DISTRIBUTION OF POLYMER TYPES IN MATAGORDA BAY & BIOFILM PRESENCE ON SURFACE OF PLASTIC POLLUTION: A STUDY USING ATTENUATED TOTAL REFLECTANCE-FOURIER TRANSFORM INFRARED SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS

A Thesis

by

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This thesis meets the standards for scope and quality of Texas A&M University-Corpus Christi and is hereby approved.

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Jeremy Conkle, PhD Co-Chair/Committee Member Mark Olson, PhD Committee Member

December 2023

ABSTRACT

Global plastic pollution presents significant environmental and economic challenges, exacerbated by mismanagement and low recycling rates. Studies have shown other pollutants like persistent organic pollutants (POPs) and heavy metals can sorb to plastic debris in aquatic ecosystems, making them more readily dispersed throughout ecosystems. This study (1) quantified the spatial and seasonal distribution of different plastic polymer types along the Matagorda Bay system, and (2) explored the nature of the biofilm form on these plastic debris and any correlation between biofilm type and polymer type throughout different seasons. This comprehensive study, the most extensive of its kind with over 3,000 samples, investigates the distribution of plastic polymers AND biofilm formation in the Matagorda and San Antonio Bays across three seasons in 2022. Attenuated total reflectance-Fourier Transform-Infrared Spectroscopy (ATR-FTIR) along with Principal Component Analysis (PCA) was employed to identify polymer types and investigate biofilm formation on the collected samples. Polyethylene and polypropylene were the predominant polymer types observed across all sites and seasons. PCA suggested that biofilm was prevalent across all polymer types and seasons, and it is made mainly of extracellular polymer substances (EPS) that are rich in carbohydrates and proteins. Spectra integration showed a positive linear relationship between carbohydrate and protein biofilm components. This study not only provides a deeper understanding of biofilm roles in pollutant adsorption, but also introduces a novel, nondestructive approach for examining bacterial biofilms, paving the way for improved environmental management strategies.

DEDICATION

This work is dedicated to anyone who desires to somehow make a difference in this big world, but may think they are too small to do anything of importance. If I can chase the passion, so can you.

To my parents, Darrell and Marsha, thank you for your unwavering support and love. I hope I make you proud. I love you both to the moon and back.

To my incredible friends: Will Richeson, Cecily Kemp, Elizabeth Anderson, Aleece Moerbe, Gina Gainer, Alexis Harborth, and J.C. Lundburg, I would not have survived this experience without you. I love you all more than words. I am eternally grateful for your kindness, patience, love, and support. It truly takes a village.

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1. BACKGROUND

1.1. Introduction

Plastic pollution in the environment has become a prolific, pervasive problem worldwide. There is a vast accumulation of plastic in terrestrial and aquatic environments on every continent. In the United States and several other countries, plastic is classified as solid waste and has minimal regulations for its release into the environment (EPA). Studies have shown that other pollutants classified as hazardous within the ecosystem, such as persistent organic pollutants (POPs), can sorb to plastic waste, both at the micro and macro level, and be more readily dispersed throughout ecosystems.¹⁻³ Additionally, additives introduced during the production of plastic can leach into the environment. These additives include plasticizers such as bisphenols and phthalates, fillers like calcium carbonate, and organic halogenated compounds used as flame retardants.⁴ This interaction between plastic and other pollutants increases the potential for easier transport, bioaccumulation, and biomagnification of hazardous pollutants throughout and within our ecosystems.⁵ This study investigated the relationship and interaction between plastic debris found and the biofilm formation on plastic in the Matagorda Bay system. Attenuated total reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR) was employed to confirm polymer classification. Polymers of interest are polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), polyvinyl acetate (PVA), polyimide (PI), polyurethane (PU), nylon, polycarbonate (PC), neoprene, and polyethylene terephthalate (PET). Because PI, PVA, neoprene, PI, and PC were so few, they were combined and classified as "other". Principal component analysis (PCA) was conducted on FTIR spectra collected to determine if there were any variations or trends between polymer type, sampling site location, or season. Based on variance in functional groups within the spectra, these differences can be used

to assess the leaching and degradation of the plastics and what pollutant is potentially sorbed to these plastics. The information gleaned from this analysis could be used to inform policymakers, stakeholders, and other decision-makers on how best to approach the classification of plastic pollution, and to support the reclassification of plastic waste from solid waste to hazardous waste, helping to reduce and mitigate the release of plastic into the environment.

1.2. A Brief History of Plastic

Plastic is a petrochemical product, made from petroleum sources, such as naphtha, ethane, propane, and butane. Today, it is used in almost every aspect of society: agriculture, construction, healthcare, packaging, and transportation. The material is convenient, inexpensive, lightweight, disposable, durable, and moldable. There are five general shape classifications of plastic waste: fibers, foam, fragments, films, pellets, and four size classifications: macro, pieces greater than 20 millimeters (mm) in diameter, meso, 5-20 mm in diameter, micro, less than 5 mm in diameter, and nano, plastic with a diameter less than 1000 nanometers (nm).¹

Most of the plastic produced is made for single use, and with our current technology, all plastic ever made, unless incinerated, still exists in some form on the planet. Our current waste stream is linear because the product is used and discarded. If the material is not recycled, it is discarded as solid waste, incinerated facilities to generate energy, or buried appropriately. These three disposal methods are in place to minimize the amount of plastic released into the environment. However, as plastic waste has little to no regulation, appropriate management of plastic waste is not a high priority, and the major release of plastic into the environment results from improper human behavior.² A push for a circular economy aims to minimize plastic waste, promote recycling and reuse, and reduce the environmental impact of plastics. In an ideal circular economy, a product at the end of its life would be recycled or reused, if possible, to keep

the product in circulation. Of all global solid municipal waste, which is the current classification of plastic waste, plastic makes up 10% by volume, but composes up to 80% of the debris found on beaches and floating on the ocean surface.² It was calculated that 4,900 million metric tons (MMT) of plastic, or 60% of all plastic produced, was discarded into landfills and the environment since mass production began in the 1950s to 2015.³

The amount of recycled plastic varies depending on factors such as geographic location, infrastructure, and the type of plastic. Though plastic recycling rates also differ between countries and regions, global plastic recycling rates are generally low. According to the United Nations Environment Program (UNEP), only around 9% of the 9 billion tons of plastic waste produced up to September 2021 had been recycled. The majority of plastic waste ends up in landfills, incinerators, or as litter in the environment. However, it's worth noting that efforts to improve plastic recycling rates and reduce plastic waste have been gaining momentum in recent years. Specifically, UNEP is taking strides in uniting countries in discussing global plastic pollution management. Many countries and organizations are implementing measures to promote recycling, such as setting recycling targets, implementing extended producer responsibility programs, and developing better recycling technologies. It is important to continue promoting and expanding recycling initiatives, requiring a certain percentage of recycled content in products, investing in recycling infrastructure, and promoting awareness, education about the importance of recycling, and accessibility to increase plastic recycling rates and reduce the environmental impact of plastic waste. If production, recycling, incineration, and disposal trends continue in the current fashion, an estimated total of 26,000 MMT of plastic will have been produced by 2050 with at least 12,000 MMT ending up in landfills and the environment.³ With such an enormous and sustained global growth in plastic production and use, and so much of it

ending up as litter, there is a great need to consider the behavior of plastic pollution in the environment.

