

# Assessment of Organic Pollutants in Nueces Bay's Petroleum Brine Impacted Sediments

Final Report

Publication CBBEP – 145 Project Number – 1910 June 2021

Prepared by:

Hussain Abdulla, Ph.D. Assistant Professor of Chemistry Center for Water Supply Studies Texas A&M University-Corpus Christi 6300 Ocean Drive, Corpus Christi, Texas, 78412 Phone: (361)825-6050 E-mail: Hussain.abdulla@tamucc.edu

Dorina Murgulet, Ph.D. Associate Professor of Hydrogeology Director Center for Water Supply Studies Texas A&M University-Corpus Christi 6300 Ocean Drive, Corpus Christi, Texas, 78412 Phone: (361)825-2309 E-mail: <u>Dorina.murgulet@tamucc.edu</u>

Submitted to: Coastal Bend Bays & Estuaries Program 615 N. Upper Broadway, Suite 1200 Corpus Christi, TX 78401

The views expressed herein are those of the authors and do not necessarily reflect the views of CBBEP or other organizations that may have provided funding for this project.

## Assessment of Organic Pollutants in Nueces Bay's Petroleum Brine Impacted Sediments

Hussain Abdulla, Ph.D. Assistant Professor of Chemistry Center for Water Supply Studies Texas A&M University-Corpus Christi 6300 Ocean Drive Corpus Christi, Texas, 78412 Phone: (361)825-6050 E-mail: Hussain.abdulla@tamucc.edu Dorina Murgulet, Ph.D. Associate Professor of Hydrogeology Director Center for Water Supply Studies Texas A&M University-Corpus Christi 6300 Ocean Drive Corpus Christi, Texas, 78412 Phone: (361)825-2309 E-mail: Dorina.murgulet@tamucc.edu

Date of submission: April 30<sup>th</sup>, 2021

#### SUBMITTED TO:

Adrien Hilmy Coastal Bend Bays & Estuaries Program 615 N. Upper Broadway, Suite 1200 Corpus Christi, TX 78401

# **Table of Contents**

Li	ist of Tables	2
Li	ist of Figures	3
Ex	xecutive Summary	4
1.	Introduction	5
2.	Methods	7
	2.1. Study Site	7
	2.2. Sample Collection	7
	2.3. Analytical Methods	8
3.	Results	10
	3.1. Physicochemical Parameter Measurements	10
	3.2. Sediment analysis	13
	3.2.1. Porosity	13
	3.2.2. Grain Size Analysis	14
	3.3. Petroleum Aromatic Hydrocarbons	18
	3.4. Organophosphorus Pesticides and Herbicides (OPs)	21
4.	. Conclusion and Recommendations	23
5.	. Literature Cited	24

# List of Tables

Table 1   Nueces Bay surface seawater field physicochemical parameters measured in November-December 2019     11
<b>Table 2</b> Nueces Bay surface seawater field physicochemical parameters measured in September 2020.   12
<b>Table 3</b> Porosity Values by core and by sample depth. Table split into two parts for ease ofdisplay. All porosities are unitless and displayed as decimals
<b>Table 4</b> Median grain size presented in phi by core and by sample depth. Table shown in twoparts for ease of display. All phi is unitless and displayed as decimals or integers
<b>Table 5</b> Average concertation (ng/g dried sediment) of 12 individual PAH compounds detectedin Nueces Bay sediments. The averages value represents the average of three top sedimentslayers (0-2 cm, 2-4 cm, and 4-6 cm depth) for a core at the specific stations. Table shown in twoparts for ease of display

## List of Figures

Figure 1 Study area and stations of Nueces Bay using map line7
Figure 2 Surface water salinity interpolation map of Nueces Bay's during the two field sampling
<b>Figure 3</b> Porosity inverse distance weighted interpolation map by core depth A) 0-2 cm, B) 2-4 cm, C) 4-6 cm, D) 6-8 cm, E) 8-10 cm, F) 10-20 cm, G) 20-30 cm. Warm colors show higher porosities, cool colors lower porosities. The porosity distribution median of 0.52 dominates the maps, showing a typical porosity for unconsolidated sediments ranging from sand to clay 15
<b>Figure 4</b> Median grain size (Phi) inverse distance weighted interpolation map by core depth A) 0-2 cm, B) 2-4 cm, C) 4-6 cm, D) 6-8 cm, E) 8-10 cm, F) 10-20 cm, G) 20-30 cm. Warmed colors represent smaller size grains, cooler colors showing larger size grains, ranging from <0.25 mm (blue) to >4 mm (red). Median grain size average ( $\overline{x}$ : 0.7 phi) is between 1-0.5 mm in diameter, typical for coarse sand (n=106)
<b>Figure 5</b> Interpolation maps of the average concertation (ng/g dried sediment) of 12 individual PAH compounds detected the total PAHs in Nueces Bay sediments. The averages value represents the average of three top sediments layers (0-2 cm, 2-4 c,m, and 4-6 cm depth) for a core at the specific stations
Figure 6 Depth profiles of some altered organophosphorus pesticide and herbicide detected in porewater of Nueces Bay

### **Executive Summary**

In Nueces Bay, there have been numerous sites of petroleum brine discharge since the early 1900s until around 1993. While many previous studies point out the high toxicity of these petroleum brine discharges and the potential adverse impacts on the ecosystem health, there is limited information about the current level of pollution, types of pollutants trapped in the sediments and released into the water column, and their contribution to toxicity levels. This study's goals were to help: (1) identify and quantify the size of the impacted area in the bay and 2) measure organophosphate pesticides in the bay, including all the possible alterations (oxygenation, reduction, dehydration, desaturation, methylation, and acetylation) of these contaminants, not limited to only indicators as the commonly used whole toxicity tests. Surface water and sediment samples were collected from 18 stations along six transects (3 stations along each transect) during field sampling expeditions in November-December 2019 and September 2020. Three types of samples (surface water, pore water, and sediment) were processed and analyzed for polycyclic aromatic hydrocarbons (PAHs) and structural elucidation and quantification of organophosphorus compounds (OPs.) A total of twelve PAHs were identified: Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, and Benzo[ghi]perylene. The highest total PAH concentrations were found to cluster near the Nueces River mouth. Using the Fluoranthene/(Fluoranthene+Pyrene) ratio, it was determined that PAHs at stations NB2, NB5, NB6, NB7, NB8, NB10, NB12, and NB18 are of petroleum/petrogenic origin, while those at stations NB4, NB13, NB16, and NB17 are of liquid fossil fuel combustion (i.e., gasoline, diesel, and crude oil) source. Based on the Fluoranthene/(Fluoranthene+Pyrene) ratio, sources such as grass, wood, or coal combustion source were not present in any of the samples/locations. Thus, the results indicate a plausible on-going point source (less than 2 years) contamination rather than historical trapped brine water contamination.

Organic compound analyses identified 11,802 organic compounds in both porewater and surface water samples in 2019. Out of these, 2,283 were OPs compounds, which account for 19% of the total compounds detected. In 2020, 10,872 organic compounds were detected, of which 16% were OPs compounds (1745 compounds). It was found that Nueces Bay has a significantly higher percentage of OPs compounds relative to other estuaries and open ocean systems, with levels not exceeding 8% of the total organic compounds detected. A non-targeted screening (NTS) of the 190 known organophosphorus pesticides and herbicides showed none of the intact structures were present in the Nueces Bay samples, both surfaces, and porewater. However, 1995 OPs compounds that can be a product of chemical transformations of the 190 OPs were found. The most abundant presence of these altered OPs was found in the sediment porewater at NB16, NB17, NB18, and NB13 in the Rincon Bayou `surveyed area. This area is also characterized by finer sediments (e.g., large porosities) with a larger affinity for trapping contaminants and a favorable environment for chemical transformations. Also, given the reduced inflows through the delta, this area is likely not well flushed unless during high precipitation/flow events.

