Semi-quantitative analysis of plastic additives within marine derelict fishing gear and post-industrial plastic compatibilized for use in asphalt

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ABSTRACT

In Hawai’i, public roadways and airports are required to be paved with State Polymer Modified Asphalt Mix IV consisting of 95% aggregate and 5% polymer-modified bitumen or binder. Virgin styrene-butadiene-styrene (SBS) polymer is utilized to make this asphalt polymer-modified. In recent years, the asphalt industry has become interested in replacing a portion of this virgin polymer with post-consumer plastic and marine derelict fishing gear (DFG) in order to reduce the production of virgin plastics and create an alternative solution for the disposal or recycling of plastic waste and marine debris. Plastics are not pure polymers as they consist of up to 70% plastic chemical additives by weight, some which are toxic to humans and to marine animals. Concern of replacing the virgin styrene-butadiene styrene with recycled plastics or marine derelict fishing gear is present in the environmental field as the recycled plastics could potentially contribute additional leaching of toxic chemicals. This thesis presents the preliminary results of a forensic analysis evaluating the plastic additives found within different formulation of recycled plastics compatibilized for the addition into asphalt roadways. The results of this study indicated that high-density polyethylene (HDPE) marine derelict fishing gear, HDPE NewRoad post-industrial plastic, and low-density polyethylene GreenMantra post-consumer plastic contained lower ratio values of the plastic additives Irgafos® 168O and Irganox® 1076 than the standard SBS utilized in the current asphalt in Hawai’i. Additionally, the results of this study showed that through the extraction of target chemicals, LDPE produces a greater diversity of hydrocarbons than the extraction of HDPE. This thesis prepares the Center for Marine Debris Research (CMDR) for the undertaking of a research project funded by the Hawai’i Department of Transportation (HDOT). The results of this thesis will aid in the detection of microplastics and plastic additives in water samples from mechanical performance testing performed at the

University of Hawaii’s Asphalt Testing Laboratory and from simulated stormwater runoff on a trial roadway section paved with the NewRoad post-industrial recycled plastics.

ACKNOWLEDGEMENTS

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CHAPTER 1

Plastic additives in the ocean: Use of a comprehensive database for meta-analysis and method development

ABBREVIATION GLOSSARY

GC – Gas Chromatography

Py-GC – Pyrolysis Gas Chromatography

LC – Liquid Chromatography

SEM – Scanning Electron Microscope

EDX – Energy-Dispersive X-Ray Microanalyzer

XRF – X-ray Fluorescence

TGA – Thermogravimetric Analysis

ICP/OES – Inductively Coupled Plasma/Optical Emission Spectrometry

ICP/MS - Inductively Coupled Plasma/Mass Spectrometry

MS – Mass Spectrometry

MS/MS – Tandem Mass Spectrometry

ECD – Electron Capture Detector

FID – Flame Ionization Detector

AED - Atomic Emission Detector

INTRODUCTION

Since the mid-20th century, global production of plastic has continued to increase exponentially reaching approximately 390 million metric tonnes in 2021 (Plastics Europe, 2022). Rising production and use of plastic has resulted in a diverse waste stream with a large amount of mismanaged plastic waste (Hahladakis et al., 2018; Jambeck et al., 2015). It is predicted that by 2050, 12,000 million metric tons of plastic waste will be in landfills or in the natural environment (Geyer et al., 2017).

Plastics are man-made synthetic organic polymers with production mainly dominated by thermoplastics such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polystyrene (PS). However, plastic products are not pure polymers as they can consist of up to 70% chemical additives by weight (Andrady & Rajapakse, 2019). These so-called “plastic additives" are intentionally added into the polymer matrix during production to enhance the functional properties, performance, or appearance of the plastic product (Hahladakis et al., 2018; Lynch et al., 2022; Wiesinger et al., 2021). Additives used at high weight loadings include plasticizers (to enhance flexibility and elasticity), flame retardants (to impart fire resistance), and fillers (to provide reinforcement or cost reduction), while antioxidants (prevent discoloration and degradation) and heat stabilizers (prevent thermal degradation) are used at much lower weight loadings (Andrady and Rajapaske, 2019). Table 1 shows an overview of the chemical class, purpose, and weight loadings of certain additive types.

The majority of additives within plastic products are not chemically bonded to the polymer matrix, allowing them to flow freely within the polymer and between the polymer and the surrounding environment (Hermabessiere et al., 2017; Lynch et al., 2022; Weisenger et al., 2021). Studies have shown that transport of additives into the marine environment occurs through industrial releases, wastewater effluent, runoff and river transport in addition to leaching from plastic marine debris directly into the surrounding seawater (Lynch et al., 2022). The leaching of additives from plastic waste into the marine environment has been documented for multiple additive classes including plasticizers, BPA, flame retardants, antioxidants, and light stabilizers (Mato et al., 2001; Rani et al., 2015; Teuten et al., 2009). Exposure to weathering processes can enhance the release of the chemical additives to the environment by accelerating diffusion rates at higher temperatures and lowering the surface area to volume ratio when the plastic piece is fragmented (Lynch et al., 2022). This raises great concern about the ingestion of plastic additives by marine organisms since some of these compounds are known toxicants.

