans (DBF), a small number of lower chlorinated PCDD will also be detected due to pulp chlorination (Dimmel et al., 1993). This also held true for the sludge pit samples.

At the pulp waste pit site (SG-6), approximately 50 to 70 percent of the total amount of dioxins present in each sediment depth interval were 2,3,7,8-TeCDF, which is primarily associated with pulp mills by-products (Macdonald et al., 1992; Plumb, 2004) (Figure 27). 2,3,7,8-TeCDF was 2- to 6-fold higher than OCDD, the second most common congener in these sediments. 2,3,7,8-TeCDD was also significant, but TeCDF was still approximately four to six times more prevalent. This distribution of congeners is expected for bleached pulp (Dimmel et al., 1993) (Figure 28).

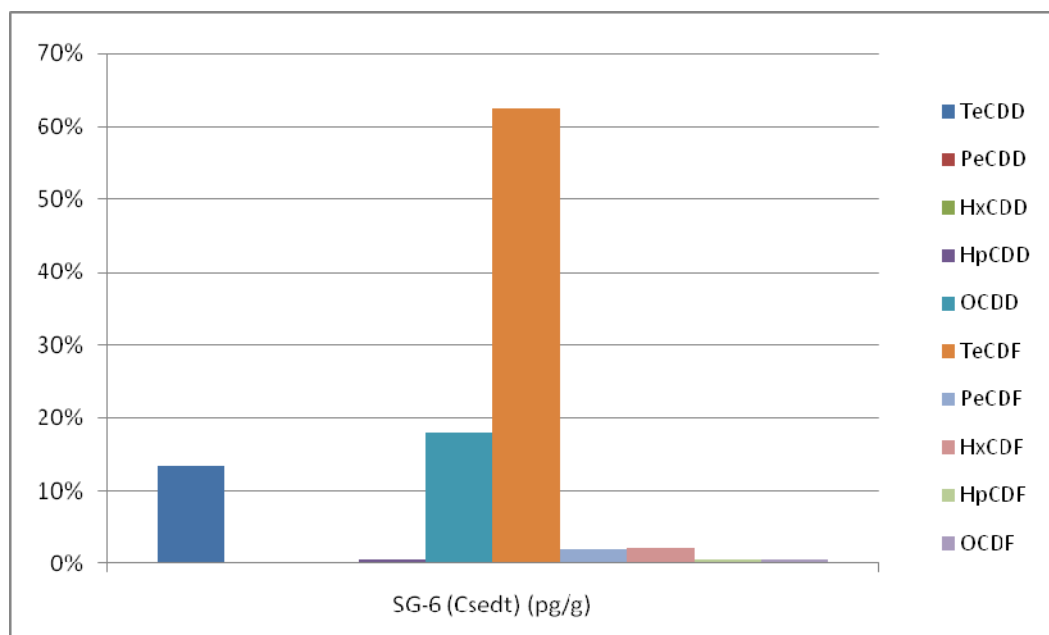


Figure 27. The percent concentration of dioxin congeners in SG-6 sediments.

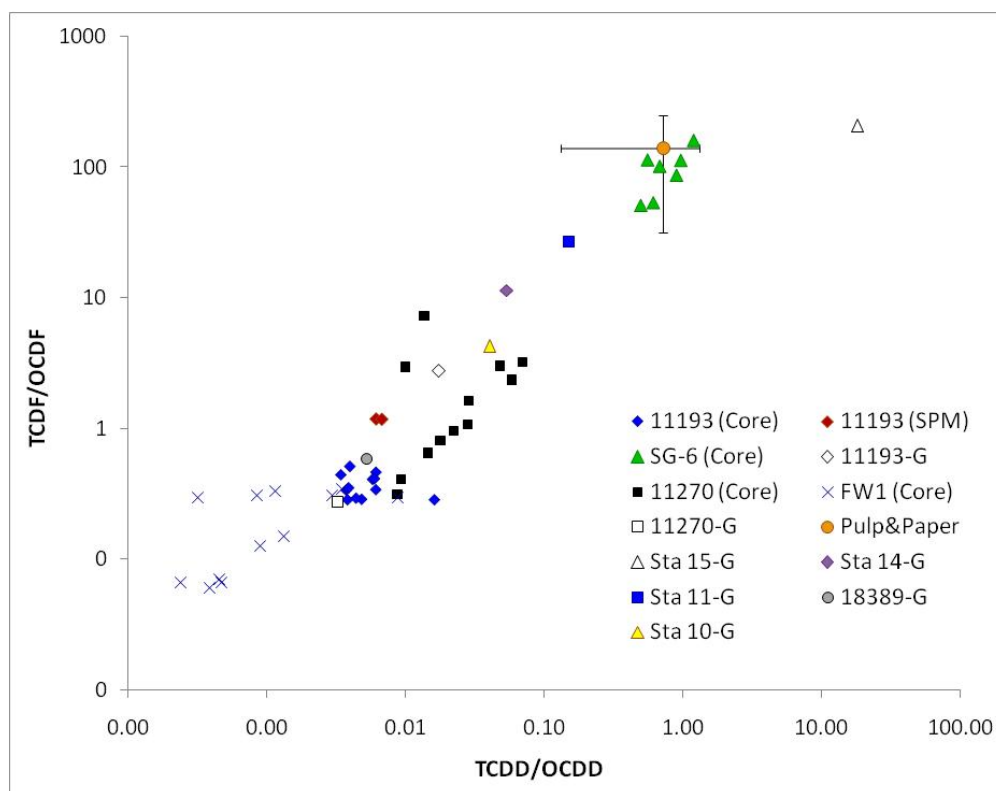


Figure 28. Ratios of tetra- to octa-chlorinated congeners in sediments at the HSC stations. The orange circle with error bars represents values typical of pulp and paper mills from literature (Rappe et al., 1987; MacDonald et al., 1998).

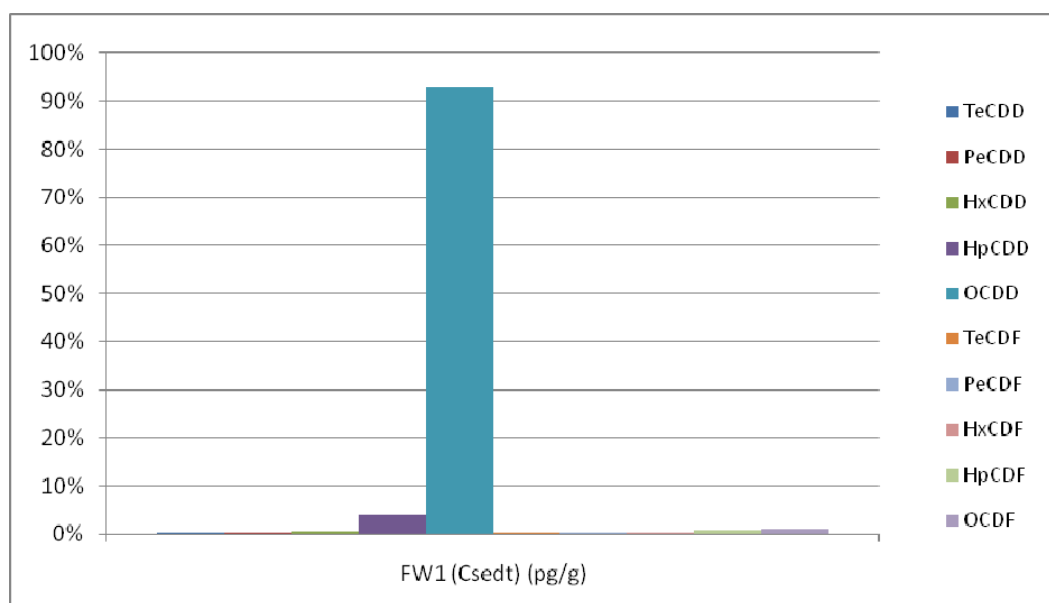


Figure 29. The percent concentration of dioxin congeners in FW1 sediments.

Different industrial processes produce PCDD and PCDF in different proportions. Therefore, as shown in Figure 28, congener ratios can be used as first-hand indicators of source fingerprints of dioxins in sedimentary systems. At the locations in the HSC away from the pulp mill, PCDD values averaged 26 times higher than those of PCDF. On the other hand, at the pulp mill site, the majority of dioxins present were PCDFs. The difference between the isomeric distributions found in these samples and those of the pulp waste site suggest different sources. Therefore, the pulp mill is a point source to the SG-6 site, but seems to have little to no influence on areas away from the mill.

In FW1, 93 percent of dioxins present in the analyzed sediments were OCDD (Figure 29). This was expected since this signature, with high proportions of OCDD, is more typical of atmospheric deposition (Baker and Hites, 2000). These sediments had ratios of OCDD/2,3,7,8-TeCDF ranging from 78 to 2174, showing just how different the

fingerprint of these dioxins is from that of the waste pit site. In UH11193, over 91 percent of dioxins can be attributed to the OCDD congener (Figure 30). OCDD/TeCDF ratios in these sediments ranged from 38 to 109. And in UH11270, over 81 percent of the dioxins were OCDD with OCDD/TeCDF ratios of 6 to 82 (Figure 31). OCDD is by far the most important congener in these areas.

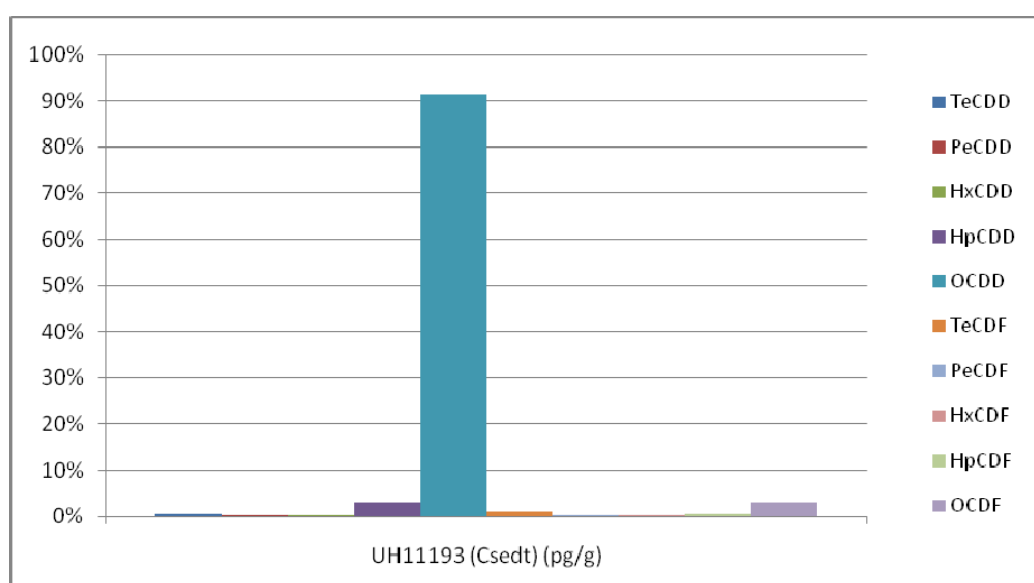


Figure 30. The percent concentration of dioxin congeners in UH11193 sediments.

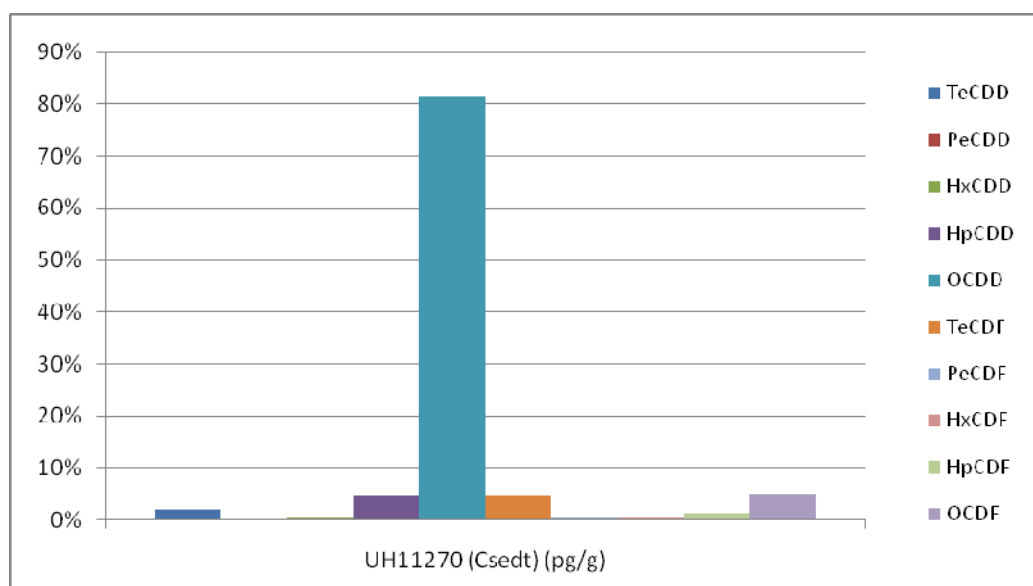


Figure 31. The percent concentration of dioxin congeners in UH11270 sediments.