The findings of this study will help guide management decisions and ensure that water quality standards and sediment quality criteria are adequate and appropriate for the living organisms (e.g., oyster reefs) and recreational use of the bay.

### 1. Introduction

Petroleum brine is one of the major environmental issues associated with oil field exploration. In 1979, it was estimated that over 32 million gallons of petroleum brine were discharged daily to Texas tidal waters (Liebow et al., 1980). In 1989, Louisiana discharged approximately 84 million gallons of petroleum brine per day from 700 sites among the 70 oil and gas fields (Boesch and Rabalais 1989). In Wyoming, a total of 58.8 billion gallons of petroleum brine were generated in 1997, 30% of that was discharged into surface waters (Ramirez, 2002). Globally, it is estimated that over 10.5 billion gallons/day of petroleum brine was produced in 2007, of which 80% was produced from onshore oil fields. For every gallon of oil, there are three gallons of petroleum brine being produced and subsequently discharged (Dal Ferro and Smith 2007). Typically, the discharged volume of petroleum brine increases several times as the oil field/exploration wells age (Somerville et al., 1987; Stromgren et al., 1995).

Besides containing high concentrations of dissolved hydrocarbons, petroleum brines have an elevated concentration of volatile organic compounds (e.g., acetic, propionic, and butyric acids), heavy metals, radionuclides, additive chemicals (e.g., biocides, demulsifiers, and corrosion inhibitors), and total suspended solids (Somerville et al., 1987; Ahmadun et al. 2009). For example, the lead, zinc, and iron concentration could reach up to 8, 35, and 1,100 mg/L in some petroleum brine discharges, respectively (Fillo and Evans 1990). Many previous studies have shown that the geochemical signatures of petroleum brine could be preserved in the sediment and pore water for many years. For example, a recent study on sediments from the Allegheny River watershed, N.J., by Burgos et al. (2017) identified a peak in Ra and Sr isotopes that correspond to the peak period of industrial activity and could be tracked to the Marcellus Shale formation. The fate of many contaminates traces, and heavy metals depend on the redox condition of the sediments. A study conducted on Humble Canal's sediment (Louisiana) (a site that has been exposed to petroleum brine discharge for many years) shows that as the redox potential of the sediment increased, the affinity between iron [Fe (III]) and manganese [Mn (IV)] oxide and arsenic [As], cadmium [Cd], chromium [Cr] and zinc [Zn] also increased. They observed a higher degradation rate of petroleum hydrocarbon in oxidized sediments relative to reduced conditions (DeLaune et al. 1999).

In Nueces Bay (South Texas Gulf coast), a shallow bay located near oil and gas fields (See Fig.1), several sites of petroleum brine discharge were active since the early 1900s until the restriction around 1993 (Railroad Commission of Texas, 1993). Many previous studies have identified the adverse impact of highly toxic petroleum brines on ecosystem species. For example, Caudle (1995) related the widespread denuded marsh on the Nueces bay to the longterm exposure to petroleum brine. Another study found that the Western Sandpipers (Calidris mauri) exposed to petroleum brine in Nueces Bay have a tenfold higher aromatic hydrocarbon concentration in their stomach contents relative to the birds collected a reference site (Rattner et al. 1995). In 1990, D'unger et al. (1995) conducted toxicity tests on the sediment and sediment pore waters near petroleum brine discharge sites in the bay. They concluded that these sediments are highly toxic relative to the reference sediment or pore water from unimpacted areas. A recent study showed that the tissues of Crassostrea Virginia (the Eastern or American oyster), collected from the northern Nueces Bay (near the impacted area), had the highest toxicity index relative to other local coastal areas (Palmer et al. 2015). In addition to hydrocarbons, petroleum brine is rich in Fe (III) oxyhydroxide as part of the suspended solid which has a high affinity for organophosphorus and phosphates (e.g., Gunnars and Blomqvist 1997; Gunnars et al. 2002; Hupfer and Lewandowski, 2008). We hypothesize that a large proportion of the pesticide

compounds present in the agricultural runoff was adsorbed on the Bay's fine sediment particles, which have been enriched in iron from the petroleum brine. Over time, and with sedimentation, these insoluble organophosphorus containing iron deposits would have become buried beneath layers of sediment and hidden away for decades. However, as the redox condition of these impacted sediments starts to change, Fe (III) starts to reduce to Fe (II) by anaerobic bacteria leading to the release of organophosphorus compounds to the pore water and diffused into the water column.

Many earlier studies have identified the high toxicity of the petroleum brine discharged on the Nueces Bay ecosystem. However, there is limited information about the size of the impacted area in the Bay, the current level of pollution, the types of pollutants these sediments are releasing into the water column, and their contribution to toxicity levels. Our preliminary research in Nueces Bay identified over 4,000 organic compounds in the water column with an increased abundance of oxygenated hydrocarbon compounds, unique signatures of petroleum hydrocarbons, and organophosphate compounds, likely of anthropogenic origin. The samples were collected from sites in proximity to the historical oilfield discharge sites.

This proposed study goals were to help:

- 1. Identify and quantify the size of the impacted area in the bay and ensure that water quality standards and sediment quality criteria are adequate and appropriate for the living organisms (e.g., oyster reefs) and recreational use of the bay.
- 2. Develop a new method for measuring organophosphate pesticides in estuaries, including all the possible alterations (oxygenation, reduction, dehydration, desaturation, methylation, and acetylation) of these contaminants, not limited to only indicators as the commonly used whole toxicity tests. In multiple contaminant scenarios, such as indicated for Nueces Bay by the numerous contaminant compounds, it is problematic to partition contributions of individual contaminants to overall toxicity.

## 2. Methods

## 2.1. Study Site

This study was performed in the semi-arid Nueces Bay, Texas. Nueces Bay, located on the south Texas Gulf Coast, is contiguous to Corpus Christi Bay in the Nueces Estuary system (Figure 1). The area is characterized by dry to sub-humid climates with annual precipitation averaging around 76.2 cm and an average evaporation rate of 145 cm (Ockerman 2001; Shafer 1968). Due to low rainfall in the watershed and dams and diversions on the Nueces River, riverine discharge into the Bay is typically minimal, resulting in high average salinities and often low nutrient levels (Longley et al. 1994). Nueces Bay has a long history of anthropogenic disturbances, including oil/gas development, pipelines transecting the bay, dredging, and agricultural land use. Dryland crop agriculture (i.e., grain sorghum, corn, and cotton) and ranching activities dominate the area's land use (TDWR 1981). Nueces Bay and Nueces, and San Patricio Counties immediately surrounding the Bay have been heavily developed for oil and gas extraction (D'Unger et al. 1996; Douglas et al. 2020). The long-term discharge of oil-brine to surface water and other disturbances associated with the oil/gas industry into coastal estuaries was a longstanding practice in Texas until a new rule, 40 CFR Part 435, was passed in 1996 and effectively banned such practices (D'Unger et al. 1996).



Additionally, the surrounding area has been subjected to farming practices since 1909, but regulations on organophosphorus insecticides and herbicides have not been implemented until the 21<sup>st</sup> century. These organophosphorus compounds most likely reached the Bay through runoff (San Patricio

Figure 1 Study area and stations of Nueces Bay.

County Economic Development Corporation, 2020; EPA, n.a.). According to these sources, the study site has a long history of exposure to hydrophobic and amphiphilic compounds. However, the Fe (III) oxyhydroxide from the petroleum brines could redistribute organophosphorus compounds over a wider area. Additionally, these decades-old herbicides and insecticides could have been trapped in the sediment for several years and with delayed exposure due to disturbances such as intense storms (Herndon et al., 2019; Herndon et al., 2020).

## 2.2. Sample Collection

Surface water and sediment samples were collected from 18 stations along six transects (NB3 stations along each transect), as illustrated in Figure 1. Field sampling expeditions were conducted in November-December 2019 and September 2020 Field parameters (i.e., temperature, dissolved oxygen, salinity, and pH) were measured at each site before sample collection using a multi-probe YSI series 6 sonde.

