CHARACTERIZING RECREATIONAL EXPOSURE TO CONTAMINANTS IN HOUSTON, TEXAS PARKS AFTER HURRICANE HARVEY

A Dissertation

by

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ABSTRACT

In Houston, flooding is controlled in part by a system of creeks and bayous that include a network of recreation areas, such as parks, trails, playgrounds, and picnic areas. The effects of flooding can have devastating impacts on communities, changing both the physical landscape, and in heavily industrialized communities such as the Greater Houston Area (GHA), altering the chemical profiles of parks and recreation areas. This change in chemical profile can potentially lead to adverse health outcomes in residents using parks. Shortly after Hurricane Harvey, the Texas A&M Superfund Research Center partnered with a local health department to understand the distribution of different chemicals in four park areas near Buffalo Bayou in the GHA in a post flooding environment. Soil samples were collected from the four parks one week after Hurricane Harvey made landfall, and seven weeks later to better understand the distribution of these chemicals over time as the city returned to its typical levels of activity. All environmental sediment samples were analyzed for the U.S. Environmental Protection Agency's (USEPA) 16 priority polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), legacy organochlorine pesticides, and heavy metals.

PAHs were analyzed in the sediment samples at the four park locations. Diagnostic ratios were created using the concentrations of specific priority PAHs in order to broadly predict the potential sources for PAHs in the parks. Potential sources for PAH concentrations in the parks are pyrogenic and vehicular combustion sources. Toxic equivalence factors (TEF) were assigned to give toxicity values to the 16 priority PAHs

that did not have specific toxicity values. Only one park area, Addicks Reservoir, showed levels amounting to slight contamination.

Heavy metals were analyzed in the sediment samples to better understand the potential ingestion and dermal exposures in the park areas. The metals concentration in the soil was compared to the Texas Commission for Environmental Quality (TCEQ) average background metal concentrations in soils across the State of Texas. Specific sampling points in the park areas presented with some heavy metals over the average background concentration in Texas, but none of the concentrations were above the USEPA's ingestion screening levels.

PCB's and legacy organochlorine pesticide concentrations were analyzed in the sediment samples from the four park locations. Mason Park was shown to have elevated PCB and legacy organochlorine pesticide concentrations relative to the other park areas. Hazard indices were developed for understanding exposures to the communities of PCBs and legacy organochlorine pesticides.

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NOMENCLATURE

PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyls
LOP	Legacy Organochlorine Pesticides
GHA	Greater Houston Area
TCEQ	Texas Commission for Environmental Quality
HI	Hazard Index
HQ	Hazard Quotient
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
HSC	Houston Ship Channel
USEPA	United States Environmental Protection Agency
EPA	Environmental Protection Agency
GPS	Global Positioning System
GIS	Geographic Information System
TERL	Trace Elements Research Laboratory
An	Anthracene
Phe	Phenanthrene
BaA	Benzo(a)anthracene
Chy	Chrysene

IPy	Indeno(1,2,3-cd)pyrene
BgP	Benzo(g,h,i)perylene
Fl	Fluoranthene
Py	Pyrene
Al	Aluminum
Ba	Barium
Be	Beryllium
Cr	Total Chromium
Cu	Copper
Fe	Iron
Pb	Lead
Mn	Manganese
Hg	Mercury
Ni	Nickel
Sr	Strontium
V	Vanadium
Zn	Zinc
ANOVA	Analysis of Variance

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CHAPTER I

INTRODUCTION

Hurricane Harvey made landfall on the Texas coast August 26, 2017, as a category 4 hurricane with wind speeds of 130 miles per hour, making it the strongest storm to hit the Texas coast since Hurricane Carla in 1961 (NOAA). Along with being a powerful hurricane, Harvey was also the wettest tropical storm to make landfall in the U.S., depositing 40 to 56 inches of rain across the Greater Houston Area. In an area of 29,000 square miles, with a population larger than 6.7 million people, there was an average of approximately 20 inches of rain over seven days (NOAA). This storm was categorized as a 1-in-1,000 storm indicating that within any one year there is a 0.001 chance of this class of storm occurring (NOAA). The Texas Gulf is highly vulnerable to tropical storms and hurricanes. With the rapid growth of the petrochemical industry on the U.S. Gulf Coast (focusing around the City of Houston and the Houston Ship Channel) along with subsidence, sea level rise, and rapid development, it is unclear what effects major storms will have on exposing socially and physically vulnerable populations to industrial chemicals. After Hurricane Katrina dissipated, research in New Orleans, LA, demonstrated that public parks were an instrumental part of community resilience and recovery from devastating natural disasters (Rung et al). Therefore, we explored the potential for parks and recreation areas in Houston to be impacted by contamination from a variety of substances including: legacy organochlorine pesticides, polychlorinated biphenyls (PCBs), heavy metals, and polycyclic aromatic hydrocarbons

(PAHs), which are monitored by the Texas Commission on Environmental Quality (TCEQ) Joint Groundwater Monitoring and Contamination Program (TCEQ 2015).

Background

Buffalo Bayou History

Buffalo Bayou is a systems of creeks and rivers that flow through the Greater Houston Area in Southeast Texas, which was developed as part of a diverse storm water management system. The Bayou begins in the Katy, Texas area where the Addicks and Barker reservoirs are located, and flow east through Houston, terminating at the Houston Ship Channel near Galveston Bay (Figure 1).

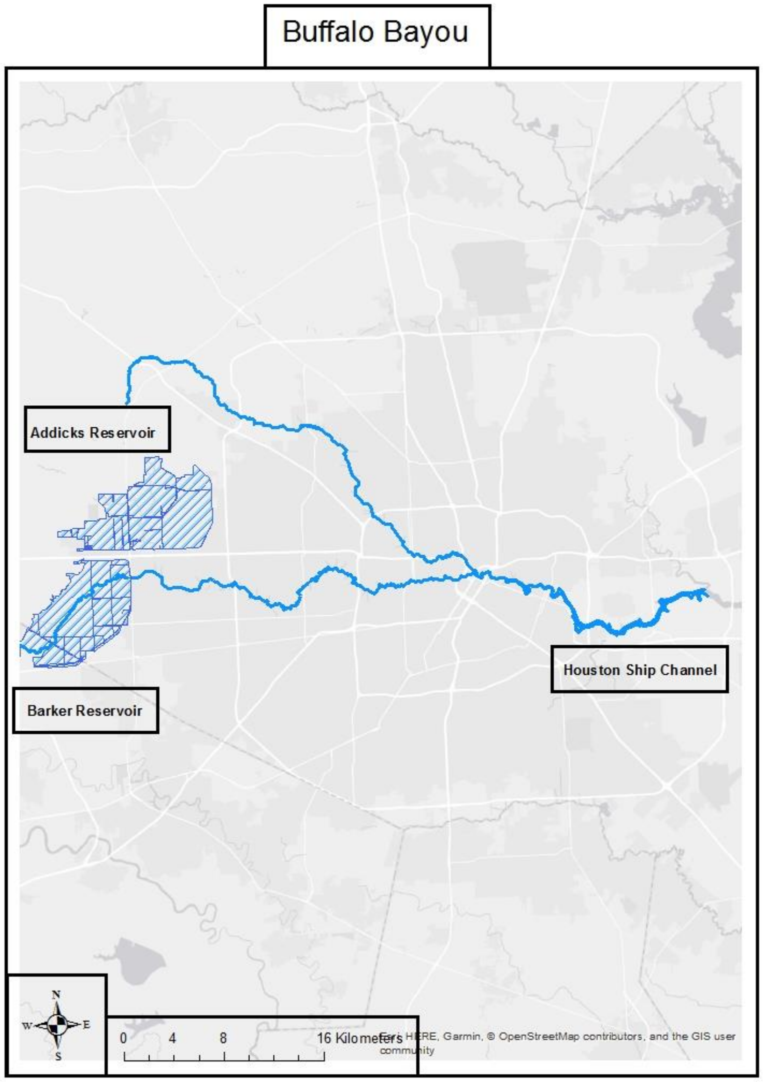

Figure 1. Buffalo Bayou

The Bayou itself is around 53 miles long and encompasses many parks and recreation areas in the Houston area. These parks vary in size from the Buffalo Bayou Park that is 160 acres to the Yolanda Black Navarro Buffalo Bend Nature Park that is 10 acres; there are also many small family neighborhood parks (buffalobayou.org). The parks, as well as adjacent recreational areas and open spaces are a hot spot for wildlife in the Houston area, including migratory birds and native Texas amphibians.

Besides offering parks for public recreation, the Bayou offers a major buffer against flooding in the Houston area with a watershed area of approximately 500 square miles. (Ecological cities project, University of Massachusetts) However, the watershed area is highly urbanized (almost 80% of the watershed is urbanized and it has a population of over 450,000 residents), which has led to increased flooding around the Bayou. (Ecological cities project, University of Massachusetts). The Addicks and Barker reservoirs, which are the headwaters of the Bayou, are extremely important in mitigating the outflow of the Bayou during periods of heavy rainfall.

In the 1940's after several flooding events impacted the Houston area, the U.S. Army Corps of Engineers built the Addicks and Barker reservoirs, which contain 410,000 acre-feet of run off storage. (Addicks and Barker Dams and Reservoirs Flood Release Procedures) Starting in 1960's, Terry Hershey and Congressman George H.W. Bush were able to block the federal government from lining the straight sections of the Bayou with concrete, which led to the formation of the Buffalo Bayou Preservation Association. After the passage of the Clean Water Act in 1972, Houston spent another $3 billion on improved sewage treatment and pumping stations linked to the Bayou throughout the City. (City of Houston Wastewater History)

The Bayou had historically been a run off site for both agricultural pesticides and sewage before the renovations that began in the 1940's. These factors, combined with the fact that the Bayou was used as a source of drinking water, prompted efforts to clean up the Bayou (City of Houston Wastewater History). According to the 2016 Basin Summary Report, Buffalo Bayou still faces several contamination concerns, including heightened levels of indicator bacteria and heavy nutrient pollution. Since contaminated soils lining the Bayou can easily be picked up and transported downstream, there is a concern that when there is a flooding event like Hurricane Harvey, residents of Houston could be exposure to chemical contaminants. These chemicals can be deposited in soil anywhere downstream; however, the soil's deposition may be based on several factors including: surface gradients, slide volumes, density of chemicals, flow velocity, and other environmental factors (Göransson et al. 2012).

Chemical Backgrounds for the Study

PAHs

PAHs are chemicals composed strictly of carbon and hydrogen atoms through the incomplete combustion of organic substances such as oil, gas, plants, and meats (ATSDR 2014). There are over 100 PAHs identified in the literature; of those 100, 16 have been designated priority pollutants by the Environmental Protection Agency (EPA) (Hussar et al. 2012). The EPA has classified 15 of the priority 16 PAHs in the Group 2B classification indicating that these PAHs are reasonably anticipated to be human carcinogens (NTP 2016). PAHs are ubiquitous in the environment with a tendency of higher concentration in urban areas due to anthropogenic sources such as fuel combustion (Abdel-Shafy and Mansour 2016; Ciesielczuk et al. 2014). PAHs deposited into the air can travel great distances from the source via winds in the atmosphere (Abdel-Shafy and Mansour 2016). PAHs have two primary methods through which they are deposited onto soil or sediment - dry deposition and wet deposition. Dry deposition is the PAH settling onto the soil or sediment from the air, wet deposition indicates that the PAH movement was influenced by a precipitation or vapor phase before settling on the soil or sediment (Abdel-Shafy and Mansour 2016). Soils that are contaminated with PAHs can also be redistributed through flooding and heavy rains (EPA 1999). These attributes of PAHs place Houston urban recreational parks along the Buffalo Bayou in a vulnerable position for exposure after flooding events, including the floods associated with Hurricane Harvey.

PCBs and Legacy Organochlorine Pesticides

PCBs are man-made chemicals comprised of carbons, hydrogens, and chlorine atoms (US EPA 2015). PCBs are a varied class of chemicals ranging from oils to waxy solids (US EPA 2015). PCBs were manufactured in the US from 1929 until 1979 and were used in a multitude of industrial applications from dyes to plasticizers to electrical and hydraulic equipment (US EPA 2015). PCBs do not break down readily in the environment, and bind strongly to soils (ATSDR 2014). Due to the strength of binding to soils, during flooding PCBs remained attached to sediments and can be transported with the flood waters (US EPA 2015). PCBs are associated with specific cancers in humans including cancer of the liver and biliary tract (ATSDR 2014). The Department of Health and Human Services considers PCBs to be reasonably anticipated as carcinogenic, the EPA considers PCBs probably carcinogenic, and the International Agency for Research on Cancer have concluded PCBs to be carcinogenic. PCBs primarily enter the environment through mismanagement of hazardous waste sites and illegal or improper disposal of industrial waste (ATSDR 2014). They can also reach the environment through leaks in older transformers that originally contained PCBs (ATSDR 2014). The potential for PCB release into the environment and the affinity to soil PCBs have make several of the Houston parks along the Buffalo Bayou susceptible to exposure through flooding of PCBs.

Legacy organic pesticides, such as DDT, were created to serve multiple purposes including protecting plants from weeds, insects, and fungi, as well as popular insecticides (CDC). Similar to PCBs legacy organic pesticides are currently banned due to health and environmental concerns (NPIC 2018). DDT is labeled as a Group 2A, probable carcinogen by the IARC. The EPA has listed DDT as a B2, probable carcinogen. Legacy organic pesticides are persistent in the environment taking several years to break down (NPIC 2018). DDT and other legacy organic pesticides can travel large distances once in the upper atmosphere, causing contamination far from the source of the original usage (EPA). DDT and other legacy organic pesticides accumulate in fatty tissues (EPA). Although DDT and other legacy organic pesticides are banned in the US, other countries still implement tactical use of DDT to combat the spread of malaria (EPA). The continual usage around the world and the persistence of legacy organic pesticides in the environment make several of the Houston parks susceptible to exposure after large disaster events such as Harvey.

Heavy Metals

Heavy metals are comprised of several naturally occurring elements with high atomic weights and densities that are at least five times more than the density of water

(Tchounwou et al. 2012). Heavy metals have a wide range of adverse health outcomes from different routes of exposures including ingestion, inhalation, and absorption through the skin. Chromium, lead, and mercury are some of the poster elements for heavy metal toxicity due to the wide range of systemic adverse health effects they can have on the human body (Tchounwou et al. 2012). During flooding events the main source of contamination from heavy metals onto soils is the deposition of sediment onto the floodplain (Patrick Pease et al. 2006). Heavy metals can enter water systems through methods such as industrial or consumer waste as well as acid rain allowing for the release of heavy metals from soils ("Heavy Metals - Lenntech" 2018). This combination of the mobility of metals through sediment in flooding as well as the systemic adverse health outcomes leave parks along Houston floodplains, such as Buffalo Bayou, susceptible to heavy metal contamination after a flooding event.

Parks in the Study

Following Hurricane Harvey, unprecedented flooding and the subsequent release of floodwaters from the Addicks and Barker Reservoirs led to the movement of potentially contaminated sediments along the Buffalo Bayou. Flooding is a concern for public health, as past studies have documented the presence of pesticides from agricultural run-off, indicator bacteria from sewage, and other toxic chemicals in Buffalo Bayou (Smyer 2008; Houston Galveston Area Council 2016). These and other contaminants may be transported in soils and sediments during floods and deposited along the Bayou in areas used by residents for recreational activities.

In addition to providing a buffer against flooding, Buffalo Bayou also offers a number of parks for public recreation activities for residents and visitors, including nature trails, bike paths, children's playgrounds, and dog parks. After Hurricane Harvey, some parks near Buffalo Bayou had up to six feet of accumulated sediment covering trails (Houston Chronicle 2017; KPRC 2017). The population of heavily industrialized cities, such as Houston, are potentially vulnerable to exposure and health risks associated with contamination after major flooding events, especially in public recreation areas where it may not be clear what has been deposited after a major flooding event.

Working in partnership with the Houston Health Department, 5 areas in 6 parks were selected for sampling and analysis due to the inundation after Hurricane Harvey that these parks experienced (Figure 2). The parks chosen were: Meyers Park, Addicks Reservoir, Cullen Park, Bear Creek Park, Marron Tony Park, and Mason Park. These parks fall mostly on Buffalo Bayou, with the exception of Meyers Park, which is located along Cypress Creek. These parks span a large section of the Greater Houston Area (GHA), including the Houston Ship Channel (HSC). It is important to note that samples taken in Bear Creek Park and Cullen Park reside within the boundaries of the Addicks Reservoir area. While not completely representative of the GHA, Buffalo Bayou runs through the heart of Houston, and findings may be generalizable to other parks and recreational areas located along Buffalo Bayou.

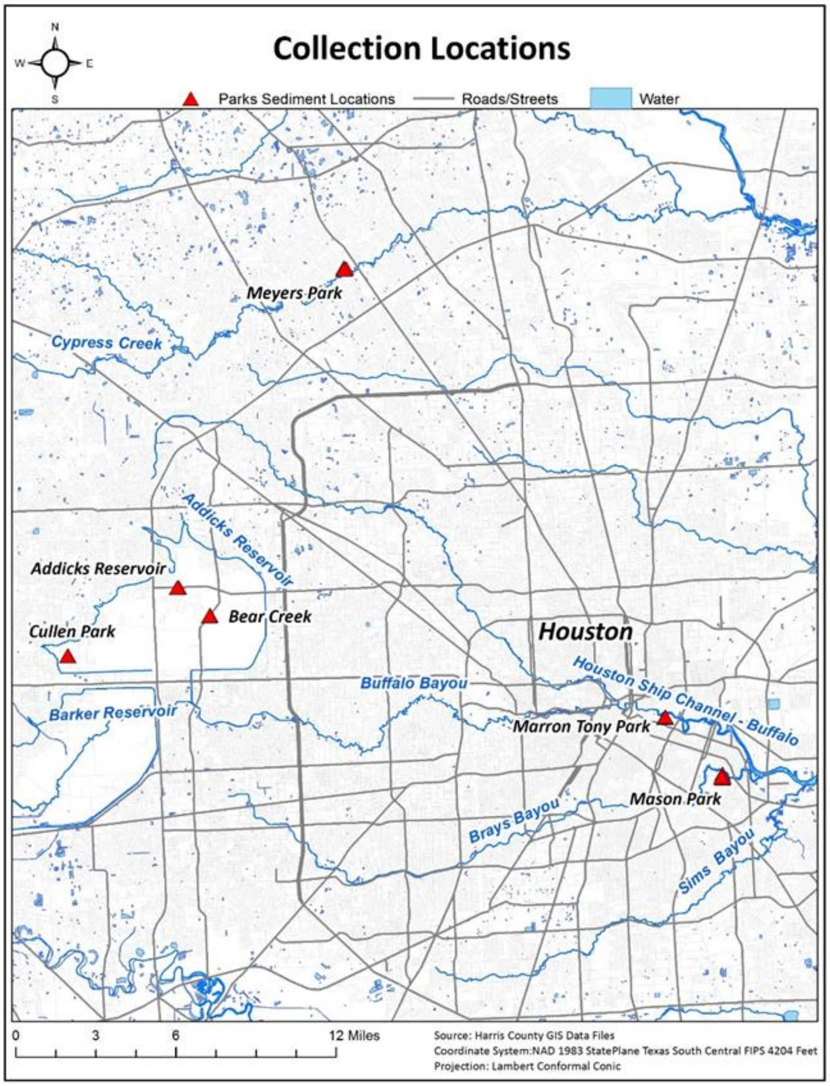

Figure 2. Sampling locations in five parks, Houston Texas

Environmental Samples

While there has been much interest in improving our scientific understanding of the potential mobilization of contaminants by disasters, little is known (Knap and Rusyn 2016). Flooding can impact groundwater chemistry and base concentration levels of chemicals in soils (Sánchez-Pérez and Trémolières 2003). To measure potential contamination, we collected soil samples in each of the 5 parks. Pilot data had been collected and analyzed in 2016 as part of a grant received by the Texas A&M School of Public Health to assess potential contamination in the environmental justice neighborhood of Manchester. Pilot data included evaluations of air quality and exposure of BTEX and PAHs to residents. After Hurricane Harvey, we attempted to compare PAHs in Manchester before (air and dust samples) and after (soil samples) Harvey. The results demonstrated that the PAH profiles tended to cluster with respect to the time the samples were taken (Horney et al. 2018). Our small pre-post Manchester PAH study demonstrated that there were large gaps in our knowledge of the potential for chemical transport during major flooding events. By taking samples in parks that were flooded after Hurricane Harvey, we might address this gap with relation to the assessment of potential environmental exposures in parks.