In past studies, OCDD was found to be widely distributed and of sufficient magnitude due to an important atmospheric source (Macdonald et al., 1992; Baker and Hites, 2000). Direct measurements of OCDD confirmed that it is a major dioxin congener in the atmosphere (Macdonald et al., 1992; Rappe et al., 1987). OCDD is supplied to the environment partly by combustion or mixed industrial and municipal sources and partly by local events (Macdonald et al., 1998). Due to the large values of OCDD and the small values of other congeners in the sediments at distances from the waste pit, it can be concluded that the pulp mill effluent has little or no effect on the OCDD in these areas. This again emphasizes the difference in sources.

CONCLUSIONS

In contrast to what was expected, there seems to be little remobilization of particles from the pulp and paper mill waste site (SG-6) in the HSC. The waste pit appears to be stable and it seems that the contaminated particles are not being exported throughout the entire system. In other words, the mill seems to have a very limited geographical influence.

Therefore, the pulp and paper mill was a point source of dioxins to the sediments in and immediately surrounding the waste pit site. Due to the presence of dioxins in sediments other than those in the pit, there has to be another source of dioxins to the HSC system. This source is probably more diffuse and industrial in origin, and enters the sedimentary environment through the air and water.

PAHs were found to be mostly of petrogenic origin (~ 75%) at SG-6. This shows the importance of oil spills in the region in and around the waste pit. Pyrogenic sources of PAHs were also significant, as well as BC inputs to the sediments. This confirms the abundance of combustion by-products in the pulp and paper waste products deposited in the pit.

CHAPTER III

ESTIMATING IN SITU POREWATER DISTRIBUTION OF DIOXINS IN SEDIMENTS OF THE HOUSTON SHIP CHANNEL

INTRODUCTION

Background Information

Dioxins are released into aquatic environments in different ways and from various sources. The main sink for dioxins in aquatic environments is sediments. These sediments can then act as a secondary source of dioxins due to the persistent presence of these compounds in this reservoir and their potential to be released back into the water column (Kitamura et al., 2009). Once back in the water phase, dioxins are available to be accumulated by aquatic organisms (Arp et al., 2009) and bioaccumulated through the aquatic food chain (U.S. EPA, 1999). Therefore, aquatic sediments are related to human dioxin exposure, especially in countries where the main source of human dioxin intake is the consumption of seafood (Kitamura et al., 2009).

Based on previous reports, most dioxins present in the water column are associated with suspended particulate matter. Sources of suspended particulate matter include biota and organic matter from rivers. Particle size is one of the main properties controlling the behavior of suspended particulate matter (Kitamura et al., 2009) (e.g., the smaller the particle, the longer it remains in the water column). Different sources of dioxins contain different particle size distributions and bulk densities (Kitamura et al.,

2009). While this can make source apportioning more difficult, it is no impediment for bioaccumulation (i.e., for filter-feeding organisms).

Toxic dioxins are less available when bound to sediment and are usually passive or harmless to biota in the sediment-bound state. However, if they can enter the porewater phase, their potential bioavailability increases by several orders of magnitude (Arp et al., 2009). This issue is exacerbated by organisms that burrow into and filter-feed on the sediments.

The contaminants are also more available to flux back to the overlying water if they are freely dissolved in the porewater phase (Arp et al., 2009). In this freely dissolved state, PCDD/Fs can diffuse to the water column and become available to bioaccumulate in organisms (Cornelissen et al., 2008a). Therefore, it is also important to understand how organic contaminants are distributed between the sediment and porewater phases, not just the total quantity found bound to particles.

Due to the hydrophobicity of dioxins (repelled from water), when introduced to aquatic systems, they are thought to rapidly partition to organic carbon (OC), especially black carbon (BC), in suspended solids and eventually become buried in sediments (Yeager et al., 2007; Cornelissen et al., 2004; Wenning et al., 1992). This strong binding between dioxins and OC helps reduce the leaching, bioaccumulation, and toxicity of dioxins (Cornelissen et al., 2008a).

All 2,3,7,8-chlorinated PCDD/F congeners are highly toxic (Cornelissen et al., 2008a). Of these congeners, 2,3,7,8-TeCDD (Figure 32) has been shown to be the most toxic and physiologically active (Wenning et al., 1992). The World Health Organization

Toxic Equivalents (WHO-TEQ) is used to summarize dioxin concentrations with emphasis on toxic compounds (Kitamura et al., 2009). The TEQ method weighs the toxicity of the less toxic compounds as fractions of the toxicity of the most toxic TCDD, 2,3,7,8-TeCDD (Executive..., 1998).

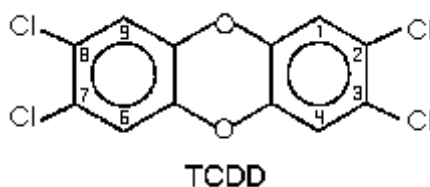


Figure 32. Diagram of 2,3,7,8-TeCDD showing the locations of its 4 chlorine atoms. (Scientific..., 2004)

Partitioning to anthropogenic impacted sediments and other environmental phases has often been found to be nonlinear (Arp et al., 2009), even though the original algorithms were based on linear relationships to OC and BC contents. Black carbon (BC), formed during incomplete combustion processes, is responsible for strong sorption behavior albeit nonlinear due to site saturation (Arp et al., 2009). For this reason, the significance of BC as a strong sorbent decreases as dioxin concentration increases. With high levels of dioxins, a critical point can be reached where OC becomes saturated and cannot absorb any more dioxins. Still, the potential for strong sorption to BC should be included when making risk assessments to the environment or when modeling transport of PCDD/Fs from sediment to the water column (Cornelissen et al., 2008a).

Several processes can impact sorption to the different absorbing and adsorbing phases. These include aging processes, surface attenuation by water and organics, pore blocking, and differences in sorption nonlinearity of both the absorbing and adsorbing phases to name a few (Arp et al., 2009). These processes could cause individual sediment components to sometimes sorb non-additively and inconsistently. These processes also challenge the idea that there are constant and standard amorphous OC and BC partitioning coefficients, K_{AOC} and K_{BC} , that are usable in predictive models, and emphasize that TOC is the carbon fraction that best accounts for general partitioning behavior (Arp et al., 2009). Therefore, two models, one including both AOC (amorphous OC)–water distribution ratio (K_{AOC}) and BC-normalized distribution coefficient (K_{BC}) values and one including just K_{TOC} values, were included in this study.

Objectives

Use two dioxin sorption models to estimate the freely dissolved distribution of dioxins in impacted sediments of the HSC. A control site from the Trinity River will be included to allow a constraint on the porewater concentrations. Since the “active” (freely dissolved) form exists in the porewater, and is the most readily available to biota, it can give a first approximation of the potential for bio-uptake and bioavailability. The toxic equivalence will also be calculated by expressing all dioxins in the system in equivalent units of toxicity. These will be used to show the environmental significance of dioxins in the system.

METHODS

Sampling

A total of 55 sediment cores were previously collected in 2004 from northwest Galveston Bay, the Houston Ship Channel, the lower San Jacinto River, and the lower Trinity River floodplain, Texas (Yeager et al., 2007). Three of these (UH11270, UH11193, and FW1) were used in this study. Seven additional cores were collected by Kevin Yeager and his group (Santschi et al., 2009). One such core (SG-6) was included in this study. Subsamples of the cores were used for analyses.

Previous Determinations

Some dioxin values were already determined for the samples from a previous study using EPA Method 1613B (Yeager et al., 2007), while the rest of the dioxin samples (core SG-6) were analyzed by Dr. Jermiah Shen (National Taiwan University) using the same method.

Theoretical Sorption Calculations

Estimated values for porewater concentrations of dioxins were calculated using empirical values for K_{TOC} and a two-phase model that assumes total organic carbon (TOC) is the main sorbent:

$$C_s = f_{\text{TOC}} K_{\text{TOC}} C_{\text{pw}}$$

where, C_s is the sediment dioxin concentration (pg/g); f_{TOC} is the sediment mass fraction of total OC; K_{TOC} is the TOC-water distribution ratio (L/kg); and C_{pw} is the freely

dissolved dioxin equilibrium concentration in porewaters (pg/L) (Arp et al., 2009). Log K_{TOC} values vary throughout the literature due to the diverse sorption behavior of the different adsorbing and absorbing components within the impacted sediments (Arp et al., 2009). Therefore, three values were used for K_{TOC} : minimum, maximum, and average, to show the sensitivity and range of the model predictions (Table 6).

The theoretical sorption and free porewater concentrations (C_{PW}) (pg/L) of dioxins were also estimated based on a three-phase model which incorporates both amorphous OC (i.e., difference between TOC and BC concentrations) and soot-derived BC as sorbents:

$$C_s = f_{AOC}K_{AOC}C_w + f_{BC}K_{BC}C_{PW}^{\eta_{F,BC}}$$

where, C_s is the sediment dioxin concentration (pg/g); f_{AOC} and f_{BC} are, respectively, the sediment mass fractions of amorphous OC and BC; K_{AOC} is the AOC-water distribution ratio (L/kg); C_{pw} is the freely dissolved dioxin equilibrium concentration in porewaters (pg/L); K_{BC} is the concentration-independent Freundlich BC-water distribution coefficient ((pg/kg BC)/(pg/L)); and $\eta_{F,BC}$ is the Freundlich exponent of BC sorption (Cornelissen et al, 2008a). No literature value is available for $\eta_{F,BC}$ for dioxins. Therefore, the value determined for phenanthrene (0.61) was used in this model to calculate the sorption to BC (Cornelissen et al, 2008a).

Table 6. Literature values for K_{TOC} . (Cornelissen et al., 2008a; Cornelissen et al., 2008b; Cornelissen et al., 2006; Arp et al., 2009)

Congener	K_{TOC} Avg	K_{TOC} Min	K_{TOC} Max
2,3,7,8-TeCDD	7.81	7.53	8.10
1,2,3,7,8-PeCDD	7.96	7.73	8.30
1,2,3,4,7,8-HxCDD	8.42	8.22	8.63
1,2,3,6,7,8-HxCDD	8.52	8.23	8.86
1,2,3,7,8,9-HxCDD	8.54	8.32	8.73
1,2,3,4,6,7,8-HpCDD	8.94	8.70	9.19
OCDD	9.34	9.14	9.58
2,3,7,8-TeCDF	7.70	7.50	8.03
1,2,3,7,8-PeCDF	8.04	7.74	8.50
2,3,4,7,8-PeCDF	8.12	7.81	8.66
1,2,3,4,7,8-HxCDF	8.48	8.29	8.83
1,2,3,6,7,8-HxCDF	8.48	8.28	8.82
1,2,3,7,8,9-HxCDF	8.32	7.95	8.93
2,3,4,6,7,8-HxCDF	8.04	7.02	8.88
1,2,3,4,6,7,8-HpCDF	9.01	8.76	9.15
1,2,3,4,7,8,9-HpCDF	8.99	8.77	9.26
OCDF	9.41	8.90	9.67

In the K_{AOC-BC} model, theoretical values of C_{PW} were modeled based on known solid-phase dioxin, amorphous organic carbon (AOC), and BC concentrations in the sediments of study and empirical K_{AOC} (L/kg) and K_{BC} ((pg/kg BC)/(pg/L)) values. K_{AOC} and K_{BC} were obtained from extensive studies in comparable environments (Cornelissen et al., 2008a; Cornelissen et al., 2008b). Then, the values obtained from the two different models (K_{TOC} and K_{AOC-BC}) were compared. This allowed for verification of the results and further discussions of implications as to the sensitivity of the models.

The results of the models also allowed for the calculation of the potential saturation of the sorbents or, on the other hand, the preservation of hydrophobic

contaminants in the solid phase. These calculations showed that either dioxins are being released into the water column or dioxins are being taken out of the water column with a subsequent decrease in their potential bioavailability through sorption.

