ANALYSIS AND QUANTIFICATION OF THE CONTENT OF

MICROPLASTICS IN GALVESTON BAY

An Undergraduate Research Scholars Thesis

by

BRIANNE WHARTON

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Dr. Karl Kaiser

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ABSTRACT

Analysis and Quantification of Microplastics in Galveston Bay

Brianne Wharton Department of Marine and Coastal Environmental Sciences Texas A&M University

Research Faculty Advisor: Dr. Karl Kaiser Department of Marine and Coastal Environmental Sciences Texas A&M University

Plastics and their consequent microplastics have become omnipresent throughout the globe. Microplastic pollution has been observed in the marine environment, by direct observation and by analyses of organisms. The microplastics in the ocean and their chemical composition must be analyzed in order to determine the current health of the ocean and its inhabitants. Eight sites were sampled in Galveston Bay to analyze the microplastic content of the samples. FT-IR was performed on each microplastic found in a given sample. The IR spectra was then compared to a database to determine the chemical composition of the microplastics. The microplastics most frequently found in the samples were polypropylene and polyethylene.

DEDICATION

To my friends, families, instructors, and peers who supported me throughout the research

process. Thank you.

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Contributors

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The data and materials analyzed/used for Microplastics in Galveston Bay were provided by Dr. Kaiser, Laura Leonard, and the MCES department. The analyses depicted in Microplastics in Galveston Bay were conducted in part by the MCES department at Texas A&M University at Galveston and were unpublished.

All other work conducted for the thesis was completed by the student independently.

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NOMENCLATURE

PP	Polypropylene
PE	Polyethylene
MP's	Microplastics
CTD	Conductivity, Temperature, Depth Instrument
FT-IR	Fourier-transformed Infrared Spectroscopy

1. INTRODUCTION

1.1 Present Plastic Production and Microplastics

Plastic first began being mass produced in the early 20th century, and have only increased in production and prominence since then (Hidalgo-Ruz et al., 2012). As of 2017, plastics were produced of about 300 million metric tons annually (Andrady.). Plastics are synthetically produced by the polymerization of small molecules, usually consisting of carbon, sulfur, nitrogen, oxygen (Wayman and Niemann, 2020). They are long-chained, have a high molar mass, and are generally hydrocarbon based. The synthetic deriving of these materials is from fossil fuel feedstocks (Law, 2017).

Plastic proved to be a cheap and durable material to be used in any industry (Peters et al., 2017). They, by their extensive material abilities, including durability, thickness, insulation, have allowed for an assortment of uses. This results in them being used as fibers, films, adhesives, or foams. Today, their main use is as packaging materials, with up to 35% of plastics being used as such – these are produced specifically for disposal (Law, 2017). This is especially useful in maintaining safety and health standards in preventing the spread of germs, viruses, or diseases in a controlled environment. Despite allowing for technological advancement in an affordable matter, these have become so omnipresent that it has developed into a global problem. The problem largely lies in the fact that plastics are not readily biodegradable and will persist within the environment for many years, and that plastics are lightweight and can be transported easily into bodies of water and sediments (Law, 2017). Some of these transport methods include wind or water, which requires no human intervention, yet is initiated by humans consistently and constantly when plastics are polluted. From there, river flows, ocean currents, wave action, or

wind circulation will distribute and degrade the plastics, spreading them everywhere (Windsor et al., 2018). This problem is further exacerbated by the sheer volume of plastics being produced worldwide, most of which are only produced with intent to be disposed. Up to 79% of plastics made so far have been disposed of into landfills already (Windsor et al., 2018).

The first notice of plastic litter being found in the ocean was in the 1970's (Andrady, 2011). The topic drew little concern until recently, when more studies were performed upon the obvious exponential increase of plastic usage and litter. Any plastic litter in the ocean is called "marine debris", which comprises of any manmade solid material that has been disposed of in the ocean. To date, plastics are the prominent marine debris material found in surface waters of the ocean (Law, 2017).

Microplastics are derived from plastic materials and are essentially just smaller pieces of these larger plastics if not initially a small plastic. They are the result of the degradation of plastics from natural occurrences such as UV radiation, water currents, and abrasion (Frias & Nash, 2019). They are considered to be plastic materials less than 5 mm in size (Arthur et al., 2009). These abrasive materials have accumulated throughout the sediments and different zones of the ocean (Thompson et al., 2004). These are a fairly new concern that still pose a great threat to the health of the ocean.

