Characterizing PCBs and Dioxins in the Houston Ship Channel and Galveston Bay Post Hurricane Harvey

Final Report

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Abbreviations

Dioxins	Dibenzo-p-dioxins and dibenzofurans
DL	Detection limit
DO	Dissolved oxygen
DOC	Dissolved organic carbon
GB	Galveston Bay
GBEP	Galveston Bay Estuary Program
GBF	Galveston Bay Foundation
GBS	Galveston Bay System
HSC	Houston Ship Channel
HSC-GB	Houston Ship Channel – Galveston Bay
HSC-SJR	Houston Ship Channel – San Jacinto River

K-L	Kullback-Leibler
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mS/cm	millisiemens per centimeter
ng/kg	nanograms per kilogram
NSF	National Science Foundation
OCDD	Octachlorodibenzo-p-dioxin
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated Dibenzo-p-Dioxin
PCDF	Polychlorinated Dibenzo-p-Furan
ppt	Parts per thousand (when used for salinity)
QAPP	Quality Assurance Project Plan
SJR	San Jacinto River
SJRWP	San Jacinto River Waste Pits
STORET	Storage and retrieval
SWQM	Surface Water Quality Monitoring
SWQMIS	Surface Water Quality Monitoring Information System
TCDD	Tetrachlorodibenzodioxin
TCDF	Tetrachlorodibenzofuran
TCEQ	Texas Commission on Environmental Quality
TDSHS	Texas Department of State Health Services
TEF	Toxic Equivalency Factor
TEQ	Toxic Equivalency
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TMDL	Total Maximum Daily Load
UGB	Upper Galveston Bay
UH	University of Houston
USEPA	United States Environmental Protection Agency

Executive Summary

The purpose of this project was to collect and analyze fish and crab tissue and sediment samples to quantify the levels of polychlorinated biphenyls and dioxin post Hurricane Harvey in the Houston Ship Channel and Galveston Bay system. This project leveraged a previous effort funded by the Galveston Bay Foundation (2020) that was aimed at examining fish and crab dioxin and polychlorinated biphenyls levels in the San Jacinto River and the Houston Ship Channel post Hurricane Harvey within a 5-mile radius around the San Jacinto River Waste Pits Superfund site. This project extends beyond the 5-mile radius. The project also leveraged sediment polychlorinated biphenyls and dioxin data collected by the University of Houston in 2017 post Hurricane Harvey with funding from the National Science Foundation at 15 sites located in the Houston Ship Channel, the San Jacinto River and Galveston Bay in addition to Galveston Bay sediment dioxin data gathered by University of Houston with funding from the Texas Commission on Environmental Quality in support of Total Maximum Daily Load studies. The data were collected over a period of almost 15 years from 2003 through 2017. Overall, two observations after Hurricane Harvey motivated this study: (i) some parts of the Houston Ship Channel and Galveston Bay exhibited higher sediment concentrations of dioxin and polychlorinated biphenyls after the hurricane relative to historic levels, and (ii) it has been reported that the protective cap on the San Jacinto River Waste Pits site incurred failures during the hurricane, potentially exposing waste material in the pits to the San Jacinto River waters.

Field activities began on Dec. 14, 2021 and concluded on Dec. 16, 2021. A total of 28 samples for sediment and water quality analyses were collected. Two fish samples collected in January 2019 were composited from multiple fish (red drum and black drum from two different sites) and analyzed. Source association analysis, sediment dynamics analyses, and data management compilations were all completed as part of the scope of the project.

Overall, total suspended solids values ranged from a low of 8.1 milligrams per liter to a high of 31.6 milligrams per liter, and the total organic carbon ranged from 2.5 milligrams per liter to 5.6 milligrams per liter in the gathered water quality samples. The total organic carbon in sediment ranged from 3740 milligrams per kilogram to a high of 23500 milligrams per kilogram; it was observed that most sites had mainly silt and clay with only two sites that had sand exceeding 50% in their grain size distributions. The measured toxic equivalencies for dioxin ranged from a low of 0.74 nanograms per kilogram to a maximum value of 30.4 nanograms per kilogram; whereas, the measured total polychlorinated biphenyls ranged from a low of 814.84 nanograms per kilogram to a high of 130974.1 nanograms per kilogram just downstream of Patrick Bayou. The analyzed fish tissue samples had dioxin toxic equivalency values ranging from 0.388 nanograms per kilogram to 0.649 nanograms per kilogram, and total polychlorinated biphenyls ranging from 10199.1 nanograms per kilogram to 39870.1 nanograms per kilogram.

When compared to historical data, the results from the December 2021 sampling conducted in this project indicated that dioxin in sediment toxic equivalencies exhibited lower concentrations relative to their counterparts from 2011-2012 with few exceptions at some of the monitored sites (11261, 13363, 14560). The observed increases at the aforementioned sites that did not exhibit declines, however, were relatively small and may not be statistically significant. It was noted that the dioxin toxic equivalencies in sediment that were measured in 2017, 2019, and 2021 after Hurricane Harvey showed increases in concentrations from 2017 to 2019 and declines from 2019 to 2021 at some stations. A similar conclusion was made for polychlorinated biphenyls in sediment when compared to 2011-2012; the exceptions in this case where concentrations increased relative to 2011 and 2012 were 11261, 13342, and 15301. Comparing the sediment polychlorinated biphenyls concentrations measured between 2017 and 2021, all measured concentrations were lower in 2021 relative to 2019 with two exceptions in one of the side bays and downstream of Patrick Bayou where concentrations had increased. When compared to 2017, concentrations in 2021 increased at three locations (11261, 11285, and 13344). Tissue concentrations were interpreted with caution since red and black drum are not species that have been sampled regularly. It was noted that the toxic equivalencies in black drum was one order of magnitude smaller than historical concentrations for other fish species from the same site, whereas total polychlorinated biphenyls in red drum was of the same order of magnitude quantified in other species from the same site. It is not clear whether this indicates a trend or a one-off observation.

Congener profiling indicates associations of sediment concentrations mainly with air deposition and effluent sources, whereas tissue data can be more strongly associated with the San Jacinto River Waste Pits site for blue catfish and blue crab, whereas other fish species reflect additional source associations. Source apportionment analyses using statistical methods supported the previously confirmed patterns of weak correspondence between observed dioxin congener patterns and those of the San Jacinto River Waste Pits in the Houston Ship Channel – Galveston Bay system with notable exceptions in 2005 and 2017 that might be associated with extreme events.

Further analyses of flow and sediment dynamics completed in this study points to the importance of flows and sediment loads from the San Jacinto into the Houston Ship Channel – Galveston Bay system. The San Jacinto River has the highest historical median flows of all streams discharging into this system and the highest total suspended solid loads, pointing to its relative importance in terms of pollutants entrained in its sediment that significantly impact their concentrations in the remainder of the system. Additionally, it is noted that modeling and other analyses (not part of this project and not included here) support the “flow-back” of San Jacinto River water and sediment into segment 1016 of the Houston Ship Channel. It is also noted (also not part of this project and research not reported here) that, in addition to the San Jacinto River Waste Pits, Patrick Bayou and the Champions Paper Mill site along the Houston Ship Channel remain important continuing sources of dioxin and polychlorinated biphenyls into the system (other sites and sources have not been specifically studied).

Introduction

The purpose of this project was to collect and analyze fish and crab tissue and sediment samples to quantify the levels of polychlorinated biphenyls (PCB) and dioxin post Hurricane Harvey in the Houston Ship Channel (HSC) and Galveston Bay (GB). This project leveraged a previous effort funded by the Galveston Bay Foundation (GBF, 2020) that was aimed at examining fish and crab dioxin and PCB levels in the San Jacinto River (SJR) and the HSC post Hurricane Harvey. The GBF scope was limited to a 5-mile radius around the San Jacinto River Waste Pits (SJRWP) Superfund site. The final report from the GBF study is available upon request; results from the study will not be repeated in their entirety here but some figures or tables may be included for reference and/or context as they relate to this study.

The project also leveraged sediment PCB and dioxin data collected by the University of Houston (UH) in 2017 post Hurricane Harvey with funding from the National Science Foundation (NSF) at 15 sites located in the HSC, the SJR and GB in addition to GB sediment dioxin data gathered by UH with funding from the Texas Commission on Environmental Quality (TCEQ) in support of Total Maximum Daily Load (TMDL) studies. The data were collected over a period of almost 15 years from 2003 through 2017. Overall, two observations after Hurricane Harvey motivated this study: (i) some parts of the HSC and GB exhibited higher sediment concentrations of dioxin and PCBs after the hurricane relative to historic levels, and (ii) it has been reported that the protective cap on the SJWRP site incurred failures during the hurricane, potentially exposing waste material in the pits to the SJR waters. The main goal for this study was to expand the sampling and analysis scope beyond the 5-mile limit of the GBF study to encompass the remainder of the HSC and GB system as applicable and appropriate.

Section 2 presents background information on PCBs and dioxins and the study area in addition to placing the project in context in terms of significance. Section 3 presents the methods used in the study and Section 4 presents the results while Section 5 presents a discussion of the findings. The cited references can be found in Section 6.

Project Significance and Background

Background

PCBs and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs or ‘dioxins’) are persistent organic pollutants that are widely distributed in environmental media (UNEP, 2019). PCBs and dioxins in the environment are mainly a result of anthropogenic activities and are found in all media, including air, water, sediment, and fish tissue (Balasubramani and Rifai, 2018; Bocio et al., 2007; Haglund et al., 2007; Howell et al., 2011; Howell et al., 2008; Howell and Rifai, 2016; Li et al., 2012; Louchouarn et al., 2018; Moon et al., 2012; Moon et al., 2009; Nunes et al., 2014; Raun et al., 2005). These compounds pose significant health risks as they accumulate in the adipose tissues of organisms and become concentrated along the food chain (UNEP, 2019; USEPA, 2021a). Exposure to dioxins and PCBs is known to cause immunotoxicological, developmental, hormonal, reproductive, and neurological complications (ATSDR, 2016; WHO, 2016). The exposure of aquatic biota to PCB and dioxin concentrations in water and sediment, and the subsequent consumption of fish with the aforementioned pollutants has been a global problem. Sediments, in particular, have a significant impact on the presence and distribution of pollutants in an aquatic system and are both pollutant sources and sinks. Pollutants accumulate in the bottom sediment by organic and particulate sequestration (Howell and Rifai, 2015). Processes such as partitioning, and sediment resuspension and deposition due to flows result in the exchange of concentrations between the bottom sediment and water column phases (Burton Jr, 1991; Howell et al., 2011). Sediment dynamics and related processes in a given aquatic system, therefore, affect the fate and transport of pollutants which makes the study of concentrations in bottom sediment important in addition to the study of concentration distributions in fish tissue. In this project, sediment and tissue concentration data are studied and analyzed jointly to present as comprehensive of a status and trends picture as possible using historical data and data gathered in the study for the HSC-GBS.

Project Significance

The HSC-GBS, shown in Figure 1, is located in southeast Texas. It comprises the Houston Ship Channel-San Jacinto River (HSC-SJR), located in the SJR Basin, and drains into GB. The HSC is one of the busiest ship channels in the world, serving the Port of Houston, the largest port in Texas, and is important to the local area, the state, and the country. The HSC is a highly industrialized system with chemical and petrochemical facilities, making it susceptible to contamination, with complex interactions between chemicals and different media (Burleson et al., 2015; Kiaghadi et al., 2022; Kiaghadi et al., 2018; Rifai et al., 2021). Galveston Bay is a diverse estuarine system that supports varied recreational activities including fishing and crabbing. The marine life in GB can be adversely affected by the spills and leaks due to industrial activities in the upstream HSC. Both systems are listed for PCB and dioxin contamination of fish tissue and multiple advisories have been put in place over the years. TCEQ launched a TMDL project for both PCB and dioxins beginning in early 2000; data were mainly collected by UH starting in 2002 through 2013. In addition to the UH TMDL-specific data, other data collections were undertaken by the United States Environmental Protection Agency (USEPA) in response to the listing of the SJRWP as a Superfund site and also by the TDSHS in support of issuing seafood consumption advisories. More recent data collections include those from a UH study funded by the NSF post Hurricane Harvey and a UH study funded by the GBF to evaluate changes in concentrations within a 5-mile radius of the SJRWP Superfund site after Hurricane Harvey. Cap failure at the SJRWP site motivated the GBF study.

The current study is the most recent data gathering effort and it expands on the GBF study by collecting and analyzing sediment and tissue samples beyond the 5-mile radius. The project adds to the existing knowledge base of PCB and dioxin monitoring and analysis in the region. Historical data presented in conjunction with the results from the current sampling project provide an insight into the spatial-temporal variation of dioxins and PCBs, and noteworthy trends in the data, which may be attributed to both hydrologic events and anthropogenic inputs. Finally, using recent methods published in the literature, source associations were further elucidated using the comprehensive dataset of all information gathered for the HSC-GBS over the years.