Toxic Equivalent Calculations

The 17 dioxin congeners considered in this study (seven PCDDs and ten PCDFs) have a WHO-toxic equivalency factor (TEF) greater than zero (Kitamura et al., 2009). Each congener is given a specific TEF as shown in Tables 7 and 8. This factor indicates the degree of toxicity with respect to 2,3,7,8-TeCDD. This congener is the most toxic of the entire set and is assigned a reference value of 1 TEF. To calculate the total PCDD/F-TEQ of a dioxin mixture, the concentrations of each toxic congener are multiplied by their TEF and then totaled as shown in this equation:

$$\text{TEQ} = \sum (\text{PCDD}_i \times \text{TEF}_i) + \sum (\text{PCDF}_j \times \text{TEF}_j).$$

Table 7. Toxic equivalency factors of PCDDs. (Executive..., 1998)

Congener	2,3,7,8- TeCDD	1,2,3,7, 8- PeCDD	1,2,3,4, 7,8- HxCDD	1,2,3,6,7,8 -HxCDD	1,2,3,7,8,9 -HxCDD	1,2,3,4,6,7 ,8-HpCDD	OCDD
TEF	1	0.5	0.1	0.1	0.1	0.01	0.001

Table 8. Toxic equivalency factors of PCDFs. (Executive..., 1998)

Congener	2,3,7,8- TeCDF	1,2,3,7,8- PeCDF	2,3,4,7,8- PeCDF	1,2,3,4,7,8- HxCDF	1,2,3,6,7,8- HxCDF	1,2,3,7,8,9- HxCDF	2,3,4,6,7,8- HxCDF	1,2,3,4,6,7, 8-HpCDF	1,2,3,4,7,8, 9-HpCDF	OCDF
TEF	0.1	0.05	0.5	0.1	0.1	0.1	0.1	0.01	0.01	0.001

The TEQ method only refers to potential adverse effects such as cancer that follow interactions with the cellular Ah receptors (Executive..., 1998). Other toxic effects of dioxins are not accounted for by this method.

EXPECTED RESULTS

Due to the differences between the stations for dioxin concentrations and sources of dioxins in the sediment, there should also be differences in porewater concentrations and toxic equivalence. SG-6 should have by far the highest values for both of these between the stations, with UH11270, UH11193, and FW1 having successively lower values, based on previously determined data.

Since BC is present in the system based on assumed natural and anthropogenic inputs, the effects of dioxins present should be ameliorated and buffered somewhat by sorption to BC. In other words, sorption to BC is expected to decrease the bioavailability of dioxins in these sediments.

RESULTS AND DISCUSSION

Estimated Freely Dissolved Concentrations of PCDD/F

It has been shown that the *in situ* sediment-porewater distribution behavior of organics within impacted sediments is rather varied and difficult to generalize. Even at regional scales, the differences between sediment and porewater concentrations have been found to span up to 3 orders of magnitude (Arp et al., 2009). This is why it is important to note the median sorption behavior, but to also account for the possibility that different areas of the impacted sediments have minimum and maximum sorption coefficients (i.e. K_{TOC}) of this median value (Arp et al., 2009). Therefore, a sensitivity analysis was run on the first model by using three different K_{TOC} values to calculate the concentration of each congener in every sample. In addition, theoretical values of C_{PW} in the K_{AOC-BC} model were derived from known solid-phase dioxin, AOC, and BC concentrations in the sediments of study and empirical K_{AOC} and K_{BC} values (Arp et al., 2009; Cornelissen et al., 2008a; Cornelissen et al., 2008b). Therefore, a sensitivity analysis was not necessary for this second model.

The results from both of the estimated porewater dioxin concentrations (C_{PW}) are presented in Table A-8. The K_{TOC} model predicted that station SG-6 had porewater concentrations of dioxins ranging from 11.5 pg/L (15 cm depth) to 20.9 pg/L (8 cm depth). The lowest value for C_S (about 9300 pg/g) was also found at the 15 cm depth. However, 8 cm did not correspond to the depth with the highest C_S value (40 cm). Therefore, the sediments at SG-6 have slightly different sorption capacities and porewater concentrations.

Using the K_{TOC} model, station UH11270 showed estimated C_{PW} from 0.02 (2 cm) to 1.71 pg/L (12 cm). Station UH11193 had even lower estimated C_{PW} ranging from 0.19 (3 and 5 cm) to 0.54 pg/L (2 and 4 cm), and station FW1 showed estimated C_{PW} values of less than 0.04 pg/L. These values average about 8, 38, and over 1300 times less than those for SG-6, respectively. These values confirm the expectations of the significance of dioxin concentrations in the porewaters and their potential bioavailability at SG-6.

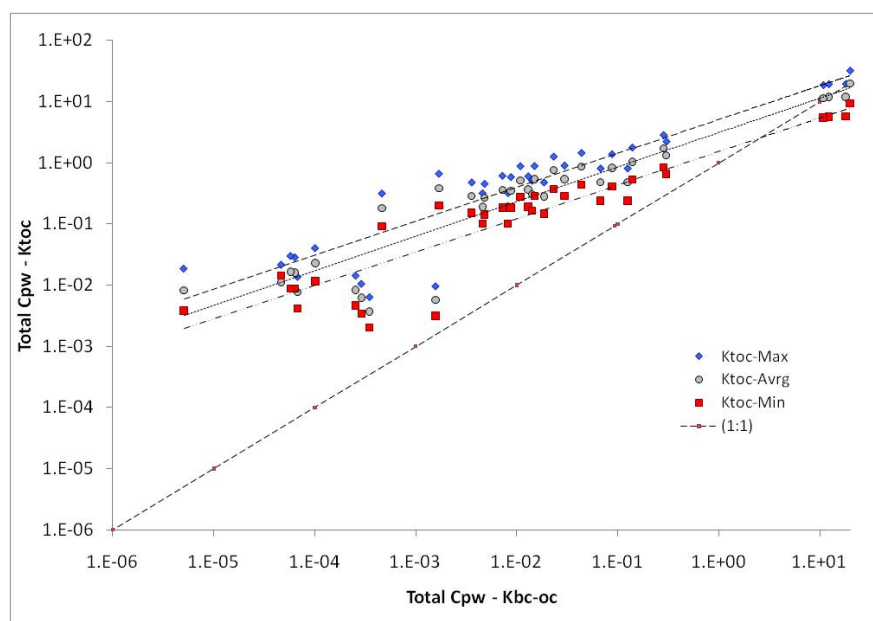


Figure 33. Estimated porewater dioxin concentrations (C_{PW}) using the K_{TOC} and K_{AOC-BC} methods.

Potential sources of error could cause some uncertainty in the reported data, but would not influence any of the conclusions drawn from this work. For instance, as shown in Figure 33, either the K_{TOC} model overestimates C_{PW} at low total dioxin concentrations or the K_{AOC-BC} model underestimates them. These differences point to the

heterogeneous nature of the total OC and its incorporation of carbonaceous geosorbents such as BC (Louchouart & Brinkmeyer, 2009). The presence of these carbonaceous geosorbents increases the sorption capacity of the total OC with respect to the ideal provided by amorphous OC one (Louchouart & Brinkmeyer, 2009), causing the C_{pw} values from the two models to be different.

Although it seems that the K_{AOC-BC} model is more conservative in predicting C_{pw} values in low to moderately impacted sediments, as is the case for most HSC sediments studied here, one could assume that field C_{pw} values might plot in between the lower range estimated by the K_{AOC-BC} model and the upper range estimated by the K_{TOC} model. The results from both models thus suggest that in the HSC system, and to the exception of the waste pit and its close surroundings, the sediments may have enough sorption capacity (despite low TOC and BC content) to keep the freely dissolved fraction of HOCs to a level <0.1 pg/L. In contrast, despite relatively high TOC and BC content in the waste pit, the extreme PCDD/F concentrations seem to exceed the sorption capacity (in particular for geosorbents such as soot-BC) leading to orders of magnitude higher values for estimated freely dissolved PCDD/F concentrations.

Toxic Equivalency of PCDD/Fs

The Swedish generic guideline value for less sensitive land use is 250 pg TEQ/g (Cornelissen et al., 2008a). All HSC sediments show potential risk since the toxicity of C_s exceeds this criterion by factors of 80 (SG-6), 12 (UH11270), and 8 (UH11193). The control site sediments (FW1) showed C_s values (in TEQ/g) about equal to this guideline

value. In Kitamura et al. (2009), TEQ concentrations in sediment samples ranged from 7 to 40 pg TEQ/g dry weight. Values of TEQ for C_s for SG-6 were far higher than these, ranging from over 1800 pg TEQ/g in the surface sediment (1 cm depth) to over 5000 pg TEQ/g at 40 cm depth. Even though more PCDFs were present in these samples than PCDDs, the majority of the TEQ was due to the PCDDs (62-69%).

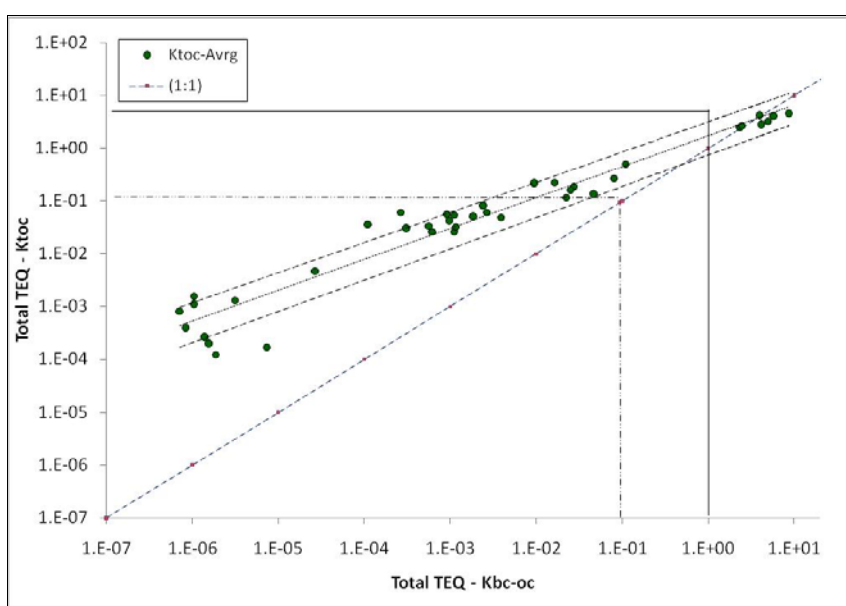


Figure 34. Calculated toxic equivalents for the estimated porewater dioxin concentrations from the K_{TOC} and K_{AOC-BC} models. The Texas Surface Water Quality Standard (0.0933 pg/L) is indicated with a broken dashed line and the Dutch limit for groundwaters (1 pg/L) is indicated with a solid line.

At station UH11270, TEQ concentrations in the sediment were found to span two orders of magnitude, from 2 at 41 cm depth to over 240 pg TEQ/g at 12 cm depth. At station UH11193, values ranged from 9 at 15 cm depth to 26 pg TEQ/g at the surface (1 cm depth). Station FW1 showed even lower toxic equivalents with values less than 1 pg

TEQ/g throughout most of the core. The highest value found at FW1 was 4 pg TEQ/g at the surface (1 cm depth). Contrary to SG-6, more PCDDs were present in these samples than PCDFs. However, as found at SG-6, the majority of the TEQ was due to the PCDDs. This is because 2,3,7,8-TeCDD is the most toxic congener, causing the PCDD-TEQ to be higher than that of PCDF.

The corresponding potential toxicities of the porewater concentrations were also calculated. The Dutch risk limit for serious groundwater contamination is 1 pg TEQ/L (Van De Gucht et al., 2000). Since this value leads to 50 percent death in organisms (H_{50}), it is used as a standard to identify highly polluted sites that require immediate attention (Van De Gucht et al., 2000). We are not aware of any similar standard in the U.S. However, the Texas Surface Water Quality Standard (0.0933 pg/L) is one order of magnitude lower. The estimated TEQ of porewater concentrations exceeded this risk limit by a factor of 3 at station SG-6 (Figure 34). The values for this location ranged from 2.5 to 4.5 pg TEQ/L. The K_{TOC} model also suggests that several sediment intervals from UH 11270 may have TEQs that exceed this limit (Fig. 34). Estimated dissolved TEQs were lower than this 'intervention value' limit at station UH11193 (0.03-0.08 pg TEQ/L) and station FW1 (0.00 pg TEQ/L).

Potential Bioavailability of PCDD/Fs

The samples with the highest sediment dioxin concentrations and the lowest estimated porewater dioxin concentrations are believed to have the highest sorption capacity. If dioxins are found in porewaters, they are not bound to OC present in the sediments. This lack of binding between dioxins and OC could cause an increase in the leaching, bioaccumulation, and toxicity of dioxins. Thus, it is very important to compare the dioxin concentrations between the sediment and aquatic phases.

A comparison of the dioxin values between the sediment and porewater of the HSC samples can be found in Table A-9. For station FW1, even though there was only limited amounts of OC present for dioxin sorption, the smallest amounts of dioxins were also found in these sediments. Therefore, there was enough OC with respect to dioxins to trap most of the dioxins in the sediments and buffer the majority of their effects.

The next lowest amount of bioavailable dioxins was found at station UH11193. In these sediments, most of the dioxins are sorbed to OC and will remain in the sediment phase. Still, this site has very low OC and BC concentrations, and can only absorb so much of dioxins. This is similar to what is occurring at station UH11270.