Studies on the interactions between plastic and the environment have shown detrimental effects in numerous ways. World Wildlife Fund's 2018 Living Planet Report discussed that over eight hundred species are negatively impacted by plastic waste, and global biodiversity declined by 60% between 1974 and 2014.⁴ Wildlife such as marine mammals, birds and turtles can become entangled in floating plastic debris like fishing nets six-pack rings, and discarded ropes. This entanglement can hinder movement, and lead to injuries, amputations, suffocation, and death. Additionally, animals often mistake plastic items for food or accidentally consume plastic while feeding⁵. For example, sea turtles may eat plastic bags thinking they are jellyfish, and seabirds often ingest tiny plastic particles, mistaking them for fish or plankton.⁵ Ingestion can cause pseudo satiation and blockages in the digestive system leading to malnutrition, internal injuries, starvation, and death.⁵ Plastics manufactured with chemical additives can potentially leach these chemicals into the environment, especially in aquatic ecosystems. Large accumulations of plastic waste on land and in water bodies can smother and destroy habitats like coral reefs, seagrass beds, and mangrove forests. These habitats provide essential breeding and feeding grounds for numerous species, and their degradation can lead to population decline and biodiversity loss.⁶ A species decline can disrupt predator-prey relationships, upset nutrient cycling, and have cascading effects throughout the food web, compromising ecosystems' overall balance and function.⁷ Currently, many studies are underway investigating the accumulation of microplastics (MP) within fish tissues and the bioaccumulation and biomagnification of MP within different trophic levels.^{5,8–12} These studies have found that MPs are pervasive in the environment, including oceans, freshwater systems, and soil. These tiny particles can be ingested

by a wide range of organisms, from plankton to large marine animals, causing internal damage, reduced feeding efficiency, and potential transfer of sorbed contaminants up the food chain.⁵ With so much plastic produced, low recycling numbers or some plastics not being recyclable, and little to no regulation after disposal, much of the plastic waste ends up in the environment.³ Therefore, studying the transport and fate of plastic pollution throughout ecosystems is paramount, and even more paramount is the efficient identification of sorbed compounds or leached materials from plastic pollution.

1.3. Polymer Types

Plastic is a general term given to a wide range of polymers. There are two groups of polymers in this study: thermoplastics and elastomers. Thermoplastic refers to polymers with the capability to be heated to their melting point and cooled again without losing or changing any chemical properties. Elastomers are polymers that have a high viscosity and elasticity, and can return to their original state after being stretched to great extents. Both thermoplastic and elastomer polymers, which are inexpensive and mass-produced, are often colloquially termed commodity plastic. While many polymers are in production, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS) and polyurethane (PU) make up 92% of all plastics made. ³ Understanding the properties of each polymer type is important for implementing effective production and recycling of goods, and studying how different pollutants interact with each polymer type differently. Polymers of interest are defined below and shown in Table 1.

1.3.1 Polyethylene (PE)

Polyethylene is the most prevalent polymer type found in the environment, even though it is readily recyclable. PE is known for its versatility, durability, and excellent chemical resistance.

It is a long-chain aliphatic hydrocarbon consisting of repeating ethylene monomers (C₂H₄)_n. PE is widely used and found in almost every major industry. There are four common types: ultrahigh molecular weight (UHMW), high-density (HDPE), low-density (LDPE), and linear lowdensity PE (LLDPE). HDPE has a higher density and a more linear structure compared to LDPE. It possesses excellent strength, stiffness, and chemical resistance. HDPE is used in pipes, containers, toys, automotive parts, and industrial products. LDPE has a low density and a highly branched structure. It is flexible, resistant to impact, and has good transparency. LDPE is commonly used in packaging films, plastic bags, squeeze bottles, and various consumer products. LLDPE has a structure that falls between LDPE and HDPE. It has a higher tensile strength, improved puncture resistance, and better heat-sealing properties than LDPE. LLDPE is commonly used in packaging films, gricultural films, and geomembranes.

1.3.2 Polypropylene (PP)

Polypropylene is the second most abundant polymer type found in the environment, and is made of repeating propylene monomers, $(C_3H_6)_n$, and is classified as either homopolymers or copolymers. It is a light but stiff, very durable plastic that is not easily recycled. PP has extensive applications in packaging, automotive, electrical appliances, textiles, medical devices, and various consumer products. It is used in to produce packaging films, bottles, containers, automotive parts, fibers, ropes, non-woven fabrics, and more. It is quite often combined with stabilizers and antioxidants during synthesis.

1.3.3 Polyvinyl chloride (PVC)

PVC is the third most produced polymer type widely used in construction. PVC has various extensive uses in the automotive, electrical, medical, and packaging industries, commonly taking the form of pipes and fittings, window profiles, flooring, cables, medical

tubing, inflatable products, and packaging films. It is comprised of repeating vinyl chloride monomers (C₂H₃Cl)_n, and is regularly produced with additives such as plasticizers, heat stabilizers, fillers, and lubricants. PVC is 100% recyclable.

1.3.4 Polystyrene (PS)

PS is composed of monomers of the aromatic hydrocarbon styrene, $(C_8H_8)_n$, and is solid, foam, or film. It is used in various industries and applications, including packaging, construction, automotive, appliances, and food service. It is commonly used as foamed polystyrene, known as expanded polystyrene (EPS) or Styrofoam, which is lightweight and provides excellent thermal insulation. Polystyrene is also used in solid forms for items such as disposable food containers, packaging materials, toys, and household items. It is important to note that polystyrene is not readily biodegradable or recyclable and can contribute to environmental concerns, especially when not properly managed. Several US states have banned the production and use of PS, as recent studies have found that it is prone to and acts as a potential human carcinogen.19

1.3.5 Polyurethane (PU)

PU is unique among commodity plastics as it is not a simple hydrocarbon. It consists of repeating units of urethane, R2NC(O)OR. These linkages are formed through the reaction between diisocyanate groups and hydroxyl groups. PU is widely used and finds applications in a wide range of industries, including construction, automotive, furniture, electronics, packaging, and footwear. PU is used in products such as insulation foams, mattresses, adhesives, coatings, sealants, gaskets, wheels, and many others. It is flammable and therefore is treated with flame retardants. PU is not readily recyclable.

1.3.6 Polyethylene terephthalate (PET)

PET, C₁₀H₈O₄, is produced from the polymerization of ethylene glycol and terephthalic acid. PET is widely used in the packaging industry, particularly for beverage bottles, food containers, and thermoformed trays. It is also utilized in producing fibers for textiles commonly referred to as polyester fabrics. Additionally, PET is employed in applications such as films, sheeting, engineering components, and electronic devices. It is readily recycled, and is currently the most recycled plastic.

1.3.7 Other: Polycarbonate (PC) Nylon, Neoprene, Polyisoprene (PI)

Polycarbonate is an engineering thermoplastic (as opposed to commodity), and is typically derived from the polymerization of bisphenol A (BPA) with phosgene or other carbonate precursors. The resulting polymer has a linear structure with repeating carbonate groups. It is an extremely strong thermoplastic polymer, making it a substantial component in electrical components, construction materials, 3D printing, data storage, automotive, aircraft, and security components, medical applications, and smartphones. Due to PC being composed of BPA, it is somewhat controversial in regard to its environmental impact, which will be discussed further when discussing additives. Recycling PC can be challenging, and therefore is limited.

Nylon is a thermoplastic polymer that belongs to a class of materials called polyamides. It is known for its high strength, toughness, and durability. Nylon is formed through the condensation polymerization of diamines and dicarboxylic acids or by the ring-opening polymerization of lactams. The resulting polymer has a repeating amide group in its backbone structure. The specific type of nylon is often identified by a number, such as nylon-6, nylon-6,6, or nylon-12, which refers to the quantity of monomers used in its synthesis. Nylon is used in a wide range of applications, including textiles, automotive components, electrical insulation,

mechanical parts, packaging, and sports equipment. It is commonly found in products such as clothing, carpets, toothbrush bristles, hoses, gears, and bearings. Nylon is recyclable.

Neoprene is an elastomer, or synthetic rubber material, known for its excellent resistance to water, oil, heat, and weathering. Its structure consists of repeated units of chloroprene. Neoprene has extensive use in various industries and applications, including automotive, marine, sports, electrical, and industrial sectors. It is commonly used for wetsuits, gloves, footwear, orthopedic braces, gaskets, hoses, seals, laptop sleeves, and many other products that require flexibility, durability, and resistance to water or chemicals. It is not readily recyclable.

Polyisoprene (PI) is also an elastomer and is derived from the polymerization of isoprene monomers. PI is used to produce rubber goods such as tires, conveyor belts, gaskets, seals, and hoses. It is also used to manufacture medical gloves, surgical equipment, and other healthcarerelated products. It is often chosen as an alternative to natural rubber latex due to its hypoallergenic properties. It is also used in adhesives and consumer products. Like other elastomers, PI is not easily recycled.