#### Water samples

Water column samples were collected in 1 L polycarbonate bottles. The bottles were cleaned with Alconox and HCl solution and rinsed with the sample. In the field, all sample bottles were stored on ice in a dark cooler until return to the laboratory, where they were immediately frozen until processing occurred. All samples were sterile filtered through 0.22  $\mu$ m polyester sulfone filters conditioned with 5-10 mL of sample and kept frozen until analysis.

#### Sediment samples

Sediment cores (~0.5 m) were collected using a piston push coring that is designed to capture the sediment-water interface (e.g., nepheloid layer) (Gardner et al. 2009). Sediment core (in the core polycarbonate liner) was kept in a cooler with ice in the field and transferred to the lab. The nepheloid layer was removed from sediment cores and processed along with the pore water samples in the lab. To avoid dissolved organic matter (DOM) contamination from macrofauna rupture (Alperin et al. 1999), we collected pore waters from the core using Rhizon samplers (<0.2  $\mu$ m pore size) inserted through ports pre-drilled into the core liners (Seeberg-Elverfeldt et al. 2005). The cores were extruded and sliced into 2.0 cm intervals for the first 10 cm, then every 10 cm for the rest of the core (10 samples total per core including the nepheloid layer) in an N<sub>2</sub> atmosphere glove box. The sediment samples were frozen and then freeze-dried. Sediment fractions for each of the intervals mentioned above were analyzed for grain size, permeability, and petroleum hydrocarbons.

#### 2.3. Analytical Method

<u>Grain size analysis</u>: For grain size distributions, 1-2cm<sup>3</sup> of sediment was allocated for laser diffraction analysis (Beckman Coulter Limit of Detection (LOD): 0.375µm-2000µm). Organic matter was oxidized from the sediment using hydrogen peroxide (up to 40% by volume) in a multi-stage process to control reaction rates (Welschmeyer, 1994). The sediment was undergone two cycles of DI washing, agitation, and centrifuging before instrumental analysis. A Ro-tap with sieves up to 4000µm was used for core sections with grains larger than 2000µm.

Porosity was measured by weighing and then drying 166cm<sup>3</sup> saturated sediment core cylinders in an oven at 105° C. After constant weight measurements; sections will be weighed for dry mass. Porosity was then derived using the relationship between bulk density and particle density (Avnimelech et al. 2001).

$$\phi = 1 - \frac{\rho_b}{\rho_g}$$

Where  $\phi$  is porosity,  $\rho_b$  is the bulk density, and  $\rho_g$  is the particle density assuming a constant value of 2.65g/cm<sup>3</sup> (Klute, 1986). Hydraulic conductivity was calculated from the grain size data using the Kozeny-Carmen Equation:

$$\mathbf{K} = \frac{\rho g}{\mu} * D_g^2 * \frac{n_e^3}{(1 - n_e)^2}$$

Where  $\rho$  and  $\mu$  are the density and dynamic viscosity of water, g is the acceleration due to gravity,  $D_g$  is the geometric referential grain size, and  $n_e$  is the effective porosity. While previous literature contests this equation for hydraulic conductivity of fine-grained sediments, recent literature shows that using the geometric mean is an acceptable surrogate in finding the effective porosity, leading to good agreement with permeameter measurements (Urumovic, K. 2016).

<u>Polycyclic Aromatic Hydrocarbons (PAHs)</u>: PAHs were analyzed following the procedure described by Tolosa et al. (2005). Briefly, freeze-dried sediments were homogenized. The homogenized sediment was spiked with internal standards (naphthalene-d8, anthracene-d10, pyrene-d10, and perylene-d12). The freeze-dried sediment samples were Soxhlet extracted for 16 hours into 100 ml of dichloromethane/methanol (1:1, v/v). Quantification of different PAHs was performed on a TSQ 9000 Triple Quadrupole GC-MS/MS in full scan and the Skyline program provided by MacCoss Lab Software. The oven temperature program and the He flow rates followed the procedure described by Tolosa et al. (2005).

<u>Structural elucidation and quantification of organophosphorus compounds (OPs)</u>: Extraction of organophosphorus compounds from the sediment samples was conducted according to Cao et al. (2017) with modifications. In brief, 5.0 grams of grinded freeze-dried sediment were extracted in 10 ml of high-purity acetonitrile. Samples were physically lysed using a combination of sonication and vortex (3 x 5 times). The sample was centrifuged for the last time at 9,500 rpm for 5 min to separate the supernatant from the solid sediment pellet. The extraction procedure was repeated for the residual sediment. The combined extract was concentrated with Savant vacuum concentrators, and 1.0 ml of water was added.

The three types of water samples (surface water, in situ pore water, and extracted sedimentwater) were prepared for mass spectral analysis using PPL solid-phase extraction cartridges (Agilent, Bond Elut PPL, 200mg resin for porewater samples, and 1 g resin for seawater samples according to the procedure recommended by Dittmar et al. (2008).

An ultraperformance liquid chromatography (UPLC) coupled to Orbitrap Fusion Tribrid Mass Spectrometer (OT-FTMS) was used for structural elucidation of intact and altered organophosphate insecticides and herbicides compounds. It allows simultaneous de novo compound structure elucidation and quantification of thousands of compounds per sample down to attomolar concentrations and has sub-ppm mass accuracy and resolution (Zubarev and Makarov 2013). For identification and structural elucidation of organophosphorus compounds, each sample was first analyzed using a full scan mode at 500,000 full widths at half maximum (FWHM) resolution in both negative and positive modes. Coupled with UHPLC system (Vanquish UPLC, Thermo Fisher) equipped with a BEH  $C_{18}$  column, with the similar elution gradient used by Cao et al. (2017). Compound Discoverer software (Thermo Fisher) was used to identify the mass features that match our in-house organophosphate insecticides and herbicides compounds database and their UPLC retention times. This database contains 190 known organophosphate insecticides and herbicides and possible alterations (oxygenation, reduction, dehydration, desaturation, methylation, and acetylation). This information was then used to create a data-dependent acquisition (DDA) method as described by Mullard et al. (2015) with some modifications (Abdulla et al. in prep.). Both collision-induced dissociation (CID) and higher-energy collisional dissociation (HCD) fragmentation techniques were applied, and their activation energies were optimized for the detected organophosphorus compounds. De novo structural elucidation was performed on these MS<sup>2</sup> fragments, and these structures were also be putatively annotated using in silico fragmentation prediction software (Mass Frontier). Organophosphate insecticides and herbicides and their alteration were identified through a combination of the following 5 multiconfidant points: 1) high mass accuracy of OT-FTMS, 2) identification and matching of isotopic patterns (at least M+1 isotopes) to confirm ionized charge and the estimated number of carbon atoms, 3) cross-referencing with in-house database, 4) matching retention times between different samples, 5) structure confirmation through MS<sup>2</sup> fragmentation by both CID and HCD techniques and verification using in silico fragmentation prediction software.

## 3. Results

In Fall 2019, we collected 54 surface water samples (triplicate from 18 stations) and 34 sediment cores from 17 stations. We were not able to collect cores at station NB3 because of the presence of hard seafloor. A total of 96 porewaters samples were extracted from the sediment cores, and 105 sediment subsamples in triplicate (a total of 315) were collected at different sediment depths. In fall 2020, an additional 54 surface water samples were collected from the 18 stations (in triplicate). Sediment cores were collected from 17 stations, with a gap at NB3 because of hard substrates and sandy sediments. From these cores, a total of 72 porewater samples and 88 sediment subsamples in triplicate (a total of 216) were collected at different sediment depths.

