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## An Analysis of the Potential Toxicological Effects of Marine Plastics and Associated Organic and Inorganic Toxic Compounds on Six Commercially Significant Fishery Species

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# Capstone of Nicole Marie Jackson

Submitted in Partial Fulfillment of the Requirements for the Degree of

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Halmos College of Natural Sciences and Oceanography

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AN ANALYSIS OF THE POTENTIAL TOXICOLOGICAL EFFECTS OF  
MARINE PLASTICS AND ASSOCIATED ORGANIC AND INORGANIC  
TOXIC COMPOUNDS ON SIX COMMERCIALY SIGNIFICANT  
FISHERY SPECIES

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## Abstract

Marine plastics are a global issue which has garnered significant support for mitigation efforts in recent history. Research on the prevalence of plastic polymers in the marine environment has also come to the forefront of the scientific community, however studies on the toxicological impacts of their presence remains to be a little studied matter to date. Plastic polymers are capable of possessing constituents within their polymeric structures, obtained either from production processes or later sorbed into their structures from their environments. These constituents can then potentially be desorbed from those plastic polymers and enter marine organisms that have unintentionally consumed those particles, allowing these constituents to enter the marine food web and additionally allowing for the potential of subjecting those constituents to the biological processes of bioaccumulation and biomagnification.

In this study, an intensive critical review of existing data was conducted to compile profiles (including: stability ranks, sorption capacities, organic and inorganic toxic constituent concentrations, bioaccumulation scores per constituent, and biomagnification scores per constituent) for the three most common plastic polymers present in the Southwestern Atlantic region: polyethylene, polypropylene, and polystyrene. These three polymer types were assessed for the toxicity threat they pose to marine organisms based upon the contents of their polymer profiles. Basic trophic structure level rankings for the six most commercially significant fishery species in the Southwest Atlantic (*Epinephelus morio*, *Lutjanus campechanus*, *Xiphias gladius*, *Scomberomorus cavalla*, *Mugil cephalus*, *Thunnus obesus*) were generated and the toxicological effects of the three polymers of interest on each species were calculated.

The majority of constituents considered in this study were reported as present in concentrations higher than the listed Minimal Risk Level concentration by the CDC before the processes of bioaccumulation and biomagnification took place. Polychlorinated biphenyls, arsenic, cadmium, and chromium were identified as the substances of primary concern based upon their toxicity threat assessment across all three polymer types and in all six species. Exposure to carcinogenic/toxic concentrations of these constituents is probable given that those concentrations will be subjected to the processes of bioaccumulation and biomagnification as the constituents climb the trophic food web structure. This could be significant in species that occupy higher trophic level positions, putting a major resource (commercial fisheries) at risk as while also placing human health at risk via the consumption of those commercially significant fishery species.

**Keywords:** polymer, constituent, bioaccumulation, biomagnification, health hazard

## Introduction

The magnitude of plastic debris has recently become a topic of significant interest. Globally, more than 320 metric tons of plastic is produced every year, with a great majority of that plastic being of single-use purpose (Browne et al., 2010; Olubukola et al., 2018). Approximately 6-26% of the plastic produced is disposed of in recycling facilities for reuse with the remaining majority of 74-94% deposited in landfills or passively transported to natural or agricultural environments due to negligent disposal. A study conducted by Olubukola et al. (2018) investigated that many pathways plastics can take to reach the ocean (Figure 1). An estimated 80% of the plastic that is present in the ocean originated from a land-based source, with the remaining 20% coming from seafaring vessels (STAP, 2011). The 20% annual input from seafaring vessels enters the oceans in spite of the fact that the dumping of plastics into any marine environment is strictly banned under Annex V of the MARPOL Convention (Rakestraw, 2012). The land-based forms of plastic pollution that enter the oceans occur as either macroplastics, or primary or secondary microplastics (particles of plastic measuring 5mm or less in diameter), and these have been identified to originate from two primary sources: outfalls from plastic production industry and irresponsible consumer disposal. Outfalls from factories often transport primary microplastics via natural and manmade waterways either directly to the ocean or into soil, which is then later eroded away and transported to the ocean (Bean, 1987).

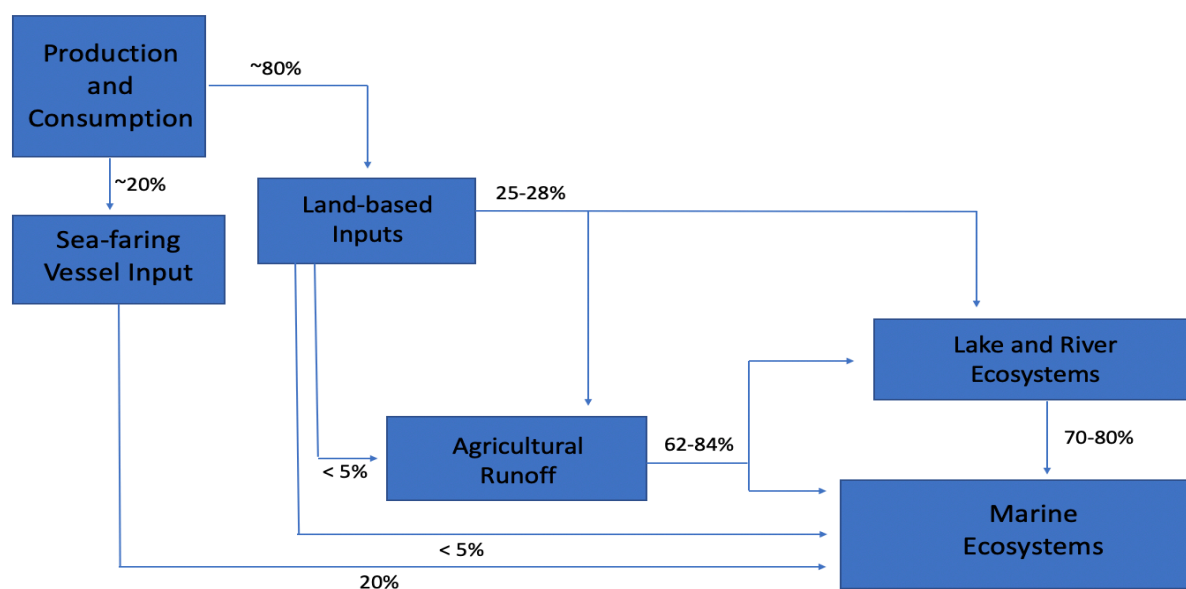


Figure 1. Estimates of sources of input of plastics to the marine environment, with approximately 80% from land-based sources and the remaining 20% from sea-faring vessels. Figure adapted from text and figures in Olubukola et al. (2018).

Plastics which make their way into the marine environment can disperse anywhere from the shoreline to the deep sea (Choy and Drazen, 2013). The stability and persistence of these synthetic polymers has resulted in a mass accumulation of plastics in the marine environment. The precise monitoring of microplastics in particular has yet to be refined due to inherent difficulties associated with the process of modeling the accumulation of microplastics in the marine environment. The inability to detect the smallest microplastics in sampling overlooks what is likely to be a significant portion of the plastic present in the ocean. Additionally, in models produced to date there is a lack of three-dimensional consideration. Models assume all plastics to be present only at the surface, and do not account for the particles that are present at varying depths in the water column due to changes and variations in density of particles (Olubukola et al., 2018). It is estimated that nearly 250 metric tons of plastic has accumulated in the world ocean either directly or indirectly as a result of anthropogenic activities. It is likely that these are low-end estimates, as these approximations are made based upon incomplete models of the transport and accumulation of plastics to the marine environment (Olubukola et al., 2018).

Little research has considered the impacts of marine plastics on organisms beyond the scope of simple physical blockage due to ingestion. Degradation of macroplastics into microplastics can be a result of abiotic processes such as UV exposure, mechanical fragmentation, and oxidation (Andrady and Pegram, 1991); and biotic processes such as digestion by microbes (Gewert et al., 2015). Because of the stability of the polymeric structure, plastic particles will continue to persist as the processes of degradation erode them down into nanoparticle size. Surprisingly, microplastics pose an even bigger threat to the marine environment than the macroplastics from which they originate. The degradation of larger plastic debris into microplastics has allowed these particles to infiltrate the marine food web at trophic levels as low as zooplankton and planktivorous fishes (Choy and Drazen, 2013; Cole et al., 2015). Biodegradation of plastics in the marine environment is affected by a variety of factors. This biodegradation is largely a factor of the stability of the polymeric structure of different plastic polymers. Degradation rates of plastic polymers are retarded by marine exposure as opposed to air exposure. The surrounding water absorbs the majority of the heat from UV radiation, slowing degradation rates significantly (Andrady and Pegram, 1991). Most research on degradation rates of plastic polymers has been conducted considering only exposure to air (Andrady, 2003). Studies have considered long-term exposure to water in order to estimate degradation rates in the marine



environment, and have found that many factors come into play when a polymer degrades in the marine environment which alter the rates of degradation of polymers with specific characteristics. During that abiotic degradation, carboxylic end groups are formed which allow for the process of biodegradation to begin on those polymers via the microorganisms and enzymes present in the marine environment (Gewert et al., 2015). Degradation into smaller fragments by abiotic processes allows for biodegradation processes to occur more quickly, increasing the potential number of byproducts released by biodegradation (for example release of plastic additive or stabilizers) (Gewert et al., 2015). Because both biotic and abiotic factors play a large role in the rate of biodegradation of polymers in the marine environment, it is important to consider simultaneous occurrence of both types of degradation.

Microplastics' decreased size results in an increased surface area to volume ratio, resulting in a higher chemical adsorption capacity, particularly for persistent organic pollutants (POPs). The weathering of plastics also further increases their surface area by creating folds and divots, resulting in increased adsorption sites for chemicals to bind to their surfaces (Crawford and Quinn, 2016). The decreased size allows for the process of bioaccumulation, or the accumulation of substances in living organisms ("Bioaccumulation" [*Miriam Webster*]), to begin at low levels of the trophic structure and magnifies the potential to impact the marine environment by increasing the potential effects of biomagnification, or the rate of increase in concentration of a toxin as it travels up the food chain ("Biomagnification" [*Miriam Webster*]). With the initial introduction of plastics into the marine food web possible at trophic structure levels as low as primary consumers, due to the small size of microplastics, plastics and their associated toxins are then potentially subject to substantial biomagnification as they climb trophic levels, which would not occur if those plastic particles were unable to enter the food web until an organism large enough to consume macroplastic particles ingested them. Operating under this idea, it could be assumed that this is a part of what makes plastic polymer particles so dangerous to marine life (Rochman et al., 2014).

Stereochemistry, or the three-dimensional arrangement of molecules, gives plastic a unique ability to sorb and desorb chemicals onto it. Sorption of chemicals can occur through two different processes: absorption and adsorption (Crawford and Quinn, 2016). Absorption refers to the diffusion of compounds into the bulk of a plastic particle, whereas adsorption refers to the adherence of a compound to the surface of a plastic particle. Which process occurs relies on the physical structure of both the polymer and of the compound in question. As discussed earlier, the

process of adsorption can occur at higher relative rates on microplastic particles in comparison to macroplastic particles as a result of their increased surface area to volume ratio (Crawford and Quinn, 2016). This allows for a variety of chemicals to be both contained within plastic polymer particles, and be taken up and transported by those particles.