Polymer Type	Molecular Structure	Chemical Properties	Recyclability
PE	$\int \int $	Melting point: 115-135 °C	Yes
	//	Density: 0.88-0.96 g/cm ³	
РР		Melting point: 130-171 °C	Yes
	$\left[\right]_{n}$	Density: 0.86-0.95 g/cm ³	
PVC	H CI H CI H CI H CI	Melting point: 100-260 °C	Yes
	LH HJ _n	Density: 1.38 g/cm ³	

PS		Melting point: 240 °C Density: 0.96-1.05 g/cm ³	Not readily
PET		Melting point: >250 °C Density: 1.38 g/cm ³	Yes
PU	$\begin{bmatrix} 0\\ 0\\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ -$	Melting point: 71.0-221 °C Density: 0.65- 1.44 g/cm ³	Not readily
PC		Melting point: 288-316 °C Density: 1.20-1.22 g/cm ³	Not readily
PI		Melting point: 64 °C Density 0.91 g/cm ³	Not readily
Nylon		Melting point: 190–350 °C Density: 1.15 g/cm ³	Not readily
Neoprene	Cl	Density: Solid: 1.23 g/cm ³ Foam: 0.1-0.3 g/cm ³	Not readily

Table 1. *Polymer Type Characteristics*. Molecular structure, density, melting point, and recyclability of some polymers of interest.

1.4. Additives, Leaching, and Weathering

Additives are substances used to alter or enhance the function and performance of a polymer and are introduced during the manufacturing process. They can be divided into four classification groups: solids, rubbers, liquids, and gases, and they include types such as stabilizers, fillers, plasticizers and softeners, colorants, antioxidants, and flame retardants. The most prevalent are fillers, flame retardants, and plasticizers, which make up about 75% of all additives³. Stabilizers are added to plastics to protect them from degradation caused by heat, UV

radiation, or oxidation. They help prevent the plastic from yellowing, becoming brittle, or losing its mechanical properties over time. Plasticizers, such as phthalates, are employed to increase plastics' flexibility, stretchability, and durability¹³. They make polymers more suitable for applications such as films, coatings, and more flexible products. Flame retardants are incorporated into plastics to reduce their flammability and improve fire resistance.¹⁴ They slow down or prevent the spread of flames, reducing the risk of ignition and enhancing the safety of plastic products. Fillers are added to plastics to modify their physical properties and reduce production costs. Common fillers include glass fibers, mineral fillers, and reinforcing fillers. They can improve strength, stiffness, thermal conductivity, and dimensional stability. Colorants, such as pigments and dyes, are used to give plastics their desired color. They enhance the aesthetic appeal of plastic products and allow for brand identification or product differentiation. Studies performed by the National Institute of Environmental Health Sciences (NIEHS), the National Toxicology Program, and the U.S. Food and Drug Administration (FDA) showed that 93% of humans involved in the study, aged 6 and older, had BPA in their urine, and that BPA is an endocrine disrupter and potential carcinogen in rats.^{15,16} Some plastic additives, such as certain flame retardants or UV stabilizers, have been found to persist in the environment and accumulate in ecosystems. This can raise concerns about potential ecological effects and the long-term environmental impact of these substances. The EPA is monitoring eight phthalates used as plasticizers, as they have been associated with endocrine disruption and reproductive issues in humans and animals.^{17,18}

Leaching, or migration, refers to the process by which substances or chemicals are released from a material, such as plastic, into the surrounding environment or the contents with which they come into contact. In the context of plastic additives, leaching can occur when the

additives migrate out of the plastic matrix and enter liquids, foods, or the surrounding environment.¹⁹ Different additives have varying degrees of mobility and propensity to leach. Some additives, such as plasticizers, are more likely to leach compared to others. Higher temperatures can accelerate the leaching process as they increase the mobility of molecules within the plastic.¹⁹ The duration of contact between the plastic and the substance it encounters influences the degree of leaching that occurs. The pH and specific chemical composition of the substance in contact with the plastic can also affect leaching¹⁹. Certain chemicals or acidic/basic conditions can enhance or reduce leaching. If potentially harmful or toxic plastic additives leach into food, beverages, or other consumables, there may be health risks associated with their ingestion or absorption. Leaching plastic additives into the environment can contribute to pollution and adversely affect ecosystems and organisms. Some pollutants, such as phthalates or bisphenol A, can leach from plastic materials and sorb onto nearby surfaces, including other plastics or sediment, which will be discussed in detail later.¹⁷ As previously mentioned, BPA has been discovered in human urine, and is being closely monitored by the EPA, the NIEHS, the FDA, and the Center for Disease Control (CDC).^{15,16,18}

The weathering of plastic debris refers to the process by which plastic materials degrade and undergo physical and chemical changes due to exposure to various environmental factors. Plastic debris can be subjected to weathering when exposed to sunlight, temperature variations, moisture, and mechanical forces over time. Ultraviolet (UV) radiation from sunlight is a significant factor in the weathering of plastic debris.²⁰ UV radiation can break down the polymer chains in plastics, leading to degrading of their physical properties. The degradation caused by UV radiation is often referred to as photo-oxidation. It can result in discoloration, loss of strength, brittleness, and the formation of surface cracks or microplastic. Fluctuations in

temperature can affect the weathering process of plastic debris. Repeated heating and cooling cycles can cause the materials' expansion and contraction, leading to stress, cracking, and accelerated degradation. Extreme temperatures can also influence the speed at which degradation occurs in that high temperatures can accelerate the breakdown of plastic polymers, while low temperatures can cause increased brittleness.²⁰ Moisture and humidity can contribute to the weathering of plastic debris, particularly in the presence of oxygen. This moisture can lead to hydrolysis, a chemical reaction that breaks down the polymer chains in plastics, resulting in the loss of mechanical strength and structural integrity.²¹ Water absorption by plastics can also facilitate the leaching of additives and other chemicals present in the plastic matrix. Mechanical forces, such as abrasion, friction, and impacts, can further accelerate the weathering process of plastic debris². Physical stressors and mechanical forces (e.g. wave action, wind, rubbing against other surfaces, or human activities) can cause surface erosion, microcracks, and fragmentation, generating smaller plastic particles.²¹ Other environmental factors, such as air pollutants, saltwater exposure, microbial activity, and chemical interactions, can also contribute to the weathering of plastic debris.²¹ These factors can vary depending on the specific environment in which the plastic debris is located (e.g., marine, terrestrial, or urban). The weathering of plastic debris can have detrimental effects on ecosystems and the environment by releasing microplastics, posing risks to wildlife, marine organisms, and even human health. Additionally, studies have shown weathering processes may favor biofilm growth due to the increase in surface area that weathering provides.²⁰

1.5. Sorption of Pollutants

The sorption of pollutants to plastic debris refers to the process by which contaminants in the environment adhere to or accumulate on the surface of plastic materials. Plastic debris,

particularly in aquatic environments, can act as a sink for various pollutants, including hydrophobic organic compounds, heavy metals, and persistent organic pollutants due to the hydrophobic nature of both the plastic and the pollutants.^{22–25} As seen in Table 1, many plastic polymer types are less dense than water, and therefore float on the ocean surface where other hydrophobic compounds tend to also accumulate at concentrations up to 500 times higher than the water column below.¹⁹ Sorption can occur through different mechanisms, including adsorption and absorption. Adsorption refers to the attachment of pollutants to the surface of the plastic material, while absorption involves the penetration and diffusion of contaminants into the plastic matrix. The sorption of pollutants to plastic is influenced by several factors, including the physicochemical properties of the plastic (e.g., surface area, roughness, polarity), the properties of the pollutant (e.g., solubility, hydrophobicity), and environmental conditions (e.g., temperature, pH).¹⁹ Various types of pollutants can sorb to plastic debris. Hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides, are known to have a strong affinity for plastics due to their nonpolar nature.^{19,23,24,26} Heavy metals, such as lead, mercury, and cadmium, can also sorb to plastic surfaces through complexation or electrostatic interactions.²⁵ Plastic debris can act as a carrier, transporting pollutants across long distances and potentially transferring them to aquatic organisms or other ecosystems, and throughout the water column and sediment layer by sinking.^{19,26–28} The Department of Health & Human Services (DHHS) and the EPA consider PCBs and several PAHs as human and animal carcinogens. A study by Mato et al. found that concentrations of PCBs found on PP pellets were up to 10^6 higher than in the surrounding water column in a marine environment in Japan.^{19,28} This same study also found that, across seven days, PCBs, nonylphenol, and a pesticide metabolite 2,2-bis(pchlorophenyl)-1,1-dichloroethene