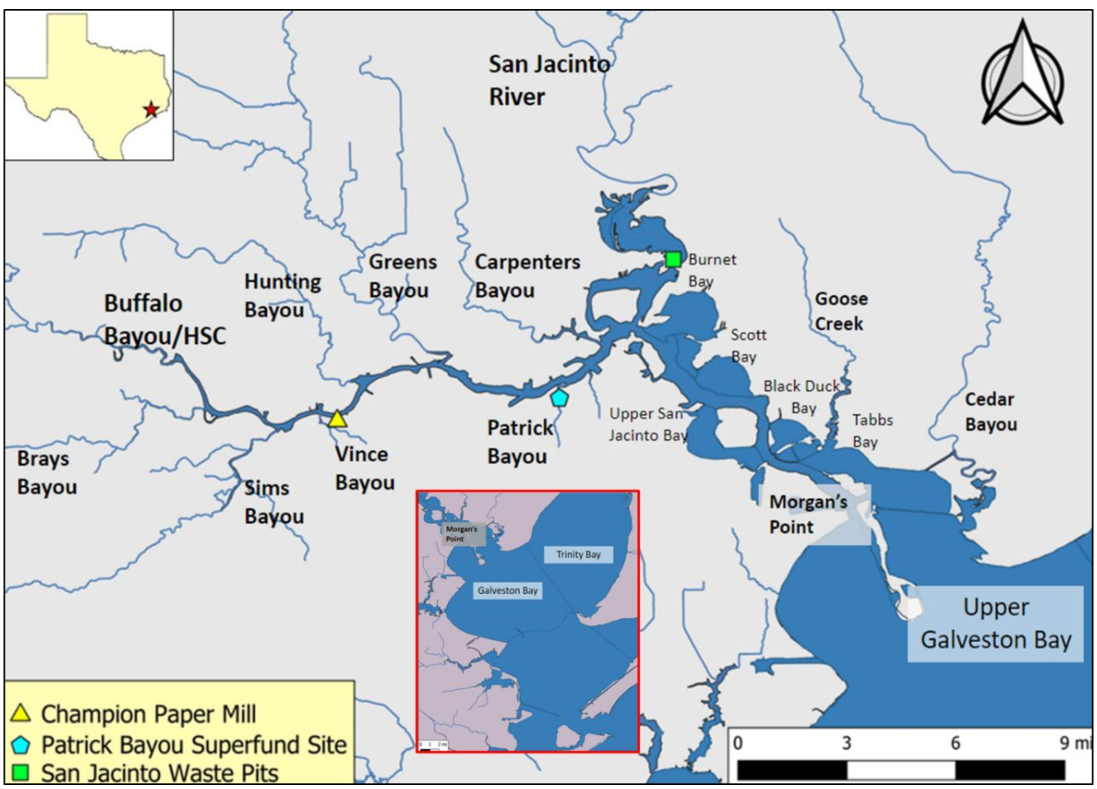

Figure 1. The HSC-GBS estuarine system with its tributaries and specific anthropogenic sources; the inset shows GB.

Historical Context of Key Sources of PCB and Dioxins in the HSC-GBS

PCBs and dioxins were introduced into the estuary many years ago from industrial sources and waste disposal. Three significant sources within the system are noted, which include two Superfund sites—the SJRWP and the Patrick Bayou Superfund sites, both on the national priorities list of the USEPA Superfund program (TCEQ, 2021)—and an industrial site where a paper mill (Champion Paper Mill) was previously situated.

The SJRWP Superfund site is located on the north bank of the SJR (north of interstate I-10) and was designated as a Superfund site in 2008. The site was first used in the 1960s as a disposal site for paper mill waste. Initially, contact between the wastes in the pits and the SJR was limited to inundation following heavy rainfall events. However, due to erosion and subsidence, direct contact between the SJR and the pits created a continuing source of dioxin into the river and estuary (Tucker, 2012). Sand mining in the SJR further exacerbated the potential for interaction between SJRWP wastes and the SJR. It is also noted that flow patterns in the SJR, especially after construction of the HSC, create a scenario whereby chemicals in the SJR can deposit at the confluence with the HSC and in some cases flow back into the HSC. The SJRWP Superfund site was capped in 2011 (USEPA, 2017 a & b). However, in 2017, damage to the armored cap due to Hurricane Harvey was reported, presumably causing potential releases of dioxins and other contaminants into the river and eventually GB (USEPA, 2017 a & b).

The Patrick Bayou site has had both PCB and dioxin inputs from surrounding industrial facilities. The Champion Paper Mill had discharges into the HSC and wastes from the paper mill were disposed of in the SJRWP. The part of the HSC near the paper mill was contaminated by dioxins from wastes generated by the facility (Suarez et al. 2005 a&b), observed to a great extent after Hurricane Harvey. As of this writing, the remediation process for the SJRWP is at the remedial design/remedial action stage (USEPA, 2021 a-d), and that for the Patrick Bayou Superfund site is at the site characterization stage (USEPA, 2021 a-d). Over time, the concentrations in water, sediment, and biota in the system have resulted in listings on the Impaired Waters list under the Clean Water Act due to the exceedance of water quality and tissue standards. The TDSHS has issued seafood consumption advisories (GBF, 2020) since 1990 directing people to minimize or avoid the consumption of fish and crab from the area due to observed levels of dioxin and PCBs in tissue.

Detailed study and quantification of dioxins and PCBs in the GBS began in the early 2000s, first initiated by the TCEQ in 2002, and has continued since then. Extensive historical sampling of PCBs and dioxins in water, sediment, air, fish tissue, effluent, sludge, and runoff has been carried out by researchers at UH; this sampling extended from 2002 to 2019 and resulted in a consistent and well-developed dataset that supports the research in this project (Balasubramani et al., 2014, 2015 and 2018; Correa et al., 2004; Dean et al., 2010; Howell, 2012; Howell and Rifai, 2015; Howell et al., 2011; Howell et al., 2008; Lakshmanan et al., 2010; Raun et al., 2005; Sappington et al., 2015; Suarez et al., 2006; Suarez et al., 2005 a & b; Yeager et al., 2007). Other important sampling entities for both sediment and fish tissue sampling in the area are the USEPA and the TDSHS. The most recent sampling was conducted in January 2019 with funding from the GBF. Fish and sediment samples were collected and analyzed for 19 sites within a five-mile radius of the SJRWP to quantify the levels of PCBs and dioxins post Hurricane Harvey (GBF, 2020). The present project expands the sampling, analysis and monitoring of PCBs and dioxins outside the five-mile radius around the SJRWP. The project also looks at the historical trends in PCB and dioxin concentrations by comparing the results from the current sampling with data from previous sampling. Sourcing of the contaminants in the system is also investigated using historical source samples.

Methods

Historical Data Gathering and Analysis

As mentioned previously, data from several sources had been gathered as part of the GBF (2020) study. The data were analyzed for spatial and temporal trends and the findings were presented in the GBF study report. In the current study, additional analyses were undertaken with the historical data and are described in Sections 3.3-3.4.

Field Sampling

Field activities for the project began on Dec. 14, 2021 and ended on Dec. 16, 2021 with a total of three active sampling days. Table 3-1 shows the total number of samples collected for each analysis for the surface water and sediment matrices. Table 3-2 presents the sampling station number and a detailed list of the number of samples collected at each site for each matrix and related analyses.

Table 3-1. Total number of samples collected for each matrix and analysis

Matrix	Analysis	# Sites sampled	# Duplicates	# Field and trip blanks	Total # samples
Surface water	Total Suspended Solids (TSS)	19	3	6	28
	Total Organic Carbon (TOC)	19	3	6	28
	Dissolved Organic Carbon (DOC)	19	3	6	28
Sediment	TOC	19	3	6	28
	Grain size	19	3	6	28
	PCB	19	3	6	28
	Dioxin	19	3	6	28

Table 3-2. Total number of sediment and water samples from each site, including field duplicates

Sampling station	Sediment samples collected				Water samples collected		
	Grain Size	TOC	PCB	Dioxin	DOC	TOC	TSS
11193	1	1	1	1	1	1	1
11252	1	1	1	1	1	1	1
11261	2	2	2	2	2	2	2
11264	1	1	1	1	1	1	1
11285	1	1	1	1	1	1	1
13342	1	1	1	1	1	1	1
13344	1	1	1	1	1	1	1
13363	1	1	1	1	1	1	1
14296	1	1	1	1	1	1	1
14560	2	2	2	2	2	2	2
15301	1	1	1	1	1	1	1
16213	1	1	1	1	1	1	1
16496	1	1	1	1	1	1	1
16622	1	1	1	1	1	1	1
17921	2	2	2	2	2	2	2
17971	1	1	1	1	1	1	1
HiRes09	1	1	1	1	1	1	1
HiRes14	1	1	1	1	1	1	1
HiRes27	1	1	1	1	1	1	1

Two fish samples collected in the January 2019 sampling effort were processed and analyzed for PCB and dioxin in tissue. The two samples were red drum collected from sampling station 11285, and black drum from 11252. For each sample, four fish were filleted, composited, and transported to the lab for PCB and dioxin analysis.

Source Apportionment

Source association of dioxins and PCBs, and the quantitative contribution of the identified sources to the observed concentrations is a topic of importance to PCB and dioxin contamination of the GBS. The system is dynamic, complex hydrodynamically, and has received PCB and dioxin loads from multiple time-variant sources. Additionally, the system receives effluent and runoff from the greater Houston area that has significantly expanded over the years. While the topic has been studied extensively in the literature for other water bodies and estuaries and multiple quantitative and qualitative methods have been used (Birch et al., 2007; Frignani et al., 2001; Hosomi et al., 2003; Liebens et al., 2011; Mohrherr et al., 2006; Okumura et al., 2004; Ruckart et al., 2008), source apportionment remains a topic requiring further study.

In 2012, Tucker at UH undertook a detailed analysis of means of interaction between the SJRWP and the HSC-GBS. They concluded that prior to subsidence, interaction was limited to severe storms and overflowing of the pits into the SJR. Subsidence, along with sand mining, however, created a scenario by which the waste pits were inundated and experienced erosion and subsequent failure such that the wastes were in direct communication with river water. Tucker (2012) developed source apportionment for dioxin concentrations in sediment using Positive Matrix Factorization (Paatero and Tapper, 1994) methods.

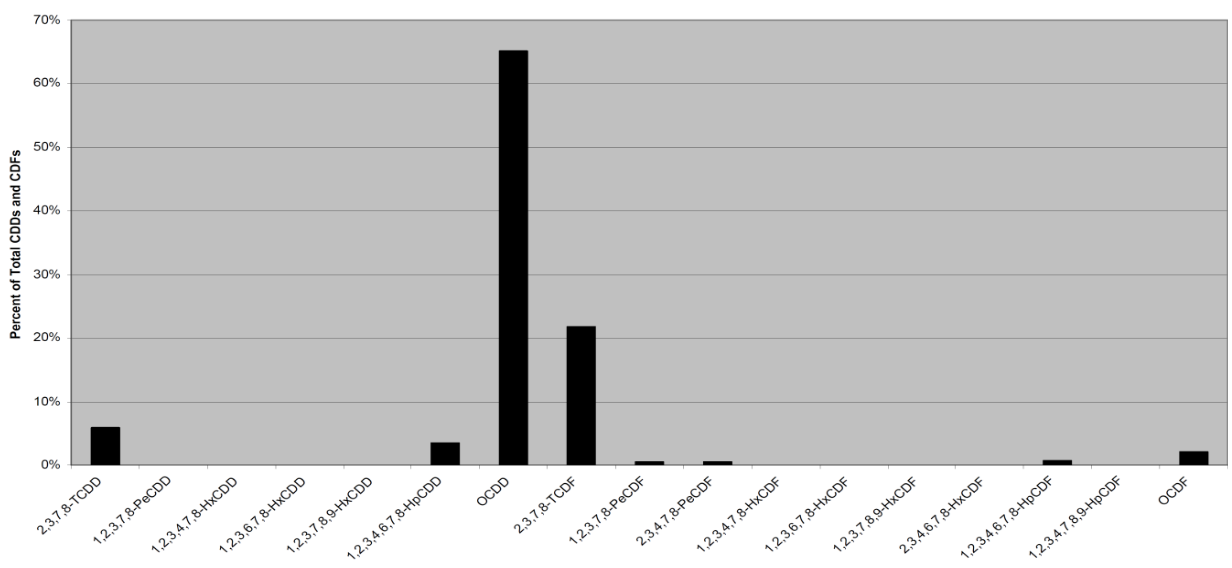

Figure 2. Papermill waste profile (Tucker, 2012 after USEPA, 2006).