Plastics can possess both constituent monomers from the manufacturing process, as well as organic contaminants (POPs) which are naturally resilient to breakdown by natural processes and can persist in the marine environment for long periods of time. Plastic polymers may possess POPs from the production process, such as hexabromocyclododecane (a commonly used flame retardant), but can also sorb these compounds into their polymeric structures and accumulate them from the water column (Tueten et al., 2007; Bakir et al., 2012; Bakir et al., 2014); (Crawford and Quinn, 2016). The transfer of these substances from plastic particles into organisms following ingestion has been shown in some experiments (Colabuono et al., 2010; Cole et al., 2011; Rochman et al., 2013) and bioaccumulation of these substances in marine organisms may have toxicological implications (Cole et al., 2011). The suite of toxic compounds associated with plastic particles may accumulate in marine organisms and result in toxicological impacts on individuals, which could eventually result in population-wide effects (Besseling et al., 2013; Ivar do Sul and Costa, 2014). A two-fold effect of bioaccumulation and biomagnification may occur in the higher trophic levels if in fact some of these compounds, such as the PBDE's, are as stable as suggested (Rochman et al., 2014). If this is true, then commercially significant fishery species, which are often secondary or tertiary predators, would accumulate greater concentrations of plastic-associated toxins compared to organisms existing lower in the trophic structure.

The prevalence of marine plastics and the potential toxicity they pose to marine organisms through their associated toxic compounds is not yet well understood, but it is becoming clear that a threat does exist for marine organisms (Rochman et al., 2013). This threat expands to human populations in a number of ways. The potential for the incorporation of toxic substances into the tissues of commercially significant fishery species at magnified concentrations could have major implications for human health, resulting in carcinogenic or otherwise negative effects (Jambeck et al., 2001). It thus poses a direct threat to the fishery industry, by compromising the quality and/or viability of the product.

The goal of this study was to investigate that concept further. A critical review of existing literature on the polymer characteristics and associated compounds was conducted, and potential

effects incorporation of those polymers in marine organisms might have was assessed. This study sought to provide insight on the scope of the toxicity threat that marine plastics pose to organisms by creating a toxicity threat scale on which each type of plastic will be ranked, based on which types of plastic particles are most pervasive in the marine environment and which toxic compounds are most commonly associated with each type of polymers. Furthermore, this study aims to estimate the threat to organisms which exist higher in the trophic structure, whom may be subject to an increased threat due to biomagnification of plastic associated compounds. This study estimates the potential exposure of upper trophic level predators to the suite of toxins associated with marine plastics, with a specific focus on commercially significant fishery resource species. This research therefore bridges the gap between human interests and the issue of plastic pollution by evaluating the unseen impacts of plastic particles in the environment, and how this translates to direct threats to a major food source for populations across the globe.

The broad scope of plastic production and use of synthetic polymers has become integral to modern society, and society has become very disconnected from its daily consumption habits. An expectation for the convenience of plastic products, specifically of single-use plastic products, is a mindset adopted in all regions of the globe. Single-use products have become the norm, and the irresponsible disposal of those waste products is an issue of rising concern. As production and consumption of plastic products continues to rise, the capacity to responsibly dispose of or recycle that waste is gradually diminishing, and an ever-increasing quantity of it winds up being lost to the environment. A subsequently larger amount of plastic makes its way to the marine environment every year (Engler, 2012; Eriksen et al., 2014). Plastic debris in the world oceans has reached a point at which it is no longer possible ignore the link between human plastic consumption and the impact that plastic waste has on the environment. The need to inform both the scientific community and the public of the full implications of plastic in the marine environment is crucial, as the abundance and durability of plastics mean that plastic polymers which have already entered the marine environment, and that have been entering the marine environment will have effects on the marine food web for many years to come (Derraik, 2002).

The understanding of the scope of the impact that plastic-associated compounds have on marine organisms is currently limited, especially in regards to toxicology. This study sought to create a direct connection between the average person and the issue at hand by assessing the potential toxicological impacts of marine plastics on a significant marine resource, fishery species.

The aim of this study was to create a general profile for the most pervasive and harmful marine plastics in a specific region in order to assess what toxic plastic-associated constituents pose the greatest threat to the marine food web that included the species of interest for the study.

The toxicological properties of marine plastics is a little studied subject. The majority of research in the past has been focused solely on the mechanical effects that plastic debris have on marine organisms, such as the blockage of gut passage, strangulation, etc. (Boerger et al., 2010; Davison and Asch, 2011). The chemical suite of toxic substances associated with macro and micro plastic debris is an invisible threat to the health of marine ecosystems. Exponential rates of accumulation of plastic debris in the marine environment over the past few decades have led to an expanded need to better understand the way these polymers interact with the environment and affect the organisms within it. Every single level of the trophic structure is impacted by the presence of plastics in the marine environment, and these effects are not limited to the direct ingestion of plastic particles themselves. The same concepts which play a key role in the transfer of nutrients through the trophic structure apply to the transfer of toxic compounds as well. The processes of bioaccumulation and biomagnification, which allow for higher trophic level organisms to obtain the energy they need, also amplify the concentration of these dangerous chemicals which have been incorporated by their prey, and their prey's prey. It is important to gain an understanding of the implications of the exposure of higher trophic level organisms to amplified concentrations as a result of these processes.

While little research exists on the rates of incorporation and the toxicological effects of plastic-associated organic and inorganic constituents, it can be useful to look at the research that does exist on these constituents in order to make an assessment of the impact they might have on marine organisms. Effects of human exposure is where the majority of research lies regarding the toxicology of the constituents in question due to ingestion or exposure. The CDC has studied and gathered toxicology data on all of the constituents in this study. The majority of the constituents being considered for this study have been listed as either positively or potentially carcinogenic to humans, and all of them are listed as having toxic effects at or above a particular concentration level, or Minimal Risk Level.

If these toxic constituents are in fact bioavailable to the organisms considered for this study, they could potentially induce population-wide impacts, a significant threat to the fisheries industry (Besseling et al., 2013; Ivar do Sul and Costa, 2014). The potential for incorporation of these

substances by marine organisms also threatens the viability of commercial fisheries' product, resulting in an unsafe product for human consumption (Carberry et al., 2018). Investigation of these potential toxicological implications of plastic-associated toxic constituents seeks to illustrate these threats posed by the infiltration of the marine food web by plastic pollution.

## **Objectives**

The overall aim of this research was to generate toxicity profiles for the three most pervasive plastic polymers present in marine litter. In order to assess the potential threat posed by exposure via incorporation into the marine food web, the organic and inorganic constituents noted to be associated with these polymers were identified and incorporated into each polymer's profile. An estimate of the potential increase in organic and inorganic compound concentrations due to these processes was then created through the calculation of threat scores for each toxin relative to both polymer and species. Additionally, this research sought to attempt to determine which plastic-associated compounds pose the most significant threat to marine life as a result of their bioaccumulation and biomagnification as they progress through the trophic structure. This in turn was used to evaluate which plastic polymers pose the greatest threat.

The objectives for this research were broken into three subcategories of discipline: toxicology, ecology, and biology. All three perspectives came together to form a more complete picture of the toxicological impacts marine plastics may have on marine organisms, especially those which occur higher in the trophic food web structure.

### **Toxicological Objectives**

The toxicological objective of this research was to determine which compounds contained within the most common forms of marine plastics in the Southwest Atlantic pose the greatest threat to marine organisms. The central goal was to narrow the working data down to the plastic polymers, and therefore the constituents, which the significant fishery species in the state of Florida are exposed to, and then decipher which of those posed the greatest toxicity threat by calculating toxicity threat scores.

## **Ecological Objectives**

Bioaccumulation of the toxic compounds associated with plastic polymers results in elevated concentrations in individual organisms due to the cumulative effects of repeated intake or ingestion of plastics or microplastics from the marine environment. To compound the effects of bioaccumulation, biomagnification can also co-occur. The process of biomagnification occurs when concentrations increase due to the transfer to the next trophic level. This trophic level exchange is accomplished by the consumption of prey by a predator, resulting in the toxins that were incorporated into the prey item then being introduced, and potentially incorporated, to the predator.

Factors including variations in metabolism and body size play a role in the uptake and concentration of chemicals within organisms in a real-world situation. However, for the purposes of this study, calculations were based upon the assumption that the concentration following the transfer to the next trophic level remains unchanged. The objective of using generalized calculations and observations on larger sets of data was intended to provide proxies for the exposure of marine organisms to toxic chemicals associated with marine plastics, not to be representative of exact rates of incorporation. The purpose of this approach was to gain a broader-scope perspective on the toxicological potential of marine plastics in commercial fishery species.

## **Biological Objectives**

The biological objectives of this study were to determine which polymer type poses the greatest threat to commercially significant fishery species in the Southwest Atlantic based upon the information gathered on organic and inorganic constituents typically present in each of the polymer types. The conclusions were intended to provide a basis on which to consider the potential health hazard implications of exposing humans to these constituents via consumption of the commercially significant fishery species examined in this study, and for this information to be of value in consideration of management and regulation policy in plastic production.

The preceding objectives for this work were addressed by obtaining the answers to the following three comprehensive questions: What are typical concentrations of toxic compounds in each of the three plastic polymers? What is the capacity of those constituents to bioaccumulate, and consequently biomagnify, in species of varying trophic levels? And, which plastic polymers

contribute the most potential to engender those increased concentrations in higher trophic level fishery species?

The role of ecosystem-wide processes was explored, such as the process of biomagnification which occur as toxins ascend the trophic structure. While both biomagnification and bioaccumulation are biological processes, understanding how the two combined create cumulative impacts not just on individuals or populations but across species and trophic levels provided insight on the ecological objectives outlined for this work. This research sought to examine if the persistence of toxic organic and inorganic constituents associated with plastic polymers in the marine trophic food web leads to increased exposure to those substances in commercially significant fishery species. This is the result of the biological processes of bioaccumulation and biomagnification, which occur following the ingestion of marine plastics by organisms. Commercially significant fishery species are consequently exposed to elevated levels of these toxic compounds compared to organisms at lower trophic levels. It was hypothesized that biomagnification scores would be significantly influenced by an organism's trophic structure rank, and that in turn it is anticipated that potentially carcinogenic levels of toxic constituents are occurring at higher trophic levels of the marine food web.

Second, cataloging which plastic polymers are most common in the marine environment, how stable their polymeric structures are, how much sorption capacity they possess, and which toxins those most common forms are likely to obtain in order to provide insight into the potential impacts those polymers might pose to the species of interest. This research also sought to examine if plastic polymers which possess a more stable structure, and experience slower rates of degradation in the marine environment, pose a significantly greater toxicity threat to marine organisms. It is vital to gain an understanding of the total toxicological threat that plastic polymers pose to marine organisms due to the compounds they inherently possess via adsorption and production processing. This work then takes that a step further, by ascertaining the biological impacts those compounds have on marine organisms if they are in fact incorporated into the tissues of the individual; shedding some light on how dangerous their presence in the marine food web could be. Because humans enter the marine food web when fishery species are consumed, these biological impacts are also of concern for human health.

## **Methods and Materials - Data Acquisition**

All data used for this study was acquired from existing databases. For the purposes of this study, the data gathered was relevant specifically to the southwestern Atlantic region, in order to illustrate the potential impacts on commercial fisheries in that area. The species of interest are those which are commercially significant fishery species in the state of Florida. Species of interest were selected using information from the Florida Department of Agriculture and Consumer Services (FDACS) (FDACS, 2015) and the Florida Fish and Wildlife Conservation Commission (FFWCC) Commercial Fisheries Landing Summaries (FWC, 2018).

Additionally, a specific region was selected to investigate, as opposed to drawing from datasets that cover a large area, in an attempt to more accurately reflect the actual profile of plastic debris and their associated toxins in a region. The toxins which are present in an environment, both naturally and as a result of anthropogenic inputs, are largely specific to that region. The level of chemicals, such as POP's, present in any particular area will vary as a product of many factors, such as river outflows, industrial inputs, etc. (Endo et al., 2005).