(DDE) readily accumulated on the surface of PP pellets.¹⁹ The high accumulation potential discovered in this study suggests that plastic pollution, particularly pellets, is a good transport medium and also a source of toxic chemicals in the marine environment.²⁸ Additionally, Liu et al. (2023) reported that several studies found that plastic debris had adsorbed persistent organic pollutants (POPs), such as perfluorooctanesulfonate, perfluorooctanesulfonamide, tetracycline, and dichlorodiphenyltrichloroethane, and heavy metals.²⁹ The presence of sorbed pollutants on plastic surfaces can lead to bioaccumulation and biomagnification in organisms that ingest or encounter the plastic. This can pose risks to the health of wildlife and potentially enter the food chain, including human consumption.^{5,30} Additionally, fouled plastics are no longer recyclable. Minimizing the sorption of pollutants to plastic debris requires addressing the root cause of plastic pollution, such as reducing plastic waste and improving waste management practices. Understanding the sorption of pollutants to plastic debris is important for assessing the potential risks associated with plastic pollution and developing effective strategies to mitigate its impacts. Efforts to reduce plastic waste, improve waste management, and address the sources of pollution can help minimize the sorption of pollutants to plastic debris and protect ecosystems and human health.

1.6. Biofilms

When plastic debris enters aquatic environments, it provides a surface for microorganisms to colonize. Biofilm, also termed "fouling" or "biofouling", is the colonization of microorganisms, plants, algae, and marine life, particularly in aquatic environments, which form a slimy, protective matrix upon surfaces, including surfaces of plastic pollution. This colonization on plastic has been recently termed the "plastisphere".³¹ Initially, microorganisms can attach to the plastic surface through physical mechanisms, such as adhesion or entrapment in surface

irregularities. These biofilms develop immediately on plastic, and can potentially change properties of the plastic like hydrophobicity or buoyancy.³² Once attached, the microorganisms start to produce extracellular polymeric substances (EPS), forming a matrix that binds them together and provides protection. This matrix allows the biofilm to grow and develop a complex structure of compounds like proteins and polysaccharides.³² Biofilms on plastic debris can have both direct and indirect effects. The biofilm matrix can physically trap additional particles, such as sediment, organic matter, and other pollutants which can further modify the surface properties and appearance of the plastic.²⁰ Biofilm formation can influence the vertical transport of plastic and associated chemicals through the water column, as well as the release and uptake of these chemicals into the environment.²⁰ This modification includes altering the density of plastic, thus the placement of the plastic pollution and associated chemicals within the water column, or even allowing plastic to settle into sediments.^{20,33} The presence of biofilms can also affect the movement and transport of plastic debris and other pollutants throughout the environment, potentially impacting their distribution and persistence in aquatic ecosystems.²⁰ Additionally, biofilms can inhibit degradation by shielding plastic from environmental factors such as UV radiation, oxidation, and physical abrasion²⁰. This protection can prolong the lifespan of plastic debris and contribute to its persistence in the environment. The presence of biofilms, microorganisms, or organic matter on the plastic surface can also influence the sorption behavior by altering the surface properties and providing additional sorption sites.²⁰ Most current studies investigated the effect of biofilm formation on plastic density and buoyancy. ^{32,34,35} Lobelle and Cudliffe (2011) found that along with a decrease in buoyancy, biofilm also decreased the hydrophobicity of plastic during their study. This decrease in these physiochemical properties can affect the fate of plastic pollution, and how polymers interact with other pollutants within

aquatic systems.36

Several studies investigated biofilm type and taxonomic groups within the biofilms, as well as if individual strains of bacteria had a polymer preference.^{34,35,37,38} Chen et al. (2019) found that biofilm development has a different growth rate and composition depending on the season. Hansen et al. (2021) reported that individual strains of microorganisms could demonstrate "polymer-specific colonization", and that microbial composition of the biofilm on the polymers was unique compared to the surrounding water environment. The strains used in their study colonized PP, PE, and PS to varying degrees. Additionally, Liu et al. (2021) studied PET, PP, PVC, and PE and biofilm production in freshwater systems. The study showed that the fouled plastic accumulated higher concentrations of heavy metals, such as barium, chromium, and zinc, than the surrounding water column. These studies demonstrate that the development of biofilms on plastics may change plastics' morphology and physiochemical properties, and the sorption capacity of pollutants of the fouled plastic. My study explored any correlation between biofilm type and plastic polymer type throughout different seasons. Understanding factors that affect and influence the behavior of plastic pollution is paramount to addressing the global plastic pollution problem. This type of investigation could assist in mitigation and cleanup efforts of plastic pollution based on polymer type. The biofilm structure's proteins, carbohydrates, and lipids may be observed by detecting corresponding functional groups within the FTIR spectra of the plastic samples collected from the environment.

1.7. Attenuated Total Reflectance-Fourier Transform-Infrared Spectroscopy (ATR-FTIR)

FTIR spectroscopy is a quick, non-destructive quantitative and qualitative analytical technique introducing infrared radiation to a sample. The molecule absorbs or transmits radiation, and the bonds react to the energy presented by moving, like bending or stretching. The

instrument records the absorption or transmittance of the energy and vibrational behavior of the bonds within the compound. Based on this information, a spectrum of absorbance or transmittance (%) versus frequency/wavenumber (cm⁻¹) is generated that gives a visual representation of the behavior of the specific functional groups and bonds found within a sample allowing for the qualitative identification or confirmation of a specific compound. The wavenumber ranges from 500 cm⁻¹ to 4000 cm⁻¹. The spectrum is divided into two parts, the functional group region (~1500 cm⁻¹ to 4000 cm⁻¹), and the fingerprint region (500 cm⁻¹ to ~1500 cm⁻¹). The fingerprint region is unique to each compound and the bands in this region are more visually complex. However, functional groups have their characteristic absorptions that allow different functional groups to be identified within a spectrum.

Traditionally, transmission FTIR (tFTIR), required that the IR light source pass through a sample completely. This could result in total absorbance, meaning too much IR light is absorbed by the sample, resulting in poor spectral quality. In order to analyze a solid sample using tFTIR, the solid would require dilution by mixing with a non-IR reactive solid, usually potassium bromide (KBr). Alternatively, ATR-FTIR introduced the use of a crystal, typically made of diamond, Zinc selenide, or germanium. The sample is placed directly on the crystal, and the IR light source is directed through the crystal and into the sample. This allows for only partial interaction (reflection) between the IR and the sample, as opposed to the IR passing through the sample completely, resulting in minimal sample preparation, and higher quality spectra.

2. SAMPLING AND METHODS

2.1. Study Area

The Matagorda Bay system, also known as the Colorado-Lavaca Estuary, is the second largest estuary and bay system located on the Texas Gulf Coast, with a surface area of 989.42 km² and a max depth of 4 m.³⁹ It is a rural area, with the largest population of 11,557 in Port Lavaca at the time of the 2020 US Census. It receives freshwater inflow from the Colorado River, the Lavaca River, and the Tres Palacios River. This bay system is of particular study interest due to the location and activity of Formosa Plastics Corporation and the Alcoa Mercury Environmental Protection Agency (EPA) Superfund site and the known accumulation of polycyclic aromatic hydrocarbons (PAHs). San Antonio Bay is a part of the Guadalupe Estuary, and is mostly closed off from the Gulf of Mexico, with its only access via the Matagorda Bay. It receives freshwater inflow from the Guadalupe and San Antonio Rivers, and is predominantly rural. These sites were chosen as control sites outside of Matagorda Bay. Twelve sites were chosen for sampling, ten in the Matagorda Bay system: Boggy Creek (BC), Baypoint (BP), Corner Beach (CB), Crossroad (CR), Lighthouse (LH), Palacios (PA), Point Comfort (PC), Six Mile (SM), Magnolia Beach (MG), and Texas Parks (TP), and two in San Antonio Bay: Austwell (AU) and Seadrift (SD), shown in Figure 1.