We can distinguish microplastics into two types, primary and secondary. Primary microplastics are produced with intent to be small, and enter the marine environment directly through runoff (Andrady, 2011). They are the plastics in raw form, such as microbeads and plastic pellets (Arthur et al., 2009). Secondary microplastics are degraded through biological, mechanical, and photo degradation into their smaller form from macroplastics or mesoplastics (Thompson, et al). The different types of microplastics consist of fragments, pellets, and fibres

(Frias & Nash, 2018). The chemical composition of these materials varies, with the most common chemical compositions being polyethylene and polypropylene.

1.2 Size Distribution of Plastics

Microplastics are considered plastics less than 5 mm in size. Any plastics above this size are considered macroplastics and can eventually be degraded into microplastics. Another category of plastics is nanoplastics. These are plastic particles less than 1 micrometer in size (Wayman & Niemann, 2020).

1.3 Where Microplastics Came From

Why are microplastics present in our environment? Microplastics have a variety of household uses that we do not recognize because they are impossible to see. Two expels of microplastics are from the washing of our clothes and the wear down of car tires (Dauvergne, 2018). An example of microplastics used every day are the fibers expelled from our clothing when we wash our clothes. Microbeads are a component of many beauty care products. They are also a format in which we consume pharmaceuticals, then passing through our systems and to the wastewater. Microplastics also lie as fibers in processes in which machinery and vessels are cleaned. The prominence of latent primary microplastics allows them to accumulate without us noticing. They pass through our wastewater systems and come back into our drinking water or the marine environment.

Poor wastewater management is one of the processes resulting in the amount of microplastics in the ocean. Another source is the degraded secondary microplastics that come into existence by the degrading of paints or other plastics. A large source of plastics in the environment is fishing gear and material that ended up in the ocean.

1.4 Types of Microplastics: Nurdles, fishing waste

Nurdles are one form of microplastic produced commercially, spherical plastic resin pellets. These are high density polyethylene particles developing from large scale plastic products, and are used in packaging. They can become marine debris by spills in transportation, packaging, production. Nurdles are most often composed of polyethylene (Figure 1), polypropylene (Figure 2), polystyrene, polyvinyldienefluoride, polycarbonate, or polyoxymethylene. These are particularly dangerous compounds because they serve as vectors for chemical pollutants. They absorb and transport dangerous hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs), and persistent organic pollutants (POPs). Some POPs include polybrominated diethyl ethers and polychlorinated biphenyls (Pozo et al., 2020). The previously discussed inherent risks of nurdles are compounded when we take into account their resistance to natural biodegradation when placed in the environment. They refuse to degrade when any biological, chemical, or photolytic processes occur (Pozo et al., 2020).



Figure 1. Structure of polyethylene.



Figure 2. Structure of polypropylene.

Commercial fishing results in a huge amount of marine debris being distributed into the ocean, including plastics. This is direct disposal of anthropogenic material. Fishing events release macroplastics such as plastic sheeting, netting, or fishing line to be degraded into microplastics. Fishing line is often made out of polyvinyldienefluoride, nylon, or polyethylene. These serve as a risk as they can get caught in the digestive tract of marine life such as fish (Wabnitz & Nichols., 2010).

1.4 Importance of Effects of Microplastics on the Marine Environment

Microplastic bring great risk to marine life and their home as marine life have been ingesting microplastics over the last few years. This is extremely dangerous to wildlife because microplastics absorb persistent bioaccumulative and toxic compounds which transfer to the organisms upon consumption. These toxic compounds contain persistent organic pollutants and metals (Hidalgo-Ruz et al., 2012). Fish in Galveston Bay have been observed to be ingesting high frequencies of these microplastics. In 2017, a study of fish in Galveston Bay revealed that of 1381 fish that were sampled, 42.2 percent had ingested a form of microplastics (Peters et al., 2017). The fish had ingested primarily fibers, then microbeads, then fragment types (Peters et al., 2017).