### **Commercially Significant Fishery Species Selection**

Selection of species was based upon the Dockside Value attributed to general groups of commercially significant fisheries by the Florida Department of Agriculture and Consumer Services (FDACS, 2015), and then species-specific selections were based upon values estimated by the Florida Fish and Wildlife Conservation Commission Commercial Fisheries Landing Summaries (FWC, 2018). In order to illustrate the effects of biomagnification and bioaccumulation across trophic levels, organisms of a range of trophic structure levels were selected for the purposes of this study. Assessing the effects of polymers on a range of organisms allowed for the effect of trophic structure rank on biomagnification scores of constituents and polymers to be realized, illustrating that organisms which occupy a higher trophic level structure will experience a more serious threat.

### **Plastic Polymers**

#### *Abundances*

In order to determine the most common forms of marine plastics present in the marine environment, data were obtained from the records for National Oceanic and Atmospheric



Administration's Marine Debris Monitoring and Assessment Project. Land-based plastic surveys were selected for this study because these have been the primary sampling method for surveying marine plastics in the scientific community in the past as they provide larger, more spatially and temporally consistent datasets, yielding greater statistical power (Browne et al., 2010; Choy and Drazen, 2013; Ryan et al., 2009). This particular monitoring project was selected with the purpose of localizing the information used. By selecting to use data that was only recorded from sites in the state of Florida, the goal is to try and emulate the circumstances that commercially significant marine organisms in the state of Florida are exposed to, in other words what plastic polymers they are most frequently exposed to in the surrounding waters.

In order to obtain access to the survey results, an account was requested through MDMAP, after which the creation of an account was approved by a NOAA Affiliate. Access to data collected from all surveys conducted under this program can then be accessed using that account. Data from the monitoring locations MDMAP ID#: 277 and 1115 were used, as these are located on the east coast of Florida DMM: 29.102087, -80.973691 and 26.89241, -80.05675. By selecting these specific survey sites, the aim was to keep the estimates of plastic debris abundances as close to the real-world abundances seen by commercially significant fishery species in the Western Atlantic. The most pervasive forms of marine plastics in the southwest Atlantic were identified using information gathered from these surveys conducted under the program from 01/17/2017 to 01/24/2018.

### *Stabilities*

Many plastic polymers contain a carbon backbone and are more susceptible to abiotic degradation, thus their degradation rates are quite different in the marine environment than in a laboratory setting (Gewert et al., 2015). A centralized way to quantify polymer degradation rates in the marine environment has not yet been determined. Some general relationships between the three polymers of interest were drawn from a review of previous studies in order to create a rank scale for stability. The use of information from studies conducted on polymers present in the marine environment was important in order to have a more accurate idea of the rates at which these polymers biodegrade relative to one another. Using the following information, stability ranks were assigned to each polymer of interest and incorporated into that polymer's profile in order to address the inherent differences in degradation rates due to their differing polymeric structures.

Information on polypropylene and polyethylene stability was obtained from studies by Sudhakar et al. (2007) and Gewert et al. (2015). Sudhakar et al. (2007) determined that biodegradation of polypropylene is significantly slower than that of polyethylene in the marine environment. A review by Gewert et al. (2015) confirmed that polypropylene possesses a less stable structure than polyethylene as a result of the molecular structure carbon backbone, which the researchers stated reduces the polymer's susceptibility to microbial degradation; implying that this would cause biodegradation of polypropylene to occur more quickly than polyethylene. A study by Andrady and Pegram (1991) investigated the biodegradation rate of polystyrene in the marine environment and found that it was highly susceptible to biodegradation by the many factors present in the marine environment, and that it in fact degrades more rapidly in water than it does in air, the contrary being true for polyethylene and polypropylene (Andrady, 2003). Gewert et al. (2015) confirmed that polystyrene is the most susceptible to biodegradation of the polymers being considered.

### *Sorption Capacities*

The sorption capacities of the three plastic polymers of interest were obtained from Olubukola et al. (2018). The following average sorption capacity rankings for the plastic polymers of interest, as well as a variety of other polymers, with one being the highest sorption capacity rank and 5 being the lowest were ascertained from this study (Olubukola et al., 2018): Polyethylene- 1.4, Polystyrene- 1.8, and Polypropylene- 2.6.

### **Plastic-Associated Toxic Constituents**

A list of the toxic organic and inorganic constituents added to polyethylene, polypropylene, and polystyrene polymers, as well as those which sorb into these polymers from the water column, and a ranking of their hazard levels and potential health hazards due to exposure were compiled from multiple sources and used in building the toxicity profiles of each polymer. The POP's known to associate with the selected polymers and which are present at toxicologically significant concentrations were obtained from previous studies (Rios et al., 2007; Ogata et al., 2009; Hirai et al., 2011). Persistent organic pollutants considered included: polychlorinated biphenyls, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, dichloro diphenyl trichloroethane, and chlordane. These were the organic compounds on which the most comprehensive data could be found for known, relative concentrations in the three plastics

polymers of interest. Polyethylene and polypropylene were assessed for polychlorinated biphenyls, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, and dichloro diphenyl trichloroethane concentrations (Hirai et al., 2011). Polystyrene was assessed for polychlorinated biphenyls, dichloro diphenyl trichloroethane, polycyclic aromatic hydrocarbons, and chlordane concentrations (Van et al., 2011). In the case of the POPs, all data collected on concentrations were obtained from samples recovered from the marine environment (i.e. marine microplastics). A record of the most common and well-documented inorganic, toxic constituents and their average concentrations in the three different plastic polymers were compiled. The inorganic constituents of arsenic, aluminum, bromine, cadmium, cobalt, chromium, antimony, selenium, and zinc were considered for all three polymers with the exception of aluminum for polystyrene polymers as it was not found in detectable concentrations (Nomura et al., 2000). In the case of inorganic constituents, data collected on concentrations were not obtained from samples that had been recovered from the marine environment as was the case with those samples used for POP concentrations.

Minimal risk levels (MRLs) for each organic and inorganic constituent were obtained from the Agency for Toxic Substances and Disease Registry. These concentrations values are similar in acquisition and function to the reference dose and reference concentration values maintained by the Environmental Protection Agency and provide concentrations at which humans can be exposed to a substance over specified time periods without experiencing health effects as a result of exposure to that substance (ATSDR, 2019). Concentrations for intermediate oral exposures were extracted from information compiled by the CDC for use in this study, with a few exceptions where intermediate oral values were not listed as noted in Table 4.

Centered and scaled bioaccumulation factors (B-scores) for each constituent were obtained from RIVM Report 601356001/2011. These values expand upon the typically used bioconcentration factors by incorporating the potential for biomagnification of substances via trophic level exchanges. These considerations are useful when considering how a substance will behave in higher trophic structure organisms, and more specifically in air-breathing organisms (Rorije et al., 2011). This allowed for what may be a potentially more accurate representation of the increases in organic and inorganic toxic constituents' presence in the polymers of interest when considering their infiltration of the food web at the highest trophic level, that of humans.

## **Data Analysis**

### **Most Abundant Polymer Types**

Raw data counts from MDMAP surveys were used to determine which types of plastic polymers are most common in the region of interest, the southwestern Atlantic off the coast of Florida (Table 1). From analysis of the datasets provided by the MDMAP program, it was determined that the six most common forms of marine plastics found represented 80% of the total samples collected over all surveys. The results of this analysis are verified by the findings of other studies (Lee et al., 2014; Olubukola et al., 2018). These six groups of marine plastics were comprised of three types of plastic polymers: polypropylene, including both high-density and low-density polypropylene; polystyrene, including both high-density and low-density polystyrene; and polyethylene, including both high density and low-density polyethylene.

Table 1. Plastic Polymer Abundances<sup>a</sup>

MDMAP ID #	Survey ID #	Survey Date	Hard Plastic	Foamed Plastic	Filmed Plastic	Food Wrappers	Beverage Bottles	Other Jugs/ Containers	Bottle/ Container Caps	Cigar Tips	Cigarettes
<b>1115</b>	6444	9/23/17	83	89	18	26	13	4	102	4	2
<b>1115</b>	8115	10/22/17	139	84	12	2	5	0	34	0	20
<b>1115</b>	8169	11/19/17	59	59	8	2	0	0	13	0	11
<b>1115</b>	8241	12/14/17	60	67	5	2	1	0	4	0	19
<b>1115</b>	8288	1/16/18	173	68	25	14	0	0	23	0	14
<b>1115</b>	8363	2/14/18	128	171	16	0	0	1	21	0	25
<b>277</b>	5363	1/17/17	10	24	16	24	12	4	13	3	3
<b>277</b>	5468	2/17/17	25	33	7	4	6	1	6	0	0
<b>277</b>	5560	3/21/17	10	0	0	13	7	1	4	0	0
<b>277</b>	5735	4/20/17	24	6	112	12	4	11	9	0	1
<b>277</b>	5894	5/19/17	10	1	2	7	1	0	4	0	1
<b>277</b>	6026	6/15/17	3	0	7	3	1	3	2	0	0
<b>277</b>	6142	7/17/17	5	2	17	1	4	0	1	0	1
<b>277</b>	6268	8/14/17	10	4	1	6	4	0	2	0	1
<b>277</b>	6520	9/25/17	4	3	12	3	1	2	2	0	1
<b>277</b>	8129	10/30/17	7	3	14	0	10	3	3	0	2
<b>277</b>	8228	11/30/17	17	3	4	4	2	1	1	0	0
<b>277</b>	8268	12/15/17	3	1	3	0	1	1	0	0	0
<b>277</b>	8361	1/24/18	7	1	34	0	2	1	0	0	0
<b>Avg. Counts</b>			<b>40.89</b>	<b>32.58</b>	<b>16.47</b>	<b>6.47</b>	<b>3.89</b>	<b>1.74</b>	<b>12.84</b>	<b>0.37</b>	<b>5.32</b>
<b>Primary Polymer (s)</b>			<b>HDPP</b>	<b>PS</b>	<b>PE</b>	<b>PE</b>	<b>PE</b>	<b>PE</b>	<b>PE</b>	<b>LDPE</b>	<b>Cellulose Acetate</b>
<b>Most Common Rank</b>			<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>10</b>	<b>13</b>	<b>4</b>	<b>18</b>	<b>7</b>

<sup>a</sup>Raw data count values obtained and compiled from MDMAP database for determining the relative abundances of most common plastic polymers found at monitoring sites 277 and 1115.

Table 1 Continued. Plastic Polymer Abundances<sup>a</sup>

MDMAP ID #	Survey ID #	Survey Date	Disposable Lighter	6-Pack Rings	Bags	Plastic Rope/ Net Pieces	Buoys & Floats	Fishing Lures & Line	Cups	Plastic Utensils	Straws
1115	6444	9/23/17	3	0	0	6	1	2	7	14	24
1115	8115	10/22/17	1	0	0	7	0	1	6	9	9
1115	8169	11/19/17	0	0	0	5	0	1	0	1	6
1115	8241	12/14/17	0	0	2	1	0	2	0	0	4
1115	8288	1/16/18	0	0	5	11	1	2	3	0	17
1115	8363	2/14/18	0	0	2	13	0	32	3	0	12
277	5363	1/17/17	0	0	37	0	0	0	12	0	1
277	5468	2/17/17	0	0	10	0	0	2	1	0	2
277	5560	3/21/17	0	0	13	0	1	0	4	0	1
277	5735	4/20/17	1	0	5	0	0	0	7	0	4
277	5894	5/19/17	0	1	7	1	1	1	0	1	0
277	6026	6/15/17	0	0	3	0	0	1	10	0	1
277	6142	7/17/17	0	0	6	0	1	0	1	0	0
277	6268	8/14/17	0	2	5	1	0	2	8	0	2
277	6520	9/25/17	0	0	5	0	0	1	3	0	0
277	8129	10/30/17	0	0	6	0	0	0	0	6	2
277	8228	11/30/17	3	0	3	0	0	0	7	0	1
277	8268	12/15/17	0	0	2	1	0	0	3	0	0
277	8361	1/24/18	0	0	3	0	0	2	2	0	0
<b>Avg. Counts</b>			<b>0.42</b>	<b>0.16</b>	<b>6</b>	<b>2.42</b>	<b>0.21</b>	<b>2.58</b>	<b>4.05</b>	<b>1.63</b>	<b>4.53</b>
<b>Primary Polymer (s)</b>			<b>Poly-acetal</b>	<b>HDPE</b>	<b>LDPE</b>	<b>PP, PE</b>	<b>HDPE</b>	<b>Nylon, PVDF, PE</b>	<b>PE, PP</b>	<b>PP, PS</b>	<b>PP</b>
<b>Most Common Rank</b>			<b>17</b>	<b>21</b>	<b>6</b>	<b>12</b>	<b>20</b>	<b>11</b>	<b>9</b>	<b>14</b>	<b>8</b>

<sup>a</sup>Raw data count values obtained and compiled from MDMAP database for determining the relative abundances of most common plastic polymers found at monitoring sites 277 and 1115.