## **3.1.Physicochemical Parameter Measurements**

The salinity in Nueces Bay ranged from 30.0- 32.0 (average  $31.2 \pm 0.6$ ) in November- December 2019 and from 26.3- 33.6 (average  $31.3 \pm 2.0$ ) in September 2020. September 2020 shows slightly higher freshwater flow contribution near the Nueces River mouth (Figure 2a &b). But in general, salinity indicates minor fresh riverine influence on the bay in both seasons. The bay is under high oxygen saturation during the two seasons, as indicated in Tables 1 and Table 2.

Station	Latitude	Longitude	Date	Time	Salinity	pН	Temp (°C)	Conductivity (µS)	D.O. %	D.O. mg/L
NB1	N27.85163	W97.38290	11/05/19	8:22	31.1	7.37	19.9	47659	256.3	20.67
NB2	N27.86796	W97.36926	11/05/19	9:31	32.0	7.56	20.3	48765	285.3	21.21
NB3	N27.86723	W97.38532	11/05/19	10:34	31.7	7.69	21.0	48286	288.5	21.29
NB4	N27.84912	W97.40296	11/05/19	11:19	32.0	7.52	20.8	48969	298.5	22.10
NB5	N27.83705	W97.40296	11/05/19	11:54	31.7	7.62	20.8	48482	226.6	16.98
NB6	N27.83376	W97.43598	11/05/19	12:44	31.7	7.67	21.4	48450	197.2	14.42
NB7	N27.82865	W97.46236	11/19/19	10:40	30.0	7.71	16.2	46145	95.1	7.81
NB8	N27.84586	W97.44076	11/19/19	11:25	30.7	7.39	15.3	47200	91.2	7.58
NB9	N27.86637	W97.42125	11/19/19	12:05	31.2	7.59	16.8	47828	73.9	5.92
NB10	N27.86634	W97.43768	11/19/19	12:40	31.0	7.65	16.4	47594	69.9	5.68
NB11	N27.85095	W97.45381	11/19/19	13:10	30.2	7.68	15.3	46597	92.0	7.64
NB12	N27.83539	W97.47196	12/03/19	8:32	30.7	8.71	11.5	47484	55.4	6.96
NB13	N27.84317	W97.48256	12/03/19	9:31	30.9	8.83	17.0	47437	84.7	6.83
NB14	N27.86497	W97.45096	12/03/19	10:17	31.2	8.84	17.5	47930	61.4	5.14
NB15	N27.85318	W97.46476	12/03/19	11:14	31.8	8.88	16.9	48672	63.3	5.12
NB16	N27.86886	W97.48928	12/03/19	13:56	31.2	8.48	18.5	47863	75.9	5.93
NB17	N27.86228	W97.49699	12/03/19	13:12	31.2	8.97	18.4	47817	74.9	5.83
NB18	N27.85553	W97.50561	12/03/19	12:33	31.4	8.91	17.8	49848	81.8	6.92

Table 1: Nueces Bay surface seawater field physicochemical parameters measured in November- December 2019

Station	Latitude	Longitude	Date	Time	Salinity	pН	Temp (°C)	Conductivity (µS)	D.O. %	D.O. mg/L
NB1	N27.85163	W97.38290	09/07/20	8:34	33.2	8.14	28.8	50716	96.2	6.18
NB2	N27.86796	W97.36926	09/07/20	9:07	33.5	8.05	28.6	51142	82.3	5.30
NB3	N27.86723	W97.38532	09/07/20	9:33	33.6	7.98	28.6	51263	69.7	4.48
NB4	N27.84912	W97.40296	09/07/20	10:03	32.6	8.09	28.8	50047	96.0	6.19
NB5	N27.83705	W97.40296	09/07/20	8:01	32.4	9.03	29.5	49800	89.8	5.72
NB6	N27.83376	W97.43598	09/07/20	10:31	31.2	8.12	29.2	48079	101.9	6.57
NB7	N27.82865	W97.46236	09/07/20	11:08	30.2	8.16	29.3	46744	109.3	7.09
NB8	N27.84586	W97.44076	09/12/20	8:07	31.6	8.06	26.8	48467	101.1	6.77
NB9	N27.86637	W97.42125	09/12/20	8:36	32.9	8.12	26.9	50306	98.0	6.51
NB10	N27.86634	W97.43768	09/12/20	9:02	33.1	8.11	27.0	50619	97.7	6.48
NB11	N27.85095	W97.45381	09/12/20	9:39	32.0	8.11	26.9	49086	101.5	6.78
NB12	N27.83539	W97.47196	09/12/20	10:19	28.8	8.14	26.6	44597	111.4	7.60
NB13	N27.84317	W97.48256	09/12/20	10:39	26.3	8.24	26.8	41154	123.1	8.50
NB14	N27.86497	W97.45096	09/12/20	11:04	32.1	8.13	27.3	49229	111.5	7.39
NB15	N27.85318	W97.46476	09/25/20	8:11	31.3	7.95	24.9	47990	98.70	6.87
NB16	N27.86886	W97.48928	09/25/20	9:58	30.1	8.16	25.9	46445	101.5	6.98
NB17	N27.86228	W97.49699	09/25/20	9:18	29.4	8.1	25.6	45506	93.5	6.53
NB18	N27.85553	W97.50561	09/25/20	8:48	28.6	8.06	25.9	44327	92.5	6.42

Table 2 Nueces Bay surface seawater field physicochemical parameters measured in September 2020.



*Figure 2* Surface water salinity interpolation maps of Nueces Bay during the two field sampling events

### 3.2. Sediment Analysis

### 3.2.1. porosity

The porosity of each sediment sample was calculated via the bulk density method. The average porosity of all samples was  $\bar{x}$ : 0.52 (maximum of 0.77, minimum of 0.21, n=106; Table 3), which is well within the range for unconsolidated sediments from sand to clay (Todd and Mays 2004). Initial distribution analysis indicates that the system is dominated by porosities near 0.52, typical for unconsolidated sediments. These data show relatively porous sediments are abundant and widespread throughout the system.

The most porous sediments were found near the Nueces Bay mouth (adjacent Corpus Christi Bay) and in Rincon Bayou (Figure 3), likely a low flow area where finer grain sediments can settle leading to the higher porosities. This matches what was observed from the grain size analysis. The oyster reefs located on the northern shoreline and Rincon Bayou's mouth likely act as baffles, slowing the water current and allowing larger sediment grains to settle out and only finer, more easily entrained grains to pass. For example, near station NB15, where porosities are lower, larger grains are deposited when water flow is slowed down when it passes over the reefs. On the other hand, in Rincon Bayou, water from the Bay has already passed reefs resulting in only finer grain sediments entrained and carried into the area. Rincon Bayou also receives water

from a diversion from Nueces River, released into the marshland west of the Bay proper, likely also only containing fine grained sediments that deposit into the bayou.

#### 3.2.2. Grain Size Analysis

The grain size analysis showed an average median grain size of 0.7 phi (n=106) with a median grain size between 1 and 0.5 mm in diameter (Table 4.). This is the range of coarse grains, which are as likely to be fragments of a calcareous shell as quartz sand grains. Median grain sizes are the smallest in Rincon Bayou and the eastern half of Nueces Bay (Figure 3). These are also the areas with the greater porosities. Finer unconsolidated particulates are known to have greater porosities, as validated by the porosity results. The southwestern portion of Nueces Bay has the largest median grain sizes due to the abundant shell hash. Shell hash, coming from oyster reefs and fine grain particulates from fine sand to silt and clay, makes up most sediment cores in this area.

Most cores had one predominant median grain size through all of the depths sampled; 16 out of 17 cores sampled had the same median grain size for 50% or more of the sampled depths. Therefore, the cores were mainly homogenous; some were mostly fine sands and silts, some mainly were shell hash. The median grain size for all depths in the core NB15 was a phi of 2 or greater ( $\leq 0.25$  mm), the most homogenous core in grain size. This shows that there are not too many different depositional environments captured to the system's sampled depth (20 cm). If the sediments reflect a poor variability in depositional environments and sediment types (oyster reef and silty-sandy bay bottom), then changes in porewater organic compounds should result from other factors such as local disturbances or variable inputs.