Based on the consistent and constant reveal of microplastics in the marine environment and inside of marine life, it is important to quantify the amount and type of microplastics truly in the ocean ecosystem at present. The most common chemicals found in microplastics as of 2012 were polyethylene, polypropylene, and polystyrene (Hidalgo-Ruz et al., 2012). Galveston Bay hosts a plethora of marine organisms and is surrounded by humans and their prevalent anthropogenic effects. Therefore, it serves as a perfect representation of a coastal environment heavily effected by plastic pollution. It is important that we determine the microplastics present throughout Galveston Bay, and several sites were sampled throughout the Bay. These sites were

Texas City, San Leon, South of Island, Midpoint, Morgan's Point, Upper San Jacinto Bay, Confluence SJR and BB, and Monument. These sites follow inputs to Galveston Bay and grow closer to the ocean output itself.

1.5 Importance of Effects of Microplastics on the Human Population

Microplastics are known to have harmful effects on humans as they do not belong in the body. In recent years, potential particle and chemical toxicity effects have been studied. Some plastics, such as polystyrene and polycarbonate, are considered endocrine disrupting materials. Humans are exposed to these EDC's by ingestion, inhalation, or even just physical contact with the chemical. Even reproductive problems are suspected of developing by exposure to these plastic particles (Rist et al., 2018).

Microplastics are exposed to humans in a variety of ways. This includes drinking or tap water, bottled water, seafood, products such as salt, honey, beer, or sugar. Not only is the human population exposed to microplastics by direct contact between the products consumed and the plastics, but by our clothing and items as well (Rist et al., 2018).

The main pathway of which microplastics end up in the body is by endocytosis. Whether or not the ingested plastic ends up in organs depends on qualities of the plastic such as surface charge, hydrophobicity, and especially particle size. Smaller plastics (<2um) will end up in the bloodstream or organs, while larger microplastics (2um-5mm) primarily end up in the gut. However, plastics with range up to 50 um will end up in the liver and spleen, where the body will take an inflammatory response - possibly activating cytokines and macrophages (Rist et al., 2018).

Microplastics are also inhaled, that is, they circulate in the air and atmosphere. Densities of over 700,000 plastics per meter cubed flow through the air in textile making workplaces.

Synthetic materials being used on a daily basis result in the particles being everywhere, including in the air, where we breathe them in. Storage and packaging materials also significantly contribute to the free-floating plastics in air (Rist et al., 2018).

1.6 Potential Inputs to the Bay

The inputs of anthropogenic plastics to the bay must be determined so that we can improve upon current methods of pollution reduction. Over 50% of earth's population resides less than 40 kilometers away from the coast (Small and Cohen, 2004). The bay receives river runoff from the San Jacinto River and Buffalo Bayou. This could be amplifying the sources of plastic found in water samples in the Bay because rivers are considered a hotspot for plastic waste with some of the highest concentrations of plastics found there. The river is essentially the connect between any terrestrial, benthic, riparian, transitional, or floodplain environments that are then connected to the bay and ocean (Windsor et al., 2018).

A major input of plastics to the Bay to be considered is the Houston Ship Channel's pollution. As seen in Figure 3, the sample sites involved in the project directly interfere with the Houston ship channel. There are terrestrial environments throughout the sampling area as well, with these being sources of plastic input to the bay. Other prominent anthropogenic inputs to the bay would consist of nurdles, fishing line, water bottles.

The global plastic industry rakes in over \$600 billion annually as of 2018 (Dauvergne.). Most of these are manufactured with intent to be disposed of, eventually ending in landfills or the environment. The ocean is the endpoint of most of these plastics, and we must determine the quantity of them in the marine environment.

2. METHODS

2.1 Sample Collection

Microplastics were collected with a 200 μ m neuston net (d = 50 cm) on two separate cruises on the R/V Trident in Galveston Bay. Six sites were selected along a salinity gradient in 2021, and four sites were selected in 2021. Water samples were grabbed at each station at the surface level water by the macro troll, 200 μ m net, and the sample grab (0-0.5 cm). The samples from the sample grab were stored in polypropylene jars with caps.

Sample sites along with date taken, location coordinates, and description can be found in tables 1 and 2. Sample sites as mapped can be found in Figure 3. After successful collection of the microplastic samples, the samples in their polypropylene jars were stored in the freezer at 4°C in an insulated container. They were removed when ready for FTIR analysis.