Table 1 Continued. Plastic Polymer Abundances<sup>a</sup>

MDMAP ID #	Survey ID #	Survey Date	Balloons	Personal Care Products	Other
1115	6444	9/23/17	0	4	1
1115	8115	10/22/17	0	0	0
1115	8169	11/19/17	1	0	0
1115	8241	12/14/17	0	2	0
1115	8288	1/16/18	3	0	0
1115	8363	2/14/18	0	3	0
277	5363	1/17/17	0	4	2
277	5468	2/17/17	0	0	1
277	5560	3/21/17	0	1	0
277	5735	4/20/17	0	1	1
277	5894	5/19/17	0	2	0
277	6026	6/15/17	0	0	0
277	6142	7/17/17	0	0	0
277	6268	8/14/17	1	0	0
277	6520	9/25/17	0	0	1
277	8129	10/30/17	0	0	1
277	8228	11/30/17	0	0	0
277	8268	12/15/17	0	0	3
277	8361	1/24/18	0	0	2
	<b>Avg. Counts</b>		<b>0.26</b>	<b>0.89</b>	<b>0.63</b>
	<b>Primary Polymers (s)</b>		<b>Rubber, Latex, Polychloroprene, Nylon</b>	<b>PP, PE, Nylon</b>	
	<b>Most Common Rank</b>		<b>19</b>	<b>15</b>	<b>16</b>

<sup>a</sup>Raw data count values obtained and compiled from MDMAP database for determining the relative abundances of most common plastic polymers found at monitoring sites 277 and 1115.

## **Most Commercially Significant Species**

The species selected for the purposes of this research, using data from FDACS and FWC surveys, were: Red Grouper (*Epinephelus morio*), Red Snapper (*Lutjanus campechanus*), Swordfish (*Xiphias gladius*), King Mackerel (*Scomberomorus cavalla*), Black Mullet (*Mugil cephalus*), and Bigeye Tuna (*Thunnus obesus*). These species have been selected based upon their relative economic significance for fisheries in the state of Florida. Estimates of trophic level position for each species of interest were based on values calculated by Arreguín-Sánchez et al. (1993) on coastal species of the southwestern Gulf of Mexico. The six species of interest were assigned the following trophic level ranks: *Epinephelus morio*- 4.3, *Lutjanus campechanus*- 4.0, *Xiphias gladius*- 4.8, *Scomberomorus cavalla*- 4.0, *Mugil cephalus*- 3.2, *Thunnus obesus*- 4.6. These values were drawn from a study modelling the trophic structure of coastal fishes in the southwestern Gulf of Mexico (Arreguín-Sánchez, 1993). Some values were approximations, based upon the calculated values for similar species in the trophic food web structure. For species which were not included in that study by Arreguín-Sánchez, the trophic level rank of the species that most closely resembled them was selected. This was the case for *Xiphias gladius*, *Thunnus obesus*, and *Mugil cephalus*. This determination was based on information from a similar study conducting trophic structure modeling by Pauly and Palomares (2005). These trophic level rank values were intended to illustrate the number of trophic exchanges each chemical could potentially undergo if it had entered the marine food web at the lowest trophic level.

## **Building of Polymer Profiles**

The plastic polymers of interest were assigned the following stability ranks on a scale of one to four, with four being the most stable polymer and one being the least: polystyrene- 1, polyethylene- 3, and polypropylene- 4. These are based on the literature review described in the Data Acquisition section. This considers how the stability of a polymer will play a role in its impact on the marine environment; if a polymer particle can remain in the marine environment for a longer duration in spite of degradation, resulting in microplastic polymer, it has an increased probability of accumulating more toxic constituents, and of entering and remaining in the marine food web.

For the purposes of this study, bioaccumulation potential was estimated using a simple model. All values were intended to provide a basic understanding of capacity for a constituent to



bioaccumulate within the marine environment. This is especially true in the case of the inorganic constituents. The use of the B-score, a centered and scaled bioaccumulation factor calculated by the National Institute for Public Health and the Environment (Rorije et al., 2011), in the calculation of the organic constituents' bioaccumulation scores incorporates an extra layer of complexity in understanding how that constituent behaves in the marine environment and what concentrations of constituents may be in plastic polymers present in the marine environment.

The purpose of this model is to use the basic ideological format of the process of bioaccumulation to estimate the tendency of a constituent to bioaccumulate, and is meant to provide a score that represents the greatest potential for bioaccumulation. The model has two parts. The first part considers the integrity of the polymer, taking the stability of that polymer (on a normal scale) and the capacity of that polymer to sorb constituents (on a reverse rank scale) into account. Research has shown that polymers with more stable structures are capable of having more associated constituents (Crawford and Quinn, 2016). The second part considers the availability of the constituent to that polymer, assuming that the total constituent concentration is able to be sorbed into the polymer.

As previously discussed, little literature exists on the presence of toxic constituents in the marine environment due to plastic association. All research that does exist typically operates based upon the assumption of the worst-case scenario (Lusher et al., 2017), so the complete sorption of constituent into polymeric structure and then the complete desorption of that constituent out of the polymeric structure and into the organism it was consumed by. The design is intentionally uncomplicated, using only what is known about the polymers and the constituents on the surface, without situational context and the many factors that have an impact upon sorption of constituents into and out of plastic polymers as well as into and out of the tissues of marine organisms. The considerations for the polymer integrity and the availability of constituents were intended to model the maximum capacity for bioaccumulation.

Bioaccumulation scores for the constituents, organic and inorganic, of each plastic polymer estimated the total rates of bioaccumulation in each polymer type. The stability rank of the polymer with which the constituents (organic or inorganic) is associated was multiplied by the estimated concentration in which that component is present. From this, a basic interpretation of which constituents are most rapidly accumulating in the marine environment was inferred, as well as which plastic polymers had the most capacity to bioaccumulate toxic constituents.

Bioaccumulation rates of both organic and inorganic constituents associated with the three plastic polymers being considered were estimated using a simple model:

Organic Constituent Bioaccumulation Model:

$$(\text{Stability Rank of Polymer} \div \text{Sorption Capacity Rank of Polymer}) \times (\text{Concentration of Organic Constituent} \times \text{B-score}) = \text{Bioaccumulation}$$

Inorganic Constituent Bioaccumulation Model:

$$(\text{Stability Rank of Polymer} \div \text{Sorption Capacity Rank of Polymer}) \times (\text{Concentration of Inorganic Constituent}) = \text{Bioaccumulation}$$

Information on B-scores were only available for persistent organic pollutant constituents and were incorporated into the calculations in an attempt to provide a more comprehensive estimation for those data. Calculations for inorganic components were conducted using the available information on those substances. For this reason, organic and inorganic constituents were considered and calculated separately throughout this study when bioaccumulation scores were considered.

The bioaccumulation scores were then considered in conjunction with a trophic structure rank in order to estimate biomagnification of the constituents. The trophic structure rank represented an estimation of the degree of biomagnification of compounds by organisms of various trophic levels. There are countless factors that could alter the effect of these biological processes on the concentrations of the constituents, ranging from water salinity, to water temperature (Karlsson et al., 2002), size/age/sex of fish (Mizukawa, 2009), etc. Because this model was based upon the bioaccumulation calculation, the goal set forth was the same: achieve a very simplistic understanding of the greatest capacity for biomagnification without the complications of circumstance. Biomagnification of both inorganic components and persistent organic pollutants associated with the three plastic polymers being considered was estimated using the following model:

$$\text{Bioaccumulation} \times \text{Trophic Structure Rank} = \text{Biomagnification}$$

By using the previously calculated bioaccumulation capacity value for each constituent according to the polymer being considered, and multiplying that value by the trophic structure rank of the organism of interest, a generalized value for the potential for biomagnification of that specific constituent when being transported by that specific plastic polymer in that specific organism was estimated.

### **Assessing Toxicity Threat**

Toxicity threats of the three polymer types, and of their associated constituents, were assessed by drawing together all of the information compiled within the polymer profiles as well as ATSDR substance priority ranks and hazard data on each of the constituents. From this information the polymers with the highest bioaccumulation and biomagnification rates were identified. The constituents with the highest bioaccumulation and biomagnification rates across all polymer types were also identified.

Constituents were assessed for their relative toxicity threats and the substances of primary concern were identified amongst both the organic and inorganic constituents. In order to make this assessment bioaccumulation rates, biomagnification rates, recorded concentrations in polymer types relative to listed MRLs, and ATSDR Substance Priority Ranks for each constituent were taken into consideration. Organic and inorganic constituents were assessed separately.

## **Results**

### **Plastic Polymer Profiles**

Concentrations of constituents for each polymer type were compiled from the best available data (Tables 2 and 3). Biomagnification and bioaccumulation scores were calculated for each plastic polymer type and each species of interest and were compiled into the polymer profiles. The calculated bioaccumulation and biomagnification scores for each polymer type and each species of interest can be seen in Table 4. Table 4 is not the complete polymer profiles, but simply the bioaccumulation and biomagnification scores extracted from the full profiles as these were the values relevant for illustrating the results of the analyses. All information on polymers, including stability ranks, B-scores, etc. were included in complete profiles. Bioaccumulation and biomagnification scores were calculated using the methods outlined for the building of polymer profiles in the Data Analysis section.