There is a two-fold increase of OC between UH11193 and UH11270, causing the sorption capacity of UH11270 to be greater than that at UH11193. However, since station UH11270 has double the C_S and C_{PW} , sorption to OC has the same effectiveness at both sites. In addition, the bioavailability at UH11270 seems to be similar but slightly higher than that at UH11193.

The highest sorption capacity and potential bioavailability occurs at station SG-6. This site has the highest OC values, but it also has the highest dioxin values. Because the dioxin concentration present in these sediments is so high, the influence of sorption to OC is decreased. Not enough OC is present in the sediments to reduce the availability of dioxins, causing some of the dioxins to be released into the porewaters. These dioxins then have the potential to move into the water column through hydrological pumping or passive diffusion and become available to biota.

CONCLUSIONS

In such instances where it is necessary to have porewater concentrations as accurate as possible, it is best to directly measure the concentrations and not rely on inferences from sediment concentrations (Arp et al., 2009). Since it was not possible to have exact values for this study, porewater concentrations were determined from sediment concentrations and sorption models using measured concentrations of geosorbents. This gave good enough data for the purposes of this work: to estimate the freely dissolved distribution of dioxins in impacted sediments and in turn estimate the potential bioavailability of those dioxins.

The pulp mill waste pit site (SG-6) showed estimated C_{PW} values well above the Dutch 'intervention value' of 1 pg TEQ/L (i.e., about 2-5 pg TEQ/L) (Van De Gucht et al., 2000; Cornelissen et al., 2008a). Values of TEQ for C_S for SG-6 were also very high (~ 2000-5000 ng TEQ/g). Despite relatively high TOC and BC contents, the sediments at

the waste pit showed a low sorption capacity for dioxins due to their extremely high dioxin concentrations with respect to OC and BC. Station UH11270 also showed substantial C_{PW} values, up to half the 'intervention value' (0.50 pg TEQ/L). Station UH11193 and especially station FW1 showed even lower C_{PW} (0.2-0.5 TEQ pg/L and < 0.04 pg/L, respectively) due to sufficient sorption capacity for the concentrations of dioxins present.

Based on estimated porewater concentrations, the waste pit is a likely source of dioxins for bioaccumulation by biota. Dioxins present in the pit have been found to remain where they are and not spread through the HSC system away from their source (Chapter II). However, biota are mobile and can transport these toxins throughout the system, causing them to spread and contaminate areas at greater distances from the pit. Dioxins are also probably bioavailable at UH11270, even though their source seems different than that of the waste emplacement at SG-6.

CHAPTER IV

CONCLUSIONS

SUMMARY

The results of this study have provided a basis for understanding the behavior of dioxins and other contaminants in the HSC system. The lignin and dioxin data from the SG-6 waste pit site verified that this core was collected at the site of a pulp and paper mill. This verification was based off the high amounts of lignin and dioxins in these sediments and their respective characteristic phenol and dioxin congener signatures (fingerprint).

The pulp and paper mill was a point source of dioxins to the sediments in and immediately surrounding the waste pit site with dioxin concentrations around 20,000 pg/g and high values of TEQ (5000 pg TEQ/g dry weight of sediment). The waste pit sediments also contain high levels of combustion-derived contaminants (pyrogenic PAHs and soot-BC), suggesting the wastes were either pre-combusted or combined with combustion waste material.

At present, the remobilization of dioxin-rich particles from the waste pit (SG-6) does not seem to occur beyond the close vicinity of the pit itself. Due to the presence of dioxins away from the waste pit site, there has to be at least one other source of dioxins to the HSC system. The source at SG-6 is the pulp and paper industry. The second source is probably more diffuse and industrial in origin, entering the sedimentary environment through the air and water.

Using two different sorption models, estimated porewater concentrations (C_{PW}) in the pulp mill waste pit showed astounding values well above the Dutch ‘intervention value’ of 1 pg TEQ/L and TEQ values around 5 pg TEQ/L. Station UH11270 also showed significant C_{PW} up to half the ‘intervention value’ (0.50 pg TEQ/L), depending on the model used. SG-6 and UH11270 sediments showed low sorption capacities for dioxins due to their low OC and BC concentrations relative to their high dioxin concentrations.

The waste pit at SG-6 is most likely a source of dioxins for bioaccumulation by biota. Even though there seems to be little wide scale geographical remobilization of dioxin rich particles from the pit, biota themselves are mobile and can transport these toxins throughout the system, causing them to contaminate areas at distances from the pit for further bioaccumulation and food chain transfer. Based on estimated C_{PW} values, dioxins are probably available to biota at UH11270, even though their source seems different than that of the waste emplacement at SG-6. Station UH11193 and especially station FW1 showed even lower C_{PW} values due to sufficient sorption capacity for the concentrations of dioxins present.

SG-6 is a site of concern and the contaminants present in these sediments need to be dealt with for a positive future for this aquatic environment. Accurate porewater concentrations should be measured directly to produce meaningful risk assessments and remediation strategies for the Houston Ship Channel system.

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APPENDIX A

TABLES

Table A-1. Carbon and nitrogen data for stations UH11270, UH11193, and FW1.

Core	Depth (cm)	Year	OC (%)	N (%)	(C/N) _a	BC (%)	(BC/OC)
UH11270	1	2003	0.90%	0.10%	9.00	0.13%	0.15
	2	2002	0.77 ± 0.07	0.06 ± 0.02	12.83	0.15%	0.20
	4	1999	1.14 ± 0.08	0.07 ± 0.01	16.29	0.11 ± 0.01	0.10
	6	1997	0.68%	0.11%	6.18	0.07 ± 0.00	0.10
	8	1995	0.43%	0.03%	14.33	0.11%	0.26
	10	1992	0.65%	0.07%	9.29	-	-
	12	1990	0.76 ± 0.01	0.06 ± 0.02	12.67	0.10 ± 0.04	0.13
	14	1988	1.06%	0.08%	13.25	0.12%	0.11
	16	1985	1.49 ± 0.02	0.12 ± 0.02	12.42	0.09 ± 0.01	0.06
	18	1983	-	-	-	0.09%	-
	20	1981	1.06 ± 0.04	0.07 ± 0.01	15.14	0.12%	0.12
	22	1978	-	-	-	0.11%	-
	24	1976	1.07 ± 0.09	0.06 ± 0.01	17.83	0.08%	0.08
	26	1974	1.43%	0.11%	13.00	0.14%	0.10
	28	1972	0.99 ± 0.06	0.07 ± 0.01	14.14	0.08 ± 0.01	0.08
	30	1969	-	-	-	0.14%	-
	31	1968	1.16 ± 0.01	0.09 ± 0.01	12.89	-	-
	32	1967	-	-	-	0.12 ± 0.01	-
	33	1966	1.53%	0.13%	11.77	-	-
	35	1963	1.50%	0.10%	15.00	0.15%	0.10
	37	1961	0.78 ± 0.16	0.05 ± 0.00	15.60	0.15%	0.20
	39	1959	0.17%	0.05%	3.40	0.13 ± 0.04	0.76
	41	1956	0.08 ± 0.01	0.01 ± 0.01	8.00	0.05 ± 0.01	0.63
	42	1955	0.18%	0.05%	3.60	-	-
	43	1954	0.11 ± 0.02	0.02 ± 0.00	5.50	0.07 ± 0.01	0.64
UH11193	1	2004	0.67 ± 0.11	0.06 ± 0.02	11.17	0.11% ± 0.04	0.16
	2	2004	0.45 ± 0.04	0.04 ± 0.01	11.25	0.07%	0.16
	3	2004	0.53%	0.06%	8.83	0.09%	0.17
	4	2004	0.42 ± 0.00	0.05 ± 0.01	8.40	0.10%	0.24
	5	2004	-	-	-	0.06%	-

Table A-1. Continued...

Core	Depth (cm)	Year	OC (%)	N (%)	(C/N) _a	BC (%)	(BC/OC)
UH11193	8	2003	0.64%	0.10%	6.40	0.09%	0.14
	10	2002	0.40 ± 0.02	0.05 ± 0.01	8.00	0.11%	0.28
	12	2002	0.33%	0.08%	4.13	0.10%	0.30
	15	2001	0.36 ± 0.04	0.03 ± 0.02	12.00	0.11%	0.31
	17	2001	0.51 ± 0.03	0.07 ± 0.01	7.29	-	-
	18	1999	-	-	-	0.09%	-
	20	1996	0.35 ± 0.01	0.03 ± 0.01	11.67	0.07% ± 0.01	0.20
	24	1990	0.37%	0.09%	4.11	0.07%	0.19
	27	1986	-	-	-	0.13% ± 0.01	-
	31	1980	0.39 ± 0.10	0.04 ± 0.01	9.75	0.09%	0.23
	34	1975	0.32%	0.04%	8.00	0.08%	0.25
	36	1972	0.32%	0.05%	6.40	-	-
	37	1971	-	-	-	0.07%	-
	40	1966	0.26 ± 0.00	0.03 ± 0.02	8.67	0.06% ± 0.00	0.23
	43	1962	0.32%	0.03%	10.67	-	-
	45	1959	0.23 ± 0.03	0.04 ± 0.01	5.75	0.04%	0.17
	47	1955	0.44%	0.07%	6.29	-	-
	50	1952	0.62 ± 0.10	0.04 ± 0.02	15.50	0.09%	0.15
	58	1950	0.56%	0.07%	8.00	-	-
	66	1948	0.44%	0.06%	7.33	-	-
FW1	1	2001	10.98 ± 1.96	0.83 ± 0.28	13.23	0.11%	0.01
	2	1999	6.73 ± 0.28	0.58 ± 0.08	11.60	0.12%	0.02
	3	1996	3.90 ± 0.30	0.54 ± 0.08	7.22	0.14% ± 0.01	0.04
	4	1993	-	-	-	0.13%	-
	5	1988	1.50%	0.52%	2.88	0.15%	0.10
	8	1985	0.70%	0.09%	7.78	0.16%	0.23
	10	1983	0.66%	0.09%	7.33	-	-
	11	1981	0.77%	0.42%	1.83	0.12%	0.16
	15	1977	0.58%	0.17%	3.41	0.13%	0.22
	16	1976	0.52%	0.08%	6.50	-	-
	20	1973	0.55%	0.41%	1.34	0.09%	0.16
	22	1971	0.47%	0.10%	4.70	-	-
	25	1969	0.43%	0.50%	0.86	0.12%	0.28
	26	1969	0.43%	0.04%	10.75	-	-
	30	1964	0.35%	0.49%	0.71	0.12%	0.34
	33	1961	0.40%	0.06%	6.67	-	-
	34	1959	-	-	-	0.13%	-
	37	1954	-	-	-	0.20%	-
	40	1948	0.54 ± 0.01	1.02 ± 0.44	0.53	0.13% ± 0.03	0.24
	43	1940	0.54%	0.06%	9.00	-	-
	46	1929	0.71 ± 0.01	1.04 ± 1.37	0.68	0.20%	0.28
	48	1916	0.82 ± 0.01	0.08 ± 0.03	10.25	-	-
	50	1906	0.90 ± 0.08	1.80 ± 2.41	0.50	0.17%	0.19

TableA-2. Carbon and nitrogen data for sediments at station SG-6.

Depth (cm)	Age (yr)	Year	OC (%)	N (%)	(C/N) _a	BC (%)	(BC/OC)
1	0.33	2007	1.23	0.11	13.05	0.116 ± 0.046	0.09
2	1.02	2006	1.59	0.11	17.67	0.16	0.10
3	1.71	2006	2.19	0.28	9.03	-	-
4	2.40	2005	1.52	0.33	5.44	-	-
5	3.08	2004	1.13	0.07	18.83	0.08	0.07
6	3.77	2004	1.88	0.13	16.90	-	-
7	4.45	2003	1.77	0.11	18.77	-	-
8	5.14	2002	1.75	0.08	27.22	0.128 ± 0.023	0.07
9	5.82	2001	2.12	0.10	24.73	-	-
10	6.51	2001	1.73	0.08	26.91	0.200 ± 0.023	0.12
11	7.19	2000	3.04	0.21	17.30	0.16	0.05
12	7.88	1999	1.78	0.07	31.95	-	-
13	8.56	1999	2.21	0.16	16.08	-	-
14	9.25	1998	1.59	0.06	30.92	-	-
15	9.93	1997	1.17	0.08	18.20	0.11	0.09
16	10.62	1997	1.44	0.04	48.00	-	-
17	11.30	1996	1.57	0.14	13.52	-	-
18	11.99	1995	1.59	0.06	33.62	-	-
19	12.67	1995	1.67	0.14	13.92	-	-
20	13.36	1994	1.50	0.12	15.22	0.11	0.07
21	14.04	1993	2.68	0.12	26.06	-	-
22	14.73	1993	1.73	0.06	33.64	-	-
23	15.41	1992	0.99	0.08	15.32	-	-
24	16.10	1991	0.85	0.06	18.03	-	-
25	16.78	1991	1.31	0.08	20.38	0.05	0.04
26	17.47	1990	1.20	0.02	93.33	-	-
27	18.15	1989	1.49	0.08	21.73	-	-
28	18.84	1988	1.05	0.03	40.64	-	-
29	19.52	1988	3.09	0.17	21.21	-	-
30	20.21	1987	2.97	0.105 ± 0.042	34.30	0.11	0.04
31	20.89	1986	4.71	0.09	61.06	-	-
32	21.58	1986	7.31	0.22	38.77	0.31	0.04
33	22.26	1985	4.08	0.11	43.27	-	-
34	22.95	1984	4.99	0.10	58.22	0.11	0.02
35	23.63	1984	5.48	0.195 ± 0.021	32.99	-	-
36	24.32	1983	5.59	0.22	29.64	0.14	0.03
37	25.00	1982	3.73	0.16	27.20	-	-
38	25.68	1982	2.07	0.11	21.95	0.14	0.07
39	26.37	1981	2.49	0.15	19.37	-	-
40	27.05	1980	1.84	0.125 ± 0.007	17.19	0.17	0.09

TableA-2. Continued...