Following EPA guidelines for soil collection and analysis, we used metal trowels to collect a sample from the top 2-3 cm of soil in each selected locations. All samples were geocoded with latitude and longitude, the time of the sample was recorded, and the sample was stored in a cooler for same day transportation from Houston to Texas A&M, a distance of approximately 90 miles. Samples were collected in each location approximately one (September 7, 2017), fourteen (November 30, 2017), and twenty-one weeks (January 28, 2018) after Hurricane Harvey. Samples were collected in 16-gram sterile glass jars and transported to Texas A&M where they were placed in a -20 degree Celsius freezer; samples were subsequently freeze-dried and ground for extraction and analysis. All analyses were conducted at the Texas A&M Trace Element Research

Laboratory (TERL), which is located at the College of Veterinary and Biomedical Sciences and at TDI-Brooks International Lab in College Station, Texas.

Along with the gap in knowledge about the fate and transport of chemicals during disasters, little is known about the baseline exposures that may be present in soils in public parks in the Houston area. There is county-level data available about potential exposures, such as PCBs, in the Houston Ship Channel (2014 Community Health Profile Area 2014). While these studies are useful in understanding potential sources in general, they are less useful for community action or to inform residents who may use certain parks and recreation areas on a day-to-day basis. The goals of this project are to 1) longitudinally characterize and quantify the presence of heavy metals, polychlorinated biphenyls (PCBs), pesticides, and polycyclic aromatic hydrocarbons (PAHs) in six parks located along Houston's Buffalo Bayou after Hurricane Harvey, and 2) to estimate the potential public health impacts from recreational exposure to these contaminants.

Aims and Objectives

Aim 1: Calculate total PAH mass and concentration in soil samples from five Buffalo Bayou parks, as well as diagnostic ratios, to determine potential sources and health effects of recreational exposure to PAHs in Houston parks

Objective 1

Outline potential sources of PAHs in the soil for these parks.

Objective 2

Characterize exposure levels using EPA tools to determine adverse health outcomes to these specific exposure levels.

Rationale

To successfully develop mitigation strategies, we must improve our understanding of the fate of chemicals distributed to recreational parks after major flooding events. This aim will draw attention to the locations containing the highest concentrations of chemicals of concern. Diagnostic rations can be calculated from these concentrations to determining potential sources of PAHs. By comparing laboratory analyzed soil sample results with legacy data from the Houston parks using statistical analysis programs such as Microsoft Excel and EPA's Expofirst, we can determine risk assessment values. This research will contribute to our fundamental understanding of chemical movement after disasters in the Houston Area and allow for the development of tailored intervention strategies for different areas of Houston that may mitigate chemical exposures. We expect this method can become a model for the mitigation of chemical exposures in recreational parks and among vulnerable populations who use them after flooding events in other large cities with a large industrial presence.

Aim 2: Calculate total exposure to PCBs and legacy pesticides in soil samples from five Buffalo Bayou parks. Determine potential sources and health effects of recreational exposure to PCBs in Houston parks

Objective 1

Outline potential sources of PCBs and pesticides in the soil for these parks.

Objective 2

Characterize exposure levels using EPA tools to determine adverse health outcomes to these specific exposure levels.

Rationale

Similar to Aim 1, this research will allow for the investigation of potential sources of PCBs and pesticides that may contaminate parks following flooding. This type of analysis will support the development of more precise and targeted interventions that may be implemented by actions to be taken by local governments in the wake of natural disasters to prevent potential accumulations of PCBs in future flooding events.

Aim 3: Calculate total exposure to Heavy Metals in the soil samples from five Buffalo Bayou parks

Objective 1

Characterize exposure levels using EPA tools to determine adverse health outcomes to these specific exposures levels.

Rationale

This research will be descriptive in understanding the levels of exposures to heavy metals residents may experience while using these parks. This type of analysis, as with the other aims, can be used for more precise interventions in the event an intervention needs to be taken after a heavy flooding event. This analysis will also lend to future predictive studies that will better prepare industrial cities like Houston for what to expect in park areas after heavy flooding.

Methods

Overview of Methods

There are two main areas for this aim that must be addressed with their own specific methods; 1) collecting environmental samples, and 2) interpreting the results of laboratory analysis.

Environmental Samples

The soil samples were taken at five parks along the Buffalo Bayou, a river that runs through the Greater Houston Area that was designed to assist with the management of storm water. The parks were chosen by the Houston Health Department because of their potential for exposure of the public to contaminants due to the flooding of the Bayou during Hurricane Harvey. At three parks, four soil samples were collected and two parks 3 samples were collected, all samples were collected in different locations of the park that were not underwater after Harvey. Each location was marked using GPS devices to record longitude and latitude. The GIS coordinates were then plotted on a map using ArcGIS, a geographic information system software (Redlands, CA) (Figure 2). Samples were collected approximately every two months after Hurricane Harvey, with the last samples collected in March 2018. These longitudinal samples allow us to observe how the chemical profile of each park changes in the months following a massive flooding event

The soil samples were collected in 16 gram sterile glass collection jars and included only the top 2-3 cm of soil at each location. The soil was collected using a metal trowel while wearing nitrile powder free gloves. The trowel was rinsed with water between each collection and all samples were collected on the same day within 3 hours of each other. While in transit, on the day of collection, the samples were stored in a container at 23.9 degrees Celsius. Upon returning to the lab, samples were stored at -20 until analysis.

Soil samples were be submitted to TERL and TDI-Brooks International labs in College Station, Texas for analysis. Prior to submission, the samples were prepared by freeze-drying frozen samples and grinding them into a finer form for extraction and analysis.

Analysis and Overall Expectations

The environmental samples were analyzed for polycyclic aromatic hydrocarbons, polychlorinated biphenyls and pesticides using mass spectrometry. Once the samples are screened for both PAHs and pesticides in the laboratory, a data bank will be organized using Microsoft Excel to sort the data into the EPA 16 priority PAHs. PCBs were also selected from the EPAs priority pollutant list. Data will be organized by concentration per sample as well as relative concentrations per park. Other interpretations of the data will include delineating PAHs by ring number and running factor analysis to determine which PAHs or PCBs appear the most frequently in each sample. The only park analyzed for the 3 round of sampling was Mason park due to increased levels of PCBs and pesticides found in the first two rounds of analysis, the other 4 parks continued to show low detects through the first two sample rounds so were not analyzed for the third round.

We expect the environmental samples to initially be saturated with PAHs, PCBs, and pesticides due to the redistribution of contaminants from the flooding caused by Hurricane Harvey and the eventual settling of the chemicals on the parks. Due to the catastrophic volume of floodwaters present in Houston during Hurricane Harvey, there is also the possibility that contaminants would have been washed out of our sample areas, and that we could see increases over time as the City and residents return to normal routines. As the study continues we expect the parks to return to similar levels of contamination that were present before the flooding. This return to normal will likely be due to the community returning to the daily routines that occur during times not affected by flooding events.

Aim 1

This detailed analysis and profiling for each park will be completed using statistical programs. The EPA has created a risk assessment software called Expofirst that allows users to organize exposure risk scenarios to specific chemicals. This program, along with Microsoft Excel, will be used for assessing risk values. A number of PAH ratios described in the literature will be used to attempt to describe source these ratios include Fluoranthene to Fluoranthene and Pyrene (Flu/ (Flu+Pyr)), Phenanthrene to Phenanthrene and Anthracene (Phe / Phe + Ant), Benzo(a)anthracene and Benzo(a)anthracene + Chrysene (BaA / (BaA + Chr)), and Indeno[1,2,3-cd]pyrene to Indeno[1,2,3-cd]pyrene and Benzo[ghi]perylene (Ind / (Ind + Bghi)). Geospatial analysis will be performed on the parks using these ratios to assist in identifying potential sources by combining these concentrations with flood data.

Risk assessment for each park will be evaluated through individual PAH risk. The total amount of PAHs are more indicative of potential risks than each individual PAH type, unfortunately it is very difficult to categorize this risk with chemical mixtures and no clear assessment has been developed. A risk assessment will be completed for both children (6-17) and adults (18 +) as both demographics use the parks simultaneously. The risk assessment will strictly be performed on PAH's in the soil, not on PAH concentration in the air or water.

Determining the potential sources of PAHs will involve diagnostic ratio tests that can be run typically comparing pairs of PAHs. The ratios we will use are derived primarily from (Yunker et al. 2002), and Uhler, Stout and Douglas (2000) and include: Fluoranthene and Pyrene, Phenanthrene and Anthracene, Benzo(a)anthracene and Chrysene, and Indeno(1,2,3-cd)pyrene and Benzo(g,h,i)perylene. This diagnostic test will approximate the source of the PAH by attributing a range of values. If the diagnostic test for the specific ratio of PAHs falls in one range that would be the likely source of the PAH. For example, using the ratio of Anthracene and Phenanthrene can indicate whether the PAH originated from petroleum sources if the value is less than 0.1 or pyrogenic sources if the value is greater than 0.1. From these single ratios, cross plots between the ratios will yield even more detailed potential sourcesand potential exposure scenarios (Yunker et al. 2000).

Number of Samples

3 of the 5 parks have four samples and 2 of the 5 parks have three samples. The reason for the disparities in the number of samples was initial access to the parks shortly

after Hurricane Harvey. Two of the parks were heavily flooded, and the only access point was the periphery of the park. The other three parks, while affected by flooding, did not have the same problems with standing water after Hurricane Harvey. The total number of samples analyzed is 18 per collection period with a total of 54 for the three collection periods. The total number of PAHs that will be analyzed are 16, these are the 16 priority PAHs listed by the EPA.

The risk assessments will be completed for each park per sample collection based on totals for that collection date. For example the first collection date the risk assessment will be performed for each of the 16 PAHs. This will allow evaluation of how the risk assessment changes with time and concentration of these values.

Analysis

Diagnostic ratio tests for PAHs are used to determine potential sources and provide the foundation for the cross-plot comparisons that are a more comprehensive method of identifying source of multiple PAHs. The ratio of Fluoranthene (Fl) and Pyrene (Py) will be compared by dividing the Fl concentration by the sum of the Fl and Py concentrations at each sample site (Fl/(Fl + Py)). For this ratio if the value is less than 0.4 the source is likely petrogenic, if the value is greater than 0.4 and less than 0.5 the source is likely to be liquid fossil fuels, and if the value is greater than 0.5 this indicates the likely source is grass, wood, or coal combustion. The ratio of Phenanthrene (Phe) and Anthracene (An) will have two different comparisons the first being the Phe concentration divided by the An concentration (Phe/An), the second being the concentration of An divided by the sum of the concentrations of An and Phe (An/(An +

Phe)). If the first ratio (Phe/An) is greater than 15, the source is likely petrogenic ; however, if the ratio is below 10 the source is likely pyrogenic. If the second ratio (An/(Phe + An)) is less than 0.1 the source is likely petrogenic if the value is greater than 0.1 the source will likely be pyrogenic. The ratio of Benzo(a)anthracene (BaA) and Chrysene (Chy) will be the concentration of BaA divided by the sum of the concentrations of BaA and Chy (BaA/(BaA + Chy)). For this ratio (BaA/(BaA + Chy)) if the value is less than 0.2 the soruce is likely petrogenic and if the ratio is greater than 0.35 the source is likely pyrogenic. The ratio of Indeno(1,2,3-cd)pyrene (IPy) and Benzo(g,h,i)perylene (BgP) will be the concentration of IP divided by the sum of the of the concentrations of IP and BgP (IPy/(IPy + BgP). For this ratio (Ipy/(Ipy + BgP) if the value is less than 0.2 the source is likely petrogenic, if the source is between 0.2 and less than 0.5 the source is likely liquid fossil fuels, and if the source is greater than 0.5 the source is likely combustion. Implementing the cross plot allows for the cross referencing of the ratios to build a better understanding of sources. Cross plots that will be used include comparing ((An/ (Phe + An)) and (Fl/ (Fl + Py) as well as (BaA/(BaA + Chy)) and (Fl/(Fl + Py).

The risk assessment will use the standard EPA values for both children and adults. The entire risk assessment paradigm will feature all EPA standards where the standards can be applied in the equations. For example, the average weight for children and adults (BW) and the average skin surface area available for contact (SA). The risk assessment will only concern exposure through dermal surfaces not air or oral exposures. The absorbed dose per event (DA) will first be calculated using the EPA equation for

DA; DA = (Kp) (C)(t). Where Kp is the permeability coefficient, C is the concentration of the chemical in contact with the skin, and t is the time of contact. The average daily dose (ADD) will then be calculated using this equation from the EPA for dermal exposure: ADD = ((DA) X (SA) X (EF) X (ED)) / (BW) X (AT), where EF is the exposure frequency in terms of events per year and ED is exposure duration in years.

Expected Outcomes

We expect the results to show very few actionable level readings across all five parks. By actionable levels alone, interpretation of results will be insufficient for the development of a mitigation plan for these parks for future hurricane flooding events. Even without actionable levels, values are not zero and one of the most potentially valuable outcomes of this project will be the identification of physical locations where there are frequently higher levels of contaminants will allow for much easier translation into action in the parks.

Aim 2

Approach

PCBs will be organized by increasing chlorination using the homologs as the increments (Howell et al. DATE). There will be 10 groups of PCB homologs. Within each group of PCB homologs are a number of congeners, which are molecules that share the same chemical formula but the chlorine is attached in a different position on the benzene ring. There are a total of 209 PCB congeners in total, not all of which were detected in the sampling. There are also nine common mixtures of PCBs that were sold and used in the U.S., which are referred to as Aroclors. The PCBs detected within each sample and the relative frequencies will also be compared to the common Aroclors to help determine potential sources.

Analysis

In 2012, the Naval Facilities Engineering Command released a handbook for determining sources of PCB contamination in sediment. Some of these methods will be applied to this aim to determine potential sources of PCBs found in the parks in this study, mainly the development of a conceptual site model (CSM). The CSM includes the contour maps, areas of accumulation, and any preexisting data on the site related to PCB contamination. Using the CSM, a principal component analysis (PCA) will be done to determine PCB composition similarities and non-similarities at each park between the different samples taken. This CSM will then be compared against sites neighboring the park that also experienced flooding in order to determine potential exposure possibilities.

Risk assessment for each park will be evaluated through individual PCB and pesticide risk. The software program for this task of assessing the risk per chemical will be completed using the Expofirst software released by the EPA. The risk assessment will be completed for both children (6-17) and adults (18 +) as both demographics use the parks simultaneously. The risk assessment will strictly be performed on PCBs and pesticides, and be restricted to soil.

Expected Outcomes

Similar to the PAHs, the vast majority of PCB and pesticide levels will be below actionable levels. However, samples obtained as time passed after Hurricane Harvey may be representative of the potential exposure to chemicals in these parks by residents who regularly use them.

Aim 3

Analysis

15 Heavy metals will be analyzed: Cobalt, Chromium, Copper, Iron, Mercury, Potassium, Magnesium, Manganese, Nickle, Phosphorus, Lead, Sulfur, Strontium, Vanadium, and Zinc. This aim will focus on potential exposures to these metals for residents using the five parks in the study. Similar to the two prior aims above, risk assessments using EPA standards will be conducted for the analyzed metals using the EPA expofirst tool. The risk assessment will again be conducted for both children and adults as both demographics use the parks.

Expected Outcomes

The expectation is for most, if not all, to be below EPA actionable levels. Similarly, to the PAHs, PCBs, and pesticides as time passes after Hurricane Harvey the levels detected may be more representative of the concentrations typically found at these parks regularly.

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CHAPTER II

TOTAL PAH MASS AND CONCENTRATION, DIAGNOSTIC RATIOS, POTENTIAL SOURCES, HEALTH EFFECTS OF RECREATIONAL EXPOSURES

Introduction

Hurricane Harvey made landfall on the Texas coast on August 26, 2017, as a Category 4 hurricane with wind speeds of 130 miles per hour (Berg 2018). Hurricane Harvey became the wettest tropical storm to make landfall in the U.S., delivering up to 60.58 inches of rain in Nederland, Texas., with large sections of the Greater Houston Area (GHA) experiencing 1-in-1000 year flooding (Berg 2018). The most recent estimates from the National Oceanic and Atmospheric Administration (NOAA) suggest that the total damage resulting from Harvey could be as high as $160 billion (Berg 2018). Unprecedented flooding like that associated with Hurricane Harvey can result in multiple exposure opportunities for individuals in impacted communities. These include exposure to harmful chemicals in parks and recreation areas during the recovery period after the flooding event. It is important to improve our understanding of the potential for contamination in parks and recreation areas because they may play an important role in community disaster recovery. For example, after Hurricane Katrina researchers in New Orleans demonstrated that public parks were an instrumental part of community resilience and recovery from the impacts of natural disasters (Rung et al. 2011). However, to our knowledge, no other studies have addressed this potential. This study will focus on improving our understanding of potential post-Harvey contamination in four parks that experienced flooding from Hurricane Harvey across the GHA.

The four study areas include Addicks Reservoir, Meyers Park, Tony Marron Park, and Mason Park. All study areas are located along the Buffalo Bayou, a system of creeks and streams that crosses the GHA beginning in the Addicks and Barker Reservoirs and terminating in the Houston Ship Channel (Figure 3). The Buffalo Bayou is 53 mile long and has a watershed area of approximately 500 square miles; it acts as a buffer to combat flooding in the GHA (Ecological cities project, University of Massachusetts). However, Buffalo Bayou is also highly urbanized, with more than 80% of the area having been developed and a population of 450,000 residents (Ecological cities project, University of Massachusetts). Due to flooding along Buffalo Bayou during Hurricane Harvey, all four study sites experienced flooding in the days after the storm's landfall.