Using source profiles associated with dioxin in sludges from paper mills (see Figure 2), and those from dioxin in air, the HSC and the SJRWP, they delineated the areas within the HSC-GBS that could have received dioxin inputs from the SJRWP after the pits were submerged and exhibited erosion and failures. Their results indicated that effects from the SJRWP could be observed into the HSC and downgradient to Morgan's Point, with the most significant effects being at the confluence of the SJR with the HSC and in the segment between the Champions Paper Mill in the HSC and the confluence.

More recently, using a "congener-ratio method," Louchouarn et al. (2018) calculated the ratio of tetra- and octa- chlorinated dioxins and furans (TCDD/OCDD and TCDF/OCDF) as a fingerprinting indicator. They identified the fingerprints to be corresponding to those of industrial sources in the vicinity of the sample sites and the SJRWP. Also, more recently, and during the GBF study (GBF, 2020), UH undertook a congener-ratio analysis for tissue that indicated that Blue Catfish and Blue Crab tissue concentration ratios fell within or close to the SJRWP cluster. Fish other than Blue Catfish seemed to be associated with both industrial effluents and the SJRWP.

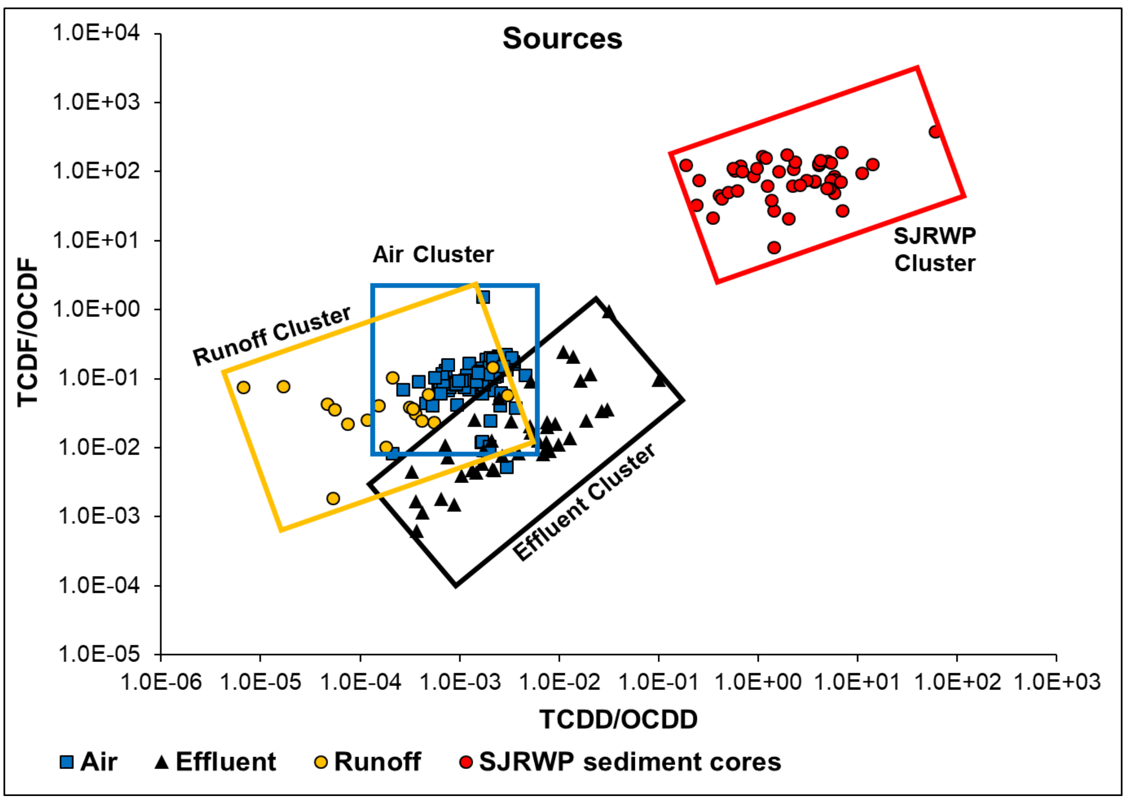

Figure 3. Dioxin Source Profiles from Historical Data (Air and effluent 2003 data, runoff 2003-2005 data, SJWRP 2005/06/09/2010/17 data).

More recently still for this project, Govindarajan (2022) utilized three qualitative methods: two distribution-based methods (the Kullback–Leibler [K-L] divergence and the Bhattacharya measure [BM]) and the congener-ratio method used by Louchouarn et al. (2018) to develop source associations using historical sediment data. The K-L divergence, also known as the directed divergence or discrimination information, is an information measure of the difference between two probability distribution functions (Kullback, 1959). The BM is a similarity metric that measures the overlap of two probability distribution functions (Bhattacharyya, 1946; Comaniciu et al., 2000). Their results using the ratio method for source concentrations in sediment from runoff, air, effluent and SJRWP data gathered by UH and others over the years are shown in Figure 3. It can be seen that the source ratio profiles cluster uniquely and distinctively with some overlap among the ratios.

Sediment Dynamics

Sediments play an important role in the distribution of dioxin and PCBs in the HSC-GBS. Detailed analyses were undertaken to develop an understanding of sediment dynamics over time and how these dynamics affect the dioxin and PCB concentrations at the various monitoring points within the GBS. Flow regimes in the GBS respond to rainfall events and depending on the severity of the events, sediment regimes in the GBS may experience changes that alter the distribution of PCB and dioxins at a given location. The analyses undertaken were aimed at elucidating the relationships between sediment dynamics under typical flow conditions and in response to rainfall events to determine to what extent events such as Hurricane Harvey alter the distribution of the two pollutant classes in the GBS.

Data Management

All field measurements and sample data collection for water, sediment and tissue were performed according to the Surface Water Quality Monitoring (SWQM) Procedures Volume 1 (RG-415). The information on field data sheets were all entered/converted to electronic formats, validated, and backed up on storage media. All laboratory results were also validated and backed up on storage media. A sample tracking database was created in excel to track each sample collected for water and sediment. The sample tracking database contains information on sample collection, sample receipt at the field office, location where sample is stored, date sample was shipped for analysis at the laboratory, and hold times for each analysis type. The sample tracking database was validated and backed up on storage media.

Results and Observations

This section will report on field data monitoring results, analyses, and data management as well as the results from comparative analysis using source apportionment. Figures 4 and 5 below show the station locations that were sampled.

Water Quality Variables

The field water quality parameters include pH, specific conductivity, salinity, dissolved oxygen (DO) and temperature. Characteristic parameters such as TSS, TOC and dissolved organic carbon (DOC) were quantified via commercial laboratories.

Table 4-1 provides the values for the measured YSI sonde variables at different depths, along with the station ID, and collection date and time. Water temperature and salinities ranged from 17.1 to 20.9 ˚C, and 1.32 parts per thousand (ppt) to 25.69 ppt respectively, with both variables showing stratification with depth as can be seen in Table 4-1. Station 14296 (see Figure 4) had the maximum salinity value of 25.69 ppt and the riverine station 16622 had the minimum values between 1.32 ppt and 3.92 ppt. As shown in Table 4-1, DO levels ranged from 3.27 milligrams per liter (mg/L) to 10.02 mg/L; pH values ranged from a low of 6.99 at station 17971 to a high of 8.29 at station 16213.

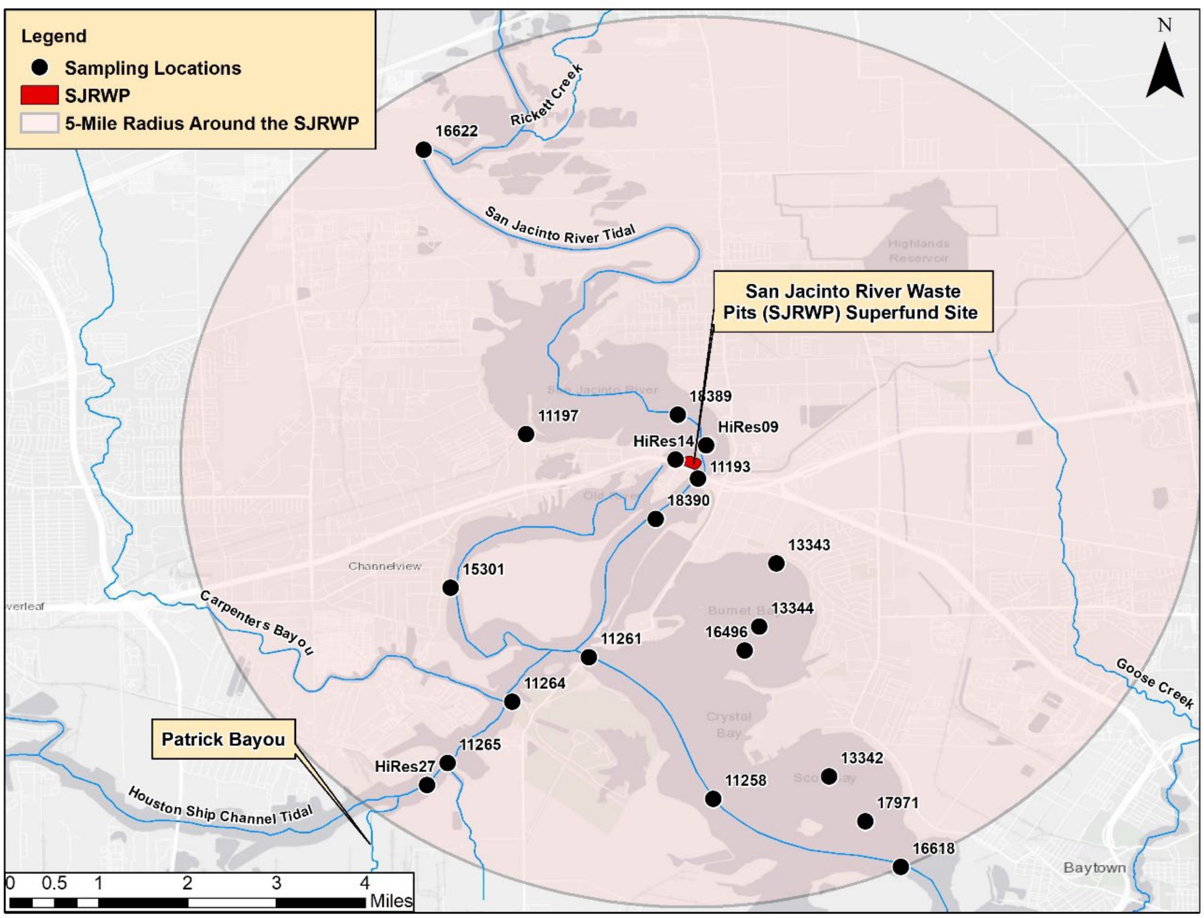

Figure 4. Map of sediment and fish sampling locations for PCBs and Dioxins within the five-mile radius of the SJRWP site.

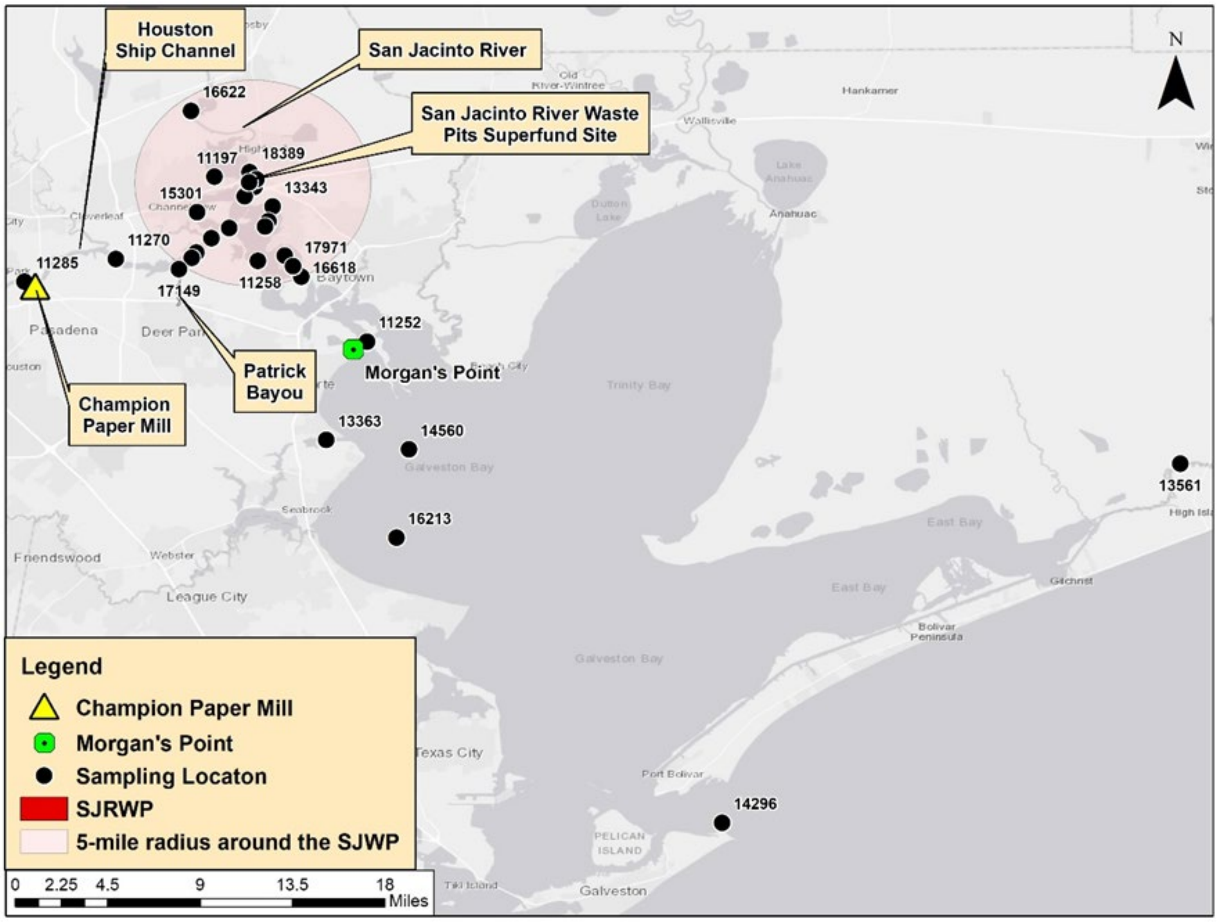

Figure 5. Map of sediment and fish sampling locations for PCBs and Dioxins outside the five-mile radius of the SJWRP site