Depth (cm)	Age (yr)	Year	OC (%)	N (%)	(C/N) _a	BC (%)	(BC/OC)
42	28.42	1979	2.09	0.12	20.32	-	-
44	29.79	1977	2.01	0.08	29.31	-	-
46	31.16	1976	2.55	0.11	27.05	0.12	0.05
48	32.53	1975	2.63	0.17	18.05	-	-
50	33.90	1973	2.31	0.120 ± 0.028	23.05	0.13	0.06
52	35.62	1972	2.44	0.22	12.94	-	-
54	36.99	1970	2.55	0.25	11.90	-	-
56	38.36	1969	2.78	0.24	13.51	0.19	0.07
58	39.73	1968	2.41	0.30	9.37	-	-
60	41.10	1966	2.38	0.185 ± 0.021	15.02	0.17	0.07
62	42.47	1965	1.51	0.14	12.58	-	-
64	43.84	1963	2.97	0.28	12.38	-	-
66	45.21	1962	2.67	0.27	11.54	0.22	0.08
68	46.58	1961	2.78	0.32	10.14	-	-
70	47.95	1959	3.47	0.270 ± 0.014	15.00	-	-
72	49.32	1958	2.43	0.22	12.89	-	-
74	50.69	1957	2.14	0.23	10.86	-	-
76	52.06	1955	2.26	0.16	16.48	0.26	0.12
78	53.43	1954	4.33	0.35	14.43	-	-
80	54.80	1952	4.75	0.290 ± 0.000	19.09	0.37	0.08

Table A-3. Lignin phenol data for HSC stations.

Core	Depth (cm)	V (mg/g)	S (mg/g)	C (mg/g)	Sig8 (mg/g)	Lambda (mg/g)	S/V	C/V
UH 11270	1	0.2394	0.1214	0.0184	0.3792	4.2135	0.5070	0.0769
	2	0.2451	0.1180	0.0149	0.3781	4.5549	0.4813	0.0609
	4	0.1904	0.0725	0.0136	0.2765	2.6337	0.3811	0.0717
	6	0.1757	0.0793	0.0129	0.2680	3.9408	0.4492	0.0740
	8	0.0912	0.0580	0.0077	0.1569	3.6489	0.6356	0.0840
	12	0.1794	0.0465	0.0108	0.2366	3.0734	0.2589	0.0600
	16	0.3254	0.0725	0.0177	0.4156	2.7985	0.2229	0.0543
	20	0.2703	0.0981	0.0204	0.3888	3.7745	0.3629	0.0757
	24	0.1889	0.0892	0.0180	0.2961	2.9612	0.4724	0.0951
	28	0.1800	0.0918	0.0197	0.2915	3.0680	0.5096	0.1092
	35	0.1409	0.0858	0.0193	0.2460	1.6401	0.6086	0.1373
	37	0.0890	0.0308	0.0058	0.1255	1.4101	0.3457	0.0648
	39	0.0064	0.0020	0.0004	0.0089	0.5239	0.3180	0.0684
	41	0.0020	0.0014	0.0000	0.0034	0.4834	0.6821	0.0000
	42	0.0024	0.0031	0.0003	0.0058	0.3206	1.2903	0.1385
	43	0.0029	0.0014	0.0000	0.0044	0.3626	0.4929	0.0000
UH 11193	1	0.0674	0.0548	0.0130	0.1351	2.0171	0.8131	0.1926
	2	0.0678	0.0518	0.0118	0.1314	2.9195	0.7647	0.1735
	3	0.0588	0.0532	0.0099	0.1218	2.2985	0.9047	0.1676
	4	0.0477	0.0386	0.0091	0.0954	2.2726	0.8101	0.1905
	8	0.0948	0.0754	0.0169	0.1871	2.9232	0.7950	0.1777
	10	0.0495	0.0384	0.0076	0.0955	2.3881	0.7760	0.1526
	15	0.0660	0.0456	0.0087	0.1202	3.3399	0.6913	0.1311
	20	0.0352	0.0244	0.0045	0.0641	1.8322	0.6930	0.1292
	24	0.0400	0.0359	0.0066	0.0825	2.2297	0.8991	0.1648
	31	0.0480	0.0345	0.0073	0.0898	2.3033	0.7188	0.1514
	34	0.0312	0.0208	0.0030	0.0550	1.7190	0.6670	0.0970
	40	0.0295	0.0201	0.0043	0.0539	2.0726	0.6801	0.1451
	45	0.0422	0.0281	0.0047	0.0750	3.2594	0.6662	0.1116
	50	0.4470	0.2169	0.0384	0.7023	11.3282	0.4853	0.0860
FW1	1	1.5644	1.1038	0.4492	3.1173	2.8404	0.7055	0.2871
	2	0.9527	0.6875	0.3055	1.9457	2.8932	0.7216	0.3207
	8	0.0243	0.0145	0.0090	0.0478	0.6827	0.5967	0.3719
	10	0.0360	0.0212	0.0081	0.0653	0.9890	0.5906	0.2248
	15	0.0126	0.0043	0.0008	0.0176	0.0003	0.0003	0.0001
	16	0.0136	0.0070	0.0039	0.0246	0.4736	0.5156	0.2889
	25	0.0093	0.0038	0.0009	0.0140	0.0003	0.0004	0.0001
	26	0.0113	0.0062	0.0028	0.0203	0.4715	0.5421	0.2468
	30	0.0110	0.0001	0.0000	0.0111	0.0003	0.0000	0.0000
	39	0.0119	0.0086	0.0030	0.0235	0.4048	0.7191	0.2483
	40	0.0149	0.0025	0.0012	0.0185	0.0003	0.0002	0.0001
	46	0.0079	0.0036	0.0015	0.0129	0.1831	0.4497	0.1846
	48	0.0123	0.0056	0.0026	0.0205	0.2510	0.4557	0.2112
	50	0.0152	0.0072	0.0026	0.0250	0.2793	0.4758	0.1711

Table A-3. Continued...

Core	Depth (cm)	V (mg/g)	S (mg/g)	C (mg/g)	Sig8 (mg/g)	Lambda (mg/g)	S/V	C/V
SG-6	1	0.1736	0.1515	0.0430	0.3681	3.2115	0.8831	0.2517
	2	0.1760	0.1720	0.0478	0.3958	3.5985	0.9773	0.2714
	5	0.1937	0.1824	0.0552	0.4313	3.7766	0.9419	0.2874
	8	0.3557	0.3376	0.0759	0.7691	4.2270	0.9487	0.2137
	10	0.4678	0.4525	0.1243	1.0446	4.5446	0.9692	0.2666
	15	0.1974	0.1824	0.0573	0.4765	3.2947	0.9296	0.2948
	20	0.2759	0.2539	0.0745	0.6874	3.7917	0.9217	0.2727
	25	0.0950	0.0126	0.0005	0.1080	0.8209	0.1321	0.0053
	29	0.6060	0.5000	0.1660	1.2720	5.3220	0.8250	0.2739
	30	1.6798	1.3194	0.3495	3.3487	9.0066	0.7855	0.2080
	31	2.4299	2.1821	0.5362	5.1482	9.5584	0.8980	0.2207
	32	4.5549	4.4466	1.4213	10.4228	11.7589	0.9762	0.3121
	33	1.4618	1.3804	0.4401	3.2822	9.9204	0.9443	0.3010
	34	3.5337	3.0519	0.8721	7.4576	12.2522	0.8637	0.2468
	35	3.8159	3.5805	1.2790	8.6754	13.5094	0.9383	0.3352
	36	3.4529	2.8024	0.8989	7.1541	11.6812	0.8116	0.2603
	37	1.7661	1.2518	0.4480	3.4660	8.0587	0.7088	0.2536
	38	0.6042	0.5075	0.1156	1.2273	5.3704	0.8399	0.1914
	40	0.5271	0.3935	0.0563	0.8005	4.8452	0.8861	0.1548
	42	0.4558	0.4505	0.0749	0.9812	4.1196	0.9884	0.1643
	44	0.4890	0.4443	0.0907	1.0240	4.9120	0.9086	0.1855
	46	0.9059	0.8261	0.2095	1.9415	7.0693	0.9120	0.2312
	50	0.6653	0.5528	0.1531	1.3712	5.2392	0.8310	0.2301
	56	0.4916	0.3826	0.0669	0.9411	3.2989	0.7783	0.1361
	60	0.2437	0.2061	0.0378	0.4876	2.1166	0.8458	0.1550
	66	0.3974	0.3783	0.0776	0.8534	2.8005	0.9518	0.1953
	70	0.6050	0.5404	0.0547	1.2001	3.6949	0.8933	0.0904
	76	0.4696	0.4025	0.0639	0.9360	4.1528	0.8571	0.1360
	80	0.8190	0.7230	0.1062	1.6707	4.2597	0.8829	0.1297

Table A-4. PAH data for stations UH11270 and UH11193.

Core	Depth (cm)	Total PAH Conc. (ng/g)	Pyrogenic PAHs (ng/g)	Pyrogenic PAHs (% of total)	Flu/(Py+Flu)	InP/(BgHi P+InP)	Ret/(Ret+Chy)	1,7-DMP/(1,7-+2,6-DMP)	MP/P	C0/C0+C1 P/A	Phen/Ant h	Fla/Pyr
UH 11270	4	2077.749	1303.775	62.75%	0.501	0.441	0.391	0.513	2.146	0.439	1.473	1.005
	8	2608.179	1958.367	75.09%	0.362	0.326	0.347	0.423	0.657	0.646	4.993	0.567
	12	1464.250	963.427	65.80%	0.490	0.560	0.319	0.453	1.855	0.566	0.705	0.963
	16	2068.714	1414.743	68.39%	0.463	0.570	0.336	0.519	2.021	0.456	1.447	0.863
	20	1887.542	1315.331	69.68%	0.554	0.591	0.290	0.551	2.232	0.449	1.218	1.241
	24	2768.004	1988.606	71.84%	0.559	0.599	0.233	0.517	2.143	0.479	1.034	1.267
	28	1281.639	913.639	71.29%	0.514	0.367	0.100	0.469	1.747	0.518	1.137	1.057
	37	1160.475	643.200	55.43%	0.633	0.424	0.553	0.509	1.632	0.433	4.085	1.722
	41	45.242	8.872	19.61%	0.358	0.157	0.719	0.595	0.996	0.501	-	0.559
	43	99.179	17.094	17.24%	0.508	0.426	0.760	0.317	0.658	0.606	99.210	1.032
UH 11193	1	456.585	233.407	51.12%	0.439	0.367	0.378	0.552	1.881	0.383	6.043	0.783
	2	402.465	211.463	52.54%	0.476	0.336	0.290	0.542	0.985	0.547	5.264	0.907
	3	321.779	145.702	45.28%	0.446	0.326	0.339	0.591	1.422	0.463	4.475	0.805
	4	282.672	129.697	45.88%	0.412	0.263	0.385	0.613	2.296	0.345	4.745	0.701
	5	417.849	221.910	53.11%	0.462	0.376	0.277	0.578	1.252	0.503	3.745	0.858
	8	604.378	325.473	53.85%	0.476	0.627	0.317	0.489	1.439	0.471	3.586	0.910
	10	334.383	158.975	47.54%	0.468	0.465	0.343	0.560	1.078	0.525	5.264	0.881
	15	1010.981	775.538	76.71%	0.516	0.465	0.080	0.545	1.082	0.523	5.388	1.067
	20	236.976	110.552	46.65%	0.512	0.362	0.317	0.618	1.176	0.503	5.217	1.048
	31	2042.573	1643.963	80.48%	0.424	0.485	0.016	0.638	1.413	0.658	0.582	0.737
	40	185.753	75.279	40.53%	0.379	0.281	0.657	0.613	1.464	0.427	10.811	0.610
	50	1559.309	1211.505	77.69%	0.285	0.457	0.115	0.545	2.332	0.449	1.111	0.398

Table A-5. PAH data for stations FW1 and SG-6.