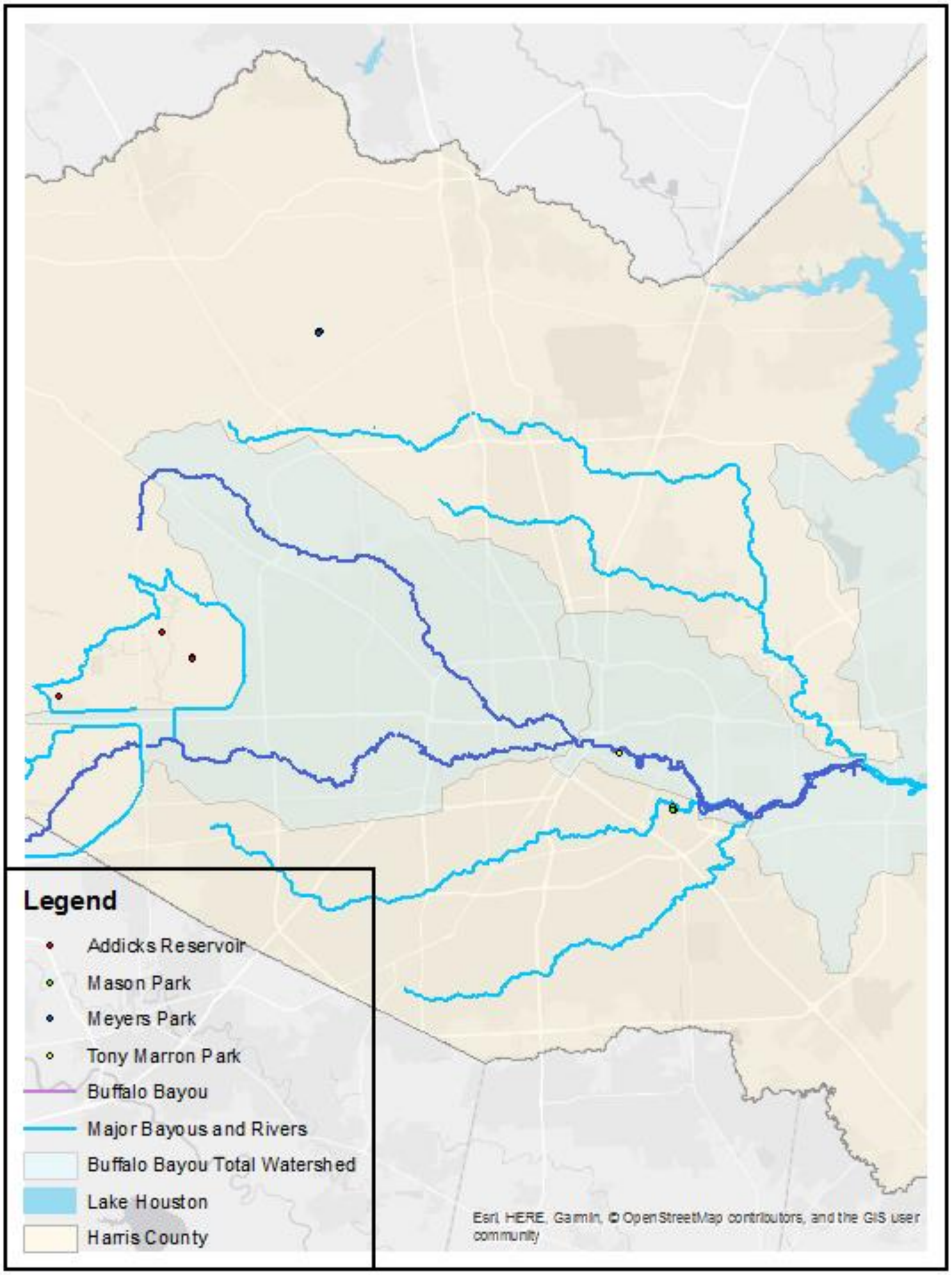

Figure 3. Map of Harris County portion of Greater Houston Area Bayou System with sampling locations

Addicks Reservoir is located to the West of the GHA (Figure 3). The Army Corp of Engineers constructed the Addicks Reservoir in the 1940's to help mitigate flooding in the GHA (HCFCD - Addicks Reservoir 2019). The Reservoir was designed to discharge flood water from Langham Creek into Buffalo Bayou (HCFCD - Addicks Reservoir 2019). Addicks Reservoir park is approximately 26,000 acres with a drainage area of 183 square miles (HCFCD - Addicks Reservoir 2019). The area provides several recreational facilities for community use, including baseball fields, soccer fields, picnic locations, and playgrounds (HCFCD - Addicks Reservoir 2019). The total population living within the Addicks Reservoir watershed is 295,694 (HCFCD - Addicks Reservoir 2019). Over the course of Hurricane Harvey associated precipitation, the Addicks Reservoir received 33 inches of rain (Harris County Flood Control District 2018). This flooding forced the city to release levees around Addicks Reservoir, which resulted in flooding of several neighborhoods in the West Houston Area.

Meyers Park is a 180 acre park located in Northwest Houston (Harris County Precinct 4 n.d.). Meyers Park is located on the Cypress Creek watershed, which drains into Buffalo Bayou. Meyers Park offers several recreational areas for community use such as soccer fields, basketball courts, playgrounds, nature trails, and fishing ponds (Harris County Precinct 4 n.d.). This park received approximately 30 inches of rain before Hurricane Harvey dissipated from the Houston area (Harris County Flood Control District 2018).

Tony Marron Park is a 19 acre park located in Southeast Houston ("Tony Marron Park" 2019). The park was acquired by the City of Houston in 1987 and offers walking trails, playgrounds, and soccer fields for recreation ("Tony Marron Park" 2019). The park is located just across Buffalo Bayou from a non-ferrous metal and electrical waste recycling facility. Tony Marron Park received 35 inches of rainfall during Hurricane Harvey (Harris County Flood Control District 2018).

Mason Park is 104 acre park located in Southeast Houston (City of Houston 2019). The park, established in 1930, offers several recreational and community services including a community center, baseball and softball fields, walking trails, and playgrounds (City of Houston 2019). The park is located on Brays Bayou, which is a major tributary of Buffalo Bayou. In 2006, Brays Bayou was widened in an attempt to reduce flooding in the watershed (City of Houston 2019). The park received approximately 35 inches of rain during Hurricane Harvey (Harris County Flood Control District 2018).

Polycyclic Aromatic Hydrocarbons (PAHs) are chemicals comprised of multiple aromatic rings (Abdel-Shafy and Mansour 2016). The largest PAH included in this study, Benzo(g,h,i)perylene, contains 6 aromatic rings. PAHs form as a result of the incomplete combustion of organic matter (ATSDR 2014). Organic matter is further broken down into three categories for determination of source: pyrogenic, petroleum, and biomass. PAHs are typically ubiquitous in the environment due to the multiple forms of exposure including cars, cooking, and other combustion sources (Abdel-Shafy and Mansour 2016). Chronic exposure to PAHs in the workplace has been shown to have adverse health outcomes such as increased incidence of lung, sink, and bladder cancer (ATSDR 2014). The EPA has designated 16 PAHs as priority pollutants. For this study, we have organized the 16 priority PAHs into four groups by ring structure starting with two rings and increasing incrementally by one aromatic ring to the five and six ring categories.

Methods

Sediment samples were collected two times over the course of two months, after Hurricane Harvey made landfall, across the four parks and recreation areas in the Harris County. The first round of samples were collected 7 days after Hurricane Harvey, at which time many locations across Harris County were still submerged by floodwater and some roads remained impassable. Therefore, soil collection points were in locations where there was little or no standing water. The latitude and longitude of each collection site was recorded using Global Positioning System (WHAT APPLICATION OR SOFTWARE). Non-powder nitrile gloves were used for collection and a new pair was used for each sample. Samples were collected in 8 ounce glass jars using a metal trowel. The metal trowels were rinsed after each collection. The collection jars were filled approximately three fourths full due to the saturation of the soil. The second round of sediment samples was collected in November 2017, 7 weeks after Hurricane Harvey landfall, at the same geocoded locations using the same methods.

After collection, samples were stored in a cooler for transport from the Houston area to the Texas A&M School of Public Health (SPH) in College Station, Texas, approximately 90 miles. Once the samples arrived at SPH they were placed in a – 20 C freezer for storage. Frozen samples were freeze dried at SPH and transported to TDI-Brooks International in College Station, Texas, for analysis using gas chromatography mass spectrometry (GC-MS). Output data were analyzed using Microsoft Excel (Redmond, WA) , Systat Sigmaplot V12.5 (San Jose, CA), and R (R Core Team).

Neither Harris County nor the City of Houston have well defined chemical profile backgrounds for parks and recreation areas. This lack of background data makes understanding the chemical profiles of parks after flooding events more difficult. The focus for this study is on potential PAH exposure via park-based sediment. To improve understanding of potential post-disaster recreational exposure to PAHs, we have describe the distribution of PAHs after a major flooding event and identify potential sources. Concentrations were recorded in two time intervals, 7 days and 7 weeks after Hurricane Harvey made landfall to understand how the concentration of PAHs in sediment changes with respect to time since major flooding. The toxic equivalent factor of the PAH concentrations are used to better understand exposure risk to individuals in communities that use these parks frequently.

Both the U.S. and Canada have established contamination concentration levels for PAHs using the TEF (Figure 6). The contamination levels are divided into three categories, below 100 ng/g is defined as uncontaminated, above 100 ng/g and below 1000 ng/g is defined as slightly contaminated, and between 1,000 ng/g and 10,000 ng/g is defined as significantly contaminated, which may pose human health risk.

Anthracene vs phenananthrene

Potential sources of PAHs can be identified based on the calculation of ratios between different PAH concentrations in sediment samples (Yunker et al. 2002; Abdel-Shafy and Mansour 2016). The concentration of anthracene is compared to the combined concentrations of anthracene and phenanthrene (An / An+Phe). If this ratio is greater than 0.1, this is indicative that the PAHs come from pyrogenic or combustion sources. If the value is less than 0.1, it indicates that the source of the PAHs in the sediment is most likely originating from petroleum products in the sediment and not from combustion sources. Pyrogenic source meaning PAHs that originated from combustion and petrogenic sources indicating PAHs formed in the crude oil maturation process or other similar process (Abdel-Shafy and Mansour 2016).

Fluoranthene vs Pyrene

The ratio of the concentration of fluoranthene to fluoranthene and pyrene (Fl / Fl+Py) can also be used to assess the source of PAHs. Values from this ratio fall into three potential source categories: < 0.4 is indicative of a petrogenic source; ratios between 0.4 and ≥ 0.5 indicate petroleum combustion as the source, while ratios > 0.5 indicate combustion of biomass.

Indeno(1,2,3-cd)pyrene vs Benzo(ghi)perylene

The ratio of the concentration of Indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene (IPy / BgP), which can also be used to assess potential PAH sources (Tobiszewaki and Namiesnik, 2012). Ratios < 0.2 indicate a potential petrogenic source, while ratios ≥ 0.2 and ≤ 0.5 indicate petroleum combustion, and ratios > 0.5 indicate of grass, wood, or coal combustion.

Benzo(a)anthracene vs Chrysene

The ratio of Benzo(a)anthracene vs Chrysene has 3 categories. A ratio below 0.2 indicates a petrogenic source, a ratio ≥ 0.2 and ≤ 0.35 is indicative of coal or petroleum combustion, a ratio greater than 0.35 is indicative of combustion or vehicular emission.

Benzo(a)pyrene vs bezno(ghi)perylene

The ratio of Benzo(a)pyrene vs Benzo(g,h,i)peryleneis used to indicate if the source for the PAH concentration in the sediment is due to vehicular emissions or non-traffic emissions. A ratio below 0.6 indicates non – traffic emissions as the potential source for PAH concentration in the sediment samples, a ratio greater than 0.6 is indicative of vehicular emissions as the potential source for PAH concentration in the sediment samples.

Results

Figure 4 shows the total concentration of PAHs (ng/g) in sediment samples at each location and sampling time. In three of the four sampling locations, the total concentration of PAHs declined over the 2-month period. The one exception was Tony Marron Park, where total PAH concentration more than doubled between seven days after Harvey and two months after Harvey. Most of the PAHs in the sediment samples were 4 – ring and 5/6 – ring PAH groups.

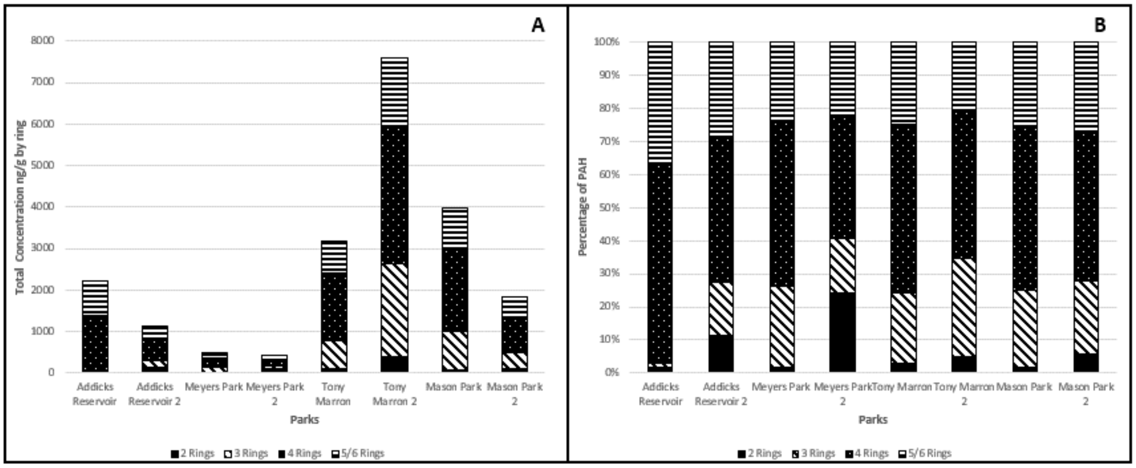

Figure 4. A: Total PAH concentration comparison between the individual parks, PAHs organized by ring number. B: Percent composition of PAHs per park, organized by ring number.

More than 70% of the PAHs present in the park sediment samples 1 week after Hurricane Harvey landfall were comprised of either four ring PAHs or 5/6 ring PAHs (Figure 4B). Samples taken 7 weeks after Hurricane Harvey landfall were also predominantly comprised of 4 - ring (44 %), 5/6 – ring (23 %), and 3 – ring (26 %) PAH structures. Both Addicks Reservoir and Tony Marron Park samples indicated an increase in the percentage of 3 – ring PAHs from the first sample collection (1.3%) to the second (16.2%) In the Addicks Reservoir and 21.4% from the first sample collection to 29.7% in the second sample collection at Tony Marron Park. In both the Addicks Reservoir and Meyers Park samples, the concentration of 2 - ring PAHS were approximately 10% and 20% at the first and second sampling time, respectively. For all other parks, 2 – ring PAHs comprised less than 10% at both sampling times.

Another way to assess potential changes in PAH concentrations over time is to conduct one-way analysis of variance tests (ANOVA) between the samples collected 1 week and 7 weeks after Hurricane Harvey landfall. ANOVA can identify pairs of samples where there is a statistically significant ($\alpha = 0.05$) difference between the total concentrations, organized by the number of rings, between the samples from the same location at the two time points. For 2 – Ring PAHs, there were statistically significant differences between first and second round samples only from Addicks Reservoir and Tony Marron Park.

Toxic Equivalence Factor

The Toxic Equivalence Factor (TEF) is a method used to describe the potential toxicity of a chemical with no known toxicity value based on the chemical structure in relation to a chemical with a similar chemical structuring that has known toxicity information. For the 16 priority PAHs the EPA uses Benzo(a)pyrene as the TEF for other PAHs. To create a toxicity factor value, the concentration of other PAHs is multiplied by a TEF based on the similarity of the chemical structure to the structure of a known toxin. The TEF maintains the same units as the total mass (ng/g).

A One-Way ANOVA was also used to compare concentrations of total PAH organized by ring number as well as TEF organized by ring number between the four park study locations. The one-way ANOVA test showed that each individual park in the study was statistically significantly unique.

One week after Hurricane Harvey, 4 of the 18 samples collected across the 4 parks had an A / A+P ratio of less than 0.1 (Figure 5A). Three of these samples were located in Meyers Park (0.06, 0.04, and 0.08) and one was located in Mason Park (0.10). In the second round of samples, only one sample from Meyers Park had an A / A+P ratio below 0.1. The An / An+Phe ratio for all other samples were indicative of combustion as the primary source of PAH concentration in park sediment.

In the samples collected one week after Hurricane Harvey, 3 samples had a Fl / Fl+Py ratio between 0.4 and 0.5, indicative of petroleum combustion. Two of the three samples (0.49 and 0.50) were collected at the Addicks Reservoir and one (0.46) was from Meyers Park. All other samples collected one week after Harvey had Fl / Fl+Py ratios that indicated biomass combustion as the main source for PAHs. Of the later samples, 6 had Fl / Fl+Py ratios between 0.4 and 0.5, indicating petroleum combustion as the potential source. Three of these samples (0.47, 0.44, 0.44) were collected at Addicks Reservoir, two (0.43 and 0.47) were from Meyers Park, and one (0.45) was from Mason Park. These six samples All other samples had a Fl / Fl+Py ratio of > 0.5, indicating the source of PAHs in the parks was the combustion of biomass.

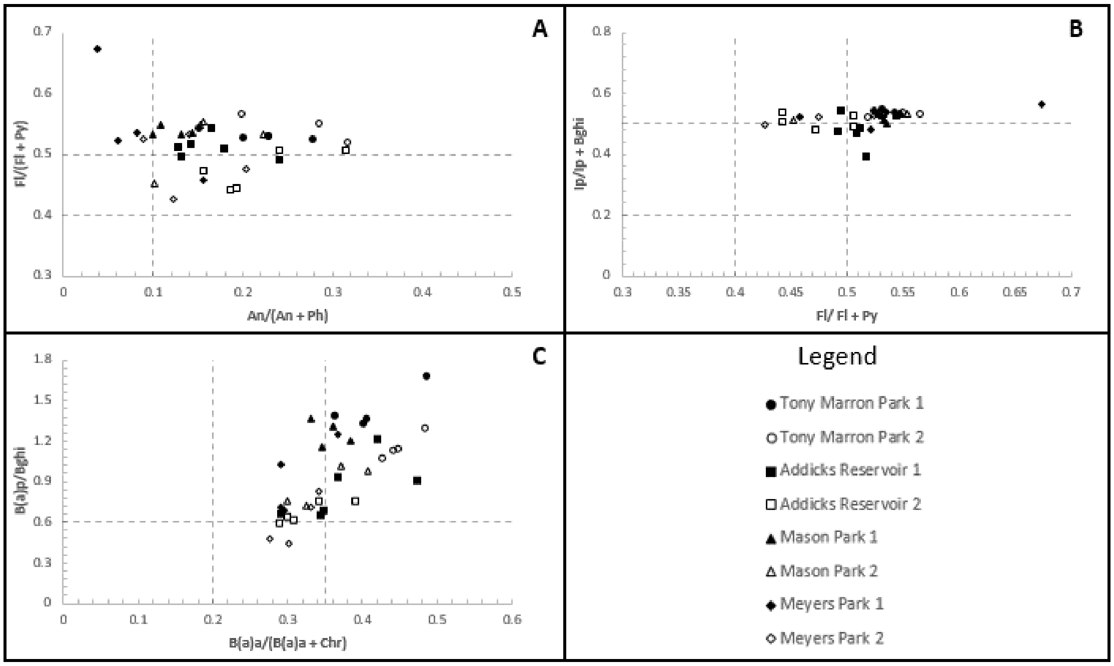

Figure 5. Several diagnostic ratios used to predict potential sources of environmental PAH concentrations in sediment. Sample 1 was taken 1-week post Hurricane Harvey and sample 2 was taken 7 weeks after Hurricane Harvey made landfall. A: ratio of anthracene to anthracene combined with phenanthrene and the ratio of fluoranthene to fluoranthene combined with pyrene. B: ratio of fluoranthene to fluoranthene combined with pyrene, and the ratio of indeno(1,2,3-cd)pyrene to indeno(1,2,3-cd)pyrene combined with benzo(g,h,i)perylene. C: ratio of benzo(a)anthracene to benzo(a)anthracene combined with chrysene, and the ratio of benzo(a)pyrene to benzo(g,h,i)perylene.