Table 2. Concentrations of Organic Constituents from Hirai et al. (2011) and Van et al. (2011) in each Polymer type

	Organic Constituents	Concentration in ug/kg
Polyethylene	PCBs	2.9
	PAHs	105
	PBDEs	15.7
	DDTs	4.8
Polypropylene	PCBs	1
	PAHs	88
	PBDEs	9.1
	DDTs	0.4
Polystyrene	PCBs	5.5
	PAHs	600
	DDTs	27.5
	Chlordane	21.5

Table 3. Concentrations of Inorganic Constituents from Nomura et al. (2000) in each Polymer type

	Inorganic Constituent	Concentration in ug/kg
Polyethylene	Arsenic	3.65
	Aluminum	33182.79
	Bromine	8.19
	Cadmium	12.846
	Cobalt	235.186
	Chromium	95.229
	Antimony	3.85
	Selenium	0
	Zinc	2587.1
Polypropylene	Arsenic	48.333
	Aluminum	45517.79
	Bromine	135
	Cadmium	1340.48
	Cobalt	400875
	Chromium	2028.031
	Antimony	56.867
	Selenium	1239.767
	Zinc	10768.03
Polystyrene	Arsenic	96
	Bromine	54
	Cadmium	0
	Cobalt	0
	Chromium	148
	Antimony	0.14
	Selenium	165
Zinc	81	

Table 4. Bioaccumulation and Biomagnification Scores

Species	Trophic Structure Rank	Polymer	POP	Bioaccumulation Score	Biomagnification Score	Inorganic Component	Bioaccumulation Score	Biomagnification Score
<i>Epinephelus morio</i>	4.3	Polyethylene	PCBs	58.8804	253.18572	As	7.82142857	33.632143
			PAHs	121.05	520.515	Al	71105.9786	305755.71
			PBDEs	31.6243	135.98449	Br	17.55	75.465
			DDTs	9.8743	42.45949	Cd	27.5274643	118.3681
			Co	503.970857	2167.0747			
			Cr	204.063236	877.47191			
			Sb	8.25	35.475			
			Se	0	0			
			Zn	5543.78571	23838.279			
		Polypropylene	PCBs	1.4577	6.26811	As	74.3589692	319.74357
			PAHs	72.8369	313.19867	Al	70027.3692	301117.69
			PBDEs	88.9616	382.53488	Br	207.692308	893.07692
			DDTs	7.0892	30.48356	Cd	2062.27692	8867.7908
			Co	616730.769	2651942.3			
			Cr	3120.04769	13416.205			
			Sb	87.4871846	376.19489			
			Se	1907.33385	8201.5355			
			Zn	16566.2	71234.66			
		Polystyrene	PCBs	3.0654	13.18122	As	56.4705882	242.82353
			PAHs	189.8824	816.49432	Br	31.7647059	136.58824
			DDTs	15.5294	66.77642	Cd	0	0
Chlordane	12.3941		53.29463	Co	0	0		
Cr	87.0588235		374.35294					
Sb	0.08235294		0.3541176					
Se	97.0588235		417.35294					
Zn	47.6470588	204.88235						

Table 4 Continued. Bioaccumulation and Biomagnification Scores

Species	Trophic Structure Rank	Polymer	POP	Bioaccumulation Score	Biomagnification Score	Inorganic Component	Bioaccumulation Score	Biomagnification Score
<i>Lutjanus campechanus</i>	4	Polyethylene	PCBs	58.8804	235.5216	As	7.82142857	31.285714
			PAHs	121.05	484.2	Al	71105.9786	284423.91
			PBDEs	31.6243	126.4972	Br	17.55	70.2
			DDTs	9.8743	39.4972	Cd	27.5274643	110.10986
		Co	503.970857	2015.8834				
		Cr	204.063236	816.25294				
		Sb	8.25	33				
		Se	0	0				
		Zn	5543.78571	22175.143				
		Polypropylene	PCBs	1.4577	5.8308	As	74.3589692	297.43588
			PAHs	72.8369	291.3476	Al	70027.3692	280109.48
			PBDEs	88.9616	355.8464	Br	207.692308	830.76923
	DDTs		7.0892	28.3568	Cd	2062.27692	8249.1077	
	Co		616730.769	2466923.1				
	Cr		3120.04769	12480.191				
	Sb		87.4871846	349.94874				
	Se		1907.33385	7629.3354				
	Zn	16566.2	66264.8					
	Polystyrene	PCBs	3.0654	12.2616	As	56.4705882	225.88235	
		PAHs	189.8824	759.5296	Br	31.7647059	127.05882	
		DDTs	15.5294	62.1176	Cd	0	0	
Chlordane		12.3941	49.5764	Co	0	0		
Cr		87.0588235	348.23529					
Sb		0.08235294	0.3294118					
Se		97.0588235	388.23529					
Zn		47.6470588	190.58824					

Table 4 Continued. Bioaccumulation and Biomagnification Scores

Species	Trophic Structure Rank	Polymer	POP	Bioaccumulation Score	Biomagnification Score	Inorganic Component	Bioaccumulation Score	Biomagnification Score
<i>Xiphias gladius</i>	4.8	Polyethylene	PCBs	58.8804	282.62592	As	7.82142857	37.542857
			PAHs	121.05	581.04	Al	71105.9786	341308.7
			PBDEs	31.6243	151.79664	Br	17.55	84.24
			DDTs	9.8743	47.39664	Cd	27.5274643	132.13183
			Co	503.970857	2419.0601			
			Cr	204.063236	979.50353			
		Sb	8.25	39.6				
		Se	0	0				
		Zn	5543.78571	26610.171				
		Polypropylene	PCBs	1.4577	6.99696	As	74.3589692	356.92305
			PAHs	72.8369	349.61712	Al	70027.3692	336131.37
			PBDEs	88.9616	427.01568	Br	207.692308	996.92308
	DDTs		7.0892	34.02816	Cd	2062.27692	9898.9292	
	Co		616730.769	2960307.7				
	Cr		3120.04769	14976.229				
	Polystyrene	Sb	87.4871846	419.93849				
		Se	1907.33385	9155.2025				
		Zn	16566.2	79517.76				
		PCBs	3.0654	14.71392	As	56.4705882	271.05882	
		PAHs	189.8824	911.43552	Br	31.7647059	152.47059	
		DDTs	15.5294	74.54112	Cd	0	0	
Chlordane	12.3941	59.49168	Co	0	0			
Cr	87.0588235	417.88235						
Sb	0.08235294	0.3952941						
Se	97.0588235	465.88235						
Zn	47.6470588	228.70588						



Table 4 Continued. Bioaccumulation and Biomagnification Scores

Species	Trophic Structure Rank	Polymer	POP	Bioaccumulation Score	Biomagnification Score	Inorganic Component	Bioaccumulation Score	Biomagnification Score
<i>Scomberomorus cavalla</i>	4	Polyethylene	PCBs	58.8804	235.5216	As	7.82142857	31.285714
			PAHs	121.05	484.2	Al	71105.9786	284423.91
			PBDEs	31.6243	126.4972	Br	17.55	70.2
			DDTs	9.8743	39.4972	Cd	27.5274643	110.10986
			Co	503.970857	2015.8834			
			Cr	204.063236	816.25294			
			Sb	8.25	33			
			Se	0	0			
			Zn	5543.78571	22175.143			
		Polypropylene	PCBs	1.4577	5.8308	As	74.3589692	297.43588
			PAHs	72.8369	291.3476	Al	70027.3692	280109.48
			PBDEs	88.9616	355.8464	Br	207.692308	830.76923
			DDTs	7.0892	28.3568	Cd	2062.27692	8249.1077
			Co	616730.769	2466923.1			
			Cr	3120.04769	12480.191			
			Sb	87.4871846	349.94874			
			Se	1907.33385	7629.3354			
			Zn	16566.2	66264.8			
		Polystyrene	PCBs	3.0654	12.2616	As	56.4705882	225.88235
			PAHs	189.8824	759.5296	Br	31.7647059	127.05882
			DDTs	15.5294	62.1176	Cd	0	0
Chlordane	12.3941		49.5764	Co	0	0		
Cr	87.0588235		348.23529					
Sb	0.08235294		0.3294118					
Se	97.0588235		388.23529					
Zn	47.6470588		190.58824					

Table 4 Continued. Bioaccumulation and Biomagnification Scores

Species	Trophic Structure Rank	Polymer	POP	Bioaccumulation Score	Biomagnification Score	Inorganic Component	Bioaccumulation Score	Biomagnification Score
<i>Mugil cephalus</i>	3.2	Polyethylene	PCBs	58.8804	188.41728	As	7.82142857	25.028571
			PAHs	121.05	387.36	Al	71105.9786	227539.13
			PBDEs	31.6243	101.19776	Br	17.55	56.16
			DDTs	9.8743	31.59776	Cd	27.5274643	88.087886
			Co	503.970857	1612.7067			
			Cr	204.063236	653.00235			
			Sb	8.25	26.4			
			Se	0	0			
			Zn	5543.78571	17740.114			
		Polypropylene	PCBs	1.4577	4.66464	As	74.3589692	237.9487
			PAHs	72.8369	233.07808	Al	70027.3692	224087.58
			PBDEs	88.9616	284.67712	Br	207.692308	664.61538
			DDTs	7.0892	22.68544	Cd	2062.27692	6599.2862
			Co	616730.769	1973538.5			
			Cr	3120.04769	9984.1526			
			Sb	87.4871846	279.95899			
			Se	1907.33385	6103.4683			
			Zn	16566.2	53011.84			
		Polystyrene	PCBs	3.0654	9.80928	As	56.4705882	180.70588
			PAHs	189.8824	607.62368	Br	31.7647059	101.64706
			DDTs	15.5294	49.69408	Cd	0	0
Chlordane	12.3941		39.66112	Co	0	0		
Cr	87.0588235		278.58824					
Sb	0.08235294		0.2635294					
Se	97.0588235		310.58824					
Zn	47.6470588		152.47059					

Table 4 Continued. Bioaccumulation and Biomagnification Scores

Species	Trophic Structure Rank	Polymer	POP	Bioaccumulation Score	Biomagnification Score	Inorganic Component	Bioaccumulation Score	Biomagnification Score
<i>Thunnus obesus</i>	4.6	Polyethylene	PCBs	58.8804	270.84984	As	7.82142857	35.978571
			PAHs	121.05	556.83	Al	71105.9786	327087.5
			PBDEs	31.6243	145.47178	Br	17.55	80.73
			DDTs	9.8743	45.42178	Cd	27.5274643	126.62634
			Co	503.970857	2318.2659			
			Cr	204.063236	938.69088			
			Sb	8.25	37.95			
			Se	0	0			
			Zn	5543.78571	25501.414			
		Polypropylene	PCBs	1.4577	6.70542	As	74.3589692	342.05126
			PAHs	72.8369	335.04974	Al	70027.3692	322125.9
			PBDEs	88.9616	409.22336	Br	207.692308	955.38462
			DDTs	7.0892	32.61032	Cd	2062.27692	9486.4738
			Co	616730.769	2836961.5			
			Cr	3120.04769	14352.219			
			Sb	87.4871846	402.44105			
			Se	1907.33385	8773.7357			
			Zn	16566.2	76204.52			
		Polystyrene	PCBs	3.0654	14.10084	As	56.4705882	259.76471
			PAHs	189.8824	873.45904	Br	31.7647059	146.11765
			DDTs	15.5294	71.43524	Cd	0	0
			Chlordane	12.3941	57.01286	Co	0	0
			Cr	87.0588235	400.47059			
			Sb	0.08235294	0.3788235			
Se	97.0588235		446.47059					
Zn	47.6470588		219.17647					

## Bioaccumulation

The data on bioaccumulation of the constituents analyzed within this study showed that among the persistent organic pollutants, polycyclic aromatic hydrocarbons bioaccumulate at the highest rate. For example, in *Xiphias gladius* PAHs received bioaccumulation scores more than two times greater than the second highest scored organic constituent of polyethylene and more than twelve times higher than the second highest scored organic constituent of polystyrene. PAHs appeared to far exceed other organic pollutants in bioaccumulation score, making them priority pollutants to be considered for regulation purposes. Succeeding PAHs in bioaccumulation scores, in order, were PBDEs, then PCBs, Chlordane, and finally DDTs (Figure 2A).

The data on bioaccumulation of inorganic constituents across all species and polymers considered showed that cobalt bioaccumulates at the highest rate, followed by aluminum, zinc, chromium, arsenic, cadmium, selenium, and antimony (Figure 2B). As mentioned previously, the bioaccumulation score calculations were less sophisticated, and therefore likely less representative of actual bioaccumulative concentrations. Information on the bioaccumulation of inorganics in the marine environment due to plastic polymer presence is not well-established.