Figure 1. *Sampling Sites within the Matagorda Bay System*. Map of the ten sample sites within the Matagorda Bay System and two in San Antonio Bay.

2.2. Sampling

Samples were collected from 12 sites throughout the Matagorda Bay system (see Figure 1) over three seasons (March, July, and October 2022). Water properties were measured at every site using a Yellow Springs Instrument (YSI), including temperature (°C), salinity, and dissolved oxygen (%). At each site, 25-meter (m) transects were measured at the newest visible wrack line, and divided into five 5x1 m sections, labeled a-e, using PVC piping. Using acid clean (10% hydrochloric acid) forceps, each section was scoured for probable plastic debris twice, and debris was placed in appropriately labeled bags for laboratory processing. The labeled bags were refrigerated until processing occurred. Each sample was cleaned using distilled water, air-dried, weighed, and a small portion of each sample was cut and placed in a 1-milliliter (mL) vial to, and

the vials were stored on the laboratory bench to await FTIR analysis. Due to the seasonal shift of sands around the bay, Point Comfort was not sampled in March 202, nor Magnolia Beach in October 2022. Due to a shoreline stabilization project that affected the previous shoreline, Seadrift site was not sampled in July and October.

2.3. ATR-FTIR Analysis and Principal Component Analysis (PCA)

ATR-FTIR analysis was performed using a Thermo Scientific[™] Nicolet[™] iS[™] 10 ATR-FTIR Spectrometer. Each spectrum was collected by collecting 50 scans at 4 cm⁻¹ resolution. Thermo Scientific[™] OMNIC[™] series software was utilized for spectra processing and identification.

Principal Component Analysis (PCA) is an unsupervised statistical analysis technique used to decrease the dimensionality of large data sets. The decrease in size allows for better comparison of variation within the data sets by reducing data sets size into smaller principal components (PCs) that still contain most of the information from the larger data sets. The first PC explains the largest variance in the dataset, and each successive PC is orthogonal to the previous PC and explains the next largest portion of the remaining variance in the dataset. Creating PC1 versus PC2 biplots of sample scores can be used to evaluate the major differences between samples. In addition, each PC carriable loading highlights the difference.

Additionally, data standardization is required to reduce large ranges in variance and minimize bias. For example, an ATR-FTIR spectrum baseline can shift up and must be able to be corrected. This baseline error can cause a high range of variation, resulting in domination over the variation in actual functional groups of the other spectra, potentially skewing the results of the PCA. Before being analyzed by PCA each spectrum was converted into absorbance units,

smoothed at 5.304 cm⁻¹ points to reduce noise, the baseline was autocorrected, and the scale normalized. An example of baseline error and removal is shown in Figure 2a & b below.

After data standardization, the first step in PCA is the computation of covariance, which summarizes correlations between all possible pairs of variables. Next, eigenvalues of the covariance matric are computed and graphed, as seen in Figure 3a. Eigenvalues refer to the variance of the data matric. The largest two variations, principal component 1 (PC 1) and principal component 2 (PC 2) are then utilized. PC 1 represents the largest possible variance in the data sets, and PC 2 represents the second largest variance uncorrelated to PC 1. PC 1 and PC 2 become new variables to explain and compare the data within the set to each other. PC 1 and PC 2 are used to explain the significant percentage of all the data sets and all data points are then compared to this variance. Next, a score plot, shown in Figure 3b, is generated plotting each spectrum (sample) relative to other samples and analyzed in the same PCA set, and the position quantifies the PC of any given sample, giving a visual representation of each spectrum compared to the variances. The score plot is used in conjunction with a loading plot (Figure 3c & 3d) to determine which functional groups/principal components are present in the sample set. This analysis can identify variations or commonalities among polymer types, sampling sites, and seasons. Using an in-house developed MATLAB script, PCA was performed on ATR-FTIR datasets. As mentioned, each spectrum consists of 7469 data points from (4000-400 cm⁻¹) that served as the PCA input variables for each sample spectrum.



b)

a)

Figure 2. *Data Standardization for PCA*. a) An example of ATR-FTIR spectra in Excel used for data standardization showing some spectra's baseline errors. b) An example of ATR-FTIR spectra in Excel used for data standardization after baseline errors were removed.

b)

a)


Figure 3. *Graphs Generated During PCA*. a) An example graph of eigenvalues generated during PCA depicting principal components. b) An example score plot generated during PCA. c) An example loading plot generated during PCA of the first principal component. d) An example loading plot generated during PCA of the second principal component.

2.4. Statistical Evaluation

Separate one-way ANOVA tests were executed using R Studio (v. 4.1.2) to determine statistical relationships between polymer type weight and three different parameters: site, season, and a combination of site and season. Pearson correlations were also employed using R Studio to evaluate associations between different polymer type weight from site by season.

2.5. Integration of Spectra Methodology

To evaluate the formation of natural organic biofilm, we integrate the main functional groups of carbohydrates and proteins. Based on Abdulla et al., we used in-house developed Python codes to integrate the band between 850-1220 cm⁻¹ as representative of the C-O stretching of carbohydrates and the amide functional group band (N-C=O) stretching of proteins between 1570-1780 cm^{-1 40}.

3. RESULTS

3.1. Polymer Distribution

3.1.1. Total Plastic Distribution

A total of 3,498 samples were collected across three seasons from March 2022 to October 2022 with 583 samples collected in March 2022, 585 in July 2022, and 2,330 in October 2022. Of these samples, 3,225 were confirmed to be plastic polymers based on the ATR-FTIR analysis with a total of 2.753 kg. Out of the 3,225 total plastic samples, 483 plastic samples collected in March with a mass of 0.585 kg, 541 plastic samples in July with a mass of 1.316 kg, and 2,201 plastic samples in October with a mass of 1.437 kg. The mass by polymer type for each sampling event is shown in Figure 4.

a)







c)





Total Mass of Polymer Type by Site for October



Figure 4. *Mass of Polymer Types Collected During Each Season*. a) Total mass of polymer types collected from each site across all seasons: Austwell (AU), Boggy Creek (BC), Baypoint (BP), Corner Beach (CB), Crossroad (CR), Lighthouse (LH), Palacios (PA), Point Comfort (PC), Six Mile (SM), and Texas Parks (TP). b) Total mass of polymer types collected from each site in March. c) Total mass of polymer types collected from each site in July. c) Total mass of polymer types collected from each site in October.

The distribution of the number of plastic debris across the 12 sampling stations showed the largest mass of plastic debris was recovered from Point Comfort (1,230), Corner Beach (853), and Lighthouse Beach (351). Point Comfort was not sampled in March due to the seasonal shift of sands around the bay, but a total of 1,230 plastic samples were collected with 188 samples in July, and 1,042 in October. The total count of each polymer type across different seasons and different sample locations is shown in Figure 5 below.

d)



a)

Total Count of Polymer Type by Site for March

b)







Figure 5. *Count of Polymer Types Collected During Each Season*. a) Total count of samples by polymer type collected in March. b) Total count of samples by polymer type collected in July. c) Total count of samples by polymer type collected in October.

3.1.2. Polymer Type Distribution

The percentage of each polymer type collected during each season is shown in Figure 6.

PE and PP are the predominant polymer type observed across all sites and seasons. The

percentage of PE for March, July and October was 30%, 42%, and 49%, respectively, and 15%,

23%, and 27% for PP. Additionally, the percentage of PVC was higher in March with 7%,

compared to only 3% in July and 1% in October.



b)





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Figure 6. *Percentage of Polymer Type by Season*. a) Side-by-side comparison of percentage of each polymer mass of season. a) Percentage breakdown by polymer type of total plastic debris across all sites for each season: b.) March 2022. c.) July 2022. d.) October 2022.