In Figure 5, of the samples collected one week after Hurricane Harvey, five had an IPy / BgP ratio between 0.2 and 0.5 (Figure 5B). Four of these five (0.48, 0.48, 0.39, 0.47) were from Addicks Reservoir and one (0.48) was from Meyers Park. In the subsequent samples, three had IPy/BgP ratios between 0.2 and 0.5. Two (0.49 and 0.48) were in Addicks Reservoir and one (0.50) was in Meyers Park, indicating that the source of PAHs in Addicks Reservoir and Meyers park may be petroleum combustion.

All other samples from both sampling times had IPy / BgP ratios above 0.5, pointing to biomass combustion as the source for the majority of the samples.

Both of the ratios presented in Figure 5C are used to predict the source of the concentration of the PAH to be vehicular emission or another source of emission. Seven days after Hurricane Harvey made landfall, 8 of the samples contained a ratio between 0.2 and 0.35. Three samples (0.2899, 0.3462, and 0.3428) from Addicks Reservoir, three samples (0.2953, 0.2905, and 0.2911) from Meyers Park, and two samples (0.3466 and 0.3319) from Mason Park. Two months after Hurricane Harvey made landfall 10 samples contained a ratio between 0.2 and 0.35. Four samples (0.3416, 0.2891, 0.3079, and 0.2996) from Addicks Reservoir, four samples (0.3009, 0.2769, 0.3416, and 0.3303) from Meyers Park, two samples (0.3000 and 0.3259) from Mason Park. These samples are all indicative of coal or petroleum combustion as a potential source for the PAH concentrations in the samples. No samples contained a ratio below 0.2, and all other samples contained ratios larger than 0.35 indicating combustion or vehicular emissions as possible sources. All of Tony Marron Park sample ratios indicate combustion or vehicular emission as the potential source for the concentration of PAHs in the sediment samples.

Seven days after Hurricane Harvey made landfall all samples contained ratios higher than 0.6 indicating vehicular emissions as the main source of the concentration of PAHs in the sediment samples. Two months after Hurricane Harvey three samples contained ratios below 0.6. One sample (0.5989) from Addicks Reservoir, and 2 samples (0.4424 and 0.4775) from Meyers Park. These three sample ratios indicate that non-traffic emissions were the potential source for the concentration of PAHs in the sediment sample. All other samples taken 2 months after Hurricane Harvey made landfall contained ratios greater than 0.6 indicating vehicular emission as the potential source for the PAH concentration in the sediment samples.

Table 1 describes the individual TEFs for the PAHs in this study. PAHs with more rings tend to have higher TEF values. All TEF values are derived from benzo(a)pyrene.

Table 1. Toxic Equivalent Factor for EPA priority 16 PAHs

Acenaphthylene	0.001
Acenaphthene	0.001
Anthracene	0.01
Benz(a)anthracene	0.1
Benzo(a)pyrene	1
Benzo(b)fluoranthene	0.1
Benzo(g,h,i)perylene	0.01
Benzo(k,j)fluoranthene	0.1
Chrysene/Triphenylene	0.01
Dibenzo(a,h)anthracene	1
Fluoranthene	0.001
Fluorene	0.001
Indeno(1,2,3-c,d)pyrene	0.1
Naphthalene	0.001
Phenanthrene	0.001
Pyrene	0.001

When converting the total PAH concentrations to TEF values both Addicks Reservoir and Tony Marron Park again showed statistically significant differences between the first and second samples. For 3 – Ring PAHs, there were no significant differences at any park, while the TEF was different only at Mason Park. For 4 – Ring PAHs, there were significant differences for both total concentration and TEF at both Addicks Reservoir and Mason Park. For 5 and 6 – Ring PAHs, there were significant differences for total concentration at both Addicks Reservoir and Mason Park, but difference in TEF were only found in the two Mason Park samples.

Figure 6 shows the total PAH concentrations converted to TEF values. Addicks reservoir had the highest TEF relative to the other parks at both sampling points. Only the Addicks Reservoir samples reached the level of slightly contaminated at both sampling periods. All other parks fell below 100 ng/g, indicating the no contamination level in the sediment.

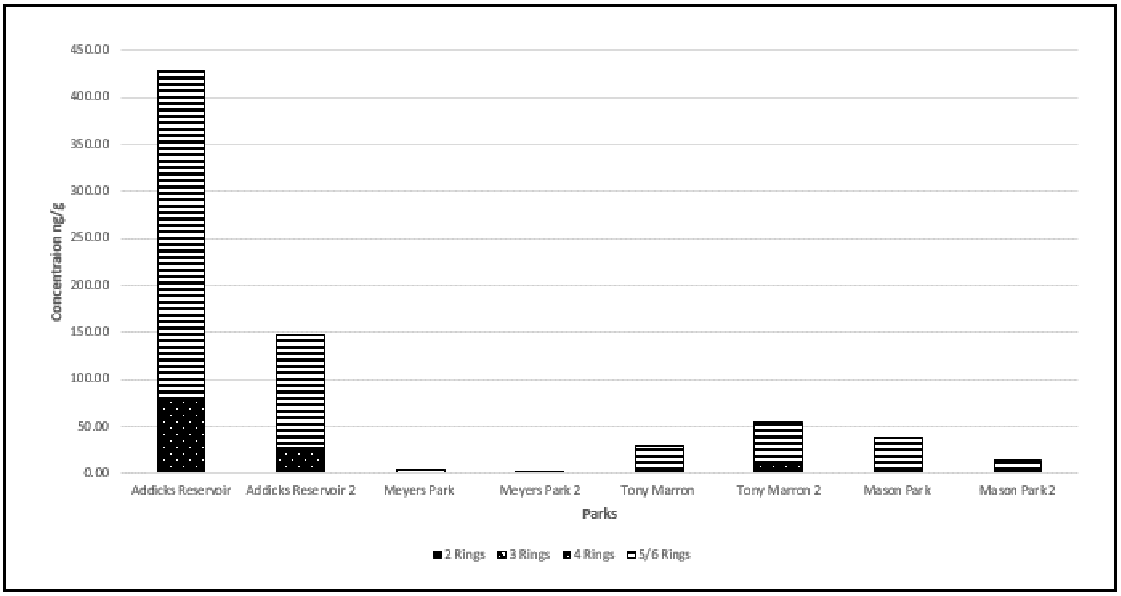

Figure 6. TEF concentration

Discussion

Little is known about baseline levels of PAHs in recreation areas in the Houston region, although the area is home to more than 40% of the nation's petrochemical industrial capacity. While TEFs across all parks sampled were well below the threshold for significant contamination, the potential for health impacts from chronic exposure to PAHs make it important to improve understanding of potential exposure and how these exposures may be impacted by a natural disaster. Addicks Reservoir was the only recreation area of those we sampled to have PAHs levels that could be characterized by the TEF as slightly contaminated. This could be due to several factors, including the park's large size and the timing of the release of water after Hurricane Harvey to prevent a possible breech in the levees.

Comparing the PAH groups by total PAH concentration the data show that the higher ring PAHs, four, five, and six rings, comprised a majority of the PAHs, including the Tony Marron Park second sample. This pattern is demonstrated again through percentage make up of each sample indicating that the higher ring PAHs comprise more than 60% of all samples taken in the study except for the second sample taken in Meyers Park where higher ring PAHs compromised 59.3%. In percent composition, there was a slight trend towards fewer higher ring PAH composition from the first sampling period to the second. This pattern is present in all four sample locations. According to the An / (An + Phe) ratios, all samples seven days after Harvey made landfall except for three are indicative of pyrogenic sources. Those three samples were collected in Meyers Park. Meyers Park is not located in close proximity to petroleum sources, making it an interesting predictive estimate. It may be the case some petroleum mixtures were deposited as the flooding rose and subsided during Harvey. The second round of sampling indicated that only one sample contained the ratio for a petrogenic source; this sample was again located in Meyers Park. Major sources of petrogenic origin to PAH contamination come in the form of oil spills as well as underground and above ground storage tanks leaks, and motor oil and gasoline leaks (Abdel-Shafy and Mansour 2016).

Meyers Park is not located in close proximity to storage tanks so these sources may have originated from vehicles in close proximity to the park. There is an uptick in ratios predicting petroleum combustion sources from the first sampling time period to the second that are not isolated to Meyers Park, rather in the second sampling round 3 of the 4 parks showed samples indicating a petroleum combustion source and could be from a variety of sources the most likely being vehicular.

The Houston Metropolitan Area is home to more than 6 million residents living in an area about the size of the State of New Jersey. Therefore, Houston has ample vehicular traffic (TxDOT 2016), which can be a main source of PAH deposition onto sediment (Abdel-Shafy and Mansour 2016; Health Effects Institute 2010). The high traffic volume is consistent with the predictive ratios highlighting the importance of combustion sources for PAHs the ratios of B(a)a / (B(a)a + Chr) and B(a)p / BgP, which are targeted ratios used to help determine traffic's contribution to the PAH sediment concentration. These ratios utilize comparisons between priority PAHs with 4, 5, and 6 rings, which comprised the majority of the priority PAH concentrations in all samples. Seven days after Harvey all samples according to the ratio of B(a)a / (B(a)a + Chr) are predicted to be sourced from vehicular emissions. Two months after all samples but three are indicative of vehicular emissions as the source for PAH contamination. The B(a)p / BgP ratio all indicated combustion as the source but contained a mixture of source from coal and petroleum combustion to specifically vehicular combustion. These ratios clearly indicate combustion as the source for the PAH concentrations in the park samples and suggest a significant amount of contribution from vehicular traffic emissions.

Conclusion

It is difficult to attribute the PAHs in Houston parks to a direct source. Vehicular traffic may be the most significant contributor to the PAH concentrations, which is not surprising given the amount of traffic the region experiences daily. Although all PAH concentrations and their TEFs were below actionable levels, residents of the Houston area still express concerns about the potential for pollution and contamination associated with flooding that results from a natural disaster. Hurricane Harvey was unique in that it was primarily an inland precipitation event; potential contaminants may have been washed downstream through the Houston Ship Channel to the Galveston Bay. Future storms with larger storm surges may bring contaminants from the Galveston Bay through the Houston Ship Channel and into the City’s neighborhoods. Therefore, residents using parks and other recreation areas after flooding should still exercise caution and best judgement when using a park after a major disaster, even if in this particular flood the concentration of PAHs in the sediment was not high enough to prevent park usage. Since there are no data on background levels of PAHs in sediment in the GHA, this research helps to describe a baseline for the next disaster. Future studies may target additional parks and sampling locations to begin to develop a library of baseline chemical profiles to improve our understanding of the potential for environmental contamination as a result of natural disasters in large urban areas at high risk of disaster impacts.

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CHAPTER III

HEAVY METAL CONCENTRATION, POTENTIAL SOURCES, AND HEALTH EFFECTS OF RECREATIONAL EXPOSURES

Introduction

Heavy metals are elements with densities over 5 g/cm3. There are 83 total heavy metals and metalloids that fall into this density category. This study focuses on 13 heavy metals: aluminum (Al), barium (Ba), beryllium (Be), total chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), strontium (Sr), vanadium (V), and zinc (Zn). While certain heavy metals such as zinc and iron have important biological functions in appropriate doses and concentrations, several heavy metals such as lead, beryllium, chromium, and mercury have deleterious health outcomes after exposure.

Sediment is defined as the conglomerate of organic and inorganic materials that can be carried away by wind, water, or ice (Fondriest Environmental, Inc. 2014). For example, large amounts of rainfall and associated flooding have the ability to displace sediment in the local area following the flow of the flood (Fondriest Environmental, Inc. 2014). In August 2017, the Greater Houston Area (GHA) experienced catastrophic flooding due to inland precipitation from Hurricane Harvey.

Sediment contaminated with heavy metals from various industrial practices has been shown to be capable of migration during heavy flooding events (Strzebonska et al. 2014). Houston is a large industrial city; the heavy flooding endured during the Harvey rainfalls raised the potential for displacement of sediment contaminated with heavy metals from industrial sites to public parks and recreation areas. This displacement of contaminated sediment can place residents and community members who use parks at risk of exposure to heavy metals in a post-disaster setting. A map of the sampling locations and the GHA is described in Figure 7.

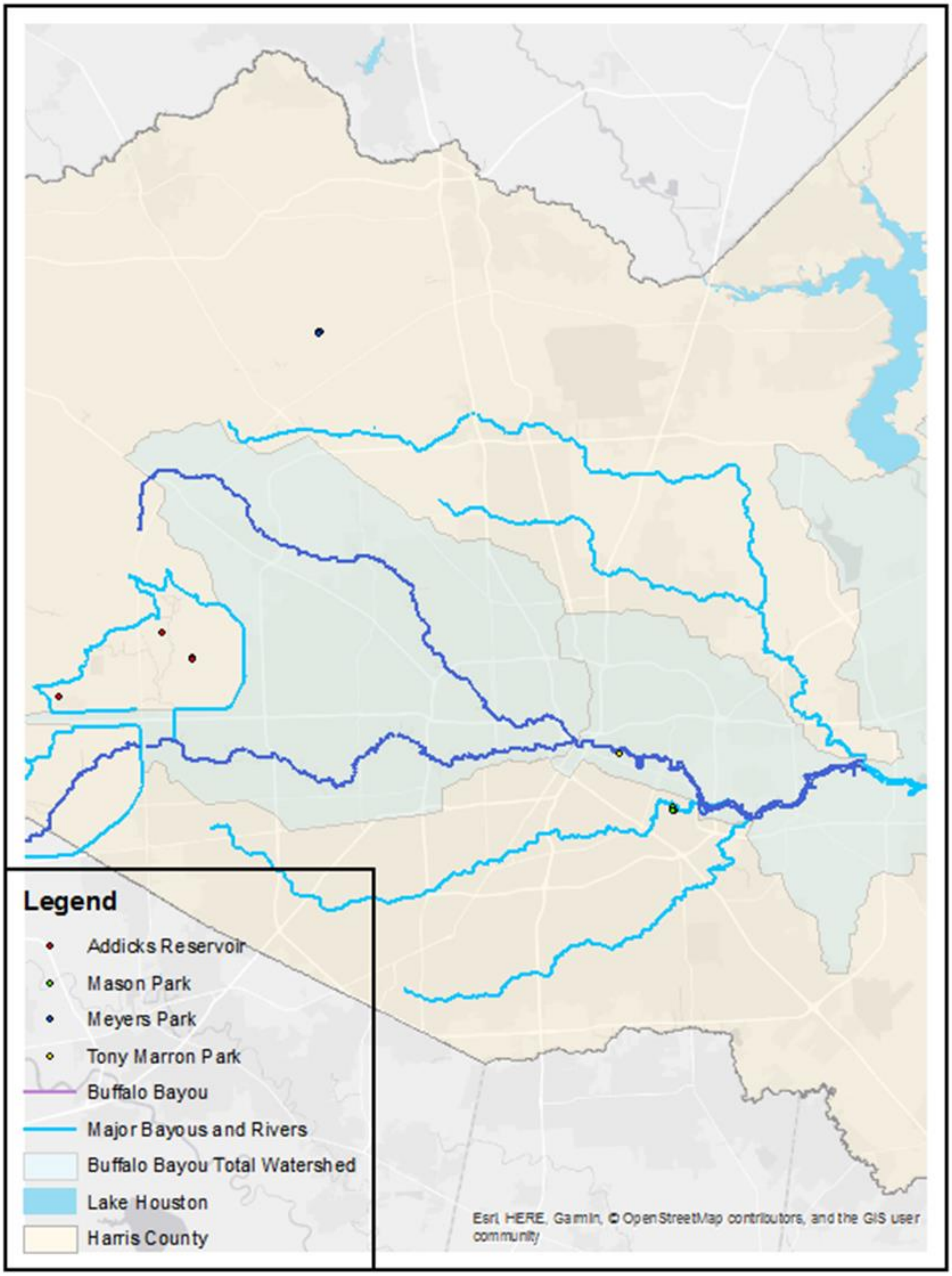

Figure 7. Map of Harris County portion of Greater Houston Area Bayou system with sampling locations

The principal source of heavy metal pollution to the environment is industrial waste from manufacturing and metal finishing operations (Table 2) (Pavan Kumar et al. 2016). The second major source of heavy metal pollution is the use of metal containing compounds such as fertilizers and pesticides in agriculture.

Table 2. Industrial uses and sources of certain heavy metals

Metals	**Industrial Uses**
Aluminum	Preparation of insulated wiring, ceramics, automotive parts, aluminum phosphates, and pesticide formation.
Barium	Manufacturing of plastics, rubbers, electronics, steel, textiles, ceramics, glass, bricks, paper, rodenticides, pharmaceutics, and cosmetics.
Beryllium	Released in the combustion of coal, fuel oil, and municipal solid waste.
Total Chromium	Used in chrome plating, petroleum refining, electroplating industries, leather tanning, textile manufacturing, and pulp processing units.
Copper	Used in the electroplating industry, the plastic industry, metal refining, and industrial emissions.
Iron	Commonly used in metals refining and engine part creation.
Lead	Used in petrol-based materials, pesticides, mobile batteries, and gasoline (not in the US).
Manganese	Usage involves municipal waste discharge, sewage sludge, mining and mineral processing, and emissions from alloy, steel, and iron products.
Mercury	Used for part creation in light bulbs, found in wood preservatives, leather tanning, ointments, thermometers, adhesives, and paints.

Table 2. Continued

Metals	**Industrial Uses**
Nickel	Used in galvanization, paints and powders, battery-processing units, metals refining, and super phosphate fertilizers.
Strontium	Common usage in pyrotechnics, can be used for many similar industries as barium, but is often not used due to higher cost than barium.
Vanadium	Released in the combustion of fossil fuels.
Zinc	Commonly used in the rubber industry, paint dyes, wood preservatives and ointments, batteries, electroplating industries, phosphate fertilizers, and detergents.

(Pavan Kumar et al. 2016; Julia Kravchenko et al. 2014; ATSDR 2002; Howe 2004; Lenntech 2019; ATSDR 2018).

Methods

Sediment samples were collected twice over the course of two months after Hurricane Harvey made landfall across four parks and recreation areas in Harris County. The first round of samples were collected 7 days after Hurricane Harvey, at which time many locations across Harris County were still submerged by floodwater and some roads remained impassable. Therefore, soil collection points were in locations where there was little or no standing water. The latitude and longitude of each collection site was recorded using Google Maps application. Non-powder nitrile gloves were used for collection and a new pair was used for each sample. Samples were collected in 8 ounce glass jars using a metal trowel. The metal trowels were rinsed after each collection. The collection jars were filled approximately three fourths full due to the saturation of the soil. The second round of sediment samples was collected in November 2017, 7 weeks after Hurricane Harvey landfall, at the same geocoded locations using the same methods.

After collection, samples were stored in a cooler for transport from the Houston area to the Texas A&M School of Public Health (SPH) in College Station, Texas, approximately 90 miles. Once the samples arrived at SPH they were placed in a – 20 C freezer for storage. Frozen samples were freeze dried at SPH and transported to the Trace Element Research Laboratory in the College of Veterinary Medicine at the Texas A&M University in College Station, Texas, for analysis using gas chromatography mass spectrometry (GC-MS). Output data were analyzed using Microsoft Excel (Redmond, WA), Sigmaplot V12.5 (San Jose, CA), and R (R Core Team).

Samples underwent analysis in the Trace Element Research Laboratory at the Texas A&M College of Veterinary Medicine. Results were initially provided in Microsoft Excel (Redmond, WA) spreadsheets, which were used to calculate hazard index equations. Sigmaplot V12.5 (San Jose, CA) was used for two-way ANOVA analysis to assess associations between samples and parks with respect to metal concentrations. Finally, R and RStudio Software (R Core Team 2013) was used to create charts to represent metal concentrations at each of the sample sites.