Core	Depth (cm)	Total PAH Conc. (ng/g)	Pyrogenic PAHs (ng/g)	Pyrogenic PAHs (% of total)	Flu/(Py+Flu)	InP/(BgHi P+InP)	Ret/(Ret+Chy)	1,7-DMP/(1,7-+2,6-DMP)	MP/P	C0/C0+C1 P/A	Phen/Ant h	Fla/Pyr
FW1	2	344.772	52.725	15.29%	0.443	0.332	0.827	0.461	1.467	0.405	-	0.795
	3	413.945	34.708	8.38%	0.563	0.333	0.937	0.355	1.238	0.447	-	1.291
	4	443.439	56.807	12.81%	0.457	0.246	0.935	0.433	2.343	0.300	202.021	0.843
	9	154.616	15.595	10.09%	0.609	0.390	0.953	0.674	2.156	0.320	71.891	1.555
	14	245.531	21.661	8.82%	0.529	0.380	0.975	0.533	4.081	0.205	18.874	1.122
	19	247.335	12.148	4.91%	0.552	0.272	0.989	0.435	2.430	0.299	27.938	1.233
	25	163.482	8.718	5.33%	0.194	0.092	0.980	0.540	2.432	0.300	24.042	0.240
	37	187.953	15.113	8.04%	0.129	0.478	0.964	0.550	2.787	0.270	32.467	0.148
	40	328.837	20.165	6.13%	0.357	0.498	0.993	0.635	1.820	0.359	58.702	0.556
	50	401.679	58.387	14.54%	0.519	0.675	0.920	0.569	3.391	0.234	28.403	1.077
SG-6	1	3349.230	588.207	17.56%	0.454	0.475	0.901	0.396	1.844	0.368	13.603	0.830
	5	3339.318	1151.483	34.48%	0.497	0.462	0.724	0.417	1.597	0.419	6.524	0.987
	8	4374.553	884.283	20.21%	0.439	0.381	0.897	0.393	2.223	0.341	6.674	0.783
	10	4449.160	780.252	17.54%	0.445	0.351	0.871	0.382	2.076	0.347	9.675	0.802
	15	1654.330	389.033	23.52%	0.439	0.344	0.725	0.415	1.774	0.393	6.792	0.784
	20	2075.733	746.187	35.95%	0.430	0.442	0.415	0.469	1.701	0.397	8.282	0.755
	25	717.618	131.831	18.37%	0.398	0.243	0.715	0.410	1.574	0.403	16.194	0.661
	30	3523.645	501.685	14.24%	0.460	0.332	0.875	0.409	1.809	0.381	8.923	0.851
	32	10933.340	2355.972	21.55%	0.495	0.406	0.700	0.382	1.804	0.387	7.152	0.979
	34	6503.753	755.259	11.61%	0.432	0.298	0.898	0.398	2.029	0.357	7.967	0.760
	36	6350.519	874.422	13.77%	0.451	0.330	0.873	0.398	1.747	0.388	9.479	0.821
	38	2850.845	725.554	25.45%	0.418	0.335	0.478	0.412	1.651	0.403	8.879	0.719
	40	3038.251	777.365	25.59%	0.398	0.303	0.427	0.422	1.697	0.400	7.552	0.662
	46	3088.220	831.625	26.93%	0.425	0.408	0.528	0.436	1.608	0.413	7.658	0.739
	50	3680.647	1345.380	36.55%	0.405	0.429	0.436	0.435	1.747	0.405	5.333	0.681
	56	3422.611	980.467	28.65%	0.379	0.309	0.479	0.454	1.843	0.390	5.572	0.609
	60	3726.130	1168.025	31.35%	0.349	0.320	0.468	0.464	1.765	0.409	4.555	0.536
	66	4053.937	1096.527	27.05%	0.384	0.293	0.523	0.421	1.955	0.381	4.946	0.624
	76	5227.924	1233.154	23.59%	0.409	0.192	0.627	0.406	2.214	0.345	5.977	0.692
	80	6821.357	1765.303	25.88%	0.399	0.307	0.574	0.400	2.142	0.355	5.634	0.665

Table A-6. Polychlorinated dibenzo-*p*-dioxin (PCDD) data for HSC sediments in pg/g.

Core	Depth (cm)	Year	2,3,7,8- TeCDD	1,2,3,7,8- PeCDD	Total HxCDD	1,2,3,4,6, 7,8- HpCDD	OCDD	Total TCDD (pg/g)
UH 11270	2	2003	1.60	0.29	0.81	4.30	110.00	117.00
	4	2000	26.00	1.40	11.60	150.00	2800.00	2989.00
	8	1996	48.00	0.70	3.38	36.00	1000.00	1088.08
	12	1991	190.00	2.30	11.10	120.00	2700.00	3023.40
	16	1986	100.00	1.80	10.30	100.00	1700.00	1912.10
	20	1982	96.00	2.10	19.60	220.00	4300.00	4637.70
	24	1977	59.00	1.60	14.40	130.00	2100.00	2305.00
	28	1972	120.00	3.10	36.10	420.00	6700.00	7279.20
	32	1968	85.00	4.60	57.70	690.00	9700.00	10537.30
	37	1962	89.00	1.60	10.30	110.00	3100.00	3310.90
	41	1957	1.25	0.35	0.87	1.65	105.00	109.12
	43	1955	3.20	0.29	1.24	4.40	490.00	499.13
UH 11193	1	2004	16.00	0.87	5.16	72.00	2600.00	2694.03
	2	2004	12.00	0.73	6.10	83.00	3000.00	3101.83
	3	2004	6.40	0.43	2.58	34.00	1100.00	1143.41
	4	2004	10.00	0.81	6.20	99.00	2900.00	3016.01
	5	2004	6.00	0.40	2.99	40.00	1000.00	1049.39
	8	2003	9.40	0.78	7.40	99.00	2500.00	2616.58
	10	2002	10.00	0.83	6.00	90.00	2600.00	2706.83
	15	2001	5.10	0.45	2.72	50.00	1300.00	1358.27
	20	1996	6.80	0.35	3.83	49.00	1400.00	1459.98
	31	1980	6.05	0.50	4.18	49.50	1180.00	1240.22
FW1	40	1966	11.00	0.46	4.05	22.00	680.00	717.51
	1	2002	0.24	0.75	6.10	59.00	1000.00	1066.09
	2	2000	0.16	0.33	2.59	21.00	410.00	434.08
	3	1997	0.19	0.31	1.95	17.00	420.00	439.45
	4	1994	0.17	0.18	2.28	12.00	360.00	374.63
	5	1989	0.16	0.20	1.04	8.20	180.00	189.60
	6	1982	0.16	0.18	0.83	5.90	120.00	127.07
	8	1978	0.16	0.18	0.68	4.50	190.00	195.52
	10	1974	0.16	0.19	1.10	12.00	500.00	513.45
	20	1969	0.25	0.23	0.64	2.55	79.00	82.66
SG-6	30	1965	0.16	0.18	0.59	0.77	18.00	19.70
	40	1949	0.16	0.23	0.71	2.80	140.00	143.90
	1	2007	1143.00	12.83	3.66	52.44	2049.00	3260.93
	5	2004	1432.00	17.35	3.93	54.18	1592.00	3099.46
	8	2002	3058.00	35.65	5.82	85.16	2562.00	5746.63
	10	2001	2780.00	32.63	6.33	93.75	2880.00	5792.71
	15	1997	1292.00	15.63	4.07	62.67	1896.00	3270.37
	20	1994	1736.00	20.04	9.43	127.10	3482.00	5374.57
	40	1980	3436.00	36.88	14.40	209.10	5606.00	9302.38

Table A-7. Polychlorinated dibenzo-furan (PCDF) and PCDD/F data for HSC sediments in pg/g.

Core	Depth (cm)	2,3,7,8-TeCDF	Total PeCDF	Total HxCDF	Total HpCDF	OCDF	Total TCDF (pg/g)	Total Dioxins (pg/g)
UH 11270	2	3.90	0.63	1.01	1.19	6.00	12.73	129.73
	4	57.00	5.80	10.90	35.80	140.00	249.50	3238.50
	8	96.00	4.10	5.24	9.50	32.00	146.84	1234.92
	12	420.00	10.60	13.70	32.90	130.00	607.20	3630.60
	16	230.00	7.80	10.24	22.90	98.00	368.94	2281.04
	20	230.00	13.60	24.70	58.80	240.00	567.10	5204.80
	24	140.00	11.00	18.50	38.40	130.00	337.90	2642.90
	28	330.00	42.00	49.90	122.00	410.00	953.90	8233.10
	32	250.00	61.00	58.80	175.00	800.00	1344.80	11882.10
	37	180.00	8.10	12.50	26.80	110.00	337.40	3648.30
	41	3.15	0.39	0.72	0.51	0.72	5.48	114.60
	43	6.00	0.51	1.78	1.24	2.00	11.53	510.66
UH 11193	1	40.00	3.10	5.62	10.30	86.00	145.02	2839.05
	2	34.00	2.80	5.94	10.60	66.00	119.34	3221.17
	3	16.00	1.26	2.64	5.36	39.00	64.26	1207.67
	4	28.00	2.60	4.72	11.10	63.00	109.42	3125.43
	5	17.00	1.45	2.73	5.85	41.00	68.03	1117.42
	8	23.00	2.20	4.39	12.80	68.00	110.39	2726.97
	10	24.00	4.40	10.70	13.00	84.00	136.10	2842.93
	15	12.00	1.31	2.57	5.05	34.00	54.93	1413.20
	20	17.00	1.77	3.39	8.40	59.00	89.56	1549.54
	31	14.50	1.38	3.21	6.87	46.00	71.95	1312.17
	40	18.00	1.38	2.13	5.01	63.00	89.52	807.03
FW1	1	1.20	1.52	3.33	11.85	18.00	35.90	1101.99
	2	0.30	0.62	1.66	3.71	5.00	11.29	445.37
	3	0.26	0.45	1.16	2.63	3.70	8.20	447.65
	4	0.24	0.43	1.09	2.30	3.60	7.66	382.29
	5	0.24	0.43	0.88	1.80	1.90	5.25	194.85
	6	0.24	0.43	0.97	1.61	1.60	4.85	131.92
	8	0.24	0.43	0.88	0.76	0.78	3.09	198.61
	10	0.23	0.42	0.90	1.13	0.77	3.45	516.90
	20	0.26	0.43	0.88	0.51	0.79	2.86	85.52
	30	0.23	0.41	0.85	0.54	0.77	2.80	22.50
	40	0.26	0.48	0.88	0.51	0.78	2.91	146.81
SG-6	1	6299.00	170.59	153.18	34.63	55.59	6712.99	9973.92
	5	6907.00	210.00	211.78	51.99	80.01	7460.78	10560.24
	8	15510.00	424.60	400.42	101.17	96.93	16533.12	22279.75
	10	14600.00	462.10	413.87	113.00	129.90	15718.87	21511.58
	15	5521.00	188.64	195.08	47.04	54.58	6006.34	9276.71
	20	7337.00	286.10	350.68	99.92	145.30	8219.00	13593.57
	40	13629.00	475.40	665.22	198.77	257.30	15225.69	24528.07

Table A-8. Dioxin porewater concentrations (C_{PW}) of HSC sediments in pg/L. The corresponding toxicities of these dioxins are also included, showing the calculated range from minimum, to average, to maximum TEQ (pg/L).