Separate one-way ANOVA tests were employed to determine the statistical significance between polymer type weight and three different factors: 1) the total mass of polymer type from each site, 2) total mass of polymer type from each season, and 3) the combination of site and season. Nylon debris total mass showed a statistical significance across sites (p-value of 0.000451), but did not show a significance when compared across seasons or across site by season (see Figure 7). There was a significance in PE mass across the different seasons (p-value of 0.000502), and site by season with a p-value of 0.000212, but no significance was observed between the total mass across different sites. There was a statistical significance in PP total mass across the sites with a p-value of 0.00197, and site by season with a p-value of 0.00693. A corresponding ANOVA heatmap is shown in Figure 8, and the total mass of polymer types is shown above in Figure 2. As the p-value decreases (becomes more significant), the dots become darker and larger. Additionally, Pearson correlations were determined between the mass of polymer type from site by season (Figure 9). A strong positive correlation exists between PE and PP of 0.75, PE and other of 0.81, and PP and Nylon of 0.93. There is a moderate positive correlation between PET and PS of 0.68, PET and Nylon of 0.67, Nylon and Other of 0.60 and PP and Other of 0.66. A positive correlation indicates that as one variable decreases, so does the correlating variable.



Figure 7. *Mass of Nylon Across Sites and Seasons*. Total mass of Nylon recovered from each site during each season.



Figure 8. *ANOVA Heatmap*. Heatmap depicting ANOVA p values of polymer type across, site, season, and site by season.



Figure 9. Peason Correlation. Pearson Correlation between polymer types by mass.

Lastly, due to Matagorda Bay having a thriving commercial and recreational fishing industry, data was sorted by "nylon" and "thread" and any fishing-related word in morphology data. With p-values of 1.02x10e⁻⁰⁶ and 0.00115, there was a significant difference across site and season, respectively. The total weight of fishing-related plastic debris is graphically represented in Figure 10. The three sites with the most fishing-related plastic debris were Point Comfort, Lighthouse, and Corner Beach. These three sampling sites had the largest count and mass of polymer type and are the easily accessible to the public. Finding more fishing-related plastic debris in these areas is consistent with the data.



Figure 10. *Fishing-related Plastics by Site and Season*. The total mass of fishing-related plastic debris recovered from each site during each season.

3.1.3. Presence of Pellets

As plastic pellets, or nurdles colloquially, are used in the manufacturing of plastic products, they are directly released/discharged from industry as opposed to public activity. In my study, I have identified 85 pellets during all seasons, with 41 retrieved from Corner Beach. The distribution of pellets recovered from each site is shown in Table 2.

Site	Bay	Pellet	
		Count	
Austwell	San Antonio	2	
Boggy Creek	Matagorda	2	
Corner Beach	Matagorda	41	
Lighthouse	Matagorda	19	
Point Comfort	Matagorda	6	
Sea Drift	San Antonio	9	
Six Mile	Matagorda	6	

Table 2. Nurdle Count by Site. Number of pellets recovered from sampling sites.

3.2. ATR-FTIR Comparison of Plastic Polymers and Environmental Samples

Most of the previous studies have used ATR-FTIR spectra of environmental plastic sample to confirm the type of polymer based on the FTIR spectra database. However, comparing the reference spectra of plastic polymer types to the environmental samples can also be used to identify the difference in functional groups between the spectra. These differences could be utilized to quickly determine the presence and type of biofilm form on the surface of environmental plastic samples or investigate the degradation of the plastic polymer's functional group due to the weathering or degradation.

In Figures 11 and 12 below, reference spectra for PE, PET, PP and PVC are shown followed by the spectrum of an environmental sample of each polymer. The environmental samples depict the presence of identifier bands of the reference spectrum, but also have additional bands within the spectrum. Also, the change in the intensity of the identifier bands between the reference and a sample can be observed, indicating a possible alteration or degradation of specific functionality of the plastic.



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Figure 11. *Comparison of PE and PET Reference Spectra and Environmental Samples*. a) A reference FTIR spectrum of PE showing the definitive bands of the polymer. b) The FTIR spectrum of a PE sample collected from Austwell in October 2022, shows the polymer's definitive bands and additional bands. c) A reference FTIR spectrum of PET showing the definitive bands of the polymer. d) The FTIR spectrum of a PET sample collected from Austwell in October 2022, showing the definitive bands of the polymer. d) The FTIR spectrum of a PET sample collected from Austwell in October 2022, showing the definitive bands of the polymer and additional bands.





Figure 12. *Comparison of PP and PVC Reference spectra and Environmental Samples*. a) A reference FTIR spectrum of PP showing the definitive bands of the polymer. b) The FTIR spectrum of a PP sample collected from Austwell in October 2022, shows the definitive bands of the polymer and additional bands. c) A reference FTIR spectrum of PVC showing the definitive bands of the polymer. d) The FTIR spectrum of a PVC sample collected from Lighthouse in October 2022, shows the polymer's definitive bands and additional bands.

3.3. Principal Component Analysis (PCA)

In order to investigate how environmental plastic samples of the same polymer type differ, I have conducted PCA analysis for four polymer types, which I have polymer standards available, which are PE, PP, PS, and Nylon. Before conducting PCA analysis, I inspected each spectrum by plotting each group of spectra on the same graph to remove any spectrum with a high or tilted baseline elevation. After removing baseline errors and outliers, there were 2,409 spectra with 1,244 PE spectra, 876 PP spectra, 186 PS spectra, and 103 Nylon spectra. For a breakdown of total spectra, the number of outliers removed, spectra used for PCA, and the number of spectra used for PCA by season, refer to Table 3.

Polymer Type	Total Spectra	Outliers Removed	Total Spectra used for PCA	Spectra from March	Spectra from July	Spectra from October
PE	1360	116	1244	74	183	987
PP	1008	132	876	77	97	702
PS	224	38	186	35	43	108
Nylon	116	13	103	30	31	42
Total	2708	299	2409	216	354	1839

Table 3. *Spectra Count for PCA*. Total spectra, outliers removed, spectra used for PCA after outliers were removed, and spectra used for PCA by season.

3.3.1 PCA of PE

The definitive ATR-FTIR absorbance bands for the PE standard are 2916 cm⁻¹, 2848 cm⁻¹, 1470 cm⁻¹, and 719 cm⁻¹, which is depicted in Figure 13 of the PE standard spectrum below. Applying PCA analysis on 1,244 PE spectra showed that PC 1 and PC 2 represent 56.8% and 14.5%, respectively, accounting for 71.3% of the variation between all PE spectra (see Figure 15). The scatter plot of the first two PCs (PC 1 and PC 2) is shown in Figure 156. There were not any clustering trends between the same seasons or sampling sites. However, the PE-PCA scatter plot showed that all the PE standard spectra clustered on the extreme left of PC 1 (the orange circles). In contrast, some PE spectra are clustered with the PE standard spectra, the majority showed large distribution along the PC 1(the major PC component). To investigate the FTIR bands behind these distributions of PE samples, I plotted the spectra loading of PC 1 and PC 2 in Figure 17. Comparing the PC 1 loading figure (Figure 16) to the standard PE spectrum in Figure 13 showed that on the negative side (downward bands) along the y axis are predominately similar to the PE standard spectrum, which corresponds to PE's definitive bands around 2920 cm⁻¹ and 2850 cm⁻¹, which indicate that some of the environmental PE samples that fall on the negative side of PC 1 in the scatter plot (Figure 15) has a higher abundance of the PE's standard definitive bands relative to the samples located on the positive side of PC 1. On the other hand, the bands with positive intensity (upward bands) of PC 1 loading (Figure 16) are a broad wide band at 3400 cm⁻¹, a band at 1630 cm⁻¹, and a band at ~1050 cm⁻¹. These band are attributed to carbohydrate bands (O-H stretching at the broad band at 3400 cm⁻¹ and C-O stretching at ~1050 cm⁻¹) and protein N-C=O stretching band at 1620 cm⁻¹ according to Abdulla et al. This indicates that the PE samples located on the right side (positive PC 1) of the scatter plot (Figure 15) have a higher content of carbohydrates and protein structure relative to the other PE samples.



Figure 13. *ATR-FTIR Spectrum of PE Standard*. An ATR-FTIR spectrum of PE standard displaying the definitive absorbance bands.