Figure 3 Porosity inverse distance weighted interpolation map by core depth A) 0-2 cm, B) 2-4 cm, C) 4-6 cm, D) 6-8 cm, E) 8-10 cm, F) 10-20 cm, G) 20-30 cm. Warm colors show higher porosities, cool colors lower porosities. The porosity distribution median of 0.52 dominates the maps, showing a typical porosity for unconsolidated sediments ranging from sand to clay. NB 3 omitted as no data was available.



Figure 4 Median grain size (Phi) inverse distance weighted interpolation map by core depth A) 0-2 cm, B) 2-4 cm, C) 4-6 cm, D) 6-8 cm, E) 8-10 cm, F) 10-20 cm, G) 20-30 cm. Warmer colors represent smaller size grains, cooler colors showing larger size grains, ranging from <0.25 mm (red) to >4 mm (blue). Median grain size average ( $\bar{x}$ : 0.7 phi) is between 1-0.5 mm in diameter, typical for coarse sand (n=106). NB 3 omitted as no data was available.

Table 3 Porosity Values by core and by sample depth. Table split into two parts for ease of display. All porosities are unitless and displayed as decimals.

			Core									
	Section	NB1	NB2	NB3	NB4	NB5	NB6	NB7	NB8	NB9	NB10	
	0-2	0.54	0.44		0.63	0.31	0.63	0.36	0.30	0.40	0.48	
	2-4	0.44	0.46		0.64	0.39	0.59	0.76	0.50	0.50	0.61	
	4-6	0.43	0.40		0.63	0.21	0.64	0.75	0.61	0.39	0.62	
orosity y Core	6-8	0.40	0.47		0.51	0.35	0.63	0.58	0.56	0.61	0.57	
ection (cm)	8-10	0.43	0.52		0.77	0.37	0.51	0.59	0.49	0.40	0.45	
(cm)	10-20	0.45	0.47		0.64	0.38	0.51	0.74	0.45	0.48		
	20-30						0.66					
	30-40											

	-		Core										
	Section	NB11	NB12	NB13	NB14	NB15	NB16	NB17	NB18				
	0-2	0.48	0.69	0.56	0.47	0.51	0.58	0.71	0.59				
	2-4	0.45	0.60	0.47	0.33	0.38	0.59	0.57	0.38				
	4-6	0.45	0.61	0.36	0.40	0.57	0.55	0.57	0.56				
orosity y Core	6-8	0.55	0.64	0.44	0.34	0.50	0.68	0.56	0.64				
ection	8-10	0.48	0.56	0.48	0.40	0.47	0.47	0.44	0.39				
(cm)	10-20	0.37	0.50	0.54	0.51	0.46	0.61	0.51	0.47				
	20-30		0.60	0.64			0.65		0.69				
	30-40								0.48				

Table 4 Median grain size presented in phi by core and by sample depth. Table shown in two parts for ease of display. All phi is unitless and displayed as decimals or integers.

	-	Core										
	Section	NB1	NB2	NB3	NB4	NB5	NB6	NB7	NB8	NB9	NB10	
Median Grain	0-2	0.5	2		2	1.5	2	1.5	1.5	-0.5	0.5	
	2-4	0.5	2		1.5	2	1.5	0.5	0.5	-0.5	0.5	
	4-6	2	2		1.5	2	0.5	-0.5	0.5	-0.5	0.5	
ize by ample	6-8	1.5	2		1.5	2	-0.5	-0.5	0.5	0.5	0.5	
epth	8-10	2	1.5		0.5	2	-0.5	-2	0.5	1.5	-0.5	
(cm)	10-20	2	0.5		1.5	2	-0.5	-0.5	-0.5	0.5		
	20-30						-0.5					

		Core											
	Section	NB11	NB12	NB13	NB14	NB15	NB16	NB17	NB18				
	0-2	1.5	1.5	1.5	-2	2	2	2	1.5				
	2-4	-0.5	-0.5	-0.5	0.5	2	2	2	-1.5				
Grain	4-6	0.5	-0.5	-0.5	0.5	2	2	2	0.5				
Size by Sample	6-8	-0.5	-0.5	-0.5	1.5	2	2	2	0.5				
Depth	8-10	-0.5	-0.5	-1.5	-1.5	2	2	2	0.5				
(ст)	10-20	-0.5	-0.5	-0.5	-1.5	2	0.5	2	0.5				
	20-30		-1.5	-1.5			0.5		0.5				

#### **3.3. Petroleum Aromatic Hydrocarbons**

A total of twelve petroleum aromatic hydrocarbons (PAHs) were identified and quantified through the TSQ 9000 Triple Quadrupole GC-MS/MS in full scan and the Skyline program provided by MacCoss Lab Software. The identified PAHs include Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, and Benzo[ghi]perylene. The total PAHs (sum of all the 12 individually identified PAHs) show the highest concertation at NB12 and NB13 with 2653.3 and 2259.5 ng. g<sup>-1</sup> sediment (dried weight), respectively (Table 5, Figure 5). The lowest concertation was 133.6 ng. g<sup>-1</sup> at station NB5. As illustrated in the interpolation map (Figure 5a), the highest total PAHs are concentrated near the Nueces River mouth. The Nueces River may be the source of some of these PAH compounds to the bay. However, according to Murgulet et al., 2016 and Douglas et al. (2020), the Bay experiences low riverine discharge due to hydrologic alterations and average low precipitation. Further investigations upstream into the river could help elucidate this hypothesis. Another consideration of sources could be introducing PAH through active oil and gas wells and pipelines located in Nueces Bay Douglas et al. (2020).

Most of the individual PAHs are concentrated between stations NB6 through NB18, except Benzo[a]anthracene, which had a concentration of 478 ng. g<sup>-1</sup> sediment (dried weight) at station one. Benzo[b]fluoranthene, Benzo[k]fluoranthene, and Benzo[ghi]perylene represent the highest contributions to the total PAHs. On the other hand, Fluoranthene, Benzo[e]pyrene, and Benzo[a]pyrene has the widest distribution in Nueces Bay, present at six or more stations. However, they have lower concentrations compared to the other detected PAHs.

Several studies were able to connect certain calculated ratios between different PAHs to specific group sources. Ratios applied to this dataset include, but are not limited to, Anthracene/(Anthracene+Phenanthrene), Fluoranthene/(Fluoranthene+Pyrene), Phenanthrene/Anthracene, Fluoranthene/Pyrene, and Benzo[a]pyrene/Benzo[ghi]perylene. The ratio Fluoranthene/Pyrene categorizes values below 1 to pyrogenic and values above 1 to petrogenic origin. Stations NB2, NB4, NB5, NB6, NB7, NB8, NB10, NB12, and NB18 have characteristics of pyrogenic PAHs; These can be sourced from a vehicle, shipping combustion, power plant fuels, and coal tar products (Essumang et al., 2011). Stations NB1, NB11, NB13, NB16, and NB17 are more dominated by petrogenic PAHs associated with fossil fuel (i.e., petroleum, coal) (Baumard et al., 1998). The ratio Anthracene/(Anthracene+Phenanthrene) separates PAH findings into either petroleum/petrogenic source or combustion source; all calculated ratios indicate a plausible combustion source (Yunker et al., 2002; Bucheli et al., 2004, Brandli et al., 2007). The ratio Fluoranthene/(Fluoranthene+Pyrene) placed stations NB2, NB5, NB6, NB7, NB8, NB10, NB12, and NB18 into the category petroleum/petrogenic source, and stations NB4, NB13, NB16, and NB17 into the category liquid fossil fuel combustion (i.e., gasoline, diesel, and crude oil). None of the stations had ratios above 0.50, which excludes any grass, wood, or coal combustion source (Yunker et al., 2002; Brandli et al., 2007). All these results indicate a plausible ongoing point source contamination (less than 2 years) rather than historical trapped brine water contamination.