Core	Depth (cm)	PCDD (Ave) (pg/L)	PCDF (Ave)	Total Dioxins (Ave)	PCDD-TEQ (Ave)	PCDF-TEQ (Ave)	Total-TEQ (Ave)	Total-TEQ (Min)	Total-TEQ (Max)
UH 11270	2	0.011	0.012	0.023	0.003	0.001	0.005	0.002	0.009
	4	0.167	0.117	0.284	0.036	0.012	0.048	0.024	0.089
	8	0.292	0.467	0.759	0.173	0.047	0.221	0.112	0.407
	12	0.573	1.141	1.715	0.387	0.115	0.502	0.255	0.924
	16	0.167	0.322	0.488	0.104	0.033	0.137	0.069	0.252
	20	0.357	0.471	0.828	0.141	0.048	0.189	0.095	0.348
	24	0.194	0.287	0.481	0.086	0.030	0.116	0.058	0.214
	28	0.560	0.756	1.315	0.190	0.077	0.267	0.134	0.493
	32	0.541	0.501	1.042	0.109	0.051	0.160	0.079	0.295
	37	0.380	0.488	0.868	0.177	0.049	0.227	0.115	0.419
	41	0.095	0.089	0.184	0.027	0.009	0.036	0.018	0.068
	43	0.260	0.124	0.384	0.047	0.013	0.060	0.030	0.114
UH 11193	1	0.231	0.134	0.364	0.038	0.013	0.051	0.012	0.098
	2	0.374	0.171	0.544	0.043	0.017	0.060	0.019	0.158
	3	0.123	0.069	0.192	0.019	0.007	0.026	0.006	0.052
	4	0.387	0.152	0.539	0.039	0.015	0.054	0.019	0.159
	5	0.117	0.074	0.192	0.019	0.007	0.026	0.006	0.050
	8	0.224	0.084	0.308	0.024	0.008	0.032	0.011	0.090
	10	0.369	0.152	0.521	0.041	0.015	0.056	0.018	0.150
	15	0.207	0.078	0.285	0.023	0.008	0.031	0.010	0.083
	20	0.234	0.115	0.349	0.031	0.011	0.042	0.011	0.096
	31	0.182	0.088	0.269	0.025	0.009	0.034	0.009	0.073
	40	0.199	0.159	0.358	0.067	0.016	0.082	0.009	0.079
FW1	1	0.005	0.001	0.006	0.000	0.000	0.000	0.000	0.000
	2	0.003	0.000	0.004	0.000	0.000	0.000	0.000	0.000
	3	0.006	0.000	0.006	0.000	0.000	0.000	0.000	0.000
	4	0.008	0.001	0.008	0.000	0.000	0.000	0.000	0.001
	5	0.007	0.001	0.008	0.000	0.000	0.000	0.000	0.001
	6	0.004	0.001	0.005	0.000	0.000	0.000	0.000	0.001
	8	0.014	0.002	0.016	0.001	0.000	0.001	0.000	0.002
	10	0.038	0.002	0.040	0.001	0.000	0.001	0.000	0.002
	20	0.009	0.003	0.011	0.001	0.000	0.001	0.001	0.003
	30	0.004	0.004	0.008	0.001	0.001	0.002	0.001	0.003
	40	0.014	0.003	0.017	0.001	0.000	0.001	0.001	0.002
SG-6	1	1.523	10.466	11.988	1.435	1.064	2.499	1.240	4.429
	5	2.037	12.524	14.561	1.958	1.275	3.233	1.610	5.766
	8	2.784	18.119	20.903	2.699	1.842	4.541	2.259	8.078
	10	2.576	17.293	19.869	2.482	1.762	4.244	2.107	7.540
	15	1.795	9.692	11.487	1.706	0.988	2.694	1.345	4.833
	20	1.913	10.094	12.007	1.788	1.028	2.816	1.406	5.054
	40	2.791	13.971	16.762	2.640	1.421	4.061	2.032	7.306

Table A-9. A comparison of sediment and porewater concentrations of dioxins in HSC sediments.

Core	Depth (cm)	OC (g)	C _S (pg/g OC)	C _S (pg/g)	C _{PW} (pg/L)	C _S /C _{PW} (L/g)
UH 11270	2	0.0077	16848.0519	129.7300	0.0231	5621.6620
	4	0.0114	284078.9474	3238.5000	0.2838	11412.4515
	8	0.0043	287190.6977	1234.9200	0.7589	1627.1650
	12	0.0076	477710.5263	3630.6000	1.7145	2117.5578
	16	0.0149	153089.9329	2281.0400	0.4883	4671.6532
	20	0.0106	491018.8679	5204.8000	0.8276	6289.3707
	24	0.0107	247000.0000	2642.9000	0.4811	5493.2755
	28	0.0099	831626.2626	8233.1000	1.3152	6259.8462
	32	0.0125	950568.0000	11882.1000	1.0421	11402.0317
	37	0.0078	467730.7692	3648.3000	0.8684	4201.2617
	41	0.0008	143243.7500	114.5950	0.1835	624.3776
	43	0.0011	464236.3636	510.6600	0.3841	1329.5204
	Average	0.0083	401195.1808	3562.6038	0.6975	5107.3164
UH 11193	1	0.0067	423738.8060	2839.0500	0.3644	7791.4946
	2	0.0045	715815.5556	3221.1700	0.5443	5918.1709
	3	0.0053	227862.2642	1207.6700	0.1920	6290.0711
	4	0.0042	744150.0000	3125.4300	0.5389	5799.7097
	5	0.0052	214888.4615	1117.4200	0.1918	5825.9067
	8	0.0064	426089.0625	2726.9700	0.3083	8845.9096
	10	0.0040	710732.5000	2842.9300	0.5213	5453.9178
	15	0.0036	392555.5556	1413.2000	0.2853	4953.8786
	20	0.0035	442725.7143	1549.5400	0.3487	4443.1721
	31	0.0039	336453.8462	1312.1700	0.2694	4871.2519
	40	0.0026	309653.8462	807.0300	0.3577	2256.1399
	Average	0.0045	449515.0556	2014.7800	0.3565	5650.8572
FW1	1	0.1098	10036.3388	1101.9900	0.0057	193071.4146
	2	0.0673	6617.6820	445.3700	0.0037	119600.6490
	3	0.0390	11478.2051	447.6500	0.0062	71873.7344
	4	0.0247	15489.4933	382.2900	0.0084	45451.3250
	5	0.0150	12990.0000	194.8500	0.0077	25377.4894
	6	0.0168	7840.8141	131.9200	0.0050	26355.8969
	8	0.0070	28372.8571	198.6100	0.0161	12325.3274
	10	0.0066	78318.1818	516.9000	0.0402	12869.9512
	20	0.0055	15548.1818	85.5150	0.0112	7647.6732
	30	0.0035	6428.5714	22.5000	0.0082	2745.3588
	40	0.0054	27187.0370	146.8100	0.0165	8888.5156
	Average		20027.9421	334.0368	0.0117	28500.1655
SG-6	1	0.0123	810887.6423	9973.9180	11.9885	831.9579
	5	0.0113	934534.6018	10560.2410	14.5609	725.2460
	8	0.0175	1273128.6857	22279.7520	20.9026	1065.8863
	10	0.0173	1243443.9306	21511.5800	19.8691	1082.6660
	15	0.0117	792881.1966	9276.7100	11.4867	807.6075
	20	0.0150	906237.8667	13593.5680	12.0070	1132.1380
	40	0.0201	1220301.7413	24528.0650	16.7624	1463.2755
	Average	0.0150	1025916.5236	12467.1868	11.9562	1042.7425

APPENDIX B

FIGURES

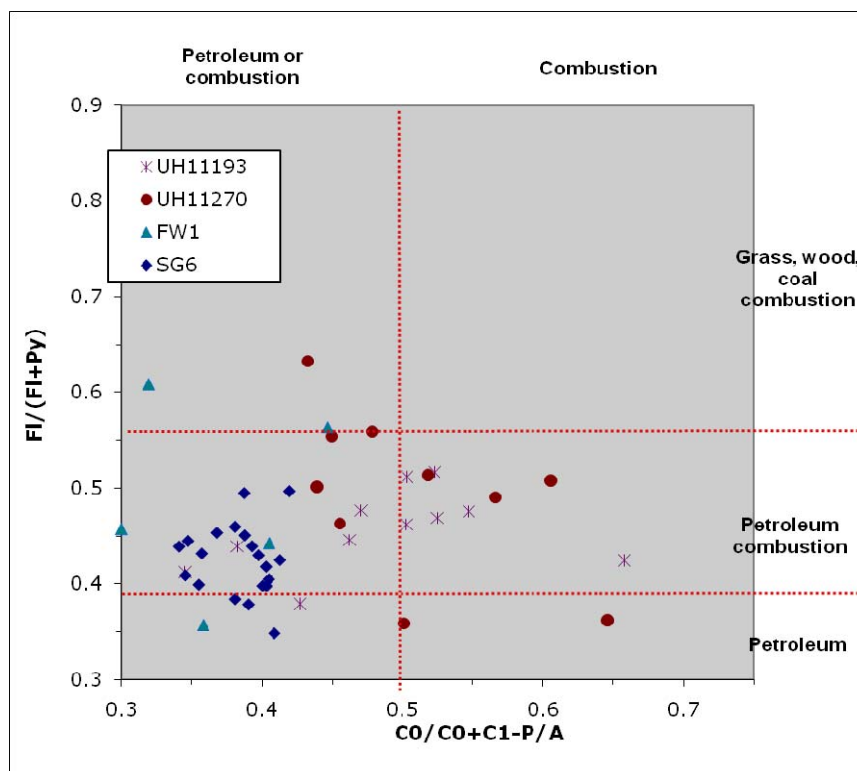


Figure A-1. Fluoranthene/(Pyrene + Fluoranthene) ($FI/(FI+Py)$) versus (Phenanthrene + Anthracene)/(Phenanthrene + Anthracene + C1-Phe/An) ($(Phen + Anth)/(Phen + Anth + C1-P/A)$) ratios for HSC stations.

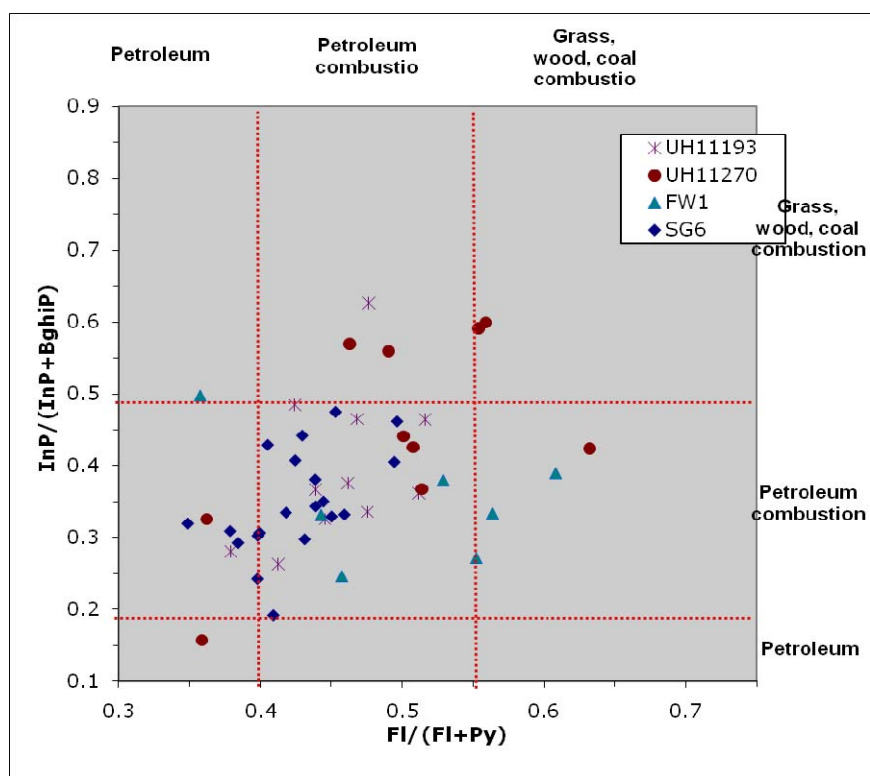


Figure A-2. Indeno(1,2,3-c,d)pyrene/(Indeno(1,2,3-c,d)pyrene + Benzo(g,h,i)perylene ($\text{InP}/(\text{InP}+\text{BghiP})$) versus Fluoranthene/(Pyrene + Fluoranthene) ($\text{Fl}/(\text{Fl}+\text{Py})$) ratios for HSC stations.