Figure 14. *Principal Components of all PE Spectra*. Eigenvalues of the principal components produced via PCA for all PE.



Figure 15. *PCA Scatter Plot of all PE Spectra*. Scatter plot of PE samples in relation to PC 1 and PC 2.



Figure 16. *PCA Loading Plots for all PE Spectra*. Loading plots of all PE spectra in relation to PC 1.

3.3.2 PCA of PP

The definitive ATR-FTIR absorbance bands for PP are 2949 cm⁻¹, 2916 cm⁻¹, 2866 cm⁻¹, 2836 cm⁻¹, 1453 cm⁻¹, 1375 cm⁻¹, and several small bands in the fingerprint region in the range 808-1200 cm⁻¹, which is depicted in Figure 17 of the PP standard below. Applying PCA analysis on 876 PP spectra showed that PC 1 and PC 2 represent 53.1% and 14.5% respectively, accounting for 67.6% of the variation between all PP spectra (see Figure 18). The scatter plot of the first two PCs (PC 1 and PC 2) is shown in Figure 19. There were no obvious clustering trends between the same seasons or sampling sites. However, the PP-PCA scatter plot (Figure 19) showed that all the PP standard spectra clustered on the extreme left of PC 1 (orange circles). The majority of the PP spectra showed a large distribution along PC 1. Comparing the PC 1 loading figure (Figure 20) to the standard PP spectrum in Figure 17 showed that on the negative side (downward bands) along the y axis are predominately similar to the PP standard spectrum, which corresponds to PP's definitive bands. The PCA scatter plot and loading plot are below in

Figures 19 and 20. The loading plot in Figure 20 can be compared to the standard PP spectrum in Figure 17 to find the corresponding absorbance bands. Loading 1 shows that the standards and samples on the negative side of zero on the y-axis are predominately composed of PC 1, which corresponds to PP's definitive bands around 2949 cm⁻¹, 2916 cm⁻¹, 2866 cm⁻¹, 2836 cm⁻¹, 1453 cm⁻¹, indicating that some of the PP samples that fall on the negative side of PC 1 has a higher abundance of PP's standard definitive bands relative to the samples located on the positive side of PC 1. On the positive intensity (the upward bands) of PC 1 loading (Figure 20) are a broad wide band at 3400 cm⁻¹ and a sharp, high intensity band around 1050 cm⁻¹ attributed to carbohydrate bands. This indicates that the PP samples located on the right side (positive PC 1) of the scatter plot (Figure 19) have a higher content of carbohydrate structure relative to the other PP samples.



Figure 17. *ATR-FTIR Spectrum of PP Standard*. An ATR-FTIR spectrum of PP standard displaying the definitive absorbance bands.



Figure 18. *Principal Components of all PP Spectra*. Eigenvalues of the principal components produced via PCA for all PP.



Figure 19. *PCA Scatter Plot of all PP Spectra*. Scatter plot of PP samples in relation to PC 1 and PC 2.





The definitive ATR-FTIR absorbance bands for PS are 2921 cm⁻¹, 1491 cm⁻¹, 1451 cm⁻¹, 748 cm⁻¹, and 694 cm⁻¹, which are shown in Figure 21 of the PS standard spectra below. Applying PCA analysis on 186 PS spectra showed that PC 1 and PC 2 represent 48.4% and 22% respectively, accounting for 70.4% of the variation between all PS spectra (Figure 22). The scatter plot of the first two PCs (PC 1 and PC 2) is shown in Figure 23. Similar to the PE and PP PCA, the PS-PCA scatter plot showed that all the PS standard spectra clustered on the extreme left of PC 1 (orange circles). There is more sample clustering around the PS standard spectra than seen previously in the PE or PP PCA, but there is a wider distribution along both PC 1 and PC 2. Comparing the loading of PC 1 (Figure 25a) to the standard PS spectrum in Figure 21 showed that on the negative side (downward bands) along the y axis are similar to that of the PS standard spectrum, which corresponds to PS's definitive bands around 2920 cm⁻¹, 1490 cm⁻¹, and 695 cm⁻¹, indicating that the samples that are clustered on the negative side of PC 1 have a higher abundance of PS's definitive bands than those on the positive side of PC 1. The upward bands (positive side of PC 1) loading (Figure 24a) show a sharp, high intensity band around 1050 cm⁻¹ attributed to carbohydrate bands (C-O stretching) and a band around 1620 cm⁻¹ attributed to protein (N-C=O). This indicates that the PS samples located on the positive side of the PC 1 scatter plot have a higher content of carbohydrates and protein structure. Additionally, looking at the loading of PC 2 (Figure 24b), the PS standard spectrum is indistinguishable, and the bands associated with carbohydrate and protein structure dominate.



Figure 21. *ATR-FTIR Spectrum of PS Standard*. An ATR-FTIR spectrum of PS standard displaying the definitive absorbance bands.



Figure 22. *Principal Components of all PS Spectra*. Eigenvalues of the principal components produced via PCA for all PS.



Figure 23. *PCA Scatter Plot of all PS Spectra*. Scatter plot of all PS samples in relation to PC 1 and PC 2.



Figure 24. *PCA Loading Plots for all PS Spectra*. Loading plots of all PS spectra in relation to a) PC 1 and b) PC 2.

3.3.4 PCA of Nylon

The definitive FTIR absorbance bands for Nylon are 3298 cm⁻¹, 2930 cm⁻¹, 2857 cm⁻¹, and 1630 cm⁻¹, 1532 cm⁻¹, and numerous variable bands between 1463-577 cm⁻¹, which is depicted in Figure 25 of the Nylon standard below. Applying PCA analysis on 103 Nylon spectra showed that PC 1 and PC 2 represent 43.2% and 27.1% respectively, accounting for 70.3% of the variation between all Nylon spectra, which is depicted in Figure 26. The scatter plot of PC 1 and PC 2 is shown in Figure 27. The Nylon-PCA scatter plot showed that all the Nylon standard spectra were on the extreme bottom left of PC 1 (the orange circles), but unlike the other polymers, there was minimal clustering observed of Nylon samples around the Nylon standard spectra. Comparing the PC 1 loading figure (Figure 28a) to the Nylon standard spectrum in Figure 26, the positive side (upward bands) along the y axis are similar to the Nylon standard, with definitive bands around 3298 cm⁻¹, 2930 cm⁻¹, 2857 cm⁻¹, and 1630 cm⁻¹, and 1532 cm⁻¹. Comparing the PC 2 loading figure (Figure 29b) to the Nylon standard spectrum in Figure 25 showed that on the negative side (downward bands) along the y axis are similar to the Nylon standard with the same definitive bands around 3298 cm⁻¹, 2930 cm⁻¹, 2857 cm⁻¹, and 1630 cm⁻¹, and 1532 cm⁻¹. However, the PC 2 loading figure also shows bands with positive intensity (upward bands) attributed to carbohydrate structures with a sharp, intense band around 1050 cm^{-1} , indicating that the samples on the positive side of the x axis have a higher abundance of carbohydrate structures.



Figure 25. *ATR-FTIR Spectrum of Nylon Standard*. An ATR-FTIR spectrum of Nylon standard displaying the definitive absorbance bands.



Figure 26. *Principal Components of all Nylon Spectra*. Eigenvalues of the principal components produced via PCA for all Nylon.



Figure 27. *PCA Scatter Plot of all Nylon Spectra*. Scatter plot of all Nylon spectra in relation to PC 1 and PC 2. a)





Figure 28. *PCA Loading Plots for all Nylon Spectra*. Loading plots of all Nylon spectra in relation to a) PC 1 and b) PC 2.

3.4. Linear Regression of Spectra Integration

In this study, to further investigate the nature of the biofilm formed on these plastic debris, I integrated the C absorbance band range of 850-1220 cm⁻¹ (C-O stretching band) as a representative of the carbohydrate portion of biofilm and the absorbance band range of 1570-1780 cm⁻¹ (amide stretching band) as representative of the protein portion of biofilm for PE, PP, and PS spectra using Python code. I did not conduct the same integration for PET, PVC, PU, and Nylon as their definitive bands interfere with the bands of the protein and carbohydrate. These integrations determined a carbohydrate to protein integration ratio (CPR) for each PE, PP, and PS using linear regression plots of all the same plastic type samples (Figures 30-32).