Results

Table 3 displays the total hazard quotient for each park during both sample times, round 1 being one week after Hurricane Harvey makes land fall and round 2 being seven weeks after Hurricane Harvey. The hazard index is created by taking the ingestion exposure or dermal exposure values for each individual metal and dividing that value by a reference dose factor (rdf) for that specific heavy metal provided by the USEPA. Once the hazard index is determined for each individual metal the sum of those indices is taken and applied to each park per each sampling time. The sum of the indices is known as the hazard quotient. According to USEPA, hazard quotients below 1 (HQ < 1) are considered safe for human health, hazard quotients between 1 and 5 ($1 < HQ \leq 5$) are considered low risk, hazard quotients greater than 5 and less than or equal to 10 ($5 < HQ \leq 10$) are considered medium risk, and any hazard quotient larger than 10 ($H > 10$) is considered high risk (Aemere et al. 2019).

Table 3. Hazard indices for both dermal and ingestion exposures to heavy metals, as well as when those metals pose carcinogenic risks and non-carcinogenic risks

Total Hazard Quotients	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age: Adult	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic Metals	0.039343	0.032727	0.048406	0.040279	0.019436	0.019304	0.053095	0.033215
Ingestion of Soil Carcinogenic Metals	0.001955	0.001879	0.003853	0.003542	0.000805	0.000843	0.003003	0.002158
Dermal Absorption of Soil Non Carcinogenic Metals	0.000426	0.000354	0.000524	0.000436	0.00021	0.000209	0.000574	0.000359
Dermal Absorption of Soil Carcinogenic Metals	2.25E-05	2.98E-06	4.17E-05	3.83E-05	8.71E-06	9.12E-06	3.25E-05	2.33E-05
Total Hazard Quotients	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age: 3 to < 6	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic Metals	0.148064	0.123165	0.182173	0.151586	0.073146	0.07265	0.19982	0.125002
Ingestion of Soil Carcinogenic Metals	0.007357	0.007071	0.014501	0.01333	0.003031	0.003172	0.011303	0.00812
Dermal Absorption of Soil Non Carcinogenic Metals	0.001601	0.001332	0.00197	0.00164	0.000791	0.000786	0.002161	0.001352
Dermal Absorption of Soil Carcinogenic Metals	8.48E-05	1.12E-05	0.000157	0.000144	3.28E-05	3.43E-05	0.000122	8.78E-05
Total Hazard Quotients	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age 6 to < 11	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic Metals	0.086603	0.07204	0.106554	0.088663	0.042783	0.042494	0.116876	0.073115
Ingestion of Soil Carcinogenic Metals	0.004303	0.004136	0.008482	0.007797	0.001773	0.001855	0.006611	0.004749
Dermal Absorption of Soil Non Carcinogenic Metals	0.000937	0.000779	0.001152	0.000959	0.000463	0.00046	0.001264	0.000791
Dermal Absorption of Soil Carcinogenic Metals	4.96E-05	6.56E-06	9.17E-05	8.43E-05	1.92E-05	2.01E-05	7.15E-05	5.14E-05
Total Hazard Quotients	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age 11 < 16	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic Metals	0.048486	0.040332	0.059655	0.049639	0.023953	0.02379	0.065434	0.040934
Ingestion of Soil Carcinogenic Metals	0.002409	0.002315	0.004749	0.004365	0.000993	0.001039	0.003701	0.002659
Dermal Absorption of Soil Non Carcinogenic Metals	0.000524	0.000436	0.000645	0.000537	0.000259	0.000257	0.000708	0.000443
Dermal Absorption of Soil Carcinogenic Metals	2.78E-05	3.67E-06	5.14E-05	4.72E-05	1.07E-05	1.12E-05	4E-05	2.88E-05

Calculations are based on equations provided by the U.S. Environmental Protection Agency (USEPA) (USEPA 2011). The equation for ingestion of metals in soil:

$$Ing_{Soil} = \frac{(CS\ x\ IR\ x\ CF\ x\ EF\ x\ ED)}{(BW\ x\ AT)}$$

Where CS – heavy metal content in soil (mg/kg); IR – soil ingestion rate (mg/day); CF – conversion factor (kg/mg); EF – exposure frequency (day/a); ED – exposure duration (a); BW – body weight (kg); AT – average time (day). All constants taken from the USEPA (USEPA 2011).

The equation for dermal absorption is calculated in the following way based on the USEPA (USEPA 2011):

$$DA_{Soil} = \frac{(CS\ x\ AF\ x\ SA\ x\ ABS\ x\ CF\ x\ EF\ x\ ED)}{(BW\ x\ AT)}$$

Where CS – heavy metal content in soil (mg/kg); AF – skin adherence factor (mg/cm^2); SA – exposed surface area of skin (cm^2); ABS – dermal absorption factor; CF – conversion factor (kg/mg); EF – exposure frequency (day/a); ED – exposure duration (a); BW – body weight (kg); AT – average time (day). All constants taken from USEPA (USEPA 2011).

The total hazard index is obtained by the following equation:

$$HI = \sum \frac{Ing_{Soil}}{Rdf} \text{ Or } HI = \sum \frac{DA_{Soil}}{Rdf}$$

Where Ingsoil – Ingestion of soil; DASoil – dermal absorption of soil; Rdf – reference dose factor.

Rdf is taken from USEPA (USEPA 2018, 2011). The hazard index from each metal is then summed to give an overall total hazard quotient for any one park

Figures 8, 9, 10, and 11 show the concentration in parts per million (ppm) of each heavy metal in each park sample organized by park location. The far right bar in each chart shows the Texas Commission on Environmental Quality (TCEQ) background concentration levels in the State of Texas for each heavy metal in soil.

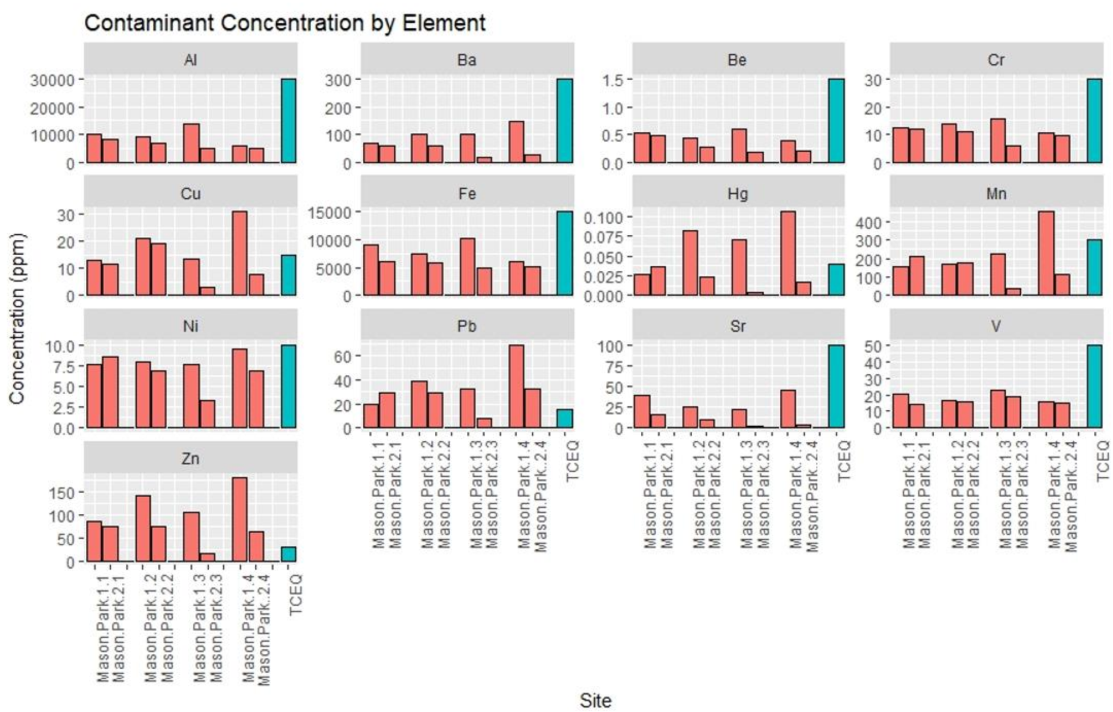

Figure 8. Comparing samples taken from Mason Park one week after Hurricane Harvey to samples taken seven weeks after Hurricane Harvey with the TCEQ average background concentrations in Texas. Mason Park samples 1.1 – 1.4 are all samples taken one week after Harvey, samples 2.1 – 2.4 are all samples taken seven weeks after Harvey.

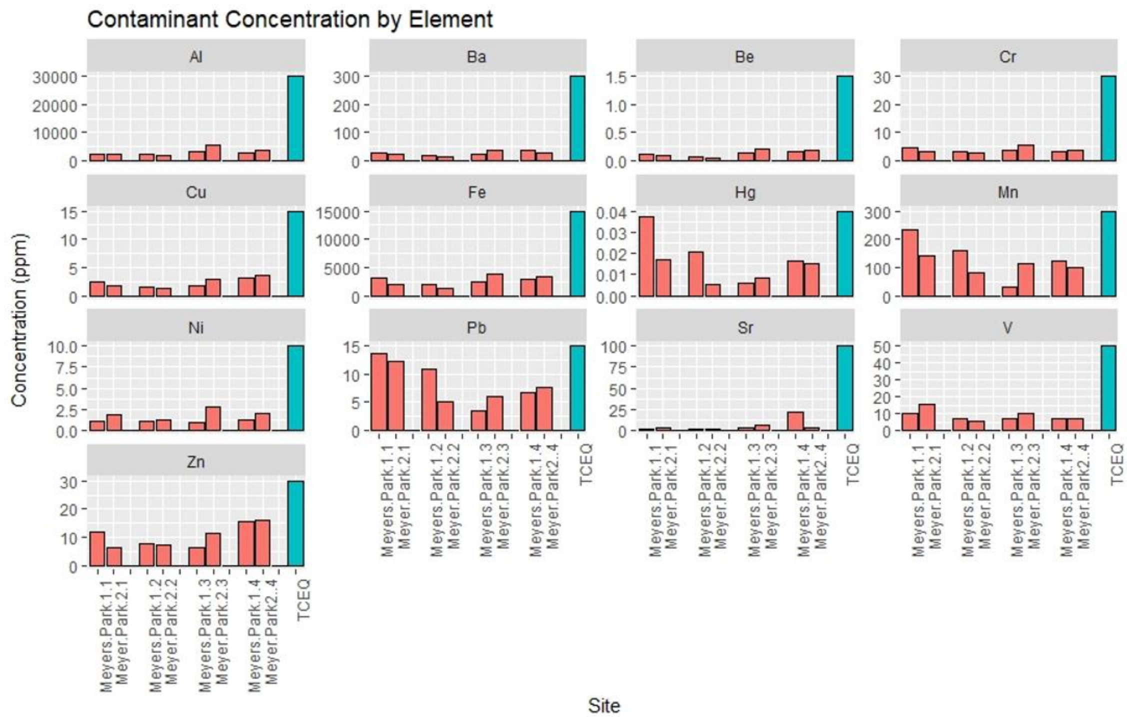

Figure 9. Comparing samples taken from Meyers Park one week after Hurricane Harvey to samples taken seven weeks after Hurricane Harvey with the TCEQ average background concentrations in Texas. Meyers Park samples 1.1 – 1.4 are all samples taken one week after Harvey, samples 2.1 – 2.4 are all samples taken seven weeks after Harvey.

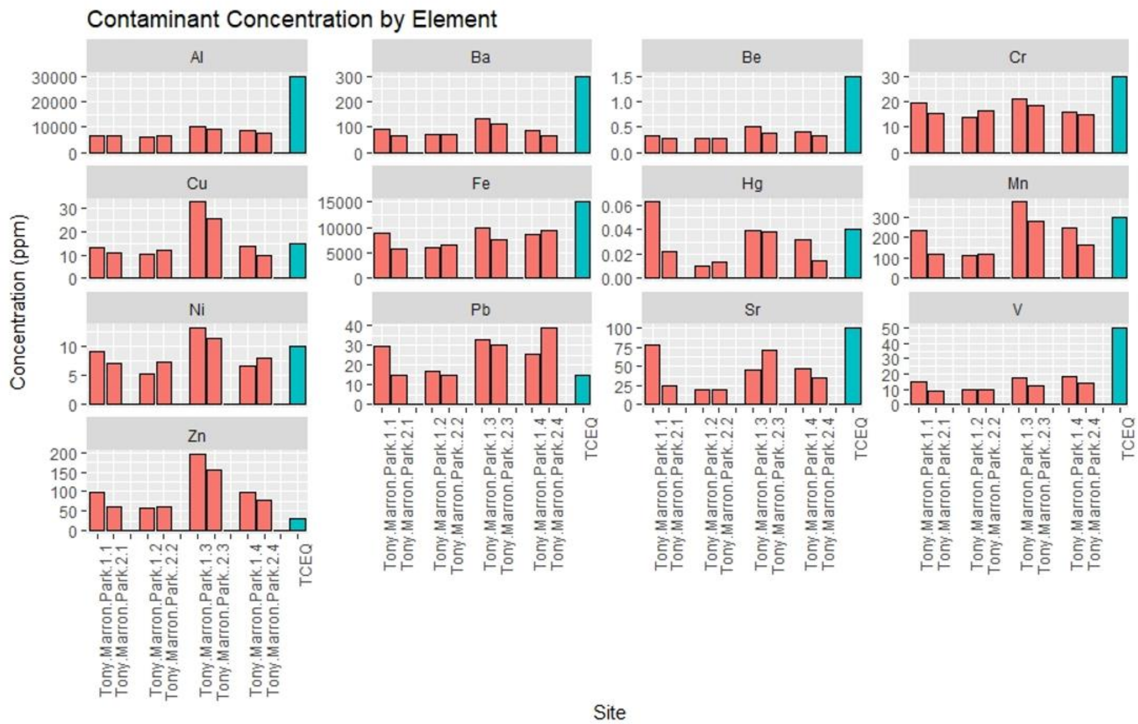

Figure 10. Comparing samples taken from Tony Marron Park one week after Hurricane Harvey to samples taken seven weeks after Hurricane Harvey with the TCEQ average background concentrations in Texas. Tony Marron Park samples 1.1 – 1.4 are all samples taken one week after Harvey, samples 2.1 – 2.4 are all samples taken seven weeks after Harvey.

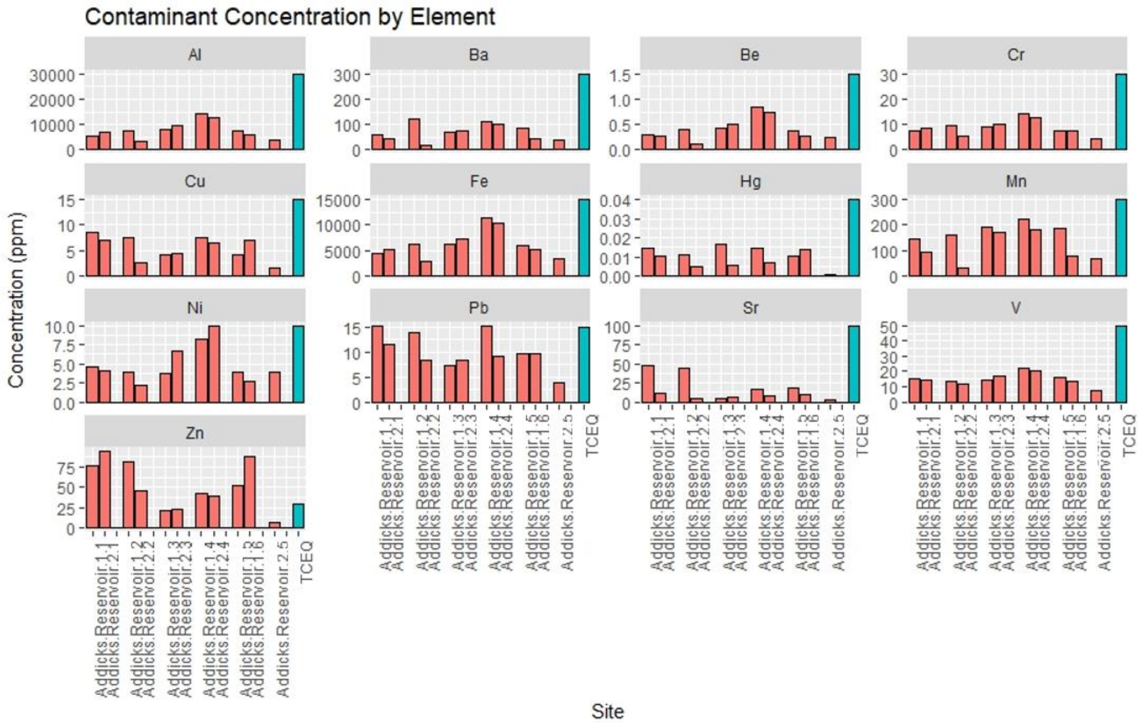

Figure 11. Comparing samples taken from Addicks Reservoir one week after Hurricane Harvey to samples taken seven weeks after Hurricane Harvey with the TCEQ average background concentrations in Texas. Addicks Reservoir samples 1.1 – 1.4 are all samples taken one week after Harvey, samples 2.1 – 2.4 are all samples taken seven weeks after Harvey.

Nickel is a medium weight heavy metal (58.693 AMU). Only one sample point showed nickel concentration in sediment above the average background concentration. This sample point was located in Tony Marron Park, and was elevated above the Texas background both one week after Harvey and seven weeks after Harvey. Copper is a medium weight heavy metal (63.546 AMU). One week after Hurricane Harvey three samples presented concentrations over the average background concentration in Texas. Two of the samples were collected in Mason Park and one was collected in Tony Marron Park. Two samples collected seven weeks after Hurricane Harvey were also above background concentrations, one sample was collected in Tony Marron Park and the other in Mason Park. Zinc is a medium weight heavy metal (65.38 AMU). One week after Hurricane Harvey made landfall, 13 samples contained concentrations over TCEQ's average background concentration for zinc in Texas. These samples spanned three of the four parks in the study; five samples from Addicks Reservoir, four samples from Tony Marron Park, and four Samples from Mason Park. Ten samples collected seven weeks after Harvey had concentrations of zinc over the background levels. Three of the samples were located in Addicks Reservoir, three were located in Mason Park, and four were located in Tony Marron Park. Mercury is a heavy weight heavy metal (200.59 AMU). Four samples collected one week after Hurricane Harvey showed mercury concentrations in sediment higher than the Texas background concentrations. One of these samples was located in Tony Marron Park and the other three were located in Mason Park. No samples collected seven weeks after Harvey had mercury concentrations higher than background concentrations in Texas. Lead is also a heavy weight heavy metal (207.2 AMU). Ten Samples collected one week after Harvey contained lead concentrations in sediment greater than the average Texas background concentrations. Two samples were collected in Addicks Reservoir, four in Tony Marron Park, and four in Mason Park. Seven samples collected seven weeks after Hurricane Harvey made landfall contained lead concentrations in sediment greater than the Texas average background lead concentration. Three samples were collected in Mason Park and four samples were collected in Tony Marron Park.