PAH compound	NB1	NB2	NB3	N	<b>B4</b>	Ν	B5	NB6	5	NB7	NB	8
Phenanthrene	$10.3\pm2.9$	$13.9\pm3.0$		25.7	' ± 6.3	15.5	$5\pm0.5$	$40.6\pm7.3$		57.6 ±1 7.	7 17.9 ±	8.5
Anthracene	$6.6\pm3.3$	$2.8\pm0.8$		19.2	±17.0	$2.4\pm1.2$		$15.6 \pm 1.4$		3.5 ± 2.5	22.1 ±	11.0
Fluoranthene	$36.6\pm34.9$	$25.3\pm2.4$		36.0	± 19.9	$7.0\pm0.7$		$29.8 \pm 11.2$		$44.3 \pm 0.5$	$29.9 \pm$	9.6
Pyrene	$1.7\pm1.5$	$60.8\pm 6.2$		43.0	) ± 9.2	38.7	± 17.1	$109.0 \pm$	56.6	94.7 ± 19.	5 130.8 81.	5 ± 2
Benzo[a]anthracene	$478.6\pm501.2$	$38.8\pm 10.4$		59.7	±23.6	22.1	$\pm 9.3$	55.6±	17.9	$212.6\pm23$	5 75.9 $\pm 3$	39.7
Triphenylene	$5.2\pm2.9$	$26.7\pm4.7$		32.7	' ± 9.1	2.6	$\pm 0.6$	$33.4 \pm$	8.7	$63.4 \pm 10.$	8 22.0 ±	4.3
Benzo[b]fluoranthene	$10.4\pm4.2$	$184.4 \pm 109.7$	·	34.0 ± 3		19.5	± 25.8	$56.4\pm0.9$		355.0± 122.3	228.0 ±	= 0.7
Benzo[k]fluoranthene	$4.1\pm0.0$	$72.0\pm52.4$		11.2	$.2 \pm 9.2$ $10.9 \pm 3$		$9 \pm 3.7$ 20.8 ± 6		0.6	$122.9\pm46$	4 76.7 ±	6.1
Benzo[e]pyrene	$4.5\pm2.0$	$10.2\pm0.6$		16.8	$3 \pm 2.7$	2.5	$\pm 0.2$	$28.6 \pm$	8.0	$37.3 \pm 7.5$	$18.7 \pm$	3.1
Benzo(a)pyrene	$3.7\pm1.2$	$10.4\pm2.3$		16.2	$\pm 0.3$	2.0	$\pm 0.1$	$31.0 \pm$	9.8	$40.3 \pm 8.7$	21.6 ±	3.7
Perylene	$2.8\pm0.4$	$10.7\pm1.6$		13.3	$\pm 4.6$	1.3	$\pm 0.3$	$11.6\pm3.9$		$18.1 \pm 4.8$	6.7±0	0.8
Benzo[ghi]perylene	$6.2\pm5.3$	$113.6\pm 66.2$		77.8	± 59.3	9.0	± 5.9	$48.0\pm10.6$		316.5 ± 105.3	170.3 17.	± 2
Total PAHs	570.6	569.7	38		35.4	13	3.6	480.3		1366.1	820.	7
	-				_							
PAH compound	NB10	NB11	NB1	2	NB	NB13		NB16		NB17	NB18	1
Phenanthrene	8.1 ±1.0	$22.2\pm2.1$	$31.8 \pm$	0.4	43.3 =	± 3.8	12.6	$12.6 \pm 4.7$ 26		$0.3 \pm 6.6$	$20.0\pm8$	3.3
Anthracene	$36.8\pm10.2$	$7.3\pm1.8$	$4.1 \pm$	1.4	33.8 ±	16.4	8.8	8.8 ± 7.7 4		$.1 \pm 0.7$	9.7 ± 2.	.5
Fluoranthene	$5.4\pm0.8$	$39.6\pm10.0$	$56.0\pm$	9.4	52.4 ±	15.6	19.0	$\pm 5.3$	34	$4.8 \pm 2.1$	$41.8\pm0$	).0
Pyrene	$41.1\pm9.2$	$31.0\pm12.4$	$73.0\pm$	0.8	63.2 ±	30.6	14.8	± 13.6	40	$0.3 \pm 2.2$	$75.7 \pm 13$	8.2
Benzo[a]anthracene	$314.5\pm33.0$	$47.1\pm10.8$	86.5±3	31.2	96.2 =	± 6.9	130.0	$\pm 69.3$	30	$5.7 \pm 1.5$	71.5 ± 10	0.0
Triphenylene	$14.0\pm1.5$	$37.9\pm 8.7$	$74.8 \ \pm$	12.1	50.3 ±	13.4	18.4	$\pm 3.1$	2:	$5.5 \pm 2.5$	$35.9\pm8$	3.5
Benzo[b]fluoranthene	$29.6 \pm 19.3$	$347.2\pm21.9$	1007.9 ±	419.5	865.0 =	± 72.7	193.5	$\pm 42.2$	130	$0.0 \pm 28.7$	82.4 ± 18	8.7
Benzo[k]fluoranthene	$10.9 \pm 7.3$	$116.5\pm1.2$	$318.1 \pm$	119.1	330.8 =	± 21.2	70.6	± 6.2	40	$0.3 \pm 7.8$	$29.3\pm7$	<i>'</i> .7
Benzo[e]pyrene	$25.7\pm7.6$	$20.6\pm6.7$	$24.7~\pm$	2.8	34.1 ±	12.2	11.3	± 1.4	9	$.7 \pm 0.5$	$13.8 \pm 2$	2.8
Benzo(a)pyrene	$12.4\pm5.0$	$21.6\pm5.2$	27.1 ±	5.9	40.6 ±	: 14.5	12.7	$\pm 0.8$	9.9 ± 1.1		13.1 ± 2	2.2
Perylene	$7.4\pm2.9$	$28.4\pm6.0$	31.7 ±	7.2	15.8 =	± 3.6	6.3	$\pm 1.0$	8	$.1\pm0.3$	50.1 ± 2	2.7
Benzo[ghi]perylene	$24.1 \pm 12.6$	$224.1\pm4.6$	917.7±	444.3	634.0 =	± 38.9	130.2	$\pm 36.2$	$73.2\pm22.8$		47.4 ± 7	.8
Total PAHs	530.1	943.5	2653	3	225	95	62	82		432.9	490.6	

Table 5 Average concertation (ng/g dried sediment) of 12 individual PAH compounds detected in Nueces Bay sediments. The averages value represents the average of three top sediments layers (0-2 cm, 2-4 cm, and 4-6 cm depth) for a core at the specific stations. NB3 omitted as no data was available. Table shown in two parts for ease of display.



Figure 5 Interpolation maps of the average concertation (ng/g dried sediment) of 12 individual PAH compounds detected the total PAHs in Nueces Bay sediments. The averages value represents the average of three top sediments layers (0-2 cm, 2-4 cm, and 4-6 cm depth) for a core at the specific stations.

#### 3.4. Organophosphorus Pesticides and Herbicides (OPs)

Over the two field sampling campaigns, we have extracted dissolved organic compounds from a total of 108 surface water samples (triplicate from 18 stations in two sampling field expeditions) and 168 porewater and nepheloid layer samples (96 in November-December 2019 and 72 in September 2020). Each organic matter extract was analyzed by UPLC-Orbitrap Fusion mass spectrometer (in positive mode) and IC-Orbitrap mass spectrometer (in negative mode). In the 2019 samples, 11,802 organic compounds were detected in both porewater and surface water samples. Out of these, 2,283 were organophosphorus compounds which account for 19% of the total compounds detected. In 2020, 10,872 organic compounds were detected, with organophosphorus compounds accounting for 16% (1745 compounds) of the total compounds detected. It was found that Nuceses Bay has a significantly higher percentage of organophosphorus in these other study systems does not exceed 8% of the total organic compounds detected (e.g., Abdulla et al. 2010, Abdulla et al. 2018).