Table 4-1. Surface water quality variables

Station	Date	Time	Total Depth (feet)	YSI Depth (meters)	Temp (˚C)	DO (%)	DO (mg/L)	Specific Conductivity (millisiemens per centimeter - mS/cm)	Salinity (ppt)	pH
14296	12/14/2021	7:47	30	8.2	18.2	93.4	7.64	40.13	25.69	8.02
				5.3	18.2	94.0	7.68	39.91	25.55	8.09
				2.3	18.2	93.7	7.66	39.98	25.58	8.01
14560	12/14/2021	10:12	40	9.8	17.8	85.0	7.18	30.33	23.00	7.94
				6.4	18.1	85.1	7.18	33.34	20.93	7.99
				3.6	18.1	83.3	7.08	32.09	20.08	8.00
				0.7	17.2	113.2	10.02	28.22	17.40	8.23
11252	12/14/2021	11:30	31	9.4	18.1	78.7	6.61	33.50	21.05	7.87
				6.5	18.1	83.8	7.09	32.68	20.47	7.94
				3.4	18.6	82.8	7.09	26.90	16.20	7.93
				0.6	18.7	84.6	7.29	25.15	15.37	7.87
16213	12/14/2021	12:21	10	3.1	17.1	91.6	7.95	30.59	19.05	8.16
				1.9	17.1	96.0	8.35	30.37	18.89	8.23
				0.7	17.7	110.1	9.80	30.03	18.66	8.29
17971	12/15/2021	7:57	5.8	2.0	19.7	82.5	6.30	23.67	14.38	6.99
				1.5	19.7	88.3	7.59	23.68	14.38	7.41
				1.0	19.7	89.5	7.59	23.73	14.42	7.49
				0.4	19.7	89.9	7.62	23.75	14.43	7.51
13342	12/15/2021	8:58	5.1	2.0	19.9	78.8	6.61	23.94	14.29	7.41
				1.5	19.8	82.2	6.98	23.60	14.33	7.46
				1.1	19.8	85.6	7.24	23.60	14.38	7.52
				0.6	19.8	85.8	7.26	23.67	14.38	7.53
17921	12/15/2021	9:46	7	2.5	19.7	83.0	7.05	23.13	14.02	7.44

Station	Date	Time	Total Depth (feet)	YSI Depth (meters)	Temp (˚C)	DO (%)	DO (mg/L)	Specific Conductivity (millisiemens per centimeter - mS/cm)	Salinity (ppt)	pH
				2.4	19.7	89.5	7.62	23.21	14.08	7.52
				2.0	19.7	90.7	7.70	23.28	14.12	7.65
				1.4	19.7	90.9	7.72	23.31	14.14	7.67
				0.6	19.7	80.9	7.71	23.33	14.16	7.68
16496	12/15/2021	10:55	6.7	2.3	19.5	100.4	8.56	22.99	13.93	7.86
				2.0	19.5	100.9	8.60	23.03	13.95	7.94
				1.4	19.6	102.8	8.75	23.03	13.96	7.99
				0.8	19.6	103.3	8.80	23.05	13.97	8.02
13344	12/15/2021	11:41	7	2.4	20.0	105.0	8.86	23.13	14.01	7.88
				2.0	19.9	105.7	8.92	23.17	14.05	7.97
				1.4	20.1	105.8	8.92	23.20	14.06	7.99
				1.0	20.0	105.9	8.94	23.20	14.06	8.00
				0.6	20.0	106.1	8.94	23.20	14.07	8.01
16622	12/15/2021	12:57	12.8	4.1	18.9	72.1	6.57	7.10	3.92	7.81
				3.5	18.7	76.4	7.03	5.84	3.20	7.73
				2.9	19.1	89.7	8.28	3.14	1.65	8.01
				2.4	19.1	90.6	8.36	2.95	1.55	7.99
				1.7	19.2	93.9	8.66	2.70	1.40	8.00
				1.0	19.4	97.2	8.95	2.58	1.34	8.03
				0.4	19.4	99.8	9.16	2.55	1.32	8.06
HiRes9	12/15/2021	14:43	3.5	1.4	19.7	94.2	8.25	13.80	8.00	7.49
				1.0	19.8	94.1	8.24	13.79	8.00	7.59
				0.4	19.7	93.7	8.21	13.90	8.06	7.63

Station	Date	Time	Total Depth (feet)	YSI Depth (meters)	Temp (˚C)	DO (%)	DO (mg/L)	Specific Conductivity (millisiemens per centimeter - mS/cm)	Salinity (ppt)	pH
HiRes14	12/15/2021	15:24	2.4	1.5	19.2	87.4	7.71	14.76	8.61	7.57
				0.6	19.7	92.9	8.14	13.76	7.99	7.65
11261	12/16/2021	7:41	46	8.1	19.7	69.1	5.80	24.70	15.30	7.54
				5.4	19.7	68.4	5.77	23.30	13.97	7.53
				2.4	19.8	67.2	5.66	22.78	13.77	7.49
				0.4	19.8	67.3	5.66	22.71	13.74	7.49
11193	12/16/2021	8:36	42.7	9.0	19.9	75.8	6.43	19.90	12.60	7.62
				6.2	20.0	80.5	6.93	15.91	9.39	7.74
				2.9	20.0	81.2	7.01	14.96	8.71	7.77
				0.5	20.1	83.3	7.20	13.88	8.03	7.80
15301	12/16/2021	9:32	21	4.8	20.4	79.6	6.70	19.80	11.83	7.70
				2.1	20.5	80.4	6.76	19.80	11.80	7.71
				0.5	20.5	80.6	6.78	19.70	11.80	7.72
11285	12/16/2021	10:37	43	9.8	19.3	53.5	4.53	23.70	14.43	7.37
				6.9	19.8	45.5	3.87	19.95	11.91	7.31
				3.9	20.2	38.2	3.27	18.10	10.74	7.16
				0.9	20.9	43.0	3.67	13.90	8.06	7.21
HiRes27	12/16/2021	11:24	48.3	8.9	19.6	66.0	5.54	24.70	15.11	7.55
				5.9	19.7	66.1	5.57	23.25	14.09	7.91
				3.2	19.8	65.0	5.48	22.60	13.65	7.46
				0.4	19.9	65.7	5.53	21.90	13.24	7.44
11264	12/16/2021	11:47	49	8.1	19.7	69.0	5.98	24.00	14.58	7.55
				5.4	19.8	69.1	5.80	23.20	14.08	7.54

Station	Date	Time	Total Depth (feet)	YSI Depth (meters)	Temp (˚C)	DO (%)	DO (mg/L)	Specific Conductivity (millisiemens per centimeter - mS/cm)	Salinity (ppt)	pH
				2.5	19.9	69.3	5.81	23.00	13.90	7.53
				0.4	20.0	69.5	5.83	22.70	13.75	7.52
13363	12/16/2021	12:49	51	9.1	18.9	78.7	6.47	32.40	20.22	8.03
				6.2	19.1	80.2	6.61	31.70	19.77	8.03
				3.1	19.4	84.4	6.93	30.90	19.23	8.04
				0.5	20.1	95.9	7.83	29.70	18.45	8.10

Table 4-2 shows the TSS, TOC, and DOC values in water samples. The TSS values ranged from a low of 8.1 mg/L at station 13363 to a high of 31.6 mg/L at station 15301. The DOC ranged between 2.8 mg/L at station 14296 to 5.9 mg/L at station 16622. The TOC values ranged from 2.5 mg/L to 5.6 mg/L at stations 14296 and 16622, respectively. It should be noted that the DOC exceeded the TOC in more than 60% of the samples, which reduces the confidence in the DOC data and points to possible laboratory variability in quantification.

Table 4-2. Water sample characteristic parameters at different locations

Station ID	Collection Date	TOC (mg/L)	DOC (mg/L)	TSS (mg/L)
11193	12/16/2021	4.9	5.2	12.7
11252	12/14/2021	4.0	4.4	15.4
11261	12/16/2021	4.2	4.6	14.1
11261-DUP	12/16/2021	4.3	4.6	13.8
11264	12/16/2021	4.1	4.2	16.6
11285	12/16/2021	5.2	5.2	10.4
13342	12/15/2021	4.1	4.6	15.9
13344	12/15/2021	4.5	5.1	13.7
13363	12/16/2021	4.0	4.0	8.1

Station ID	Collection Date	TOC (mg/L)	DOC (mg/L)	TSS (mg/L)
14296	12/14/2021	2.5	2.8	29.3
14560	12/16/2021	4.6	4.6	13.7
14560-DUP	12/14/2021	4.5	4.5	16.8
15301	12/16/2021	4.2	4.7	31.6
16213	12/14/2021	4.6	4.4	19.3
16496	12/15/2021	4.8	4.9	13.5
16622	12/15/2021	5.6	5.9	11.1
17921	12/15/2021	4.6	4.6	14.2
17921-DUP	12/15/2021	4.4	4.6	15.0
17971	12/15/2021	4.3	4.7	15.6
HIRes09	12/15/2021	4.8	5.3	15.8
HIRes14	12/15/2021	4.7	5.2	14.8
HIRes27	12/16/2021	4.2	4.6	16.7

Sediment Quality Variables

Parameters used to define the characteristics of sediment include TOC, grain size, moisture content, and grain size distribution. Table 4-3 lists the sediment properties and their values. As can be seen in Table 4-3, TOC in sediment was lowest at station 16622 (3740 milligrams per kilogram (mg/kg)) and highest at station 16213 (23500 mg/kg). It can also be seen that most sites had mainly clay and silt; only sites 14296 and 16622 had sand exceeding 50% in their grain size distribution.

Table 4-3. Properties of sediments collected at different locations

Station ID	Collection Date	TOC (mg/kg)	Median Grain Size (millimeters)	Moisture Content (%)	Grain Type Distribution (%)			
					Clay	Silt	Sand	Gravel
11193	12/16/2021	9960	0.008	120	36.53	60.81	2.67	0
11252	12/14/2021	7910	0.01	134.5	32.89	62.56	4.55	0
11261	12/16/2021	20000	0.007	206.6	40.67	59.29	0.04	0
11261-DUP	12/16/2021	17200	0.007	206.9	40.6	59.4	0	0
11264	12/16/2021	16800	0.007	173.1	40.76	58.94	0.3	0
11285	12/16/2021	15500	0.009	65	34.62	63.26	2.12	0
13342	12/15/2021	16600	0.007	170.4	41.58	58.42	0	0
13344	12/15/2021	21700	0.006	273.5	43.55	56.45	0	0
13363	12/16/2021	15400	0.006	166	44.66	55.34	0	0
14296	12/14/2021	6580	0.117	37.9	16.87	19.85	63.28	0
14560	12/16/2021	7400	0.009	144	34.34	61.51	4.15	0
14560-DUP	12/14/2021	7770	0.009	142.9	33.54	64.27	2.2	0
15301	12/16/2021	11700	0.017	52.8	29.8	47.77	22.43	0
16213	12/14/2021	23500	0.005	135.9	47.47	52.53	0	0
16496	12/15/2021	16600	0.006	231.5	45.34	54.66	0	0
16622	12/15/2021	3740	0.168	24.5	13.47	22.38	64.14	0
17921	12/15/2021	11700	0.007	156.4	42.85	57.07	0.08	0
17921-DUP	12/15/2021	13400	0.007	157.2	41.74	56.92	1.34	0
17971	12/15/2021	13700	0.006	178.1	46.93	53.07	0	0
HIRes09	12/15/2021	8140	0.026	59.6	24.36	47.27	28.36	0
HIRes14	12/15/2021	6600	0.038	43.8	21.06	46.96	31.98	0
HIRes27	12/16/2021	13400	0.006	143.5	43.08	56.92	0	0

Fish Tissue Properties

Lipid content and dry weight analyses were conducted for tissue samples. The physical properties along with the species information is provided in Table 4-4, while the laboratory analysis results are tabulated in Table 4-5. Lipid content for the two samples was approximately 0.5%, whereas % solids was around 20% (Table 4-5).