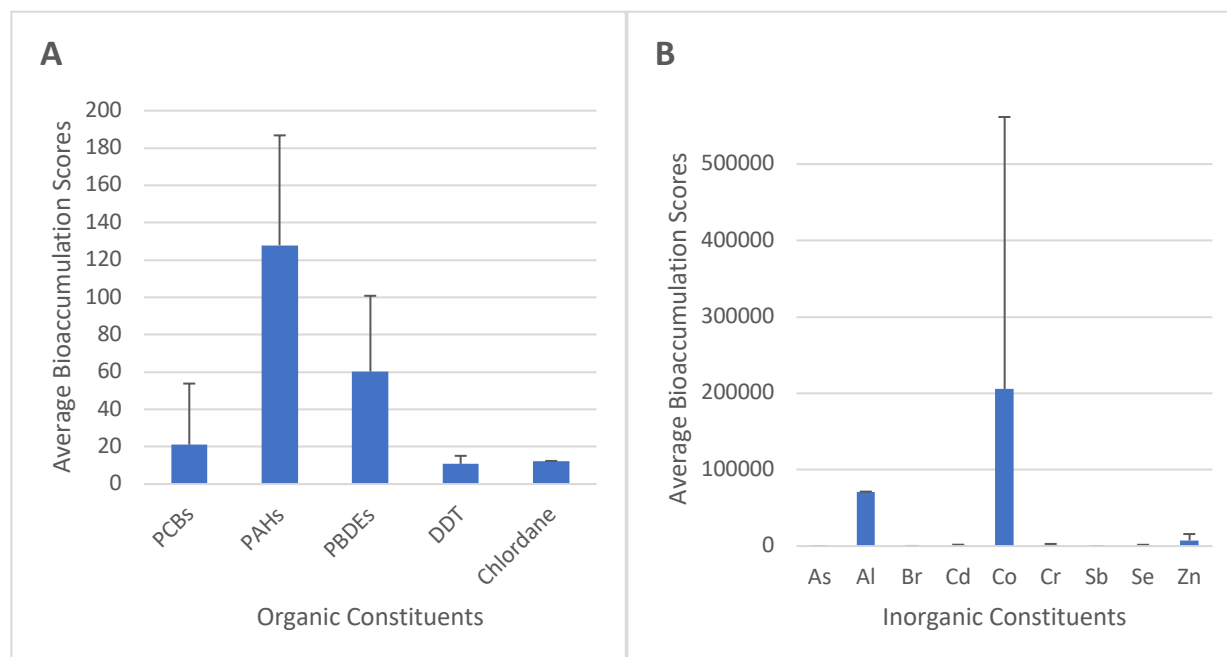


Figure 2. A) Mean ( $\pm$ SD) of bioaccumulation scores of organic constituents (from left to right: polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, dichloro diphenyl trichloroethane, and chlordane) across all three polymer types, and B) mean ( $\pm$ SD) bioaccumulation scores of inorganic constituents (from left to right: arsenic, aluminum, bromine, cadmium, cobalt, chromium, antimony, selenium, and zinc) across all three polymer types.

When comparing total bioaccumulation of all organic constituents across all three polymer types, polystyrene had the highest rates of bioaccumulation of organic constituents. Polypropylene had the second highest rates of bioaccumulation and polyethylene had the lowest rates of bioaccumulation (Figure 3A). Evaluating bioaccumulation rates of only the inorganic constituents revealed a different trend, with polypropylene exhibiting the highest rates of bioaccumulation. Polyethylene had much lower, but the second highest rates of bioaccumulation, and polystyrene had the lowest rates of bioaccumulation (Figure 3B).

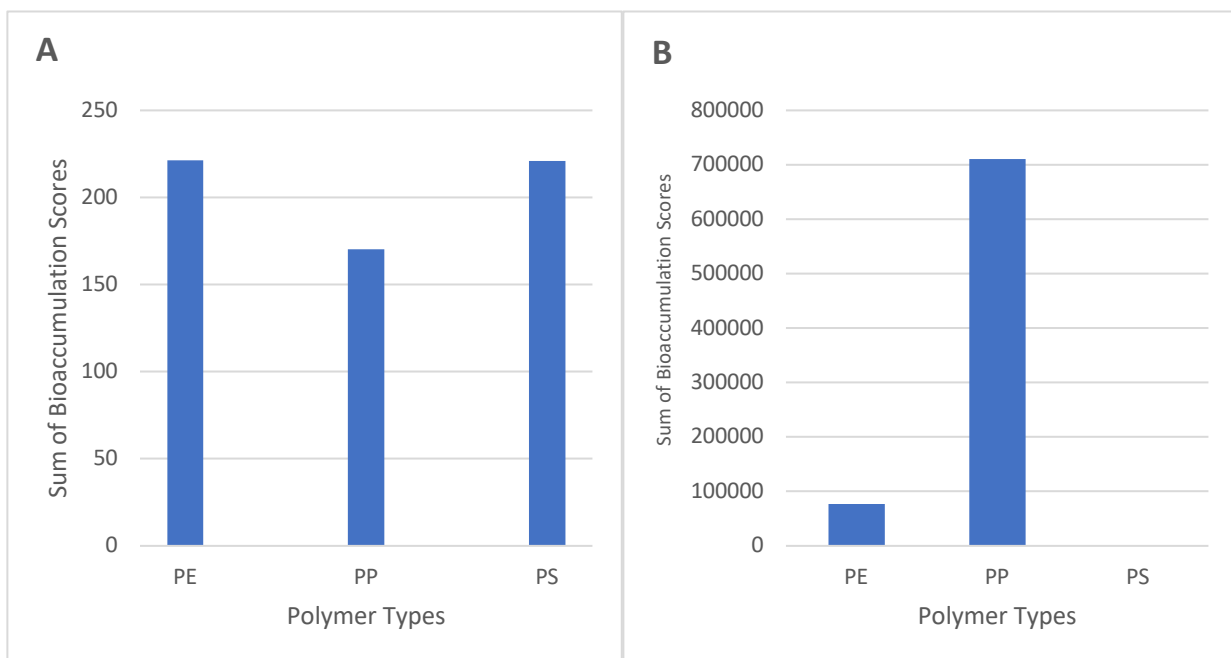


Figure 3. A) Sum of bioaccumulation scores of organic constituents in all three polymer types (from left to right: polyethylene, polypropylene, and polystyrene), and B) sum of bioaccumulation scores of inorganic constituents in all three polymer types (from left to right: polyethylene, polypropylene, and polystyrene)

## Biomagnification

Calculated biomagnification rates revealed that PAHs had the highest rates of biomagnification of organic constituents across all three polymer types. PBDEs had the second highest biomagnification rates, followed by PCBs, Chlordane, and DDTs (Figure 4A). Of the inorganic constituents across all polymer types, cobalt had the highest rates of biomagnification,

aluminum had the second highest biomagnification, and zinc had the third highest biomagnification (Figure 4B).

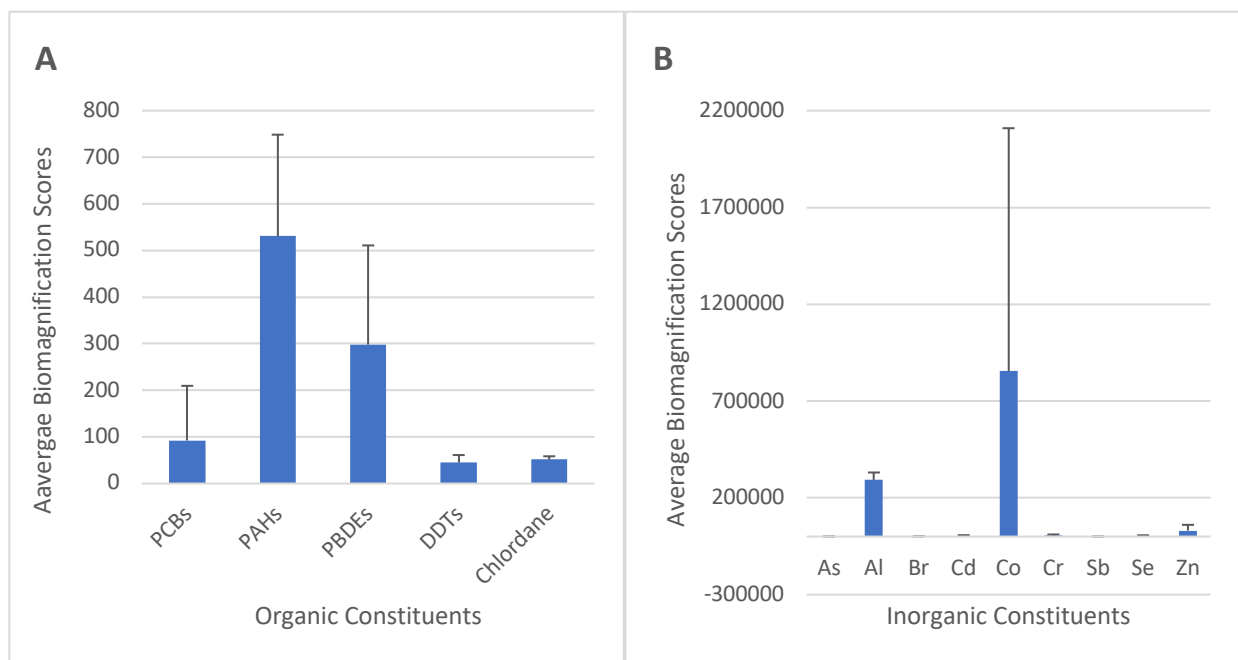


Figure 4. A) Mean ( $\pm$ SD) of biomagnification scores of organic constituents (from left to right: polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, dichloro diphenyl trichloroethane, and chlordane) across all three polymer types, and B) mean ( $\pm$ SD) biomagnification scores of inorganic constituents (from left to right: arsenic, aluminum, bromine, cadmium, cobalt, chromium, antimony, selenium, and zinc) across all three polymer types

When considering which polymer type had the highest total rates of biomagnification in its profile across all organic constituents, there was no significant difference between polyethylene and polystyrene, with polypropylene having the lowest rate of biomagnification (Figure 5A). Polypropylene had the highest rates of biomagnification of inorganic constituents. Polyethylene and polystyrene had much lower rates of biomagnification, with polyethylene having a slightly higher rate than polystyrene (Figure 5B).

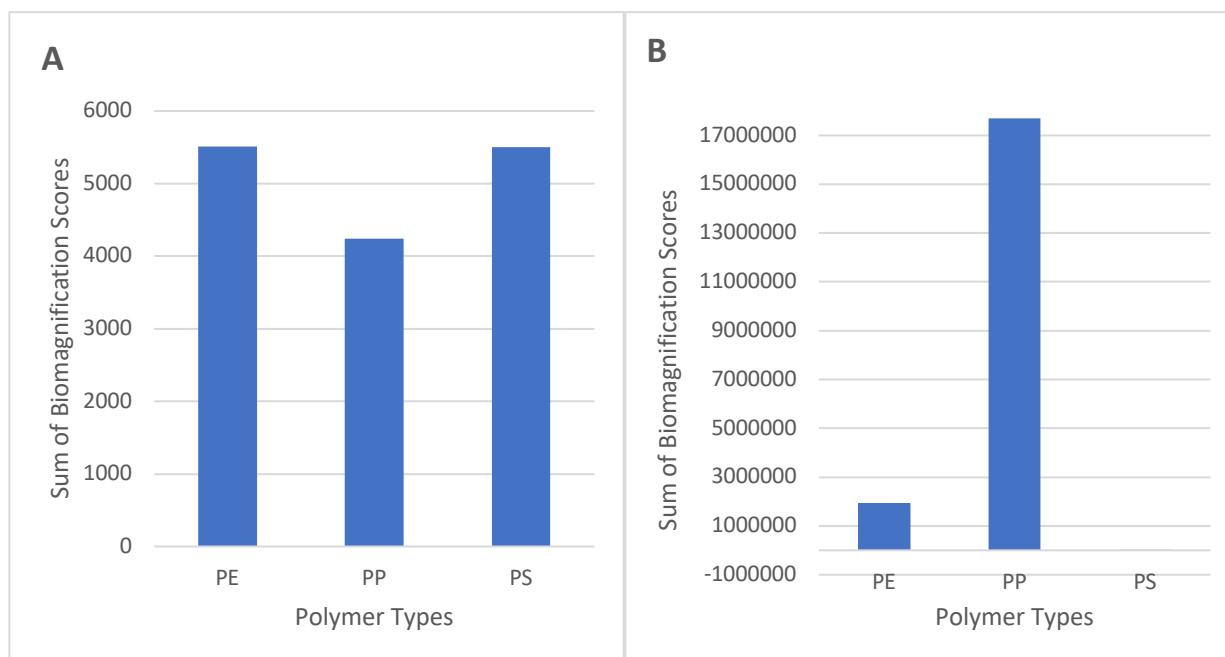


Figure 5. A) Sum of biomagnification scores of organic constituents in all three polymer types (from left to right: polyethylene, polypropylene, and polystyrene), and B) sum biomagnification scores of inorganic constituents in all three polymer types (from left to right: polyethylene, polypropylene, and polystyrene)

## MRLs and Health Hazards

Concentrations for organic and inorganic toxic substances present in each polymer type were compared to the corresponding MRL for that substance in order to determine whether exposure to plastic polymers resulted in exposure to concentrations that pose the threat of carcinogenic or toxic effects. If concentrations were at or above the intermediate oral MRL provided in a report by the CDC (ATSDR, 2019a), then a substance was considered to be a human health hazard. The results of this comparison can be seen in Table 5, in addition to whether each substance is classified as a carcinogen to humans and the physiological system to which the human health hazards of that substance poses upon exposure.