Conducting a non-target screening (NTS) of 190 known organophosphorus pesticides and herbicides (OPs) using the 5 multi-confidant points (see the method section), we didn't identify any of the 190 known intact organophosphorus pesticides and herbicides. The fate of OPs depends on the biotic and abiotic conditions of the sediment and the water column. OPs degrades much faster than organochlorine insecticides, but their degradation rate depends on sediment composition, microbial communities, and environmental factors such as pH, temperature, and sunlight exposure (Aislabie and Lloyd-Jones, 1995). However, the degradation of the OPs in the aquatic environment is relatively slow compared to that in the soil. Kumar et al. (2018) showed that the half-life of most OPs in the soil is under 100 days, while their half-life in the aquatic environment is several orders of magnitude longer. For example, chlorpyrifos has a half-life of 30.5 days in soil, but its half-life in the aquatic environment is 2118 days. The insecticide parathion has a half-life in soil between 21 to 58 days, but in the aquatic environment, its hydrolysis half-life increases to 302 days.

Organophosphorous pesticides and herbicides don't completely degrade but go through many chemical transformation pathways. The dominant transformation pathways are oxidation, hydrolysis, alkylation, dealkylation (Singh and Walker, 2006). To investigate the potential of detecting the degraded OPs in the Nueces Bay's sediment porewater and surface water, we conduct in-silico 37 different chemical transformations on each of the 190 intact organophosphorus pesticides and herbicides. Then, we conducted a non-target screening for all these transformation products. We were able to identify 1995 organophosphorus compounds that can be a product of chemical transformations of the 190 OPs. We confirmed their structures by comparing their MS/MS fragmentation to the in-silico fragmentation prediction software. The most abundant presence of these altered OPs was found in the sediment porewater at NB16, NB17, NB18, and NB13 in the Rincon Bayou surveyed area (Figure 6). This area is also characterized by finer sediments (e.g., large porosities) with a larger affinity for trapping contaminants and a favorable environment for chemical transformations. Also, given the reduced inflows through the delta, this area is likely not well flushed unless during high precipitation/flow events.



Figure 6 Depth profiles of some altered organophosphorus pesticide and herbicide detected in porewater of Nueces Bay

## 4. Conclusion and Recommendations

Three types of samples (surface water, pore water, and sediment) were processed and analyzed for polycyclic aromatic hydrocarbons (PAHs) and structural elucidation and quantification of organophosphorus compounds (OPs) in Nueces Bay. A total of twelve PAHs were identified, the highest total PAHs concentrations were found to cluster near the Nueces River mouth. Using the Fluoranthene/(Fluoranthene+Pyrene) ratio indicates that origin of these PAHs is of petroleum/petrogenic and liquid fossil fuel combustion (i.e., gasoline, diesel, and crude oil) source. The results highlight a plausible on-going point source (less than 2 years) contamination rather than historical trapped brine water contamination.

It was found that Nueces Bay has a significantly higher percentage of OPs compounds relative to other estuaries and open ocean systems. A non-targeted screening (NTS) of the 190 known organophosphorus pesticides and herbicides showed none of the intact structures were present in the Nueces Bay samples, both surfaces, and porewater. However, 1995 OPs compounds that can be a product of chemical transformations of the 190 OPs were found. The most abundant presence of these altered OPs was found in the sediment porewater in the Rincon Bayou `surveyed area. This area is also characterized by finer sediments (e.g., large porosities) with a larger affinity for trapping contaminants and a favorable environment for chemical transformations. The findings of this study will help guide management decisions and ensure that water quality standards and sediment quality criteria are adequate and appropriate for the living organisms (e.g., oyster reefs) and recreational use of the bay.

Future studies need to identify the primary sources of recent crude oil leaks to the Bay; whether these PAHs contamination leaks from the oil pipes, oil tankers, or transport through the Nueces River. In addition, new studies need to investigate the effect of the PAHs and other contaminants on the Bay ecosystem before any restoration (e.g., restore the oyster reefs).

Final remark: We have faced some issues in our building facility (the down of the fume hood system and the breakdown of the Serigraph x-ray instrument). Because of that, this report only includes one year of analysis of both Petroleum Aromatic Hydrocarbons (PAHs) and grain size analysis of the sediments. However, we are committed to finish these analyses for the 2<sup>nd</sup> year of sampling as they are also part of a student's master thesis, and we will submit the complete unofficial report to CBBEP by fall 2021.

## 5. Literature Cited

- Abdulla, H.A., Burdige, D.J. and Komada, T., 2018. Accumulation of deaminated peptides in anoxic sediments of Santa Barbara Basin. Geochimica et Cosmochimica Acta, 223, pp.245-258.
- Abdulla, H.A., Sleighter, R.L. and Hatcher, P.G., 2013. Two dimensional correlation analysis of Fourier transform ion cyclotron resonance mass spectra of dissolved organic matter: A new graphical analysis of trends. Analytical chemistry, 85(8), pp.3895-3902.
- Ahmadum, F., A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S., Abidin, Z.Z., 2009. Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials, 170(2), pp.530-551.
- Aislabie J, Lloyd-Jones G. 1995. A review of bacterial-degradation of pesticides. Aust J Soil Res. (33): 925–942.
- Aktar M W, Sengupta D, Chowdhury A. 2009. Impact of pesticides use in agriculture: Their benefits and hazards. Interdiscip Toxicol. (2): 1–12.
- Alperin M. J., Martens C. S., Albert D. B., Suayah I. B., Benninger L. K., Blair N. E., Jahnke R. A., 1999. Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope. Geochim. Cosmochim. Acta 63, 427–448.
- Avnimelech, Y., Ritvo, G., Meijer, L. E., Kochba, M. 2001. Water content, organic carbon and dry bulk density in flooded sediments. Aquacultural Engineering, 25(1), 25-33.
- Baumard, P.; Budzinski, H.; Michon, Q.; Garrigues, P.; Burgeot, T.; Bellocq, J. Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. Estuar. Coast. Shelf Sci. 1998, 47, 77–90.
- Bcesch, D. F., Rabalais N. N., 1989. Produced Waters in Sensitive Coastal Habitats : An Analysis of Impacts, Central Coastal Gulf of Mexico. OCS Report/MMS 89-0031, U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, Louisiana, 157 pp.
- Brandli R.C., Bucheli T.D., Kupper T., Mayer J., Stadelmann F.X., Tarradellas J. Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants. Environ. Pollut. 2007, 148:520–528.
- Bucheli, T.D.; Blum, F.; Desaules, A.; Gustafsson, Ö. Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. Chemosphere. 2004, 56, 1061– 1076.
- Burgos, W.D., Castillo-Meza, L., Tasker, T.L., Geeza, T.J., Drohan, P.J., Liu, X., Landis, J.D., Blotevogel, J., McLaughlin, M., Borch, T., Warner, N.R., 2017. Watershed-Scale Impacts from Surface Water Disposal of Oil and Gas Wastewater in Western Pennsylvania. Environmental Science & Technology, 51(15), pp.8851-8860.
- Dal Ferro, B., Smith, M., 2007. Global onshore and offshore water production. Oil and Gas Review, OTC edition.