Table 4-4. Tissue sample composites with constituting species and related physical measurements

Station ID	Sampling Date	Filleting Date	Species	Fish Species[1]	Species Code[2]	# Individuals in Composite	Anatomical Part[1]	Length (inches)				Weight (grams - g)			
11285	1/24/2019	1/20/2022	red drum	202	98962	4	87	14	17.5	17	16.5	510	910	850	880
11252	1/19/2019	1/20/2022	black drum	199	98970	4	87	9	13.5	15.25	12.15	150	620	530	350

[1] Based on USEPA Storage and Retrieval (STORET) Numeric Code, [2] Based on Texas Biological STORET

Table 4-5. Percentage of lipids, solids, and moisture in tissue samples

Station ID	Collected	Species	% Lipids*	% Solids	Dry weight (g)	% Moisture
11285	1/24/2019	red drum	60.3% (Dioxin)	21.1%	1.66	78.9
			58.4% (PCB)			
11252	1/19/2019	black drum	48.2% (Dioxin)	20.1%	1.67	79.9
			47.8% (PCB)			

* Different samples were used for dioxin and PCB analyses which explains the slight differences in % lipids

PCB and Dioxin Concentrations

PCB concentrations were calculated as the sum of the PCB congeners in a sample. Due to the method of analysis, some of the 209 PCB congeners are co-eluted, which results in congener groups which are then used for the total PCB calculations.

$$\text{Total PCBs} = \sum_{i=1}^{x} (\text{Congener Group})_i \quad \text{(Equation 1)},$$

where 'i' is the congener group, and 'x' is the total number of congener groups.

Dioxins are represented in terms of TEQ, a measure of dioxin toxicity, which is calculated for each sample as:

$$\text{TEQ} = \sum_{i=1}^{17} \text{Concentration}_i * \text{TEF}_i \quad \text{(Equation 2)},$$

where 'i' is the dioxin congener, and the TEF is the toxic equivalency factor for that congener.

For the purpose of calculations and analyses, non-detect congener concentrations for both PCBs and dioxins were considered as half of the detection limit (DL) for each congener per sample analyzed.

Dioxins in sediment

The measured concentrations were converted to TEQs and the resulting values are shown in Table 4-6. The TEQs ranged from a low of 0.74 nanogram per kilogram (ng/kg) at station 14296 to a maximum value of 30.4 ng/kg at station 17971. A total of eight stations had 35% or more non-detects in their congeners (the 17 congeners in the TEQ).

Table 4-6. Dioxin TEQs and percentage of non-detect congeners

Station ID	Collection Date	% of Non-detect Congeners*	TEQ at Half DL (ng/kg)**
11193	12/16/2021	6	7.72
11252	12/14/2021	6	3.62
11261	12/16/2021	6	6.49

Station ID	Collection Date	% of Non-detect Congeners*	TEQ at Half DL (ng/kg)**
11261-DUP	12/16/2021	6	6.08
11264	12/16/2021	0	7.73
11285	12/16/2021	0	18.75
13342	12/15/2021	6	13.16
13344	12/15/2021	0	12.92
13363	12/16/2021	35	3.08
14296	12/14/2021	59	0.74
14560	12/16/2021	41	2.67
14560-DUP	12/14/2021	41	2.33
15301	12/16/2021	35	4.3
16213	12/14/2021	6	4.15
16496	12/15/2021	0	14.9
16622^	12/15/2021	65	0.85
17921	12/15/2021	6	13.1
17921-DUP	12/15/2021	6	9.64
17971	12/15/2021	0	30.4
HIRes09	12/15/2021	47	3.14
HIRes14	12/15/2021	47	3.36
HIRes27	12/16/2021	0	20.38

* Calculated as the total number of congeners with concentrations reported as non-detect divided by the total number of congeners (i.e., 17), ** non-detected concentrations were replaced with half of the DL, ^average of 2 values reported by laboratory

PCBs in sediment

The measured concentrations are shown in Table 4-7. The total PCB in sediment ranged from a low of 814.84 ng/kg at station 14296 to a high of 130974.1 ng/kg at station HiRes27 near Patrick Bayou.

Table 4-7. Total PCB concentration in sediment

Station ID	Collection Date	Total PCBs at Half DL (ng/kg)*
11193	12/16/2021	12674.9
11252	12/14/2021	2833.8
11261	12/16/2021	12767.0
11261-DUP	12/16/2021	9730.9
11264	12/16/2021	12918.0
11285	12/16/2021	65818.2
13342	12/15/2021	20721.6
13344	12/15/2021	18321.5
13363	12/16/2021	2667.1
14296	12/14/2021	814.84
14560	12/16/2021	1847.5
14560-DUP	12/14/2021	2866.0
15301	12/16/2021	8356.06
16213	12/14/2021	5151.6
16496	12/15/2021	27659.1
16622^	12/15/2021	3049.9
17921	12/15/2021	24171.0
17921-DUP	12/15/2021	25093.3
17971	12/15/2021	50944.9
HIRes09	12/15/2021	3114.5
HIRes14	12/15/2021	2311.1
HIRes27	12/16/2021	130974.1

* non-detect concentrations were replaced with half of the DL, ^average of 2 values reported by laboratory.

Dioxin in fish tissue

The TEQ in the two fish samples that were analyzed was 0.59 ng/kg (average of two values in red drum) and 0.388 ng/kg in black drum at stations 11285 and 11252, respectively as shown in Table 4-8.

Table 4-8. Dioxin TEQs and percentage of non-detect congeners in fish tissue

Station ID	Species	Collection Date	% of Non-detect Congeners*	TEQ at Half DL (ng/kg) **
11285	Red Drum	1/24/2019	65%	0.649
11285-DUP			71%	0.537
11252	Black Drum	1/19/2019	76%	0.388

* Calculated as the total number of congeners with concentrations reported as non-detect divided by the total number of congeners (i.e., 17), ** non-detect concentrations were replaced with half of the DL.

PCBs in fish tissue

The total PCB in the two fish samples that were analyzed was 38,765.1 ng/kg (average of 2 values in red drum) and 10199.1 ng/kg in black drum at stations 11285 and 11252, respectively, as shown in Table 4-9.

Table 4-9. Total PCBs in fish tissue

Station ID	Species	Collection Date	Total PCBs at Half DL (ng/kg) *
11285	red drum	1/24/2019	37660.1
11285-DUP			39870.1
11252	black drum	1/19/2019	10199.1

* non-detect concentrations were replaced with half of the DL

Comparative analysis

The dioxin in sediment TEQs over time are presented in Table 4-10 (each value shown is the average based on all sediment samples collected in that year at the location in question). It should be noted that a number of stations (10) with data in 2021 were not sampled in 2011 or 2012. Almost all stations exhibited lower concentrations in 2021 than 2011-2012. The exceptions were stations 11261, 13363, and 14560; however, the increases were relatively small and may not be statistically significant. Comparing the dioxin sediment TEQs between 2017 and 2021, it is noted that some stations exhibited increases in 2019 relative to 2017 but had lower concentrations in 2021 compared to 2019. Here again, there were some exceptions; 11252, 14296, 14560, 16622, 17971, and HiRes27 all had increased concentrations in 2021 relative to 2019.

Similarly, the total PCB sediment data in Table 4-11 indicated overall declines in 2021 relative to 2011-2012 in most stations with some exceptions that had higher concentrations: stations 11261, 13342, and 15301. When comparing the concentrations in sediment between 2017 and 2021, most stations exhibited declines from 2019 to 2021 except for station 17971 and HiRes27. Similar to dioxin, it should be noted that a number of stations (10) with data in 2021 were not sampled in 2011 or 2012.

Table 4-10. Dioxin TEQs in sediment (ng/kg) over time

Station ID	2002	2003	2004	2005	2009	2011	2012	2017*	2019	2021
11193	83.6	138.4	59.4			73.3		1.9	9.8	7.72
11252	4.4	8.8	5.9					7.6	3.4	3.62
11261	8.2	15.1	14.2				3.2	3.3	8.5	6.49
11261-DUP										6.08
11264	14.7	25.1	20.6			13.2			20.7	7.73
11285								17.7	20.9	18.75
13342	28.2	29.1	29.5				19.1		19.7	13.16
13344	32.6		26.2			28.1		18.5	23.3	12.92
13363	1.4						2.6		5.1	3.08
14296								4.9	0.45	0.74
14560	13.13	1.6	1.1			4.5	2.6		2.3	2.67
14560-DUP										2.33
15301							5.04		16.07	4.3
16213	2.2	2.7				6.3		4.4	5.2	4.15

Station ID	2002	2003	2004	2005	2009	2011	2012	2017*	2019	2021
16496	35.4	33.4							22.1	14.9
16622	0.97	6.2							0.21	0.85
17921	No historical record									13.1
17921-DUP										9.64
17971	24.0								22.2	30.4
HIRes09				13.2				6.9	10.9	3.14
HIRes14				34.4				10.8	6.2	3.36
HIRes27								18.0	19.1	20.38

Blank cells indicate no sample collected that year. * Post Harvey samples collected between Oct. 9 and Oct. 27, 2017.

Tissue data were also compared to historical measurements; however, it is noted that red and black drum were not species that had been sampled regularly in prior years. The data for all species for the two stations where tissue samples were analyzed in this study are presented in Tables 4-12 and 4-13 for dioxin and total PCB, respectively. It can be seen from Table 4-12, for example, for dioxin, that the TEQs in black drum for station 11252 were one order of magnitude smaller than those observed historically in hard head catfish and two orders of magnitude than those in blue catfish. The same observation can be made for red drum collected in 11285. In comparison, total PCB quantified in red drum for 11252 and 11285 were of the same order of magnitude of prior observed total PCBs in tissue.

Table 4-11. Total PCBs in sediment (ng/kg) over time

Station ID	2002	2003	2008	2009	2011	2012	2017	2019	2021
11193	26870.5	64597.5	22581.7	1339375.	30871.1		1049889.	16579.2	12674.9
11252	7894.2	10249.5	1975.4	9942.5			9125.8	7981.	2833.8
11261	17575.5	20881.5	9080.9	43459.5		7181.4	9311.2	15561.4	12767.0
11261-DUP									9730.9
11264	105087.5	120746.	20459.9	211895.8	22179.6			75203.7	12918.0
11285				1289037.			9481.2	186759.6	65818.2
13342	44701.3	37279.	19355.3	37591.2		16097.2		31525.7	20721.6
13344	39323.8		6281.6	32865.9	30200.2		12570.3	27784.6	18321.5
13363	4822.3		2514.2			3973.1		6171.0	2667.1
14296							6846.9	5308.5	814.84
14560	18334.	5438.	2212.5		10106.	4845.7		5402.2	1847.5
14560-DUP									2866.0
15301			36427.6	14703.3		7918.2		28345.9	8356.06
16213	11879.	5930.5	2627.2		7996.1		9016.9	8152.1	5151.6
16496	41368.5	65498.5						28994.4	27659.1
16622^	18724.	20159.5	1564.6	4858.9				5308.5	3049.9
17921	No historical data								24171.0
17921-DUP									25093.3
17971	76552.5							45456.6	50944.9
HIRes09							6979.5	14533.3	3114.5
HIRes14							7472.3	6568.1	2311.1
HIRes27							57952.0	120173.5	130974.1

Blank cells indicate no sample collected that year

Table 4-12. Dioxin TEQs in tissue (ng/kg) over time

Station ID	2002	species	2003	species	2004	species	2012	species	2019*	species
11252	8.79	HH-catfish	2.33	HH-catfish	27.33	Blue catfish			0.388	Black drum
	3.12	HH-catfish			2.23	HH-catfish				
11285							6.53	HH-catfish	0.59	Red drum

Blank cells indicate no sample collected that year, * sample collected in Jan 2019 but analyzed in Jan 2022 due to COVID-19

Table 4-13. Total PCBs in tissue (ng/kg) over time

Station ID	2002	species	2003	species	2008	species	2009	species	2012	species	2019	species	2019*	species
11252	114131.	HH-catfish	21150.3	HH-catfish	51702.5	HH-catfish	70473.8	HH-catfish					10199.1	Black drum
11285									102564.1	HH-catfish			38765.1	Red drum
HiRes14											15297.2	Red drum		
15979							36478.6	Red drum						
13343											15742.8	Black drum		
17971											31651.4	Black drum		
HiRes27											35394.5	Black drum		

Blank cells indicate no sample collected that year, * sample collected in Jan 2019 but analyzed in Jan 2022 due to COVID-19

Source associations for sediments over time

The congener-ratio method described in Section 3, when applied in the GBF study indicated that the majority of concentrations in sediment can be associated with air deposition and effluent sources (Figure 6) whereas source associations with the SJRWP site could be gleaned from the tissue data as shown in Figure 7 for blue catfish (crab exhibits a similar source association; other types of fish reflect additional source influences).