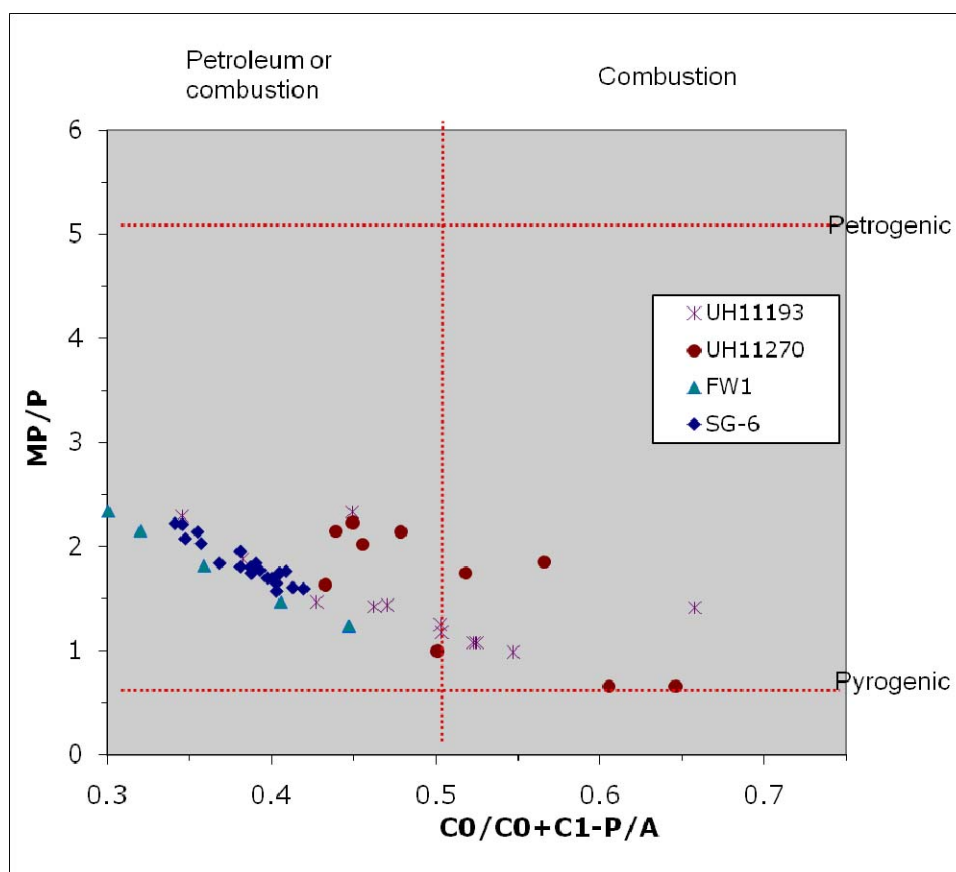


Figure A-3. Methylphenanthrenes/Phenanthrene (MP/P) versus (Phenanthrene + Anthracene)/ (Phenanthrene + Anthracene + C1-Phe/An) ((Phen + Anth)/(Phen + Anth + C1-P/A)) ratios for the HSC stations.

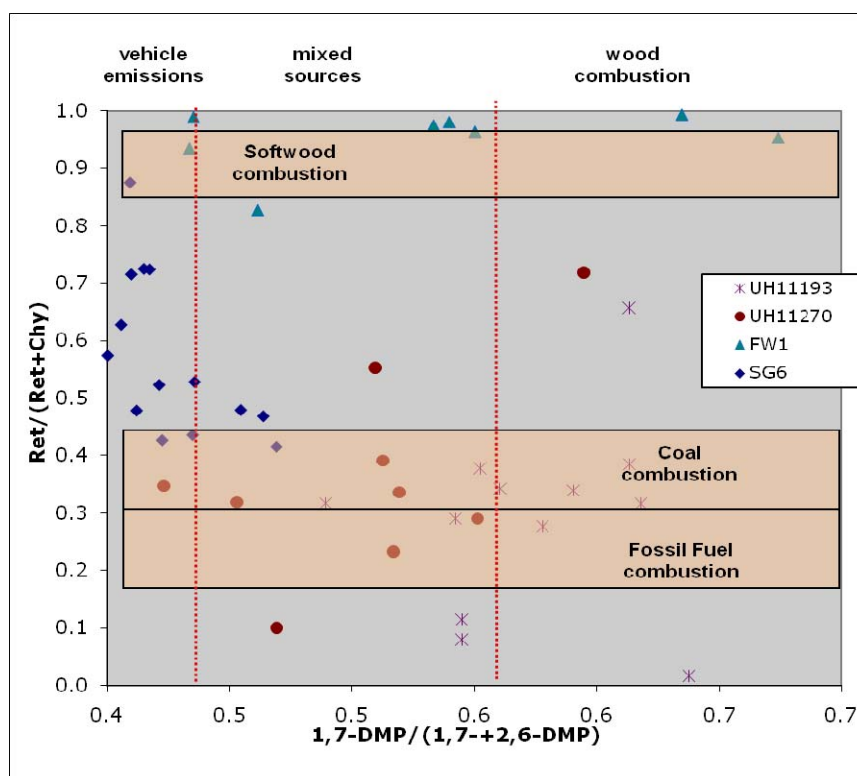


Figure A-4. Retene/(Retene + Chrysene) (Ret/(Ret+Chy)) versus 1,7-Dimethylphenanthrene/(1,7- + 2,6-Dimethylphenanthrene) (1,7-DMP/(1,7+2,6-DMP) ratios for HSC stations.

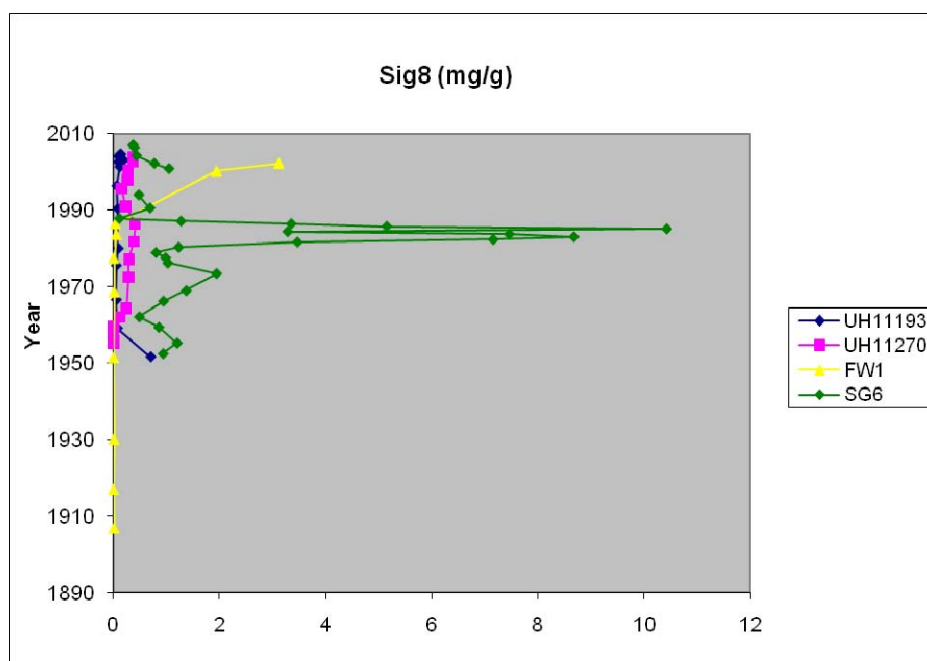


Figure A-5. A comparison of lignin phenols ($\Sigma 8$; mg/g) between HSC stations.

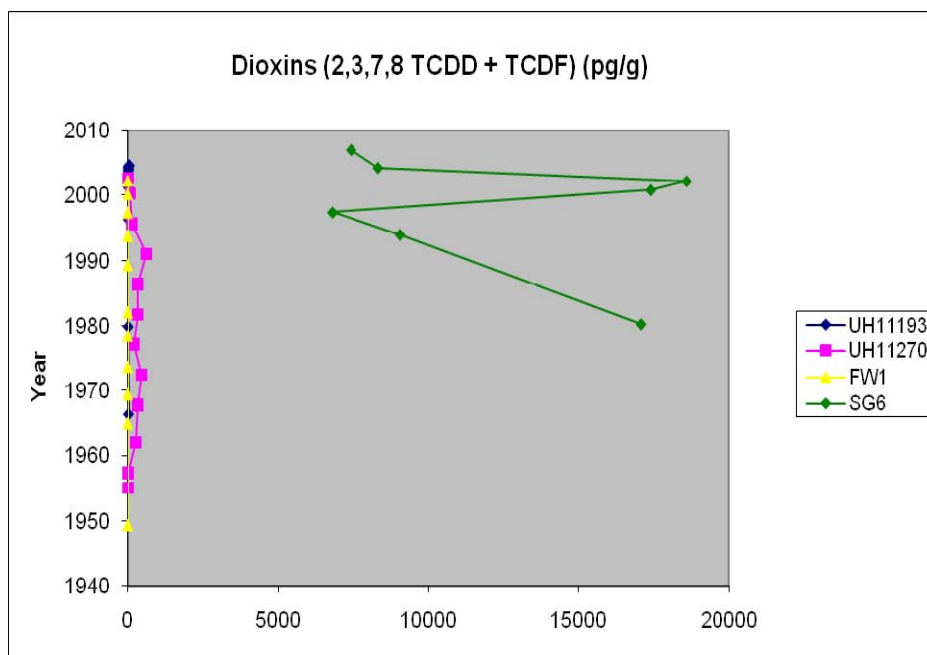


Figure A-6. A comparison of total dioxins (pg/g) between HSC stations.

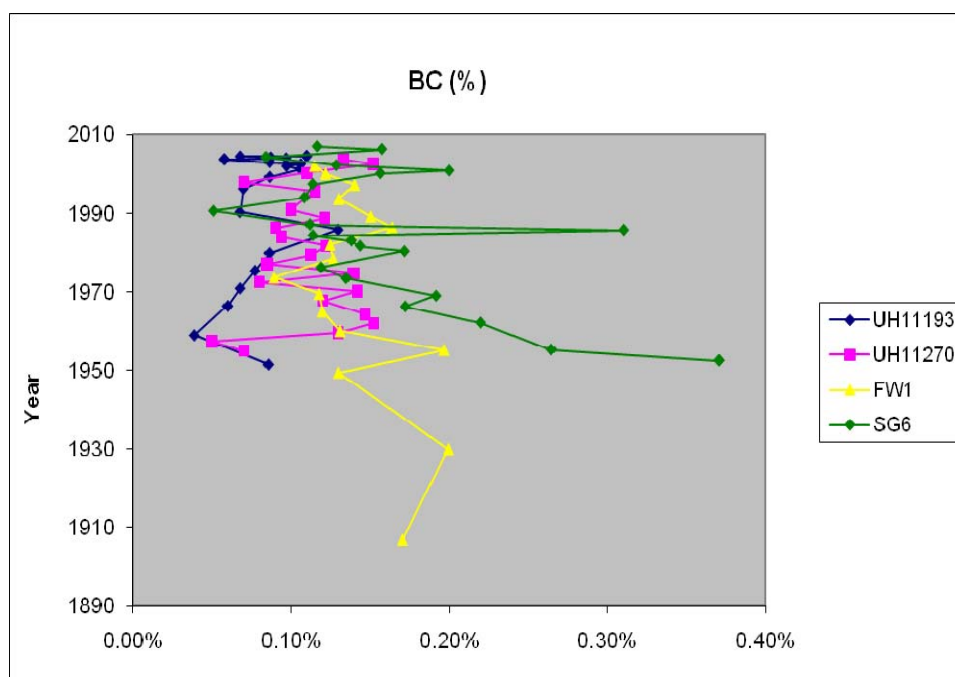


Figure A-7. A comparison of BC (%) between HSC stations.

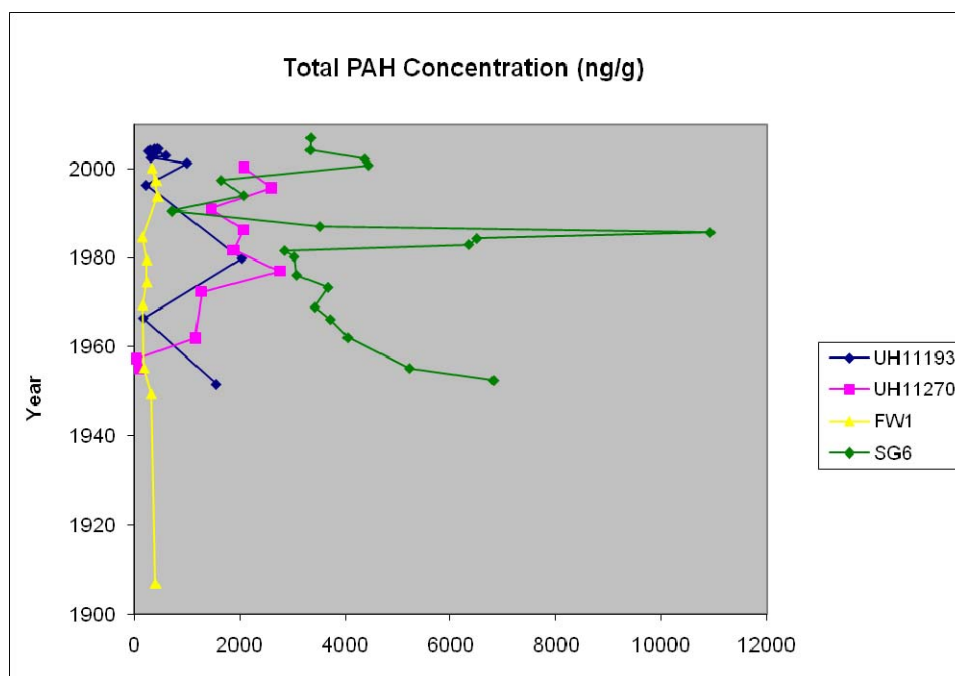


Figure A-8. A comparison of total PAH concentration (ng/g) between HSC stations.

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