The background concentrations of heavy metals in sediments compiled by TCEQ are general average concentrations for any given heavy metal in sediment of Texas. These concentrations are all below any actionable levels as described by the USEPA. A sample having a concentration higher than the average background for Texas is therefore not immediately a concern. As the background figure provided by TCEQ is an average, it is comprised of sample locations that had concentrations above and below this average value. Figure 12 compares the TCEQ average background concentrations with USEPA concentrations for levels of action for heavy metals in sediment. Any samples with concentrations exceeding the levels of action as defined by the USEPA would be cause for concern. However, no samples collected in this study exceeded actionable USEPA concentrations.

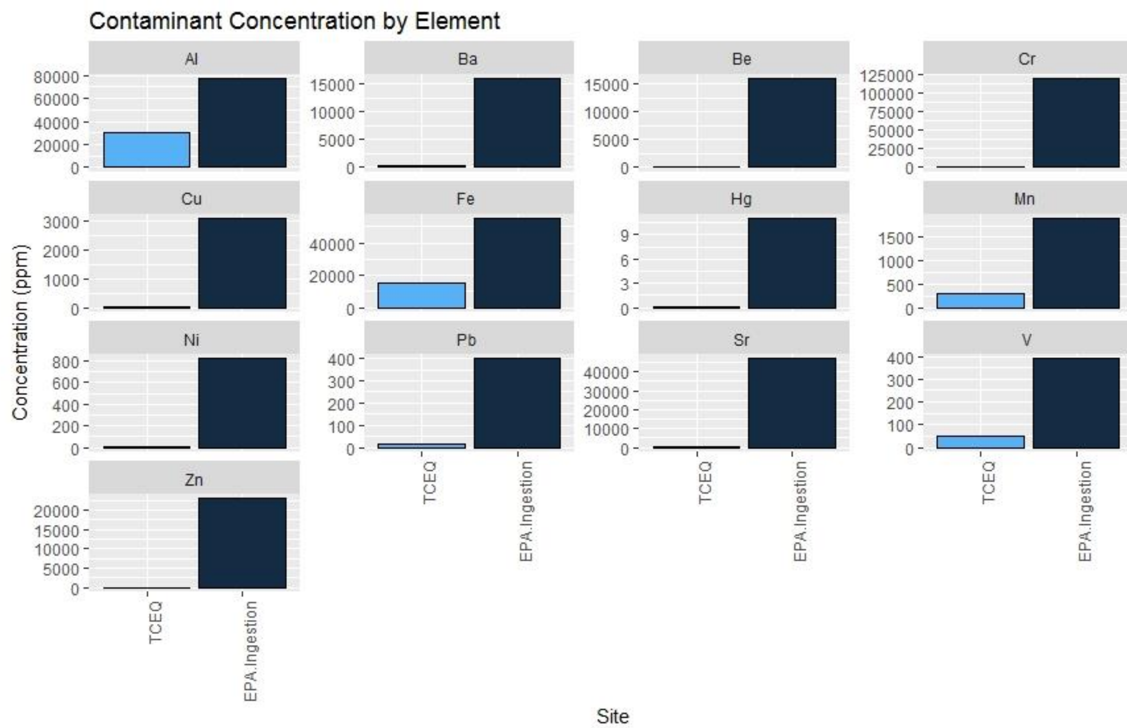

Figure 12. USEPA Regional Screening Levels for Residential Soil compared to TCEQ background soil levels

ANOVA was used to determine if the concentrations of heavy metals in parks following Hurricane Harvey were statistically different from one another or if it is more likely that each park's concentration of heavy metals in the soil was due to random chance. The concentration of nearly all heavy metals assessed were demonstrated to be significantly different and not due to random chance (Table 4). Concentrations of beryllium, manganese, mercury, and vanadium were statistically different in park soil in both the first (manganese) and second (beryllium, manganese, mercury, and vanadium) rounds of sediment collection, which were conducted one week after Harvey and seven weeks after Harvey respectively.

Table 4. One-way ANOVA comparing metals to all parks

One way ANOVA: Comparing metals between all parks		
Metals	**One Week After Harvey**	**Seven Weeks After Harvey**
Al (ppm)	0.00860 *	0.124584649
Ba (ppm)	0.00624 *	0.0465463 *
Be (ppm)	0.00963 *	0.203273751
Cr (ppm)	0.00001 *	6.21715E-05 *
Cu (ppm)	0.00265 *	0.01579089 *
Fe (ppm)	0.00224 *	0.030745776 *
Pb (ppm)	0.00222 *	0.008059737 *
Mn (ppm)	0.25534	0.49630559
Hg (ppm)	0.00236 *	0.066249121
Ni (ppm)	0.00031 *	0.009584092 *
Sr (ppm)	0.02560	0.003729434 *
V (ppm)	0.00165 *	0.103727822
Zn (ppm)	0.00190 *	0.026361894 *

*** statistical significance at (P < 0.0.5)**

ANOVA was also used to compare each individual heavy metal within each park between sample collection periods. Table 5 displays that a majority of the metal concentrations did not change significantly between sample collections one week after Hurricane Harvey made landfall and seven weeks after Hurricane Harvey made landfall. Mason Park had the most statistically significant sediment changes between sampling times. In addition, there were statistically significant changes between samples of barium, beryllium, iron, strontium, and zinc in Mason Park, mercury in both Addicks Reservoir and Mason Park, and nickel in Meyers Park.

Table 5. One-way ANOVA between sample times in parks

One way ANOVA: Comparing metals between sampling times				
Metals	**Addicks Reservoir**	**Tony Marron**	**Meyers Park**	**Mason Park**
Al (ppm)	0.75	0.79	0.42	0.11
Ba (ppm)	0.19	0.37	0.86	0.02 *
Be (ppm)	0.64	0.27	0.71	0.05 *
Cr (ppm)	0.61	0.47	0.94	0.07
Cu (ppm)	0.16	0.65	0.76	0.14
Fe (ppm)	0.63	0.42	0.96	0.03 *
Pb (ppm)	0.09	0.85	0.75	0.24
Mn (ppm)	0.16	0.32	0.55	0.19
Hg (ppm)	0.00 *	0.29	0.27	0.03 *
Ni (ppm)	0.58	0.96	0.03 *	0.20
Sr (ppm)	0.07	0.56	0.50	0.01 *
V (ppm)	0.51	0.15	0.49	0.18
Zn (ppm)	0.33	0.54	0.98	0.03 *

*** statistical significance at ($P < 0.05$)**

Finally, Table 6 displays a two-way ANOVA was used to assess potential interaction between sample times and park locations with respect to metal concentrations. Mercury is the only metal that showed a statistically significant interaction between sample time and park location.

Table 6. Two way ANOVA between Sample Time and Park

Two Way ANOVA	
Metals	**Sample Time x Park**
Al	0.43
Ba	0.13
Be	0.54
Cr	0.50
Cu	0.39
Fe	0.56
Pb	0.40
Mn	0.73
Hg	0.02 *
Ni	0.55
Sr	0.51
V	0.42
Zn	0.22

*** statistical significance at (P < 0.05)**

Discussion

To our knowledge, no background data on heavy metal concentrations in the sediment and soil of public parks and recreational areas in the Houston area are available. Many factors likely contribute to this lack of baseline data. One factor may be the cost to collect and analyze environmental samples in parks where there have been no history of community complaints due to contamination. In this case, a city like Houston may not spend a portion of a finite budget collecting background when that budget may be spent doing other actions such as cleaning up or investigating other locations that have evidence of a type of heavy metal contamination. Other factors may be lack of education in the communities and residents using the parks. A lack of education of heavy metal exposures or of facilities surrounding these parks that may release metals through industrial processes may allow for a lack of investigation where one should occur. This is because the residents that use the parks and lack education regarding heavy metals may not know to inquire an investigation from the city. Thirdly there are not enough human resources to take background of every park that every community uses, this means the city has to prioritize human resources to specific tasks and cannot take environmental samples of every park.

Therefore, we are unable to compare our data, collected following Hurricane Harvey-associated flooding, with background data. However, post-Harvey data can be compared to TCEQ average background concentrations as well as to USEPA limits. Samples taken seven days after Hurricane Harvey made landfall indicated concentrations of heavy metals that were both higher and lower than TCEQ State of Texas backgrounds levels. However, all samples taken at both time points had concentrations below actionable levels for soil according to the USEPAs soil ingestion limits.

Samples collected seven weeks after Hurricane Harvey generally had lower concentrations relative to TCEQ State of Texas background concentrations. In the initial samples taken one week after Harvey, there were 33 instances (N= 33; 14.47%) where specific metals in specific sampling locations per park were greater than TCEQ State of Texas background concentrations. These included nickel, copper, zinc, mercury, and lead. Zinc and lead samples over the TCEQ concentrations were taken from the Addicks Park, Mason Park, and Tony Marron Park (See Figure 7). Nickel was only over TCEQ concentrations at Tony Marron Park. Copper and mercury presented over TCEQ concentrations at both Tony Marron Park and Mason Park. In the second round of samples, there were only 20 instances (N= 20; 9.05%) where concentrations were greater than TCEQ State of Texas background concentrations. These included nickel, copper, zinc, and lead. Zinc concentrations exceeding TCEQ background concentrations were sampled in Addicks Reservoir, Mason Park, and Tony Marron Park. Nickel concentrations exceeding the TCEQ background were sampled only in Tony Marron Park. Copper and lead samples that exceeded TCEQ concentrations were taken in Meyers Park and Tony Marron Park.

Tony Marron Park and Mason Park are both in the Southeastern section of the GHA, within 5 miles of each other. They do not share a common tributary, however; Tony Marron Park is adjacent to Buffalo Bayou while Mason Park is adjacent to the Brays Bayou. Tony Marron Park is just across the river from a metals composting and recycling plant, which may explain some of the concentrations in the park that were elevated over TCEQs background concentrations. Mason Park has a significant amount of construction occurring on the opposite side of the Brays Bayou from the main park, including the construction of a pedestrian bridge over the Brays Bayou leading to the park. This construction may explain some of the elevated metals concentrations in the park.

When comparing the concentrations of heavy metals by sampling time across all parks, Mason Park showed the most statistically significant changes. Six heavy metal concentrations, barium, beryllium, iron, mercury, strontium, and zinc, were significantly different from sampling conducted one week after Harvey and seven weeks after Harvey. This change in concentration may be explained by the unprecedented flooding from Hurricane Harvey, which may have mobilized the top layer of sediment, depositing sediment with higher concentrations of heavy metals on the top 2 – 3 cm of sediment in the initial sample. In addition to Mason Park, Meyers Park and Addicks Reservoir each had one metal that showed statistically different concentrations between the first and second sample. In Meyers Park, that metal was Nickel and in Addicks Reservoir, the metal was Mercury. Samples collected two months after Hurricane Harvey showed metal concentrations across all parks to be generally less than in the initial sample, with the exception of a few specific sample sites. This decrease in concentration across parks for the second round of samples was not statistically different from the first round of sampling except for the metals listed above.

When comparing metals between all parks in the initial samples, the parks were statistically unique regarding metals concentration with the exception of Manganese. In the second set of samples, there were similar differences between parks, with the exception of four metals, aluminum, beryllium, manganese, and vanadium. The parks span the GHA, but all are either on the Buffalo Bayou itself or on a tributary feeding directly into Buffalo Bayou. These differences may be explained by the distance between the parks and the surrounding environment at each individual location. For example, there is, relative to Mason Park and Tony Marron Park, very little industrialization near either Meyers Park or the Addicks Reservoir.

At both sampling periods, all samples had hazard quotients below one, indicating that with respect to both dermal and ingestion exposures, these parks were safe to use immediately after major flooding like that associated with Hurricane Harvey.

This study has several important limitations. The overall sample size is relatively small; however, the catastrophic flooding after Hurricane Harvey limited travel and park access across the GHA. This study also only represents the impacts that resulted from one type of disaster, a relatively unique tropical storm that was predominantly characterized by inland flooding as opposed to storm surge, which may have resulted in a different distribution of heavy metals in soils and sediments. For example, Hurricane Ike, which made landfall in North Galveston County in 2008, included a larger storm surge that brought water into Houston from Galveston Bay via the Houston Ship Channel. Since sediment is highly mobile, it is difficult to discern the source of the heavy metals in the samples in our study. In the future, the collection of core samples may help improve understanding of the contents of soils under the sediments that were sampled here.

Conclusion

In this study, while several heavy metal concentrations were above the TCEQ State of Texas background concentrations for soils in Texas, none of the concentrations were above the USEPA ingestion concentration, meaning that the parks should be considered safe for use after Hurricane Harvey. In addition to comparing the individual concentrations over time and across parks, the cumulative hazard index for each park was below one, another indication that potential dermal or ingestion exposure was not a concern in this particular post-flood setting in these selected parks. More analyses are needed to improve our understanding of the baseline levels of heavy metals in parks across the GHA, which is highly vulnerable to future natural disasters and heavily exposed to industrial development. More data about background concentrations of heavy metals will potentially improve our understanding of the potential effects of flood-related contamination of parks and recreation areas.

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CHAPTER IV

PCB AND LEGACY ORGANOCHLORINE PESTICIDE CONCENTRATIONS AND POTENTIAL SOURCES IN HOUSTON RESIDENTIAL PARKS FOLLOWING HURRICANE HARVEY

Introduction

Polychlorinated biphenyls (PCBs) are a class of chlorinated compounds consisting of two aromatic rings. There are a total of 209 possible congeners that are the individual molecular formula for each PCB (USEPA 1983). PCB congeners can then be clustered into ten broad groups, referred to as homologs, based on the number of chlorine atoms in the compound. PCBs are man-made, and were produced in the United States between the years of 1929 and 1979 (US EPA 2015). PCBs can range from oily liquids to solids, from having no color to a yellow coloration and have no smell or taste (Illinois Department of Public Health 2009). PCBs have wide spread industrial applications ranging from dye production and plasticizers to electrical and hydraulic equipment (US EPA 2015). Monsanto Inc. was the primary producer of PCBs in the United States, under the production trade name of Aroclor (Illinois Department of Public Health 2009). There are 16 Aroclor mixtures, each of which contain a unique number of PCB congeners, with some consisting of over 100 individual congeners. The Aroclors distinct composition of PCBs allow for identification.

Measuring individual PCBs in the environment can be difficult and impractical, as different types of analysis have been developed to measure PCB concentration in environmental samples. The most common measurement for environmental samples are measuring the Aroclors (Okun 2011). There are nine common PCB Aroclor mixtures (1221, 1232, 1242, 1016, 1248, 1254, 1260, 1262, and 1268) each of which have unique gas chromatographic fingerprints (Okun 2011). Measuring Aroclors is best when the environmental samples have not been subject to heavy weathering. In the event of weathering, PCB congeners with fewer chlorine atoms favor partitioning into air and water over the PCBs with more chlorine atoms; analyzing for homologs over Aroclors can more accurately describe the sample (Okun 2011).

PCBs can enter the environment through several primary routes. One route is through spills and leaks from electrical and mechanical equipment; the other route is through poor disposal and storage of items containing PCBs (Illinois Department of Public Health 2009). A common source of environmental contamination with PCBs are leaks from old transformers containing PCBs (ATSDR 2014a). PCBs tend to bind strongly to soil and sediment, which leads to them being persistent in the environment (Illinois Department of Public Health 2009; ATSDR 2014a).

Bioaccumulation of PCBs occurs in both fish and mammals (ATSDR 2014a; Green Facts 2019; US EPA 2015). Bioaccumulation is the phenomenon of passive or active uptake and concentration of elements and compounds within an organism (Streit 1992). During bioaccumulation the lowest organism on the food chain has the smallest concentration of compound while the animals on the top of the food chain accumulate the highest concentration of the compound (Streit 1992). This accumulation can have adverse health outcomes to species along the food chain as well as humans who consume these species. PCBs, especially with a higher number of congeners, tend to bioaccumulate successfully (National Academies Press 2001)

Human exposure to high levels of PCBs occurred primarily in occupational settings (ATSDR 2014b). In high concentrations, the adverse health outcomes include possible hepatic damage, dermal lesions, and respiratory problems (ATSDR 2014b). Epidemiological studies suggest links between PCBs and thyroid hormone toxicity, while animal studies provide evidence of thyroid hormone involvement in the PCB mechanism of toxicity (ATSDR 2014b). The United States Department of Health and Human Services (DHSS) and the USEPA consider PCBs probable human carcinogens (ATSDR 2014b; US EPA 2015).

Chlorodane is an organochloride used as a pesticide in the United States from 1948 until 1988 (ATSDR 2011a). Chlorodane was used in large agricultural settings as well as residential lawns (ATSDR 2011a). Chlorodane was banned by the USEPA for all purposes with the exception of termites in 1983 and finally banned completely in 1988 (ATSDR 2011a). The USEPA banned chlorodane due to environmental impact and concerns with human ingestion (ATSDR 2011a).

Dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) are two chemicals similar to dichlorodiphenyltrichloroethane (DDT) that were used to protect agriculture from pests as well as protect human populations from insects carrying diseases such as malaria (ATSDR 2011b). DDE has no commercial use and DDD, similar to DDT, was used to remove pests (ATSDR 2011b). Both DDD and DDE were banned in the United States in 1972 due to environmental concerns. Other countries around the world have not banned the use of DDT (ATSDR 2011b).

Organochlorine pesticide general toxicity to humans in high concentrations impact the central nervous system (Jayaraj, Megha, and Sreedev 2016). Symptoms from organchlorine legacy pesticide exposure across all types include nausea, vomiting, convulsions, incoordination and tremors (Jayaraj, Megha, and Sreedev 2016). All the compounds described above have been discovered in the breast milk in the agricultural population of Guerrero Mexico (Chávez-Almazán et al. 2014). Although all of these pesticides have been banned in the US for more than three decades, their ability to persist in the environment potentially leaves residents vulnerable to exposure after flooding events in areas where the chemicals may be present in legacy electrical and mechanical equipment or due to improper disposal and storage.

Hurricane Harvey made landfall impacting the Greater Houston Area (GHA) with unprecedented flooding. The flooding and subsequent damage caused by Hurricane Harvey has the potential to increase PCB and Legacy Organochlorine pesticide concentrations in the sediment in Houston recreational parks that residents will use in the post disaster setting. Four park locations were chosen that span the Greater Houston Area (GHA) shown in Figure 13. These recreational parks are located along the Houston Ship Channel and the tributaries leading into the channel. All four parks were submerged following Hurricane Harvey's downpour and the release of the levees at the Addicks and Barkers Reservoirs.