Station #	Latitude	Longitude	Description
1	29.368847	-94.805272	Texas City
2	29.494558	-94.867653	San Leon
3	29.561219	-94.919819	South of Island
4	29.629042	-94.960381	Midpoint
5	29.675961	-94.979092	Morgan's Point
6			Confluence SJR and
	29.749992	-95.064197	BB

Table 1. Sample sites as collected on 02/28/20.

Table 2. Sample sites as collected on 02/05/21.

Station #	Latitude	Longitude	Description
7	29.36212	-94.81083	Texas City
8	29.56773	-94.9239833	South of Island
9	29.6738	-94.9801167	
			Morgan's Point
10	29.7290833	-95.0271167	Upper San Jacinto Bay

2.2 Chemical Characterization of Collected Microplastics

The sites sampled along the bay in two different microplastic trawls consisted of several areas down the bay that can be described by their nearby geographical landmarks and their coordinates.



Figure 3. The sample sites in Galveston Bay as mapped and labelled.

The sample sites used for water sampling go from near the output of the bay to the inputs of the bay such as from buffalo bayou and the San Jacinto river, as seen and labelled in Tables 1-

2, Figure 3.

After samples had been taken and stored appropriately, they were removed from storage at 4deg C to determine the type of microplastics in samples.

For each water sample, the microplastics were picked out of the sample using metal tweezers. They were placed on an Ahlstrom Quantitative Filter Paper by station number (Figures 2-11). They were allowed to dry before the spectra was taken. The microplastics found were then counted (Table 3) and analyzed with an Agilent Technologies Cary 630 FTIR. Each microplastic FTIR spectra, the data was saved as an .spc file and a .txt file to be read and analyzed.

After analysis and FT-IR data of the plastics were taken, they were weighed and the mass per site was recorded (Table 3).

The recorded FTIR spectra were compared to library spectra of pure plastics using a an in-house python code.



Figure 2. The microplastics found in Station 1 from sample taken 2/28/20.



Figure 3. The microplastics found in Station 2 from sample taken 2/28/20.



Figure 5. The microplastics found in Station 2 from sample taken 2/28/20.



Figure 4. The microplastics found in Station 4 from sample taken 2/28/20.



Figure The microplastics found in Station 6 from sample taken 2/28/20.



Figure 7. The microplastics found in Station 6 from sample taken 2/28/20.





Figure 8. The microplastics found in Station 1 from sample taken 2/5/21.

Figure 9. The microplastics found in Station 2 from sample taken 2/5/21.



Figure 10. The microplastics found in Station 3 from sample taken 2/5/21.



Figure 11. The microplastics found in Station 4 from sample taken 2/5/21.

Each spectra reading from the FT-IR was saved as a .spc file. It was opened through JupyterLab using Anaconda's software. Each recorded IR file was read against a variety of plastic IR's or other organic material's IR to determine the identity of each item picked out of water. After thorough comparison, the plastic was labelled for analysis.



Figure 6. The spectra comparison of the unknown plastic against a known plastics spectra.

3. **RESULTS**

3.1 Volume of Flow Determination

Volume flow through net was determined by speed of the boat recorded during sampling, the diameter of net which was used to sample with, and the time for which the sample was taken. This was then used in conjunction with mass of plastics and counts of plastics. The sample calculation is as follows:

Water sampling site 9:

$$3 \ knots \times \frac{1 \ m \ s^{-1}}{1.9 \ knots} = 1.579 \ m \ s^{-1}$$

 $1.579 \text{ ms}^{-1} \times 300s = 473.68 = 473.7 \text{ m flowed through net}$

$$Volume = h\pi r^{2} = \left(\frac{2}{3} \times 473.7 \, m\right) \pi (.25m)^{2} = 62 \, m^{3} = 62005 \, L$$
$$Volume = 62005 \, L$$

$$\frac{mass \ plastics}{Volume} = \frac{.097g}{62005L} = 1.56439 \times 10^{-6} \ g \ L^{-1}$$
$$\frac{\# \ plastics}{2005L} = \frac{.097g}{.00014515} \ count \ L^{-1}$$

$$\frac{\# plastics}{Volume} = \frac{9}{62005L} = 0.00014515 \text{ count } L^{-}$$

The remaining calculations were done for the rest of the sample sites.

3.2 Microplastics found in marine environment

Identified microplastics were primarily polypropylene and polyethylene in the samples of Galveston Bay.