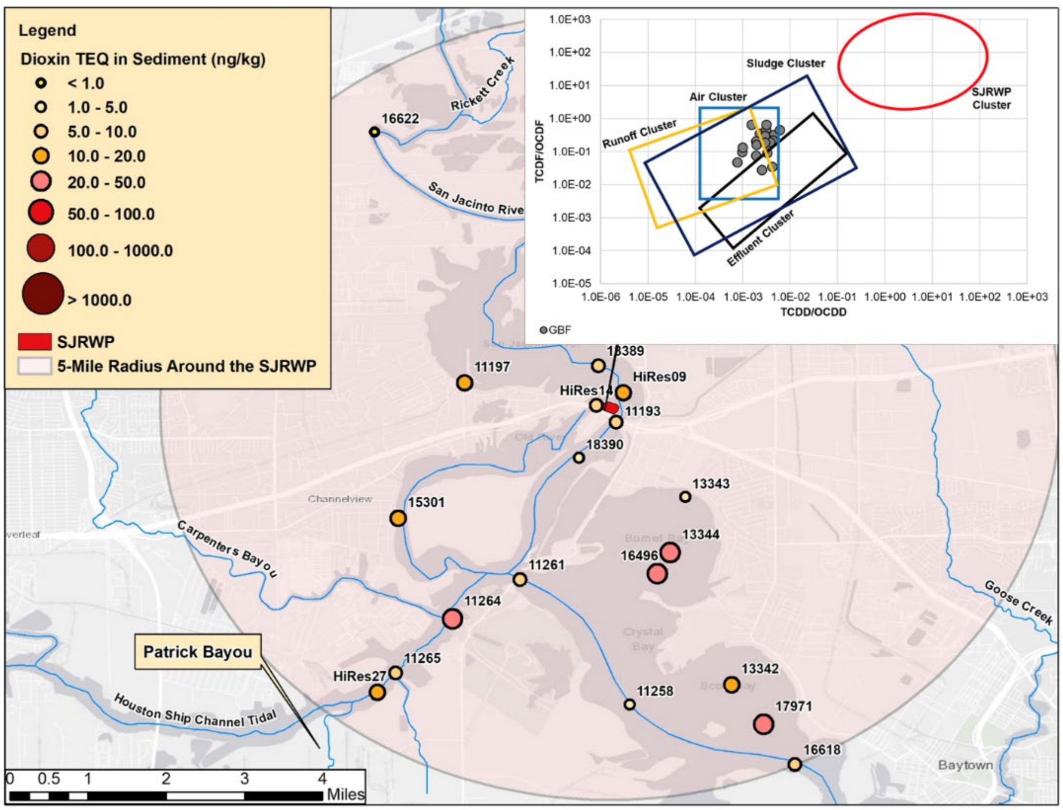

Figure 6. Clustering of dioxin in sediment samples for stations within the 5-mile radius around the SJRWP (GBF, 2020)

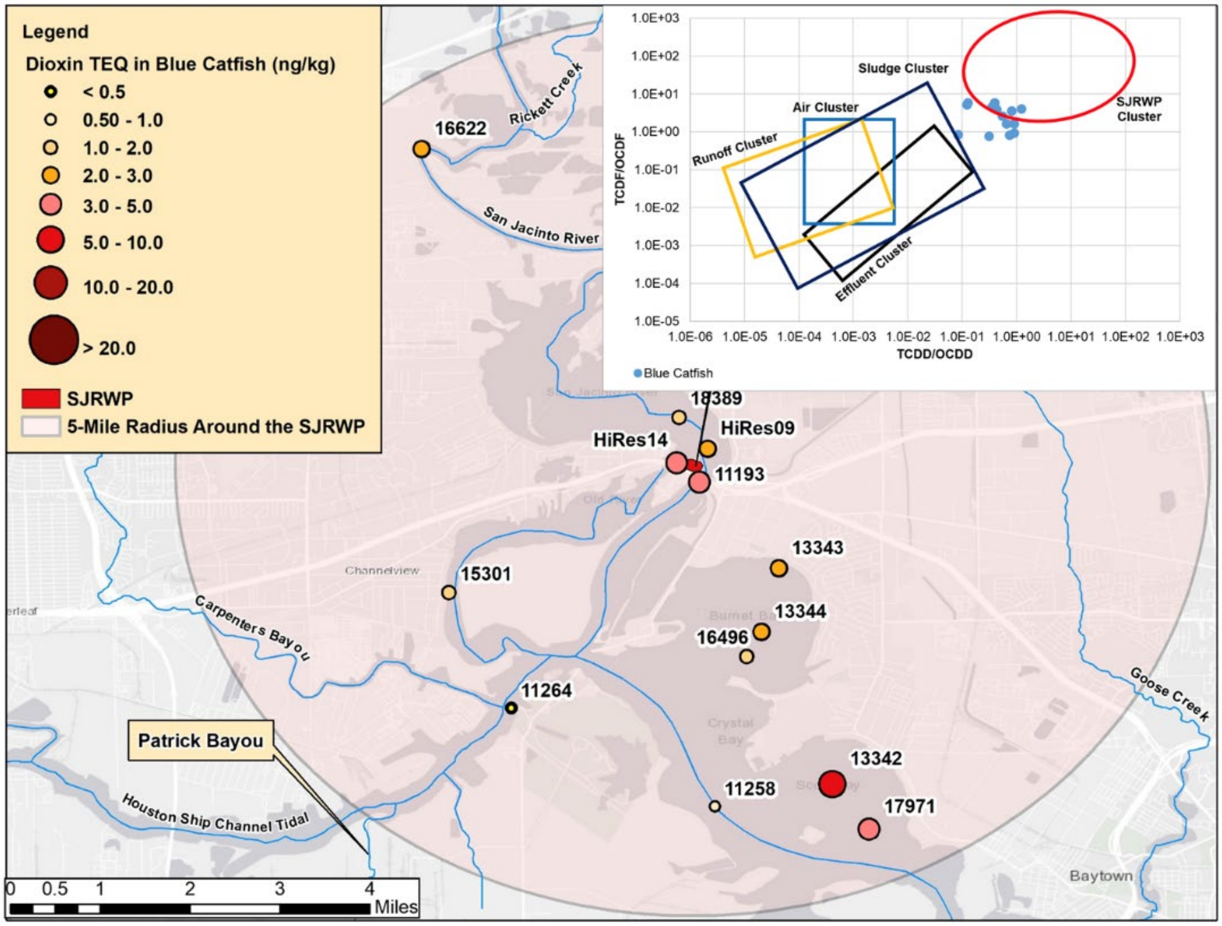

Figure 7. Clustering of dioxin in blue catfish tissue samples for stations within the 5-mile radius around the SJRWP (GBF, 2020)

When comparing historical data to the the source profiles in Figure 3 in a more detailed approach for this project, Govindarajan (2022) confirmed the weak correspondence between observed sediment dioxin congener patterns and those of the SJWRP with two notable exceptions in 2005 and 2017 (after Hurricane Harvey—Figure 8). In Figure 8, the panels representing the other sampling years (not 2005 and 2017), show the sediment data within the air, runoff, and effluent cluster with none near the SJRWP cluster. In comparison, the 2005 and 2017 panels show paired ratios (TCDF/OCDF andTCDD/OCDD) that approach the SJWRP cluster and/or are contained within it. This suggests potential mobilization of SJWRP pollutants post severe storms or hurricanes. Given the significant flows and sediment loads from the SJR as discussed in more detail in Section 5.0, measured sediment concentrations reflect these dynamics following severe events and can be used to quantify changes within the HSC-GBS as a result of extreme rainfall or storm surge.

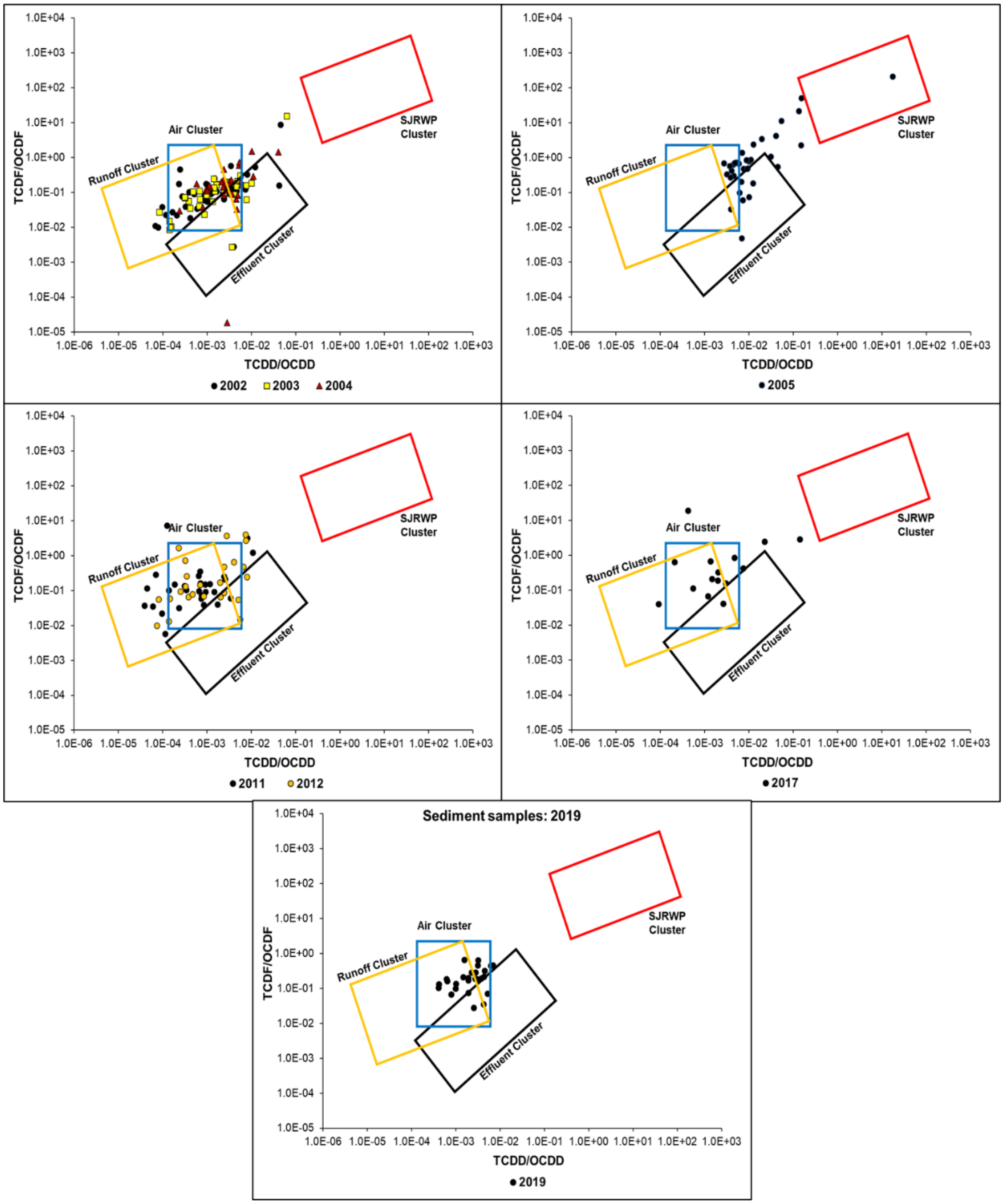

Figure 8. Clustering of dioxin in sediment for specific sampling events

Sediment dynamics and their associations with PCB and dioxin concentrations

Figure 9 shows the flow gages and the SWQM stations in the HSC-GBS. Table 4-14 lists the number of samples that were collected for sediment pollutant concentrations by UH over time up to 2019. Govindarajan (2022) undertook a detailed flow analysis for the HSC-GBS and concluded that the SJR had the highest flows into the system followed by Brays and Buffalo Bayous then Greens Bayou; although the latter three bayous had much smaller magnitudes than the SJR. This means that extreme flows in the SJR such as those in Hurricane Harvey will likely have an important impact on sediment dynamics in the HSC-GBS. Additionally, Govindarajan (2022) analyzed TSS data from the HSC-GBS and concluded that while TSS concentrations in the SJR are relatively lower than the other tributaries, the magnitude of the sediment loading would be much higher due to the higher flows in the SJR. Given that dioxins are mainly found on the suspended sediment, this emphasizes the relative importance of flows and TSS emanating from the SJR into the HSC-GBS.