Figure 29. *Linear Regression for CPR from PE*. Linear regression for Carbohydrate to protein area ratio (CPR) from PE samples.



Figure 31. *Linear Regression for CPR from PP*. Linear regression for Carbohydrate to protein area ratio (CPR) from PP samples.



Figure 32. *Linear Regression for CPR from PS*. Linear regression for Carbohydrate to protein area ratio (CPR) from PS samples.

4. DISCUSSION

4.1. Distribution of Plastic Polymers Along the Coastline of Matagorda Bay

The percentages of each polymer type observed in this study appear to follow generally the same trend as the percentage breakdown of polymer type of all manufactured polymers which is 36% PE, 21% PP, 12% PVC, and <10% each of PET, PU, and PS³ with the exception of PE having a higher percentage in the July and October sampling seasons which reflects the typical trend of personal and commercial use of these polymers. The increase in PE percentages in July and October which makes up most single-use plastic polymers in these two seasons (Figure 8), could contribute to the increase in PE plastic debris used in these two seasons. This explanation is supported by the increase in tourism and beach visitors during the summer months June-August, according to the Visit Corpus Christi quarterly data report, and hotel occupancy rates⁴⁷. This increase in tourism and beach visitors combined with PE being the most manufactured polymer, could explain the higher percentage of PE debris collected along the beaches of Matagorda Bay during these two seasons. The high abundance of plastic debris recovered from beaches like Lighthouse, Corner Beach, or Point Comfort relative to other sites could be attributed to some sample sites being more accessible, sandy public beaches. In contrast, others are more remote, rocky beaches unsuitable for recreational use. The discrepancy and large variation of samples collected across seasons could again be attributed to the peak tourist season and the increase in anthropogenic activity. Moreover, October falls at the end of the wet season and tropical storm season. An increase in tropical storm activity can increase the circulation of plastic pollution throughout the bay system due to higher wind speeds, and storm surge, and flooding. The Texas Gulf Coast experiences more onshore currents due to stronger along shore winds, particularly in the winter months⁴¹. This allows for more accumulation of

debris on the beaches during this time, as opposed to currents moving the debris out to sea. Moreover, due to the barrier islands, the Matagorda Bay system is semi-closed, so circulation is predominantly within the bay itself. This characteristic mixed with stronger onshore winds, is consistent with finding more plastic debris in October. Additionally, the wet season increases the inflow of freshwater from the local river systems. The Colorado and Lavaca Rivers discharge into the Matagorda Bay system, introducing more plastic debris from upstream.

Most previous studies that investigated the distribution of plastic debris did not include polymer type distribution. These studies focused on the percentage of plastic in debris collected, and the size, shape, and color of the plastic. For example, Wessel et al. studied the distribution of plastic debris across the northern Gulf of Mexico, from Texas to Florida. This study showed that Texas coastlines accumulated ten times more plastic debris than the other sites along the Gulf Coast. This study also argued the stronger onshore direction winds along the Texas coast as opposed to offshore direction winds in the eastern Gulf of Mexico sites as being a determining factor of the higher accumulation rates of plastic debris on the Texas barrier islands⁴².

Few studies investigate distribution of polymer types. For example, Gandhi et al. investigated the distribution of plastic polymer types pre- and post-cyclone events and found that the distribution percentage was 31.4% PP, 30.5% PE, 16.0% PS, 15.5% nylon, and 5.1% PVC⁴³. This percentage distribution trend is in agreement with my current study. Additionally, Gandhi et al. found substantially more plastic debris post-cyclone than pre-cyclone, supporting that tropical storm season might cause a higher accumulation of plastic debris collected, as we observed in the October 2022 season.

The majority of pellets were collected from sites in and near Lavaca Bay, with almost half retrieved from Corner Beach. This is expected as Lavaca Bay is the location of Formosa

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Plastics Corporation, and the known release of millions of PE and PP pellets. As mentioned, the greatest amount of nurdles was collected from Corner Beach. The circulation patterns observed using NOAA circulation data (Fig. 13) within the Lavaca Bay system corresponds with the accumulation of pellets at this site.



Figure 32. *Circulation Patterns in Matagorda Bay System*. Circulation and currents data in the Matagorda Bay system from the National Oceanic and Atmospheric Administration⁴³ (NOAA 2023).

4.2. Chemical Nature of Plastic Debris Biofilm

The PCA analyses of PE, PP, and PS showed the differences in abundance of carbohydrate and protein bands were responsible for major variation between environmental plastic debris. One of the major sources of carbohydrates and protein in plastic debris is the formation of microbial biofilm on the surface of plastic debris. As previously mentioned, many microbes biosynthesize extracellular polymers consisting of carbohydrates, protein, and DNA known as extracellular polymeric substances (EPS) to attach themselves to solid surfaces⁴⁴. Regarding current biofilm and plastic research, most studies focused on the time lapse of biofilm formation on plastic pollution or isolated target strains of microorganisms from the biofilm collected^{32,36,37}. However, Tu et al. investigated biofilm formation on PE, PP, and PS in saline conditions, and they concluded that biofilm formation is greatly dependent on incubation time and polymer type⁴⁵. Additionally, one study conducted by Battulga et al. in Mongolia used micro-FTIR to analyze biofilm formation on polystyrene microplastics in freshwater, and was able to distinguish definitive peaks of EPS on their environmental PS samples from the PS standard spectra, and that the biofilm on the PS played a part in surface changes observed on the microplastics⁴⁶.

For PE, using a total of 1,244 PE sample spectra, the linear regression plots (Figure 29) show a significant positive linear relationship between the carbohydrate and protein absorbance bands. With an R² of 0.8045, 80.45% of the variation of the protein can be explained by the variance of the carbohydrate. As the intensity of the carbohydrate absorbance band increased, so did the protein absorbance band. The CPR for the PE samples was 11.42. For PP, a positive linear relationship between the carbohydrate and protein absorbance bands was observed by plotting a total of 876 PP sample spectra with an R² of 0.7926, 79.26% of the variation of the protein can be explained by the variance of the carbohydrate (see Figure 30). The CPR for PP samples was 10.32. For PS, I also observed a positive linear relationship between the carbohydrate and protein absorbance bands for 186 PS spectra with an R² of 0.7704 (Figure 31). However, the CPR for PS samples was lower, with a value of 8.92.

The PE, PP, and PS plastic debris samples showed a different CPR, indicating that the biofilms formed on these plastic types are different, supporting that polymer type affects biofilm formation. PE showed higher carbohydrate content relative to protein contents in their biofilm, followed by PP then PS with the lowest ratio, which supports the notion that biofilm differs across polymer types. These findings help us better understand how polymer types have different interaction and sorption of various pollutants based on biofilm present.

5. CONCLUSION

Understanding the accumulation and distribution of polymer types as shown in this study could lead to identified possible sources of these plastic debris. Targeting sources of prevalent polymer types may be a better method to mitigate and manage plastic pollution. Across all seasons we have identified a total of 3,225 plastic samples collected across all seasons with 44.5% PE, 32.2% PP, 7.0% PS, 5.1% PET, 3.7% PU, 3.6% Nylon, 2.2% PVC, and 1.4% Other. The small percentage of nurdles recovered indicates that anthropogenic activity and mismanagement of waste by the public may play a more significant role in releasing plastic debris in the coastal beaches of the Matagorda Bay system than from industry. The seasonal variation suggest that onshore winds and circulation patterns play a significant role in the accumulation of plastic debris on specific beach locations. This information can be used to better plan clean-up efforts, like what time of year would be most productive in removing plastic debris. Additionally, understanding the interaction between plastic debris and biofilms can help bridge the gaps in the behavior of plastics, like leaching, sorption, and movement throughout the water column. ATR-FTIR and PCA were efficient methods to employ to find that biofilm was present on all PE, PP, PS, Nylon and PET samples. This study showed the ability also to use the FTIR spectra as a simple, non-destructive method to investigate the chemical nature of biofilm formed on plastic debris as well as identifying the polymer type.

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