Site one in 2020 revealed light-colored and dark black polyethylene material from around the Texas City Dike. These are likely outputs from the nearby Texas City plants, where people are disposing of packaging plastics, and tire shreds are released.

Site two revealed light polyethylene nurdles and other material near San Leon. Site three revealed dark polyethylene and polypropylene near the South of Island. Site four revealed light and dark polyethylene and polypropylene near Midpoint.

Site five showed a lot of polyethylene and polypropylene of varying color, including fishing line. Some of the lighter colored microplastics were likely derived from candy wrapper bars, water bottles.

Site six showed a variety of polyethylene and polypropylene around the Monument area. Some of these inputs would be plastic straws and water bottles.

Site seven showed light polyethylene near the Texas City dike. This could be any standard plastic such as product wrappings or water bottles.

Site eight showed a variety of polyethylene and polypropylene around the south of island in 2021, as the site had showed near south of island in 2020 at site 3. Many light-colored plastics were observed in both years, however, there was less dark plastics present during 2021 sampling.

Site nine showed darker polyethylene and polypropylene around Morgan's Point – this was likely the same material observed at Morgan's Point in 2020 at site 5.

Site ten showed polyethylene only in sample. An issue with identification is small size of particles, causing difficulty in reading the particles in the FT-IR. Other lack of plastic material

could have been due to filtering in the sample, or improvement in pollution policies between 2020 and 2021.

Samples five and six showed the most plastics. This is likely because the sample was taken closer to land, and the sources of anthropogenic pollution were likely greater in these areas – Morgan's Point and Upper San Jacinto Bay, respectively. A lot of dark polypropylene material was found in these sites. There were also other points of plastic, such as nurdles and fishing line. Other plastics of different colors were observed, such as of bright green or bright blue colors, even clear plastics that may have come from a water bottle.

Sites two, three, and four also displayed nurdles of beige or clear color. These were all composed of either polyethylene or polypropylene.

Date	Site	у-	Volume	Mass of plastics in	Mass/L (µg L ⁻¹)	#	# plastics per
taken		angle	Flow	sample (µg)		plastics	volume (count
			through			in	L-1)
			net (L)			sample	
2/28/20	Station	11	31002 L				
	1			106000	3.41913425	6	0.000193536
2/28/20	Station	11	225.765				
	2			162000	143.154227	7	0.006185676
2/28/20	Station	11	252.165				
	3			141000	308.401663	8	0.017497967
2/28/20	Station	11	272.080				
	4			139000	403.028738	11	0.031894361
2/28/20	Station	11	29354.3				
	5			125000	336.201558	23	0.061861087
2/28/20	Station	11	327668				
	6			220000	372.329898	16	0.027078538
2/5/21	Station	-	31002 L				
	7			25000	0.80639959	2	6.4512E-05
2/5/21	Station	-	41364 L				
	8			87000	2.10327821	7	0.000169229
2/5/21	Station	-	62005 L				
	9			97000	1.56438997	13	0.000209661
2/5/21	Station	-	20681				
	10			88000	4.25511339	4	0.000193414
Total	-	-	-	-	-	97	-

Table 3. Content of water sample plastics per site.

More plastics were found in the original data sampling that took place on February 28 2020 than were found in the data sampling taking place on February 5 2021. This could be due to smaller sampling volumes in the sampling for sites taken in 2021. The water in 2021 sample sites likely had more mixing in samples due to choppier waters.



Figure 7: Contents of the water samples as determined by IR spectra of plastics.

The analysis and spectra of microplastics at various water sampling sites throughout Galveston Bay revealed polyethylene and polypropylene materials.

As seen in Figure 7, it was determined that the primary solid constituent of the water samples at ten sampling sites were polyethylene and polypropylene. Other constituents of the water subject to FT-IR analysis were chitin, likely from crustacean shells, algae, and cellulose.



Figure 8. The mass of plastics found in sample with respect to volume flow through net in sampling process.



Figure 10. The plastic count found in sample with respect to volume flow through net in sampling process.

As seen in Figures 9 and 10, the greatest mass and plastic count with respect to the flow during sampling was in sample sites 2-6. These sites were all in the first trawl and near anthropogenic sources. As seen in the mapping of sites (Figure 3), we see that these sources are near land where they receive land sources of marine debris. Some of these include fishing line, packaging plastic, as we can see in Figures 3-7 showing plastics in sample.