Tables 4-10 and 4-11 illustrate the range of PCB and dioxin concentrations measured in the GBS over time up to 2019 and it can be seen that the range for both pollutants varies depending on the sampled year. It is noteworthy that the range for PCBs increased after Hurricanes Ike and Harvey (2008-2009 and 2017-2019). Dioxins were not sampled before or after Ike, however, as can be seen in Table 4-11, the range increased after Hurricane Harvey. The observed changes can be attributed, in part, to the significant effects of Hurricanes Ike and Harvey on flow and sediment dynamics. While Hurricane Ike was a surge event and potentially moved sediment from downstream to further upstream as a result of surge, Hurricane Harvey was a rainfall and extreme flow event that transported significant amounts of freshwater and sediment into the GBS thereby altering the salinities and pollutant concentrations across the estuary. Thus, it is important to recognize the significant impact of extreme events on sediment dynamics and pollutants in sediment that result from these events and the need for post-event sampling to understand the resulting changes.

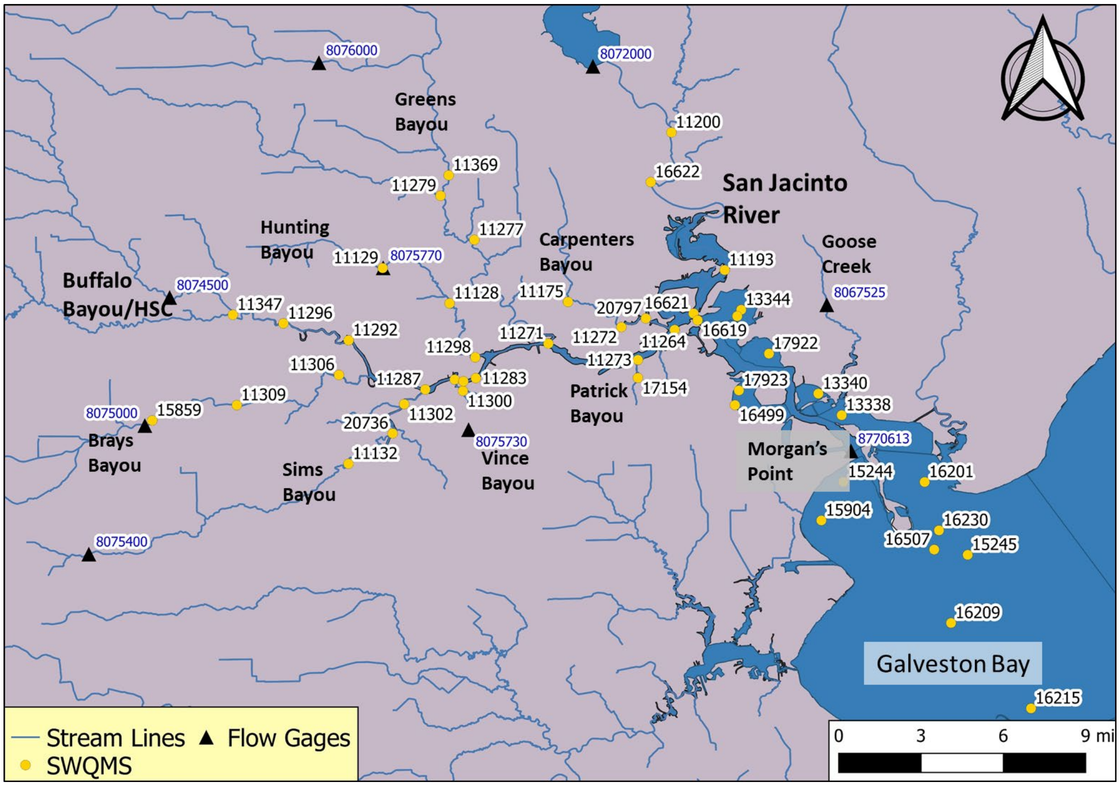

Figure 9. Flow gages and SWQM stations in the HSC-GBS

Table 4-14. The number of sediment samples collected by UH in the GBS over time

Location in the HSC-SJR-GB	**2002**	**2003**	**2004**	**2005**	**2008**	**2009**	**2011**	**2012**	**2017**	**2019**	**Total**
HSC; Upstream of Vince Bayou	5	4	6		19	5	2	2			**43**
Brays Bayou					5	1					**6**
HSC; Confluence with Brays Bayou	2	1									**3**
Vince Bayou	2	1			5	1		1	1	2	**13**
Sims Bayou	1	1			5	3		1			**11**
HSC; Between Vince and Hunting Bayous					7						**7**
Hunting Bayou	1	1				3	2				**7**
HSC; Between Hunting and Greens Bayous	3	1	4	13	3	1		1			**26**
Greens Bayou	1	2	1		6	2	1	2			**15**
HSC; Between Greens and Patrick Bayous	3	2	15	4	10	3		2	1	1	**41**
Patrick Bayou	2	2				2		1			**7**
HSC; Between Patrick and Carpenters Bayous	1	1	5	3	14	3	1	2	1	3	**34**
Carpenters Bayou	1	1						1			**3**
SJR	4	1	5		4	3		2		6	**25**
Near SJRWP	2	1	7	23	2	1	1		6	9	**52**
Confluence of HSC and SJR	2	1	2		3	1		1	1	2	**13**
South of HSC-SJR confluence	2	2	2		3	2				2	**13**
Burnet Bay	4	2	3		1	1	1		1	4	**17**
Scott Bay	6	1	2		1	1		1		3	**15**
Black Duck Bay	3	2	2								**7**
Tabbs Bay	4	1	2	1	1	2	1				**12**
Upper San Jacinto Bay	3	1	2	1	1	1					**9**
Barbours Cut	3	1			1			2			**7**
Morgan's Point	6	2	2		1	1			1	1	**14**
Goose Creek	1	1									**2**
Cedar Bayou	1	1									**2**
GB	6	5	2		2		32	22	3	4	**76**
Bayport Channel	3	1			1			2		1	**8**
Trinity Bay							4	2			**6**
Clear Lake							1	4			**5**
Total	**72**	**40**	**62**	**45**	**95**	**37**	**46**	**49**	**15**	**38**	**499**

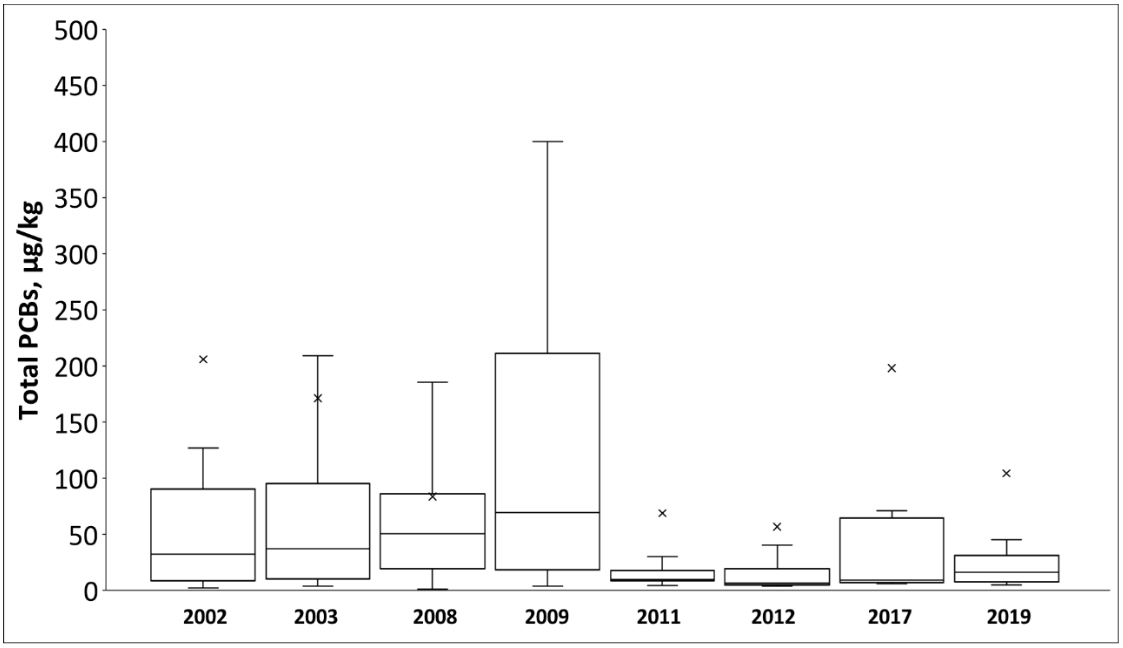

Figure 10. The range of measured PCBs over time in the HSC-GBS sediments

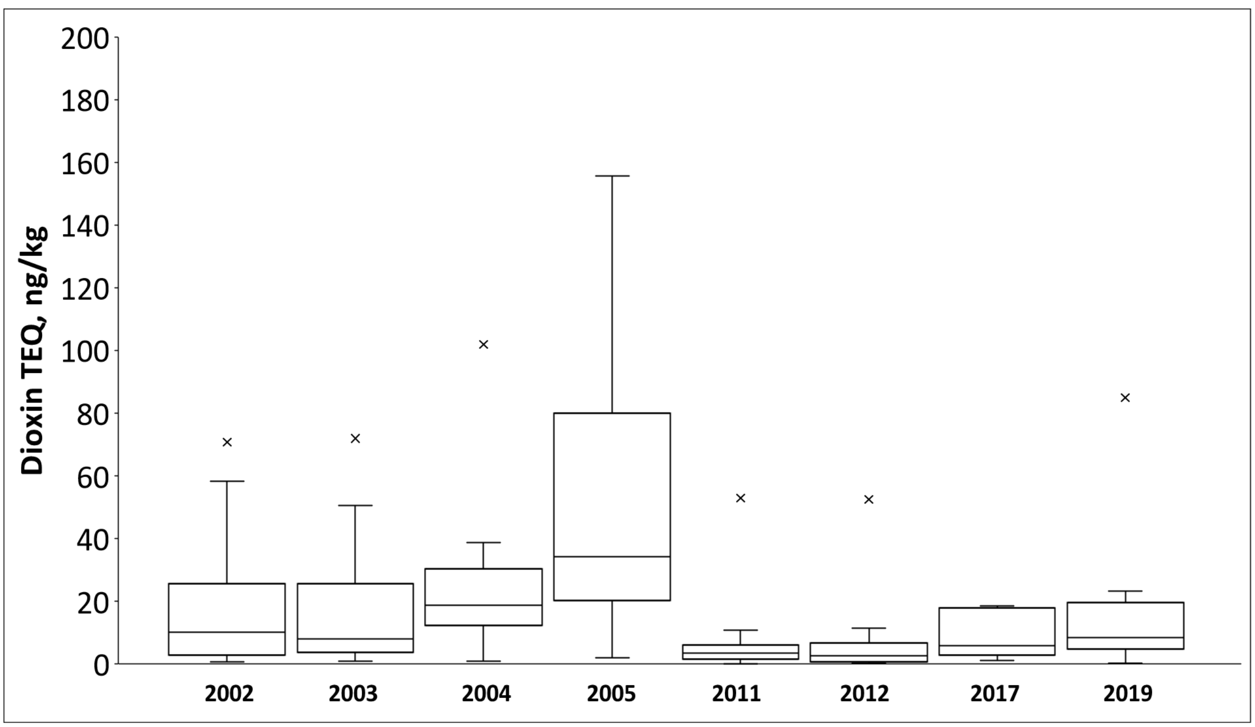

Figure 11. The range of observed dioxin concentrations over time in the HSC-GBS sediments

Discussion

Data collected by the UH Rifai research group in the HSC-GBS for dioxins and PCBs has occurred since 2002 with multiple sampling events encompassing sediment, tissue, runoff, and air. Initial studies were aimed at identifying contributions of various sources to observed levels of dioxin and PCBs in tissue with the goal of developing total maximum daily loads (TMDLs) for the estuary. During the course of these studies, sampling events coincided with the occurrence of Hurricanes Ike and Harvey (pre and post), thus enabling a closer look at the impact that natural hazards have on the distribution of the two pollutants within the estuary. While strong evidence exists pointing to the different impacts from a surge- and non-surge-based hurricane (Ike vs Harvey), specific patterns for changes in sediment and tissue concentrations associated with specific sources is harder to glean.