- Cao, D., Guo, J., Wang, Y., Li, Z., Liang, K., Corcoran, M.B., Hosseini, S., Bonina, S.M., Rockne, K.J., Sturchio, N.C., Giesy, J.P., 2017. Organophosphate esters in sediment of the Great Lakes. Environmental Science & Technology, 51(3), pp.1441-1449.
- Caudle, C.S., 1993. An impact assessment of produced water discharges to Nueces Bay. Texas Natural Resources Conservation Commission, Austin, Texas. Publication no. AS-49/SR. 30 pp.
- DeLaune, R.D., C.W. Lindau, and R.P. Gambrell, eds. 1999. Effect of Produced-Water Discharge on Bottom Sediment Chemistry. U.S. Dept. of the Interior, Minerals
- Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS
- 99-0060. 47 pp.
- Dittmar, T., Koch, B., Hertkorn, N., Kattner, G., 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnology and Oceanography: Methods 6, 230-235.
- Douglas, A. R., D. Murgulet & R. N. Peterson, 2020. Submarine groundwater discharge in an anthropogenically disturbed, semi-arid estuary. J Hydrol 580:124369.
- D'Unger, C., D. Chapman & R. S. Carr, 1996. Discharge of oilfield-produced water in Nueces Bay, Texas: A case study. Environ Manage 20(1):143-150.
- Fetzner S. 2002. Biodegradation of xenobiotics. In Doelle H W, Rokem S, Berovic M (eds.) Biotechnology. Volume 10. Encyclopedia of Life Support Systems (EOLSS). EOLSS Publishers Co. Ltd., Oxford. pp. 215–246.
- Fillo, J.P., Evans, J.M., 1990. Characterization and management of produced waters from underground natural gas storage reservoirs. American Gas Association Operation Section Proceedings, 448459
- Gardner, W.D., Gundersen, J.S., Richardson, M.J., Walsh, I.D., 1999. The role of seasonal and diel changes in mixed-layer depth on carbon and chlorophyll distributions in the Arabian Sea. Deep Sea Research Part II: Topical Studies in Oceanography, 46(8), pp.1833-1858
- Grube A, Donaldson D, Kiely T, Wu L. 2011. Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates. Office of Pesticide Programs, Office of Chemical Safety and Pollution Prevention, U.S. Environmental Protection Agency, Washington, D.C.
- Gunnars, A. and Blomqvist, S., 1997. Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions an experimental comparison of freshwater and brackish-marine systems. Biogeochemistry, 37(3), pp.203-226.
- Gunnars, A., Blomqvist, S., Johansson, P. and Andersson, C., 2002. Formation of Fe (III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. Geochimica et Cosmochimica Acta, 66(5), pp.745-758.
- Herndon, E. M.; Kinsman-Costello, L.; Duroe, K. A.; Mills, J.; Kane, E. S.; Sebestyen, S. D.; Thompson, A. A.; Wullschleger, S. D. Iron (Oxyhydr)Oxides Serve as Phosphate Traps in Tundra and Boreal Peat Soils. Journal of Geophysical Research: Biogeosciences 2019, 124 (2), 227–246.

- Herndon, E.; Kinsman-Costello, L.; Domenico, N. D.; Duroe, K.; Barczok, M.; Smith, C.; Wullschleger, S. D. Iron and Iron-Bound Phosphate Accumulate in Surface Soils of Ice-Wedge Polygons in Arctic Tundra. Environ. Sci.: Processes Impacts 2020, 22 (7), 1475– 1490.
- Hupfer, M. and Lewandowski, J., 2008. Oxygen Controls the Phosphorus Release from Lake Sediments–a Long-Lasting Paradigm in Limnology. International Review of Hydrobiology, 93(4-5), pp.415-432.
- Klute, A. 1986. Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods. Madison, WI: Soil Science Society of America, American Society of Agronomy.
- Kumar S., Kaushik G., Dar M. A., Nimesh S., Lopez-Chukenu I. J., Villarreal-Chui J. F. 2018. Microbial degradation of organophosphates pesticides: A review. Pedosphere. 28(2): 1-20.
- Liebow, E.B., Butler, K.S., Plaut, T.R., Arnold, V.L., Ford, G.H., 1980. Texas barrier islands region ecological characterization: A socioeconomic study. Volume 1: Synthesis Papers (No. FWS/OBS-80/19).
- Longley, W. L., G. L. Powell, A. W. Green & T. W. D. Board, 1994. Freshwater inflows to Texas bays and estuaries: ecological relationships and methods for determination of needs. Texas Water Development Board, Austin, TX.
- Murgulet, Dorina, et al. "Impact of hydrological alterations on river-groundwater exchange and water quality in a semi-arid area: Nueces River, Texas." Science of the Total Environment 572 (2016): 595-607.
- Mullard, G., Allwood, J.W., Weber, R., Brown, M., Begley, P., Hollywood, K.A., Jones, M., Unwin, R.D., Bishop, P.N., Cooper, G.J., Dunn, W.B., 2015. A new strategy for MS/MS data acquisition applying multiple data dependent experiments on Orbitrap mass spectrometers in non-targeted metabolomic applications. Metabolomics, 11(5),1068-1080.
- Ockerman, D. J., 2001. Water Budget for the Nueces Estuary, Texas, May-October 1998. U.S. Geological Survey.
- Palmer, T.A., Uehling, P., Pollack, J.B., 2015. Using oyster tissue toxicity as an indicator of disturbed environments. International Journal of Environmental Science and Technology, 12(6), pp.2111-2116.
- Railroad Commission of Texas. 1993. Permit to dispose of non-hazardous oil and gas waste by injection into a porous formation not productive of oil and gas. Permit No. 09802. Oil and Gas Division, Railroad Commission of Texas, Austin, Texas.
- Ramirez Jr, P., 2002. Oil field produced water discharges into wetlands in Wyoming. U.S. Fish and Wildlife Service. Contaminant Report Number: R6/718C /02.
- Rattner, B.A., Capizzi, J.L., King, K.A., LeCaptain, L.J., Melancon, M.J., 1995. Exposure and effects of oilfield brine discharges on western sandpipers (Calidris mauri) in Nueces Bay, Texas. Bulletin of environmental contamination and toxicology, 54(5), pp.683-689.
- Seeberg-Elverfeldt J., Schlüter M., Feseker T., Kölling M., 2005. Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. Limnol. Oceanogr. Methods 3, 361– 371.

- Shafer, G. H., 1968. Ground-water Resouces of Nueces and San Patricio Counties, Texas. U.S. Geological Survey.
- Singh B K, Walker A. 2006. Microbial degradation of organophosphorus compounds. FEMS Microbiol Rev. (30): 428-471.
- Somerville, H.J., Bennett, D., Davenport, J.N., Holt, M.S., Lynes, A., Mahieu, A., McCourt, B., Parker, J.G., Stephenson, R.R., Watkinson, R.J., Wilkinson, T.G., 1987. Environmental effect of produced water from North Sea oil operations. Marine Pollution Bulletin, 18(10), pp.549-558.
- Stromgren, T., Sorstrom, S. E., Schou, L., Kaarstad, I., Aunaas, T., Brakstad, O. G., Johansen, O. (1995) Acute Toxic E ects of Produced Water in Relation to Chemical composition and Disper- sion. Marine Environmental Research 40.
- TDWR (Texas Department of Water Resources), 1981. Nueces and Mission-Aransas Estuaries: A Study of the Influence of Freshwater Inflows.
- Todd, D. K. & L. W. Mays, 2004. Groundwater hydrology. John Wiley & Sons.
- Tolosa, I., De Mora, S.J., Fowler, S.W., Villeneuve, J.P., Bartocci, J. and Cattini, C., 2005. Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman. Marine pollution bulletin, 50(12), pp.1619-1633.
- Urumovic, K. 2016. The referential grain size and effective porosity in the Kozeny-Carman model. Hydrology and Earth System Sciences 20: 1669-1680.
- Welschmeyer, N.A. 1994. Fluorometric Analysis of Chlorophyll-a in the Presence of Chlorophyll-B and Pheopigments. Limnology and Oceanography 39: 1985-1992.
- Yunker, M.B.; Macdonald, R.W.; Vingarzan, R.; Mitchell, R.H.; Goyette, D.; Sylvestre, S. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Organ. Geochem. 2002, 33, 489–515.