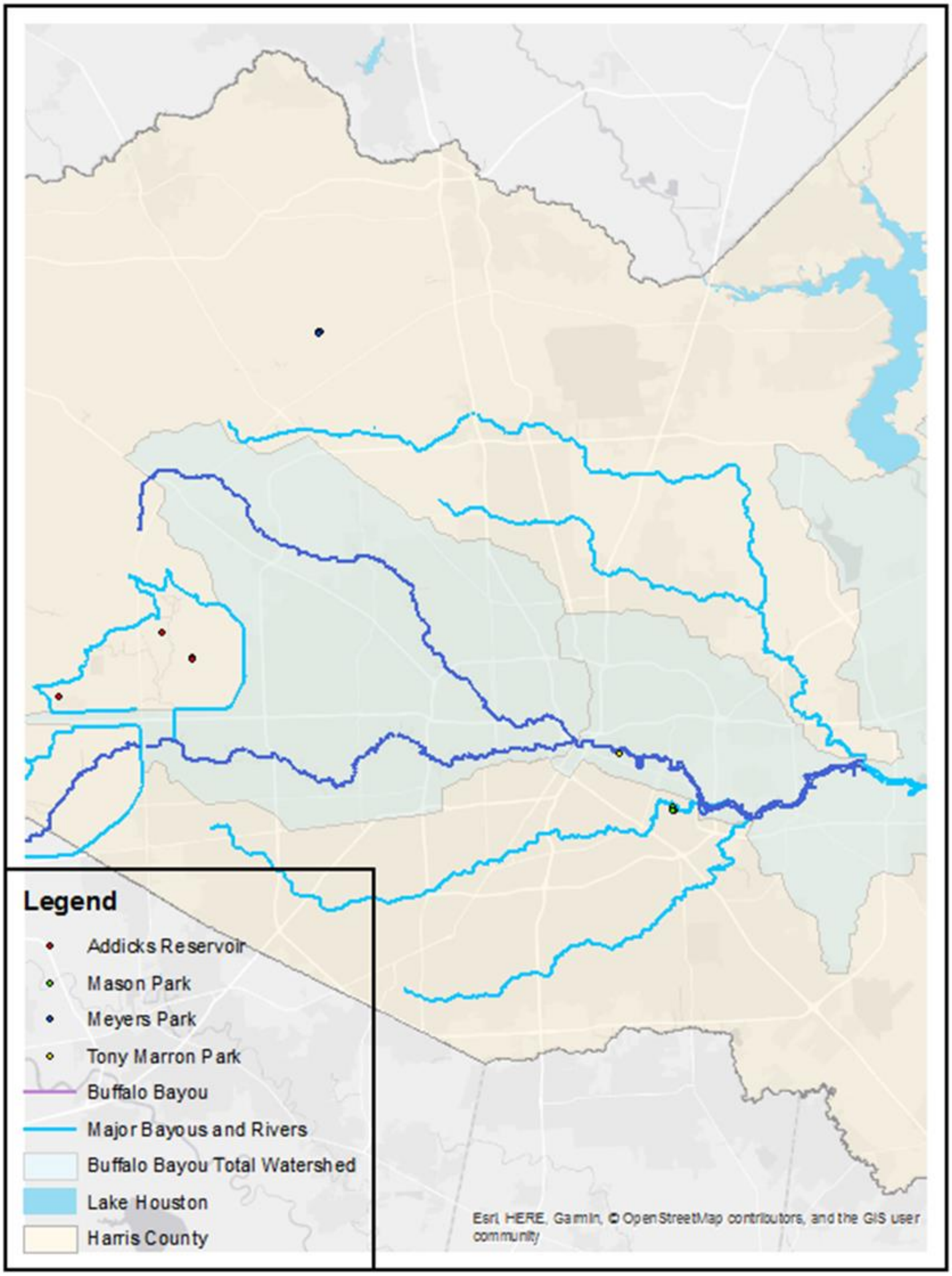

Figure 13. Map of Harris County portion of GHA Bayou System and sampling locations

Methods

Sediment samples were collected two times over the course of two months after Hurricane Harvey made landfall in four parks and recreation areas in Harris County. The first round of samples were collected one week after Hurricane Harvey, at which time many locations across Harris County were still submerged by floodwater and some roads remained impassable. Therefore, soil collection points were in locations where there was little or no standing water. The latitude and longitude of each collection site was recorded using Global Positioning System, Google Maps. Non-powder nitrile gloves were used for collection and a new pair was used for each sample. Samples were collected in 8 ounce glass jars using a metal trowel. The metal trowels were rinsed after each collection. The collection jars were filled approximately three fourths full due to the saturation of the soil. The second round of sediment samples was collected in November 2017, 7 weeks after Hurricane Harvey landfall, at the same geocoded locations using the same methods.

After collection, samples were stored in a cooler for transport from the Houston area to the Texas A&M School of Public Health (SPH) in College Station, Texas, approximately 90 miles. Once the samples arrived at SPH they were placed in a – 20 C freezer for storage. Frozen samples were freeze dried at SPH and transported to TDI-Brooks International in College Station, Texas, for analysis using gas chromatography mass spectrometry (GC-MS). Output data were analyzed using Microsoft Excel (Redmond, WA), Systat Sigmaplot V12.5 (San Jose, CA), and R (R Core Team).

Results

The PCBs that have been analyzed in the parks environmental samples have been organized into ten homolog categories and a category that displays certain PCBs that clustered together in the analysis but overlap two homolog groups (example: the cluster of PCB 33/53/20) this category is noted as, "PCBs across homologs." Figure 14 displays PCBs in each park in two ways, total percentage make-up by homolog for each park and average concentration in mg/kg of each homolog per park.

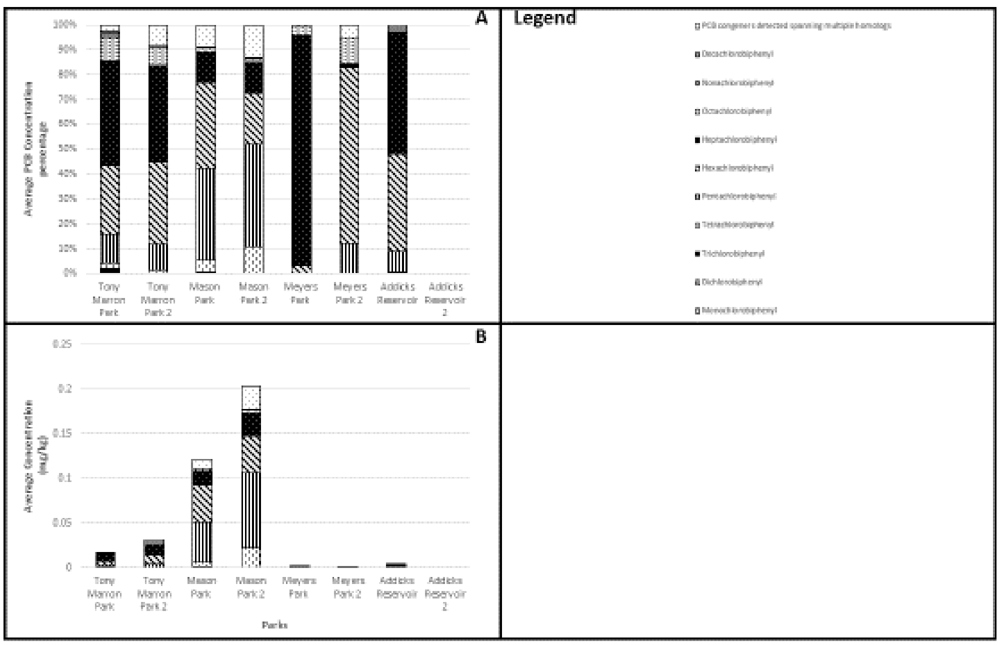

Figure 14. PCB (mg/kg) one week and seven weeks after Harvey, organized by homologs. A: Average PCB concentration percentage per park. B: Average PCB concentration per park. Samples taken one week after Harvey are denoted with the title of the park (eg. Tony Marron Park) Samples taken seven weeks after Harvey are denoted with the title of the park followed by the number, "2" (eg. Tony Marron Park 2).

In these post-Harvey samples, the combined PCB concentration in sediment approaches 1 mg/kg, with the highest concentration of combined PCBs in Mason Park (0.81652 mg/kg) in the second round of sampling. At both sampling time points, samples from Mason Park had significantly higher total concentrations of PCBs than the other three parks that were sampled. Table 7 Examines the content of total PCBs by homolog the homolog groups, the majority of the PCB concentrations in Mason Park were pentachlorobiphenyl, hexachlorobiphenyl and heptachlorobiphenyl. The Short-term action level for recreational areas column was adapted from the USEPA working with the Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup in 1997 to release short-term action levels for PCBs.

Table 7 Concentration of pentachlorobiphenyl, hexachlorobuphenyl, and heptachlorobiphenyl in Mason Park, Harris County, Texas, round 1 taken one week after Hurricane Harvey made landfall and round 2 taken 7 weeks post Harvey.

PCB homolog	Round 1 (mg/kg)	Round 2 (mg/kg)	Short-term action level: Recreational Area (mg/kg)
Pentachlorobiphenyl	0.17909	0.33728	30
Hexachlorobiphenyl	0.16483	0.16419	30
Heptachlorobiphenyl	0.05981	0.1023	30

(USEPA and Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup 1997)

Total PCB concentration in both Mason Park and Tony Marron Park increased from the first round of sampling to the second. In contrast, total PCB concentration in both Meyers Park and Addicks Reservoir decreased from the first round of sampling to the second (Figure 14).

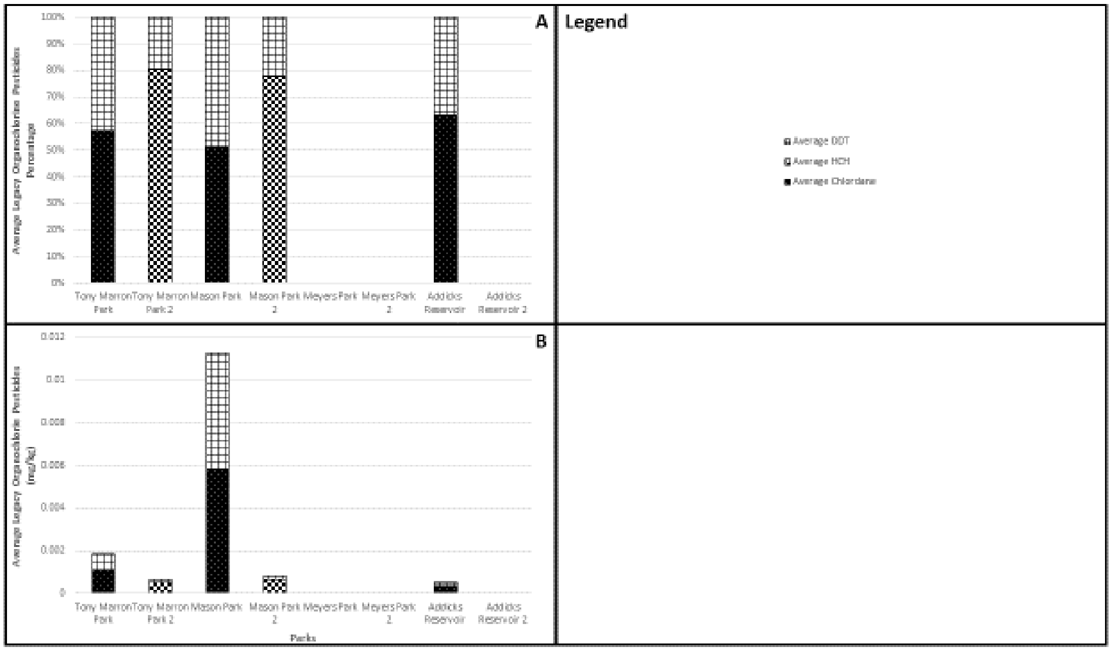

Figure 15. Legacy organochlorine pesticides (mg/kg) one week and seven weeks after Hurricane Harvey organized into three groups; average DDTs, average HCHs and average Chlordanes. A: The percent make up of each legacy organochlorine pesticide group per park. B: Average concentration of each legacy organochlorine pesticide group per park. Samples taken one week after Harvey are denoted with the title of the park (eg. Tony Marron Park) Samples taken seven weeks after Harvey are denoted with the title of the park followed by the number, "2" (eg. Tony Marron Park 2).

Figure 15 displays all legacy organochlorine pesticides decreased in total concentration from the first round of sampling to the second round. Table 8 displays two columns adapted from California human health and the TCEQ. The California human health screening levels (SL) and TCEQ protective concentration limits (PCL) for organochlorine pesticides are compared to Houston park concentrations in this table.

Table 8. Pesticide concentrations (mg/kg) in Tony Marron Park and Mason Park compared to California SL and the TCEQ protective concentration limit (PCL). The TCEQ PCL refers to soil ingestion (mg/kg). Tony Marron Park and Mason Park are samples from one week after Harvey. Tony Marron Park 2 and Mason Park 2 are samples taken from seven weeks after Harvey.

Pesticide	Tony Marron Park (mg/kg)	Tony Marron Park 2 (mg/kg)	Mason Park (mg/kg)	Mason Park 2 (mg/kg)	TCEQ Carcinogenic PCL (mg/kg)	TCEQ Noncarcinogenic PCL (mg/kg)	California SL (mg/kg)
Aldrin	0	0	0	0	0.36	2.5	0.033
Dieldrin	0	0	0	0	0.38	41	0.43
Endrin	0	0	0	0	n/a	n/a	21
DDD	0.00012	0	0.00528	0	25	n/a	2.3
DDE	0.00223	0	0.00945	0.00073	18	n/a	1.6
DDT	0.00082	0.00052	0.0071	0	18	41	1.6
Chlordane	0.00426	0.00211	0.02297	0.00254	17	41	0.43

(California Office of Environmental Health Hazard Assessment 2010; TCEQ 2018)

Discussion

PCBs environmentally degrade and bio-accumulate in a congener specific manner (National Academies Press 2001). The lower chlorinated congeners typically tend to be more volatile and soluble in water, leading to lower concentrations in the environment than the higher chlorinated congeners (National Academies Press 2001).

Higher chlorinated PCBs, in addition to increased bio-accumulation relative to the lower chlorinated species, also have a greater tendency for metabolism via an enzymatic route in both aquatic and terrestrial species (National Academies Press 2001).

In this study, Mason Park has higher PCB concentrations than other sampled parks. Mason Park is not surrounded by industry, rather it is surrounded on two sides by residential homes, on one side the Brays Bayou, and on the fourth side a city road. The land for Mason Park was originally donated to the City of Houston in 1930 and has seen incremental improvements across the decades, until present day where it is a very popular community park. Although the park buildings were renovated in 1986 and 1995, PCBs were popularly used in building caulk, paints, and other construction chemicals until 1978 (CICA 2012). The heavy flooding and quantities of rain may have dispersed old building material or revealed layers of older materials that may have seeped into the sediment in the park. If catastrophic amounts of precipitation associated with Hurricane Harvey exposed these older layers of materials from both park buildings but also from nearby homes that were damaged and downed transformers, this may explain the increase in PCB concentrations in park sediment seven weeks after the initial samples were collected. During the sampling immediately after Harvey, several parts of Mason Park were still flooded, and reconstruction to the neighborhood would not have had a chance to begin. This could mean that over time older exposed materials containing PCBs had time to continue leaking into the environment.

Concentrations of Organochlorine legacy pesticides decreased dramatically between the sampling times one week after Harvey and seven weeks after Harvey. At both time points, the chlordane group of pesticides showed to have the highest concentrations in both Mason Park and Tony Marron Park. Chlordanes have a history of use as an insecticide particularly to exterminate termites, ants, and other soil insects (Pohanish 2015). Use of the chlordane heptachlor and all heptachlor containing pesticides was banned in 1988, with the exception of fire ant control and for use in power transformers (Pohanish 2015). This continued use may have caused potential exposure in these two parks after flooding, especially in Houston, an area prone to fire ant infestation. First floor cabinets and garages are common storage for pesticide products, which are the first to flood during a flooding event. Flood waters are known to transport chemicals and deposit them in industrial settings (WHO 2018) and the same can happen with chemicals in the home during a flood. The rapid dispersal of chemicals from homes into the environment from flooding potentially explains the initial spike in chlordanes. As the flooding subsided over the course of the seven weeks, environmental weathering along with lack of pesticide supply from the flooded homes may have led to the decrease in concentration of chlordanes at the parks.

DDE and DDD are a result of degradation of DDT in the environment (ATSDR 2015). DDT's removal from usage in the USA in 1973 indicates that any DDT, DDE, DDT exposure will be primarily from the persistence of these chemicals in the environment (ATSDR 2015). DDT in surface water will bind to particulates in the water, allowing for transport of DDT from one sediment location to another (ATSDR 2011b, 2015). One week after Hurricane Harvey, the soil saturation was still extremely high, with several locations in both Mason Park and Tony Marron Park still submerged. This amount of saturation may have aided in the release of DDT, DDE, and DDD attached to particulates in sediment, mobilizing these contaminated sediment from their original resting locations to new locations, including the parks. Mobilization from their original location may explain increases in concentrations of these pesticide products one week after Harvey, with sediment saturation decreasing through evaporation and leaving pesticide particles settled on the top layer of soil. Once a majority of the flooding subsided, these parks began to see more activity from residents and wildlife, disturbing the topsoil.

It is important to put the data from park samples into context of potential action level by regulatory agencies. In all cases, the concentrations fell below the levels of action for multiple regulatory agencies. This presents a challenge for scientists in reporting results to the communities, who must stress the importance of understanding potential chemical exposure in any disaster event while ensuring residents' understanding of the actual levels needed to amount to toxic exposure. A two-part approach of education and engagement with potentially exposure residents may be the most effective way to address these issues. Focusing on the positive aspect that the concentrations immediately after the event were below any actionable level, while simultaneously educating on how to best minimize any potential exposures and what the exposure sources are.

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CHAPTER V

CONCLUSIONS

Summary

The purpose for this study was to better understand the impact major flooding events can have on the chemical profiles of public recreational parks used by residents and communities in the GHA along the Buffalo Bayou. The study is divided into three main aims. The first is describing the concentrations of PAHs in the sediments of the parks and then attempting to understand potential sources of the PAHs in a post flooding environment. The second aim, focuses on the concentration of heavy metals in the sediments of the parks and the potential for toxic exposures to residents using the parks. The third aim describes the concentration of PCBs as well as legacy organochlorine pesticides in the sediments of the park while attempting to understand the potential sources as well as any potential adverse health outcomes from exposure to these chemicals at the concentrations detected in this post disaster setting

PAHs

Samples were collected at four different parks along the Buffalo Bayou area; Addicks Reservoir, Meyers Park, Mason Park, and Tony Marron Park. The samples were collected at two time points one week after Hurricane Harvey made landfall and seven weeks after Hurricane Harvey. The sediment was collected using metal trowels then frozen at the Texas A&M School of Public Health, the samples were then freeze dried in preparation for analysis. The analyses were completed at the TDI-Brookings

Institute. These samples were analyzed for PAHs, as well as, PCBs, and Legacy organochlorine pesticides. The data analysis was completed using Microsoft Excel (Redmond, WA), Sigmaplot V12.5 (San Jose, CA), and RStudio Software (R Core Team 2013). The analysis were used to determine PAH concentrations for the EPA priority 16 PAHs, and to attempt to determine potential sources that lead to the PAH concentrations in the parks.

In nano-grams per gram (ng/g) samples taken from Tony Marron Park, seven weeks after Hurricane Harvey yielded the highest total PAH concentration. Three out of the four parks revealed an overall decrease in total combined concentration of the priority 16 PAHs. More than 70% of the PAHs detected in the park samples colleceted one week after Harvey comprised of either four ring or five/six ring priority PAHs. Park samples collected seven weeks after Hurricane Harvey were comprised of majority four ring priority PAHs at 44% composition followed by five and six ring priority PAHS composing 23% and three ring composing 26% of the total priority PAH composition. ANOVA testing comparing the total concentration of PAHs at each park revealed that all parks in the study were statistically significantly unique.

Diagnostic ratios were used in an attempt to determine potential sources of the PAHs. Five diagnostic ratios were used: Fluoranthene / (Fluoranthene + Pyrene), Anthracene / (Anthracene + Phenanthrene), Indeno(cd-1,2,3)Pyrene/ (Indeno(cd-1,2,3)pyrene + Benzo(g,h,i)perylene), Benzo(a)anthracene/ (Benzo(a)anthracene + Chrysene), and Benzo(a)pyrene/(Benzo(g,h,i)perylene. A majority of the samples both one week after Harvey and seven weeks after Harvey contained ratios indicating the source of the PAHs coming from combustion of biomass, this was obtained using the ratios of Fluoranthene/ (Fluoranthene + Pyrene), Anthracene / (Anthracene + Phenanthrene), and Inden(cd-1,2,3)pyrene / (Indeno(cd-1,2,3)pyrene + Benzo(g,h,i)perylene). The final two ratios, Benzo(a)anthracene/ (Benzo(a)anthracene + Chrysene), and Benzo(a)pyrene/(Benzo(g,h,i)perylene, are used to predict if the source of PAHs is vehicular in nature. These analyses showed that one week after Harvey only slightly more than half of the samples were predicted by the ratios to be from a vehicular source compared to seven weeks after Harvey all samples were shown to have ratios indicating a vehicular source of emissions.