Polychlorinated biphenyls were present in all three polymer types at concentrations higher than the listed MRL. Polycyclic aromatic hydrocarbons were not present at concentrations higher than the listed MRL in any of the three polymer types. Polybrominated diphenyl ethers were present at concentrations higher than the listed MRL in polyethylene and polypropylene. Dichloro diphenyl trichloroethane was present in concentrations higher than the listed MRL in polystyrene, but not in polyethylene and polypropylene. Chlordane was present in concentrations higher than

the listed MRL in polystyrene. Arsenic was present in concentrations higher than the listed MRL in all three polymer types. Aluminum was present in concentrations higher than the listed MRL in both polyethylene and polypropylene. Cadmium was present in concentrations higher than the listed MRL in both polyethylene and polypropylene but not in polystyrene. Cobalt was present in concentrations higher than the listed MRL in both polyethylene and polypropylene but not in polystyrene. Chromium was present in concentrations higher than the listed MRL in all three polymer types. Antimony was present in concentrations higher than the listed MRL in both polyethylene and polystyrene but not in polypropylene. Selenium was present in concentrations higher than the listed MRL in both polypropylene and polystyrene but not in polyethylene. Zinc was present in concentrations higher than the listed MRL in both polyethylene and polypropylene but not in polystyrene. All concentrations comparisons as well as the risks posed by each constituent, organic and inorganic, are laid out in Table 5. The organ systems affected by exposure to a constituent if it is present at or above the listed MRL are provided as well.

These results support the hypothesis that organisms of higher trophic structure are exposed to concentrations of organic and inorganic toxins that are considered toxic or carcinogenic. The majority of constituent concentrations in all three polymer types were at or above the listed MRL. These are the concentrations of constituents prior to the processes of bioaccumulation and biomagnification. Therefore, it is assumed that those concentrations have the potential to remain at these toxic levels or even experience increases through bioaccumulation and biomagnification. This would result in concentrations at or well above listed MRL in organisms occupying higher trophic levels.



Table 5. Carcinogenicity of Organic and Inorganic Constituents in each Polymer Type and Organ System Effected by Exposure at or Above MRL

<b>Constituent</b>	<b>Polymer</b>	<b>Conc. (ug/kg)</b>	<b>MRL Conc. (ug/kg)</b>	<b>Conc. Above MRL</b>	<b>Carcinogenic (Y/N/ potentially)</b>	<b>Systems Effected by Exposure</b>
<b>PCBs</b>	Polyethylene	29		YES		Immunological, neurological
	Polypropylene	1	.003	YES	Potentially	
	Polystyrene	5.5		YES		
<b>PAHs</b>	Polyethylene	105		NO		Hepatic
	Polypropylene	88	5300	NO	YES	
	Polystyrene	600		NO		
<b>PBDEs</b>	Polyethylene	15.7		YES		Developmental, endocrine
	Polypropylene	9.1	.002	YES	NO	
	Polystyrene	N/A		N/A		
<b>DDTs</b>	Polyethylene	4.8		NO		Developmental, endocrine, hepatic, neurological, reproductive
	Polypropylene	0.4	5	NO	Potentially	
	Polystyrene	27.5		YES		
<b>Chlordane</b>	Polyethylene	N/A		N/A		Developmental, hepatic, neurological
	Polypropylene	N/A		N/A	YES	
	Polystyrene	21.5		YES		
<b>Arsenic</b>	Polyethylene	3.65		YES		Dermal, gastrointestinal, hepatic, neurological
	Polypropylene	48.333	3	YES	YES	
	Polystyrene	96		YES		
<b>Aluminum</b>	Polyethylene	33182.79		YES		Developmental, neurological
	Polypropylene	45517.79	1000	YES	NO	
	Polystyrene	N/A		NO		
<b>Cadmium</b>	Polyethylene	12.85		YES		Cardiovascular, developmental, gastrointestinal, neurological, renal, reproductive, respiratory
	Polypropylene	1340.48	0.5	YES	Potentially	
	Polystyrene	0		NO		

Table 5 Continued. Carcinogenicity of Organic and Inorganic Constituents<sup>a</sup> in each Polymer Type and Organ System Effected by Exposure at or Above MRL.

<b>Cobalt</b>	Polyethylene	235.19		YES		Cardiovascular,
	Polypropylene	400875	10	YES	Potentially	developmental,
	Polystyrene	0		NO		hematological, respiratory
<b>Chromium</b>	Polyethylene	95.23		YES		Immunological, renal,
	Polypropylene	2028.03	5	YES	YES	respiratory
	Polystyrene	148		NO		
<b>Antimony</b>	Polyethylene	3.85		NO		Cardiovascular,
	Polypropylene	56.87	6	YES	NO	respiratory
	Polystyrene	0.14		NO		
<b>Selenium</b>	Polyethylene	0		NO		Dermal
	Polypropylene	1239.77	5	YES	NO	
	Polystyrene	165		YES		
<b>Zinc</b>	Polyethylene	2587.1		YES		Gastrointestinal,
	Polypropylene	10768.03	300	YES	NO	hematological,
	Polystyrene	81		NO		respiratory

<sup>a</sup>Concentrations of all constituents in all three polymer types were compared to intermediate oral MRL concentrations [exceptions marked with asterisk\* for those which did not have intermediate oral MRLs and required use of next closest value (ATSDR, 2019a); systems affected by exposure to constituent (ATSDR, 2019b)]

## Toxicity Threat

Toxicity threat of polymers was considered for each of the three polymer types based upon their constituents, considering threat due to organic constituents and threat due to inorganic constituents separately. Considering threat due to organic constituents, polystyrene was identified as posing the greatest toxicity threat, followed by polyethylene, and lastly by polypropylene. Quite conversely, when considering threat due to inorganic constituents, polypropylene was identified as posing the greatest toxicity threat, followed by polyethylene, and lastly by polystyrene.

## Polymer Stabilities and Toxicity Threat

The relationship between polymer stability and the toxicity threat followed the predicted positive correlation when considering toxicity threat posed by inorganic constituents. However,

the inverse relationship was observed for toxicity threats of polymers considering toxicity threat posed by organic constituents.

## **Discussion**

Investigation of the toxic constituents of primary concern in the three most prevalent plastic polymers of the southwestern Atlantic region brought some refinement to the understanding of the toxicity potential plastic polymers possess when they enter the marine food web. Proxies of bioaccumulation and biomagnification provided insight on which constituents, organic and inorganic, pose the greatest threat and possess the greatest potential to be present at toxic concentrations in the marine food web. While more complex methods for calculating exact bioconcentration values and biomagnification factors do exist, the magnitude of plastic debris present in the marine environment has become so significant that it is pertinent to instead attempt to quantify the overall potential for the introduction of toxic substances via plastic polymers, and not just what can be observed through a finite number of samples. Developing a more comprehensive perspective on how the principal plastic polymers that have infiltrated the marine environment behave within the trophic structure of marine organisms facilitates the ability to enact strategic actions in order to mitigate those effects.

### **Bioaccumulation**

Bioaccumulation of the organic and inorganic constituents was, in a sense, a constant within the context of this study as the value obtained from this simplified model was simply a function of properties of the constituent and polymer alone and not of the organism in question. The concentration of a substance prior to alteration by biological processes, such as incorporation and biomagnification, is independent of the organism, and the impact of an organism's place in the trophic food web structure was not considered until the bioaccumulation values were applied to the biomagnification model. While these bioaccumulation scores were relevant to consider when assessing the threats posed by each constituent, they were not the primary focus for assessment in this study. Bioaccumulation was one component in the evaluation of the potential impacts that polymers and their associated constituents can have in the marine environment.

This information could be relevant for identifying those substances which are pollutants in the marine environment as a whole, and the severity of current and potential future impacts could

be used to establish a regulatory basis to eliminate or curtail the use of the compounds that have high bioaccumulation potential. Information like this can allow for greater focus to be placed on the constituents which are present in marine plastics due to intentional incorporation into the polymers, such as polychlorinated biphenyls often used in plasticizers and polybrominated diphenyl ethers used for flame retardants in plastic polymers that pose greater bioaccumulative risks (Tueten et al., 2007).

## **Biomagnification**

Statistical support of the hypothesis that a higher trophic structure rank of an organism would positively influence the rate of biomagnification of organic and inorganic constituents was foundational to the conclusions of this study. This illustrates the concept that organisms that occupy higher trophic levels are at a greater risk from marine plastic toxicity. Calculations conducted for POPs in particular, because those calculations included B-scores and used concentration data gathered from plastic polymers recovered from the marine environment, demonstrated the impact that the process of biomagnification has on the concentrations of toxic substances and their amplification as they are passed along multiple trophic levels to reach not just top-level predators like *Xiphias gladius*, but the organisms one step further up the food chain—humans. Although humans were not considered as species of interest for this study, because human beings are the next level on the trophic food web, it is reasonable to infer that the biomagnification scores seen by the highest ranked species in this study would be even greater if calculations were to be done for those scores in human beings.

Like bioaccumulation scores, biomagnification scores for inorganic constituents are meant to serve as proxies, while the scores calculated for organic constituents are likely more representative. A significant correlation between trophic structure rank and biomagnification scores for both types of constituents is an indication that, although one set of results may be more reflective of real-world concentrations, both datasets serve as appropriate proxies for biomagnification of the constituents within their respective polymers when consumed by organisms of varying trophic level.

## **Threat Scores**

The lack of support for the hypothesis that polymer stability rank and polymer threat scores would have a significant relationship was surprising and most likely attributable to the small sample of polymers considered for this study. Future work would likely need to consider more polymer types. The lack of relationship between stability rank and threat score may be an artifact of a small polymer sample size. At this time, it is still plausible that a stable structure plays a role in a polymer having greater capacity to house more constituents or allowing for more time in the water column for those constituents to accumulate. However, this does not mean that conclusions could not be drawn on the three plastic polymers of interest based upon their calculated and assigned threat scores.