Following Hurricane Harvey, for example, it was reported that the cap deployed for the SJRWP Superfund site was damaged and may have led to further dioxin contamination emanating from the site. Additionally, existing sediment contamination outside of the SJRWP Superfund site's armored cap could have been mobilized within the watershed. The data gathered in three studies conducted by the UH Rifai research group (the NSF study, the GBF study and the current study funded by GBEP) between 2017 and 2021 have enabled the gathering of data before and after Hurricane Harvey for sediment and tissue. Associations with observed concentrations in sediment and tissue were made using the congener-ratio method to congener patterns from the SJRWP Superfund site. The effect in sediment from Hurricane Harvey indicates increased concentrations in parts of the HSC-GBS between 2017 and 2019; the observed increases, however had attenuated by 2021 at several stations but not all (Table 4-10). Station 11193, for instance maintains elevated concentrations in 2019 and 2021 relative to 2017 as does station 11261, among others. Tissue data remain largely elevated as evidenced by the tissue concentrations from the 2019 samples collected within the 5-mile radius of the site. Tissue samples outside the 5-mile radius were very limited. The two samples that were analyzed indicated that PCB levels in red and black drum remain unchanged from their 2009 (post Hurricane Ike) levels at station 11252 (Morgan's Point) and 11285 (downstream of the Champion Paper Mill). This could mean that industrial influences are more evident in tissue data outside the 5-mile radius while both tissue and sediment concentration associations can be made within the 5-mile radius of the SJWRP.

References

ATSDR (2016), Case Studies in Environmental Medicine: Polychlorinated Biphenyls (PCBs) Toxicity, https://www.atsdr.cdc.gov/csem/pcb/docs/pcb.pdf, Retrieved: Dec. 21, 2019.

Balasubramani AN, Howell NL, Rifai HS (2014), Polychlorinated biphenyls (PCBs) in industrial and municipal effluents: concentrations, congener profiles, and partitioning onto particulates and organic carbon, *Science of the Total Environment* 473-474: 702-713.

Balasubramani AN, Rifai HS (2015), Occurrence and distribution of polychlorinated dibenzo-*p* -dioxins and polychlorinated dibenzofurans (PCDD/Fs) in industrial and domestic sewage sludge, link.springer.com/journal/11356, 22(19):14801-14808.

Balasubramani AN, Rifai HS (2018), Efficacy of carbon-based materials for remediating polychlorinated biphenyls (PCBs) in sediment, *Science of the Total Environment* 644:398-405.

Bhattacharyya A (1946), On a measure of divergence between two multinomial populations, *Sankhyā: The Indian Journal of Statistics (1933-1960)*, 7:401-406.

Birch G, Harrington C, Symons R, Hunt J (2007), The source and distribution of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans in sediments of Port Jackson, Australia, *Marine Pollution Bulletin* 54:295-308.

Bocio A, Domingo JL, Falcó G, Llobet JM (2007), Concentrations of PCDD/PCDFs and PCBs in fish and seafood from the Catalan (Spain) market: Estimated human intake, *Environment International* 33:170-175.
doi: doi.org/10.1016/j.envint.2006.09.005

Burleson DW, Rifai HS, Proft JK, Dawson CN, Bedient PB (2015), Vulnerability of an industrial corridor in Texas to storm surge, *Natural Hazards* 77:1183-1203. doi:10.1007/s11069-015-1652-7.

Burton Jr GA (1991), Assessing the toxicity of freshwater sediments, *Environmental Toxicology and Chemistry: An International Journal* 10:1585-1627.

Comaniciu D, Ramesh V, Meer P (2000), Real-time tracking of non-rigid objects using mean shift, Proceedings IEEE Conference on Computer Vision and Pattern Recognition CVPR 2000 (Cat No PR00662). IEEE. pp 142-149

Correa O, Rifai HS, Raun r, Suarez MP, Koenig L (2004), Concentrations and vapor-particle partitioning of polychlorinated di-benzo-p-dioxins and dibenzofurans in ambient air of Houston, TX, *Atmospheric Environment* 38:6687-6699.

Dean K, Suarez MP, Rifai HS, Palachek RM, Koenig L (2010), Bioaccumulation of polychlorinated dioxins and furans in catfish and crabs along an estuarine salinity and contamination gradient, *Environmental Toxicology and Chemistry* 28(11):2307-2317.

Frignani M, Bellucci LG, Carraro C, Favotto M (2001), Accumulation of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments of the Venice Lagoon and the industrial area of Porto Marghera, *Marine Pollution Bulletin* 42:544-553.
doi: doi.org/10.1016/S0025-326X(00)00197-1

GBF (2020), Fish and crab dioxin tissue and sediment testing in the San Jacinto River and Houston Ship Channel.

Govindarajan, A. (2022), Sediment dynamics and Associations with Polychlorinated Biphenyls and dioxins in an urban estuary, Doctoral Dissertation, University of Houston.

Haglund P, Sporring S, Wiberg K, Björklund E (2007), Shape-selective extraction of PCBs and dioxins from fish and fish oil using in-cell carbon fractionation pressurized liquid extraction, *Analytical Chemistry* 79:2945-2951. doi:10.1021/ac0624501

Hosomi M, Matsuo T, Dobashi S, Katou S, Abe H (2003), Survey of dioxins in Tokyo Bay bottom sediment, *Marine Pollution Bulletin* 47:68-73.

Houston Chronicle (2018), Silent Spills, www.houstonchronicle.com/news/article/Texas-officials-ignore-spread-of-dioxin-in-key-12882446.php, Retrieved: Dec. 22, 2019.

Howell N (2012), Bed and suspended sediments as source and transport mechanisms for polychlorinated biphenyls in the Houston Ship Channel Estuary System, Ph.D. dissertation, University of Houston, Houston, TX.

Howell NL, Rifai HS (2015), Longitudinal estimates of sediment-water diffusive flux of PCB congeners in the Houston Ship Channel, *Estuarine, Coastal and Shelf Science* 164:19-27.

Howell NL, Rifai HS, Koenig L (2011), Comparative distribution, sourcing, and chemical behavior of PCDD/Fs and PCBs in an estuary environment, *Chemosphere* 83:873-881.
doi: doi.org/10.1016/j.chemosphere.2011.02.082

Howell NL, Rifai HS (2016), PCDD/F and PCB water column partitioning examination using natural organic matter and black carbon partition coefficient models, *Environmental Science and Pollution Research* 23:6322-6333.

Howell NL, Suarez MP, Rifai HS, Koenig L (2008), Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas, *Chemosphere* 70:593-606.

Kiaghadi A, Rifai HS, Burleson DW (2018), Development of a storm surge driven water quality model to simulate spills during hurricanes, *Marine Pollution Bulletin* 129:714-728. doi: doi.org/10.1016/j.marpolbul.2017.10.063.

Kiaghadi A, Rifai HS, Crum M, Willson RC (2022), Longitudinal patterns in sediment type and quality during daily flow regimes and following natural hazards in an urban estuary: a Hurricane Harvey retrospective, *Environmental Science Pollution Research* 29(5):7514-7531, doi.org/10.1007/s11356-021-15912-0.

Kullback S (1959) Information Theory and Statistics. John Riley and Sons. Inc New York.

Lakshmanan D, Howell NL, Rifai HS, Koenig L (2010), Spatial and temporal variation of polychlorinated biphenyls in the Houston Ship Channel, *Chemosphere* 80(2):100-112.

Li C, Zheng M, Zhang B, Gao L, Liu L, Zhou X, Ma X, Xiao K (2012), Long-term persistence of polychlorinated dibenzo-p-dioxins and dibenzofurans in air, soil and sediment around an abandoned pentachlorophenol factory in China, *Environmental Pollution* 162:138-143. doi: doi.org/10.1016/j.envpol.2011.11.015.

Liebens J, Mohrherr CJ, Karouna-Renier NK, Snyder RA, Rao KR (2011), Associations between dioxins/furans and dioxin-like PCBs in estuarine sediment and blue crab, *Water, Air, & Soil Pollution* 222:403-419.

Louchouarn P, Seward SM, Cornelissen G, Arp HPH, Yeager KM, Brinkmeyer R, Santschi PH (2018), Limited mobility of dioxins near San Jacinto super fund site (waste pit) in the Houston Ship Channel, Texas due to strong sediment sorption, *Environmental Pollution* 238:988-998.

Mohrherr C, Liebens J, Rao K (2006), Sediment and water pollution in Bayou Chico, Pensacola, FL, University of West Florida. Center for Environmental Research and Bioremediation.

Moon H-B, Choi M, Choi H-G, Kannan K (2012), Severe pollution of PCDD/Fs and dioxin-like PCBs in sediments from Lake Shihwa, Korea: tracking the source, *Marine pollution bulletin* 64:2357-2363.

Moon H-B, Choi M, Choi H-G, Ok G, Kannan K (2009), Historical trends of PCDDs, PCDFs, dioxin-like PCBs and nonylphenols in dated sediment cores from a semi-enclosed bay in Korea: Tracking the sources, *Chemosphere* 75:565-571.

Nunes M, Vernisseau A, Marchand P, Le Bizec B, Ramos F, Pardal MA (2014), Occurrence of PCDD/Fs and dioxin-like PCBs in superficial sediment of Portuguese estuaries, *Environmental Science and Pollution Research* 21:9396-9407.

Okumura Y, Yamashita Y, Kohno Y, Nagasaka H (2004), Historical trends of PCDD/Fs and CO-PCBs in a sediment core collected in Sendai Bay, Japan, *Water Research* 38:3511-3522.

Paatero P, Tapper U (1994), Positive matrix factorization - a nonnegative factor model with optimal utilization of error-estimates of data values, *Environmetrics* 5 (2): 111-126.

Raun LH, Correa O, Rifai HS, Suarez M, Koenig L (2005), Statistical investigation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the ambient air of Houston, Texas, *Chemosphere* 60:973-989.
doi: doi.org/10.1016/j.chemosphere.2004.12.057.

Ruckart PZ, Orr MF, Lanier K, Koehler A (2008), Hazardous substances releases associated with Hurricanes Katrina and Rita in industrial settings, Louisiana and Texas, *Journal of Hazardous Materials* 159:53-57.

Rifai HS, Kiaghadi A, Burleson DW (2021), Assessing damages to built and natural environments: Linking hydrodynamic and geospatial enviro-economical models, *Frontiers in Climate*, doi.org/10.3389/fclim.2021.610593.

Sappington EN, Balasubramani A, Rifai HS (2015), Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in municipal and industrial effluents, *Chemosphere* 133:82-89.

Suarez MP, Rifai HS, Schimek J, Bloom M, Jensen P, Koenig L (2006), Dioxin in stormwater runoff in Houston, TX, *ASCE Journal of Environmental Engineering* 132(12):1633-1643, 2006.

Suarez MP, Rifai HS, Palachek R, Dean K, Koenig L (2005a), Polychlorinated dibenzo-p-dioxins and dibenzofurans in Houston Ship Channel tissue and sediment, *Environmental Engineering Science* 2(6):891-906.

Suarez MP, Rifai HS, Palachek R, Dean K, and Keonig L (2005b), Distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in suspended sediments, dissolved phase and bottom sediment in the Houston Ship Channel, *Chemosphere* 62(3):417-429.

TCEQ (Texas Commission on Environmental Quality) (2021), Superfund Sites in Harris County, www.tceq.texas.gov/remediation/superfund/sites/county/harris.html, Retrieved: Dec. 23, 2019.

Tucker TY (2012), Sourcing of dioxins from the San Jacinto Waste Pit Superfund site into the Galveston Bay system. M. S. Thesis (Advisor: H. S. Rifai), University of Houston, Houston, TX.

UNEP (2019), Stockholm Convention, chm.pops.int/, Retrieved: Dec. 21, 2019.

USEPA (2017a), R6 and ERT Dive Team Operations Summary Report, Cap Assessment and Sampling Activities, San Jacinto Waste Pits, Channelview, TX.

USEPA (2017b), Record of Decision, San Jacinto River Waste Pits, Dallas, TX.

USEPA (2021a), Persistent Organic Pollutants: A Global Issue, A Global Response, www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-response#table, Retrieved: Dec. 21, 2019.

USEPA (2021b), Polychlorinated Biphenyls (PCBs), www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls-pcbs, Retrieved: Dec. 21, 2019.

USEPA (2021c), San Jacinto River Waste Pits Superfund Site, www.epa.gov/tx/sjrwp?fuseaction=second.cleanup&id=0606611, Retrieved: Dec. 22, 2019.

USEPA (2021d), Superfund Site: Patrick Bayou, cumulis.epa.gov/supercpad/cursites/csitinfo.cfm?id=0605329, Retrieved: Dec. 22, 2019.

WHO (2016), Dioxins and their effects on human health, www.who.int/news-room/fact-sheets/detail/dioxins-and-their-effects-on-human-health, Retrieved: Dec. 21, 2019.

Yeager KM, Santschi PH, Rifai HS, Suarez MP, Brinkmeyer R, Hung C-C, Schindler K, Andres M, Weaver E (2007), Dioxin chronology and fluxes in sediments of the Houston Ship Channel, Texas: Influences of non-steady state sediment transport and total organic carbon, *Environmental Science and Technology* 41:5291-5298.