Heavy Metals

The environmental sediment samples collected for analysis were collected in the same latitude and longitude locations as the samples for both PAHs and PCBs and legacy organochlorine pesticides. The samples were collected using plastic scooping shovels. The samples were analyzed in the Trace Element Research Laboratory at the Texas A&M College of Veterinary Medicine. The analysis were used to better understand the concentration of metals in sediments in a post flood setting and the potential adverse health outcomes to exposure to these concentrations through activity in the parks. Data analysis was completed using Microsoft Excel (Redmond, WA), Sigmaplot V12.5 (San Jose, CA), and RStudio Software (R Core Team 2013).

Hazard quotients were developed using the following equations:

1. $Ing_{Soil} = \frac{(CS \ x \ IR \ x \ CF \ x \ EF \ x \ ED)}{(BW \ x \ AT)}$

2. $DA_{Soil} = \frac{(CS \; x \; AF \; x \; SA \; x \; ABS \; x \; CF \; x \; EF \; x \; ED)}{(BW \; x \; AT)}$

3. $HI = \sum \frac{Ing_{Soil}}{Rdf}, HI = \sum \frac{DA_{Soil}}{Rdf}$

The Hazard quotients for all heavy metals in the analyses were below 1. This indicates, that using the USEPA risk assessment method the concentrations of metals in this sediment were not likely to post either a carcinogenic risk or a non-carcinogenic risk to residents using the parks in this particular post flooding disaster setting. The concentrations of the metals after each sampling time were compared to the closest source of background in the literature: TCEQ state of Texas average background concentration of metals in soils list. One week after Harvey copper, mercury, manganese, nickel, lead, and zinc had certain samples in the parks that surpassed the average background of those metals in the Texas soils. Seven weeks after Harvey copper, nickel, lead, and zinc had select samples from individual parks which surpassed the average background of those metals in the Texas soils. Although, in some cases the soils exceeded the average background concentration they never surpassed the USEPA Ingestion concentration for concern. The concentration in the sediment in Tony Marron Park could have been due to the nearby metals recycling facility flooding during Harvey. The Mason Park concentrations may have been sourced from the nearby construction flooding during Hurricane Harvey.

PCBs and Legacy Organochlorine Pesticides

The environmental sediment sample collection is the same as for the PAH analysis. The data analysis was completed using Microsoft Excel (Redmond, WA), Sigmaplot V12.5 (San Jose, CA), and RStudio Software (R Core Team 2013). The data analysis was used to better understand the concentration of potential PCB and legacy organochlorine exposure to residents using the parks after Harvey, as well as to attempt to better understand the potential sources of PCBs and legacy oraganochlorine pesticides to these parks.

The highest concentration of total PCBs in sediment is in Mason Park (0.81652 mg/kg) this concentration was detected seven weeks after Hurricane Harvey made landfall. Mason Park relative to the other three parks had significantly higher concentrations of PCBs both one week and seven weeks after Hurricane Harvey. Of the 10 homologs of PCBs the three that held the highest concentrations were: pentachlorobiphenyl, hexachlorobiphenyl, and heptachlorobiphenyl. Although Mason park values approached 1 mg/kg the minimum short term action level of PCBs as stated by the USEPA and Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup is 10 mg/kg.

All legacy organochlorine pesticides decrease with regards to total concentration from one week after Harvey made landfall to seven weeks after Harvey made landfall. In relation to either the TCEQ protective concentration limit or the California office of Environmental Health Hazard Assessment, the concentrations at the parks fall well below these levels. This level of concentration is indicative that short term cleaning action is not required. Sources for both PCBs and legacy organochlorine pesticides in Mason Park may have stemmed from the flooded homes that surround the park. These homes are historic and may contain materials that used these chemicals.

Future Studies

Characterizing park background levels in areas of concern

This study was in response to a disaster, which severely limited the scope of the study. With the base of knowledge, coming from this study and using Global Information Softwares (GIS) studies could identify parks of concern for flooding and collect environmental samples to gather a background chemical profile before a disaster occurs. This will increase understanding of how disasters impact communities using parks in two ways. The first, it will establish a baseline understanding of what concentration levels these communities are exposed to regularly in a non-disaster environment. The baseline will also be more robust with no limitation on areas of the park researchers will be able to sample. The second, it will allow researchers to better understand how the disaster actually impacted the chemical profile of the park. It is difficult to discern impact of a disaster without knowing the original concentrations for the chemicals in these parks.

Building community understanding surrounding disaster resilience

Using the data collected researchers can target specific vulnerable communities and develop plans of action to mitigate adverse health outcomes due to potential exposures of certain chemicals in a post disaster-flooding event. Communities that have a better understanding of the exposures and the sources, partnering with researchers, will be able to hone in specific areas of the park that have issues that can be addressed to increase resilience to disasters. Building community understanding of environmental exposures through various surveys and community engagement projects will also allow for increased communication between the communities and both government and industry. A community engagement based model for interacting with communities in a post disaster setting can be replicated outside of Houston to other communities prone to flooding and hurricanes.

APPENDIX A

ANOVA TABLES

Chapter II Tables

Another way to assess potential changes in PAH concentrations over time is to conduct one-way analysis of variance tests (ANOVA) between the samples collected 1 week and 7 weeks after Hurricane Harvey landfall. ANOVA will identify pairs of samples where there is a statistically significant ($\alpha = 0.05$) difference between the total concentrations, organized by the number of rings, between the samples from the same location at the two time points. For 2 – Ring PAHs, there were statistically significant differences between first and second round samples from only Addicks Reservoir and Tony Marron Park. for total PAH concentration, the same two parks showed statistical significance in regards to TEF. For 3 – Ring PAHs, there were no significant differences at any park, while the TEF was different only at Mason Park. For 4 – Ring PAHs, there were significant differences for both total concentration and TEF at both Addicks Reservoir and Mason Park. For 5 and 6 – Ring PAHs, there were significant differences for total concentration at both Addicks Reservoir and Mason Park, but difference in TEF were only found in the two Mason Park samples.

Table 9. One-way ANOVA between park samples and time, with both total PAH and the TEF values for total PAH concentrations

2 – Ring PAHs

Total PAH				
Park	Ring number	F	P-value	F-crit
1	2	5.433463	0.024629	4.072654
2	2	3.832116	0.059639	4.170877
3	2	5.570109	0.024969	4.170877
4	2	0.91834	0.345571	4.170877

TEF PAH				
Park	Ring number	F	P-value	F-crit
1	2	5.433463	0.024629	4.072654
2	2	3.832116	0.059639	4.170877
3	2	5.570109	0.024969	4.170877
4	2	0.91834	0.345571	4.170877

3 – Ring PAHs

Total PAH				
Park	Ring number	F	P-value	F-crit
1	3	3.124244	0.086979	4.159615
2	3	0.950727	0.340135	4.30095
3	3	2.340834	0.140275	4.30095
4	3	3.989173	0.058309	4.30095

TEF PAH				
Park	Ring number	F	P-value	F-crit
1	3	3.851455	0.058732	4.159615
2	3	0.920356	0.347807	4.30095
3	3	3.271629	0.084176	4.30095
4	3	8.267693	0.008788	4.30095

4 – Ring PAHs

Total PAH				
Park	Ring number	F	P-value	F-crit
1	4	14.46098	0.000372	4.023017
2	4	2.498346	0.122255	4.098172
3	4	3.980042	0.05325	4.098172
4	4	36.59359	4.87E-07	4.098172

TEF PAH				
Park	Ring number	F	P-value	F-crit
1	4	5.381722	0.024232	4.023017
2	4	1.2035	0.279527	4.098172
3	4	1.758344	0.192747	4.098172
4	4	6.921208	0.012236	4.098172

Table 9 Continued: One-way ANOVA between park samples and time, with both total PAH and the TEF values for total PAH concentrations
5 and 6 – Ring PAHs

Total PAH					TEF PAH				
Park	Ring number	F	P-value	F-crit	Park	Ring number	F	P-value	F-crit
1	5 and 6	8.110283	0.006785	4.072654	1	5 and 6	3.100832	0.085532	4.072654
2	5 and 6	0.436295	0.513957	4.170877	2	5 and 6	0.478805	0.494285	4.170877
3	5 and 6	3.523522	0.070259	4.170877	3	5 and 6	0.866668	0.359311	4.170877
4	5 and 6	19.11413	0.000136	4.170877	4	5 and 6	4.195626	0.049367	4.170877

A One-Way ANOVA was run comparing the concentrations of total PAH organized by ring as well as TEF organized by ring between the four park study locations. The one-way ANOVA test showed statistical significance between all park locations and all number ring groups in the study.

Table 10. One-way ANOVA between park areas and PAH concentration per sample
2 – Ring PAHs

Total PAH					TEF PAH				
Sample	Ring number	F	P-value	F-crit	Sample	Ring number	F	P-value	F-crit
1	2	5.610708	0.001695	2.739502	1	2	5.610708	0.001695	2.739502
2	2	4.524379	0.006121	2.748191	2	2	4.524379	0.006121	2.748191

3 – Ring PAHs

Total PAH					TEF PAH				
Sample	Ring number	F	P-value	F-crit	Sample	Ring number	F	P-value	F-crit
1	3	5.058592	0.00388	2.790008	1	3	14.25546	7.74E-07	2.790008
2	3	4.530761	0.007173	2.802355	2	3	5.570762	0.002357	2.802355

4 – Ring PAHs

Total PAH					TEF PAH				
Sample	Ring number	F	P-value	F-crit	Sample	Ring number	F	P-value	F-crit
1	4	35.7027	4.39E-15	2.710647	1	4	38.94706	5.4E-16	2.710647
2	4	12.78916	6.37E-07	2.717343	2	4	7.087058	0.000274	2.717343

Table 11: One-way ANOVA between park areas and PAH concentration per sample continued:
5 and 6 – Ring PAHs

Total PAH					TEF PAH				
Sample	Ring number	F	P-value	F-crit	Sample	Ring number	F	P-value	F-crit
1	5 and 6	19.82996	2.42E-09	2.739502	1	5 and 6	4.035362	0.010585	2.739502
2	5 and 6	10.61539	9.35E-06	2.748191	2	5 and 6	3.627758	0.017509	2.748191

Two-way ANOVA comparing the correlation between the sample time and the park affecting the PAH concentration. The Two-way ANOVA showed statistical significance in all parks when comparing the impact that both time and park location had on the concentration of PAHs by ring.

Table 11. Two-way ANOVA between sample time and park

Two Way Anova	
PAHs	Sample Time x Park
2 Rings	0.046 *
3 Rings	0.02 *
4 Rings	0.015 *
5/6 Rings	<0.001 *

***statistical significance at (P < 0.05)**

Table 12. Hazard Index table for PAHs

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age: 3 to < 6	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PAHs	0.000677	0.000267	0.001228	0.002346	0.000142	9.1E-05	0.001374	0.000587773
Dermal Absorption of Soil Non Carcinogenic PAHs	7.32E-06	2.89E-06	1.33E-05	2.54E-05	1.53E-06	9.84E-07	1.49E-05	6.35735E-06
Ingestion of Soil Carcinogenic PAHs	0.00029	0.000114	0.000526	0.001006	6.07E-05	3.9E-05	0.000589	0.000251903
Dermal Absorption of Soil Carcinogenic PAHs	3.14E-06	1.24E-06	5.69E-06	1.09E-05	6.56E-07	4.22E-07	6.37E-06	2.72458E-06

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age 6 to < 11	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PAHs	0.000396	0.000156	0.000718	0.001372	8.28E-05	5.32E-05	0.000804	0.000343792
Dermal Absorption of Soil Non Carcinogenic PAHs	4.28E-06	1.69E-06	7.77E-06	1.48E-05	8.96E-07	5.75E-07	8.69E-06	3.71845E-06
Ingestion of Soil Carcinogenic PAHs	0.00017	6.69E-05	0.000308	0.000588	3.55E-05	2.28E-05	0.000344	0.000147339
Dermal Absorption of Soil Carcinogenic PAHs	1.83E-06	7.23E-07	3.33E-06	6.36E-06	3.84E-07	2.47E-07	3.73E-06	1.59362E-06

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age 11 < 16	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PAHs	0.000222	8.74E-05	0.000402	0.000768	4.64E-05	2.98E-05	0.00045	0.000192475
Dermal Absorption of Soil Non Carcinogenic PAHs	2.4E-06	9.45E-07	4.35E-06	8.31E-06	5.01E-07	3.22E-07	4.87E-06	2.08181E-06
Ingestion of Soil Carcinogenic PAHs	9.5E-05	3.74E-05	0.000172	0.000329	1.99E-05	1.28E-05	0.000193	8.24893E-05
Dermal Absorption of Soil Carcinogenic PAHs	1.03E-06	4.05E-07	1.86E-06	3.56E-06	2.15E-07	1.38E-07	2.09E-06	8.92204E-07

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age: Adult	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PAHs	0.000157	6.2E-05	0.000286	0.000545	3.29E-05	2.11E-05	0.000319	0.000136657
Dermal Absorption of Soil Non Carcinogenic PAHs	1.7E-06	6.71E-07	3.09E-06	5.9E-06	3.56E-07	2.29E-07	3.46E-06	1.47808E-06
Ingestion of Soil Carcinogenic PAHs	6.74E-05	2.66E-05	0.000122	0.000234	1.41E-05	9.06E-06	0.000137	5.85674E-05
Dermal Absorption of Soil Carcinogenic PAHs	7.29E-07	2.88E-07	1.32E-06	2.53E-06	1.53E-07	9.8E-08	1.48E-06	6.33465E-07

Chapter IV Tables

Table 13. One-way ANOVA analysis comparing PCB concentrations between sampling times one week after Harvey and seven weeks after Harvey making landfall

One way ANOVA: comparing PCBs between sampling times								
PCB Homologs	**Tony Marron Park**		**Mason Park**		**Addicks Reservoir**	**Meyers Park**	
Monochlorobiphenyl	Undefined		Undefined		Undefined	Undefined	
Dichlorobiphenyl	Undefined		0.355918		Undefined	Undefined	
Trichlorobiphenyl	0.043216	*	0.026561	*	0.389283	Undefined	
Tetrachlorobiphenyl	0.678684		0.469603		Undefined	Undefined	
Pentachlorobiphenyl	0.311228		0.632733		0.371992	0.355918	
Hexachlorobiphenyl	0.397242		0.996743		0.307694	0.496916	
Heptachlorobiphenyl	0.544331		0.671829		0.094333	0.007784	*
Octachlorobiphenyl	0.680225		0.635135		Undefined	0.618261	
Nonachlorobiphenyl	0.802723		0.646953		0.389283	Undefined	
Decachlorobiphenyl	0.129712		0.078736		Undefined	Undefined	
PCB's across homologs	0.349176		0.564515		0.389283	0.355918	

***statistical significance at (P < 0.05)**

Table 14. One-way ANOVA analysis comparing PCB concentrations between all parks

One way ANOVA: Comparing PCBs between all parks			
PCB Homologs	One Week After Harvey		Seven Weeks After Harvey
Monochlorobiphenyl	Undefined		Undefined
Dichlorobiphenyl	0.342516		Undefined
Trichlorobiphenyl	0.000123	*	0.432318
Tetrachlorobiphenyl	0.002254	*	0.35278
Pentachlorobiphenyl	0.002013	*	0.315211
Hexachlorobiphenyl	0.003175	*	0.285642
Heptachlorobiphenyl	0.0000328	*	0.391874
Octachlorobiphenyl	0.061201		0.35279
Nonachlorobiphenyl	0.18631		0.332731
Decachlorobiphenyl	0.002912	*	0.383371
PCB's across homologs	0.003195	*	0.378635

***statistical significance at (P < 0.05)**

Table 15. One-way ANOVA analysis comparing legacy organochlorine pesticides between sampling times

One way ANOVA: comparing Legacy Organochlorine Pesticides between sampling times					
PCB Homologs	Tony Marron Park	Mason Park		Addicks Reservoir	Meyers Park
Total Chlordane	0.550539	0.022748	*	0.124604	Undefined
Total HCH	Undefined	0.355918		Undefined	Undefined
Total DDT	0.109012	0.027868	*	0.108554	Undefined

***statistical significance at (P < 0.05)**

Table 16. One-way ANOVA analysis comparing legacy organochlorine pesticides between all parks

One way ANOVA: Comparing Legacy Organochlorine Pesticides between all parks			
PCB Homologs	One Week After Harvey		Seven Weeks After Harvey
Total Chlordane	0.000844	*	0.062241
Total HCH	0.342516		Undefined
Total DDT	0.001136	*	0.485123

*statistical significance at (P < 0.05)

Table 17. Hazard Index for PCBs and Legacy Organochlorine Pesticides

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age: 3 to < 6	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PCBs / LOP's	0.038696	0.001474	0.167113	0.197865	0	0.003923	3.283204	4.070523
Dermal Absorption of Soil Non Carcinogenic LOP's	0.000419	0	0.001807	0.00214	0	4.24E-05	0.03676	0.044027
Ingestion of Soil Carcinogenic LOP's	0.016584	0	0.07161	0.084799	0	0.018265	1.407088	1.74451
Dermal Absorption of Soil Carcinogenic LOP's	0.000179	0	0.000775	0.000917	0	1.82E-05	0.015219	0.018869

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age 6 to < 11	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PCBs / LOP's	0.022634	0	0.097732	0.115733	0	0.002294	1.98791	2.385802
Dermal Absorption of Soil Non Carcinogenic LOP's	0.0097	0	0.001057	0.001252	0	2.48E-05	0.021501	0.025805
Ingestion of Soil Carcinogenic LOP's	0.000245	0	0.041885	0.0496	0	0.000983	0.851962	1.022487
Dermal Absorption of Soil Carcinogenic LOP's	0.000105	0	0.000453	0.000536	0	1.06E-05	0.009215	0.011059

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age 11 < 16	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PCBs / LOP's	0.012672	0	0.054716	0.064794	0	0.001285	1.11295	1.335713
Dermal Absorption of Soil Non Carcinogenic LOP's	0.000137	0	0.000592	0.000701	0	1.39E-05	0.012038	0.014447
Ingestion of Soil Carcinogenic LOP's	0.005431	0	0.02345	0.027769	0	0.000551	0.476978	0.572449
Dermal Absorption of Soil Carcinogenic LOP's	5.87E-05	0	0.000254	0.0003	0	5.95E-06	0.005159	0.006192

Total Hazard Index	Addicks Reservoir		Tony Marron		Meyers Park		Mason Park	
Age: Adult	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2	Round 1	Round 2
Ingestion of Soil Noncarcinogenic PCBs / LOP's	0.008997	0	0.038848	0.046004	0	0.000912	0.790194	0.948356
Dermal Absorption of Soil Non Carcinogenic LOP's	9.73E-05	0	0.00042	0.000498	0	9.86E-06	0.008547	0.010257
Ingestion of Soil Carcinogenic LOP's	0.003856	0	0.016649	0.019716	0	0.000391	0.338655	0.406438
Dermal Absorption of Soil Carcinogenic LOP's	4.17E-05	0	0.00018	0.000213	0	4.23E-06	0.003663	0.004396