Upon reviewing the polymer profiles, it can be seen that, in every species evaluated, the cumulative biomagnification scores for polyethylene are the highest amongst the three polymers for both organic and inorganic constituents. The same can be said for bioaccumulation scores. Patterns that can be seen in the data between threat scores and other facets of the polymers' profiles supports the validity of the threat score calculation, and should not be discounted as a means of determining which polymers pose a greater potential for ecotoxicity and should be considered for prioritization in regulatory policy.

## **Human Health Hazards**

Expanding the observed toxicity of plastic polymers on the marine food web beyond the marine environment and into the realm of human health can be accomplished by a straightforward observation of the information disseminated by the Agency for Toxic Substances and Disease Registry (ATSDR). Each constituent considered in this study is addressed by this agency and evaluated for its potential toxicity and/or carcinogenicity to human beings. The majority of the constituents for each polymer were present in concentrations at or above the listed intermediate oral MRL by ATSDR. It is assumed that the processes of bioaccumulation and biomagnification will keep those concentrations near or above the MRL, meaning that by the time these substances reach humans on the trophic food web structure, they could pose a human health hazard. Even if a plastic polymer were not to have undergone any biomagnification or bioaccumulation processes via the trophic food web before it was consumed by the highest trophic level (or one of the commercially significant species in this study), it would still possess concentrations of the vast

majority of its constituents which have the ability to pose a toxicological or carcinogenic hazard if those concentrations are available to that organism, meaning they can be translocated and are bioavailable.

## **Substances of Primary Concern**

### *Organic Constituents*

Evidence creating direct links between the presence of plastic polymers, associated organic constituents (such as PCBs), and health hazards in higher trophic level organisms such as fishery species or humans are limited. As the study of marine plastics is an emerging field in the world of marine sciences, direct support of the idea that plastic debris could be a direct cause of human food contamination is not plentiful. Rochman et al. (2013) provided evidence that the sorption of organic constituents onto marine plastics is significant enough to induce hepatic stress in medaka fish. Rochman et al. (2014) subsequently found evidence to support that those constituents are not only concentrating in the marine plastics themselves, but also in marine organisms consuming those plastics. Other researchers have also identified biomagnification of constituents of plastic polymers, or compounds often used as plastic polymer constituents, in the marine food web and the issues associated with that biomagnification. For example, Corsolini et al. (2007) was able to measure PDBE and DDT levels in a relatively isolated top-level population of organisms (in this case *Xiphias gladius* or swordfish) which had undergone biomagnification to reach detectable concentrations ( $2218 \pm 3291$  pg/g wet wt in the liver, and  $612 \pm 598$  pg/g wet wt in the muscle), and then drew comparisons between those elevated concentrations and the same MRLs used in this study in order to conduct risk level assessment of PBDE and DDT exposure to humans via swordfish consumption. Mizukawa et al. (2009) positively identified the biomagnification of both PCBs and PBDEs as the constituents worked their way up the trophic marine food web, and determined that PCBs were biomagnified more than PBDEs by marine organisms.

Of the POPs considered in this study, PCBs appear to be of the greatest concern in regards to risk of exposure to higher trophic level organisms given their high bioaccumulative and biomagnification capacity. If then the high concentrations of PCBs in all polymer types can be maintained through trophic exchanges, then a risk of exposure with potential carcinogenic and toxic effects is also present. This organic pollutant is noted as present in concentrations above the listed MRL in all three polymer types, is potentially carcinogenic, and was the POP which received

the highest threat score in all three polymer types. This indicates that PCBs have a high capacity for bioaccumulation and biomagnification in the trophic food web. Previous research has supported the idea that PCB's biomagnify in the marine food web, and experience orders of magnification in their concentrations. A study conducted in a lake ecosystem in Ontario by Rasmussen et al. (1990) demonstrated that trophic level contributed significantly to PCB concentrations. Tissue lipid content was found to be much less important in determining the concentration of PCBs present in an organism as opposed to that organism's position in the trophic food web structure, with each trophic level in the study resulting in a 3.5-fold increase in the bioconcentration factor of PCBs. Despite very small input concentrations, the tested organismal concentrations were relatively high. This rapid increase in concentration was made possible by the length of the trophic food web and the biomagnification that took place as the constituents were incorporated into one organism and passed along to another via consumption. While this was taken in the context of atmospheric inputs of PCBs, a similar situation is occurring in the marine environment, where small concentrations are introduced via plastic polymers and those concentrations undergo large increases via magnification in the trophic marine food web.

PCB concentrations listed in all three polymer's profiles as above the designated MRL also indicated that PCBs are present at concentrations which are potentially toxic or carcinogenic. This finding is supported by the listing of PCBs as chemicals of high concern by multiple organizations (European Commission, 2016; MLA, 2003; Stockholm Convention, 2016). PCBs are included in Annex 15 of the European Commission's Substances of Concern Priority List for Endocrine Disrupting Chemicals, or EDCs (European Commission, 2016). Under this Annex, listed substances are classified as Category 1 priority because of the risk they pose to humans and the environment because of their high rates of persistence and their potential for endocrine disruption. Evidence that PCBs pose these types of threats to organisms exposed to sufficient concentrations has been shown in many studies. Brouwer et al. (1989) observed and attempted to quantify the effects of PCB biomagnification in the common seal, *Phoca vitulina*. These researchers found that individuals subjected to diets that included PCB contaminated organisms, which themselves were not reported to have any negative effects to PCB exposure, lead to greater rates of biomagnification of PCBs in the individuals with those diets. The observed impacts of exposure to those concentrations included decreased plasma retinol levels, as well as effects on circulating thyroid regulating hormone levels. Maisano et al. (2016) successfully linked the accumulation of PCBs

and OCPs (organochlorine pesticides) to hepatic disruption in populations of Atlantic bluefin tuna in the Mediterranean, leading to hepatic steatosis particularly in males. Other studies have shown evidence to support that exposure to high levels of endocrine disrupting hormones (such as PCBs) in Atlantic Swordfish can lead to hormone disruptions that can alter reproductive function, posing a potentially large threat to swordfish fisheries (Fossi et al., 2001). Persky et al. (2001) sought to understand how PCB exposure can affect the biology of organisms, this time bringing the focus to the human consumer at the top of the food chain. Although this work could not conclusively link PCB exposure via fish consumption to hormone disruption in humans, it was able to show that a significant relationship exists between fish consumption and hormone disruption and that a significant relationship also exists between PCB exposure and hormone disruption. These findings provide reasonable evidence to support the idea that other constituents might contribute the negative health effects associated with the consumption of higher trophic level fishery species, warranting further investigation.

Although chlordane was also listed under Annex 15 the threat score calculated for chlordane within the context of this study was not comparable to the threat scores of the other POPs being considered. Although chlordane is a POP often considered to be of high priority, it is not present in two of the three plastic polymers considered in this study and was not present in high concentrations in polystyrene as compared to other POPs. The Stockholm Convention (2016) also listed both PCBs and chlordane under Annex A, or POPs which participating parties are required to take measures for the elimination of the production and use of. Therefore, of the organic constituents considered, PCBs received the highest priority status.

### *Inorganic Constituents*

Considering the same factors, the inorganic constituents which are of highest concern are: arsenic, chromium, and cadmium. Arsenic has been noted at concentrations above the MRL in all three polymer types and is recognized to be carcinogenic. Arsenic also received the highest threat score in all three polymer types, indicating a high capacity for bioaccumulation and biomagnification in the trophic food web. Chromium similarly is present in concentrations above the MRL in all three polymer types, recognized as carcinogenic, and received the third highest threat score amongst inorganic constituents in all three polymer types. Cadmium received the second highest threat score but was only present in concentrations above the MRL in polyethylene and polypropylene polymers and considered a potential, or unconfirmed, carcinogen.



Identification of these three inorganic constituents as substances of concern is supported by the listing of all three of these substances as Substances of Very High Concern Candidates by European Chemicals Agency (ECHA, 2013). Under this criterion, substances listed as those of very high concern are either reproductive toxicants, carcinogenic, or mutagenic to humans upon exposure, and must be closely monitored by EU authorities or banned from production processing if the substance is identified as one of very high concern. The designations of these substances by regulatory organizations is inherent support for the findings obtained from assessment of inorganic constituents in each polymer's profile.

More comprehensive support for the potential toxicological effects of these constituents on marine organisms would require studies conducted on the specific species, or species closely related to the species in question for this study, focusing on constituent concentrations and potential effects of those concentrations on these organisms due to plastic ingestion. Some research has shown that effects have been seen in some of the higher trophic level species, or species which are closely related to those considered in this study. A comprehensive study on concentrations of metals in a range of fishery species of the Mediterranean found significantly higher concentrations of lead, mercury, and cadmium (an inorganic constituent of concern in this study) in species of higher trophic levels as compared to those of lower trophic levels. For example, concentrations of about 0.06 ug/g were recorded in swordfish whereas concentrations closer 0.01 ug/g were recorded in species such as the red mullet and the mackerel (Falco et al., 2006). These studies, and others, highlight the elevated concern for higher trophic level species when considering biomagnified concentrations of toxic substances, but more research on rates of incorporation and bioavailability of specific constituents to particular species is necessary.

Because these constituents can enter the marine environment through a much wider range of inputs, unlike some of the more specific organic constituents (i.e. PCB's or PBDE's that are common plastic polymer additives and can come from a small number of other sources), targeting those which are present in the marine environment specifically because of plastic polymer introduction is more difficult. Nonetheless, this information gathered on the inorganic constituents considered for this study makes these particular substances of greater concern than other constituents of plastic polymers, and substances that should have greater regulatory restrictions in the production of plastic polymers in order to moderate their discharge into the marine environment.

## Summary and Conclusions

The idea that plastic polymers have successfully infiltrated the marine food web and undergo substantial biomagnification due to trophic structure exchanges is well supported by previous research (Engler, 2012; Avio et al., 2015; Gallo et al., 2018; Rochman, 2013). However, the complete picture of the threat that plastics pose to the marine environment, marine organisms, and to human health is much greater than this study is capable of illustrating. Much is still unknown about the exact implications of plastic polymers in the marine environment at the quantities that are present in the world ocean today. However, by focusing on a few key components of the impacts that marine plastics have on marine organisms, some important insights were highlighted that may inspire changes in perspective on marine plastic pollution and result in long term reductions of impact on human health.

Despite the fact that seafood has been definitively identified as a vector for the transfer of both microplastic particles and the toxic substances associated with them into the human diet, little work has been done to attempt to quantify those concentrations, and this lack of information has hampered efforts to put regulations in place for microplastic and plastic constituent regulations on commercial seafood industries (Carbery et al., 2018). The findings of this study are crucial to the fishery industry, as their product is directly impacted by marine plastics. Those species' fisheries which generate the greatest revenue in the state of Florida were specifically selected for the study in order to highlight the impacts not only on marine organisms, but also on humans. The results of this study have identified the most significant threats to marine life, and could be used to inform management decisions on resource allocation for the funding of programs targeted at minimizing and removing marine plastic debris, as well as those which seek to educate the public on their impacts. Knowledge acquired on the toxicological potential that plastics and their sorbed POPs (such as flame retardants) and inorganic constituents (such as metals) have when incorporated into the marine food web could also be valuable in informing regulations on the use of chemicals or compounds containing these toxic substances for production processes.

Because this work is region specific, it is not representative of the toxin load imposed by plastics elsewhere in the world ocean. More work on the toxicological impacts of plastic polymers on marine food webs is required in order to provide support for the necessary regulations on plastic production on a broader, global scale. Narrowing the focus to information obtained from a region of interest and species specific to that region allowed for a more tailored assessment to be made

on the threats present within that region due to plastic polymers and their constituents. Methods similar to those conducted in this study could be applied to larger datasets from more expansive sampling sites in order to generate a database on the presence of organic and inorganic toxic plastic constituents in marine environments across the globe.

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