Galveston Bay Microplastic Contamination in comparison to other US Estuaries 35 30.8 30 25 # plastics per Liter 20 15 10 6.6 5 1.24 0.015 0.01 0 Galveston Bay SC- Winyah Bay SC - Charleston NJ - Raritan **Delaware Bay** Harbor

3.3 **Comparison of Galveston Bay to other United States Estuaries**

Figure 10. The average microplastic content in Galveston bay in comparison to other estuaries.

When we look at microplastic content in other estuaries, Galveston is comparable to the Raritan Hudson Estuary in New Jersey and Delaware Bay. Estuaries in South Carolina range from 3-88 plastics per Liter, with average 30.8 through surface waters in Winyah Bay; in Charleston Harbor the average was 6.6. Surface waters in Raritan Hudson Estuary averaged 0.01 particles/L. Galveston Bay is considered contaminated with current levels of microplastic pollution however, more studies need to be done on Microplastic content in the ocean as it is a relatively new issue that needs more research done. Significant differences in microplastic counts per Liter can be attributed to methods used in studies, sampling sites such as open water versus direct source sampling, or mass not being considered in this value.

US Estuary

Hudson Estuary

4. CONCLUSION

4.1 Conclusion

The quantification and qualification of the microplastics present in our marine environment is important because of the effects it is having on our wildlife and our human populations. It is also a determinant of the present health of Galveston Bay. We must determine the state of the Bay's marine environment because it serves as a link between terrestrial and marine life and their respective implications.

The water in Galveston Bay and their microplastic content were determined in ten different sample sites. The microplastic content and chemical determination of these respective microplastics is pertinent in determining the health and present pollution state of Galveston Bay. The samples yielded primarily polypropylene and polyethylene microplastics. These existed in the form of nurdles, fishing lines, and other general plastic materials that we know came from humans.

Inputs of microplastics largely existed due to anthropogenic effects. Galveston Bay contains the Houston Ship Channel, as well as popular sites such as the San Jacinto Monument, Morgan's point. The bay is also popular for fishing, and the Texas City plants are accommodated on the Bay as well.

Assessing the microplastic content of the Bay is essential because it directly determined how much marine debris is being distributed into the marine environment. The synthetic polymer materials, plastics, are coming into the Bay purely by anthropogenic sources. Whether they come into the ocean as macroplastics or not, they eventually degrade into microplastics that wind up everywhere in the ocean, including surface and benthic waters. The microplastics in the marine

environment have become omnipresent, existing in living creatures and throughout the waters themselves, as we have seen at our multiple water sampling sites.

Some of these plastics we find in the bay are particularly dangerous. One of these especially detrimental plastics are nurdles because they can transport and concentrate toxic compounds. Other plastics are, still, even without transporting hazardous compounds, dangerous as well because they do not belong in the body nor environment. The plastics can disrupt normal bodily and system functions in marine life and humans alike. When marine organisms are exposed to plastics, they are at an even heavier risk than people are because they do not know that plastics cannot be eaten. This puts them at an elevated risk prospect of harm because plastics will be found in their digestive tracts, with some organisms even choking on the plastics in water.

The risks involved with the marine debris that is microplastics must be considered when we look at the coastal environment. Microplastics as a contaminant are a risk to humans and marine life alike due to their effects on bodily systems such as digestion and the endocrine system. Plastics have been found disrupting the body systems of humans and marine life such as fish. Therefore, it is pertinent that we do our best to discontinue the depositing of microplastics into the marine environment.

The project of sampling water sites throughout Galveston bay in two microplastic trawl events allowed for the determination of microplastic content in the Bay. The sample sites revealed the plastics that were present in the water. FT-IR spectra as compared to known plastic spectra determined the composition of plastics. These plastics present in the water were primarily polyethylene and polypropylene.

Microplastics as a pollution have many societal, ethical, environmental, and political implications within their existence and how they are managed. We must determine the microplastic content of the bay because it determines the health of the bay and where we stand on pollution at the moment. Analysis and determination of the mass and composition of microplastics in Galveston Bay has revealed the state and frequency of which microplastics are in the marine environment. Analysis revealed that microplastic content was primarily polypropylene and polyethylene, with some of these sources being packaging plastic, nurdles, and fishing line. From here, we can determine ways to improve upon the volume of marine debris being distributed in the marine environment.

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