Exposure to plastic additives can occur through two ways: 1) the direct ingestion of plastic additives freely floating in seawater, and 2) the leaching of plastic additives into the gastrointestinal tract of marine organisms when plastic marine debris is ingested (Koelmans et al., 2014). From there, plastic additives, depending on their pharmacodynamics, have the potential to move into the blood and tissues of the organisms, and those compounds that biomagnify can eventually bioaccumulate up food chains. Plastic additives such as phthalates, flame retardants, bisphenol A (BPA), and antioxidants are classified as endocrine disrupting chemicals (EDCs) and ingestion can cause interference with organisms' physiology resulting in long-term reproductive, behavioral, and metabolic effects (Andrady & Rajapakse, 2019; Lynch et al., 2022). Additional additive chemical classes have been shown to cause carcinogenic effects, immunosuppression, acute aquatic toxicity, and in specific cases, mortality if exposure exceeds the toxic threshold (Lynch et al., 2022; Tian et al., 2022; Weisinger et al., 2021).

The extraction, identification, and quantification of plastic additives in the marine environment is needed to evaluate their role as environmental contaminants. An array of plastic additive classes, varying in concentration, have been detected and reported around the world in multiple marine compartments such as marine debris, seawater, sediment, and biota (Lynch et al., 2022). There are numerous published reviews on the purpose of plastic additives, types of plastic additives in the marine environment, and impacts of plastic additives on marine organisms. However, no review of the analytical methods to detect and quantify plastic additives in the marine environment exists. The marine debris field is lacking reliable and reproducible methods to identify and quantify plastic additive chemicals in environmental samples. Development of these methods was named one of the top priorities in the 2018 Science and Technology for America's Oceans: A Decadal Vision report (Science Report, 2018).

This review aims to synthesize the literature surrounding the current state of plastic additive research in four different matrices of the marine environment: marine plastic debris, seawater, sediment, and biota. A comprehensive database of plastic additive studies developed by Lynch et al. (2022) was utilized to conduct a meta-analysis describing the date of study and location of study as well as laboratory methods and techniques of extraction, analytical identification and quantification of additive chemicals. The studies were tallied by environmental compartment, compound class, extraction method, and analytical method. Major findings within the data are highlighted to identify data gaps and analytical methods are developed upon to move toward standardized analytical laboratory procedures.

Table 1. Types of additive classes with typical loading, examples, and purpose of type (adapted from Lynch et al., 2022).

Additive Type	**Additive Class**	**Chemical Class**	**Purpose**	**Typical Loadings (wt %)**
Plasticizers	Functional	Phthalates, Adipates	Softens the plastic to improve flexibility, durability, and elasticity	10 % to 70 %
Flame Retardants	Functional	Brominated Flame Retardants, Phosphate Esters (Phosphate-Based)	Impart fire resistance, reduce flammability	3 % to 25 %
Fillers	Fillers	Clays, silica, glass, chalk, talc, asbestos, alumina, rutile, carbon black, carbon nanotubes	To provide mechanical reinforcement or formulation cost reductions	1 % to 50 %
Impact Modifiers	Functional	Acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA)	To increase flexibility and impact strength to meet physical property requirements of rigid parts	0.5% to 30 %
Colorants	Colorants	Cadmium, chromium, lead, and cobalt compounds, titanium dioxide, carbon black; Organic dyes	Impart color within the final product	0.25 % to 5 %
Heat Stabilizers	Functional	Dialkyl maleates or laureates and dialkyl mercaptides of tin in PVC formulations to retard HCl evolution during processing	To prevent thermal degradation	0.1 % to 8 %
Lubricants	Functional	Waxes, oils, long-chain esters of polymeric alcohols	Allows easier processing of the plastic (i.e. lower temperatures, faster processing times)	0.1 % to 3 %
Antioxidants	Functional	Alkylphenol, Hindered Phenolic Antioxidant	Prevents discoloration and degradation during processing, use, and weathering	0.05 % to 3 %
Light Stabilizers	Functional	Benzotriazole UV stabilizer	To prevent degradation of the plastic upon exposure to light sources	0.05 % to 3 %
Monomers, catalysts	Unintended Additives	Bisphenols, Styrene Analogues	Unreacted monomers or residual catalyst left over from the polymer synthesis, can act as plasticizers or flame retardants	--

METHODS

A. Identification of Literature Sources

Individual literature searches were performed for each environmental compartment (marine plastic debris, seawater, sediment, and biota). For plastics, a Web of Science search using "plastic", "marine debris", and "additive" was performed on November 18, 2020. For seawater, a Google Scholar and SciFinder search using "plastic additives", "detection", and "seawater" was performed on January 2, 2021. For sediment, a Google Scholar search using "plastic chemical additives" and "sediment" was performed on November 18, 2020. For biota, a Google Scholar search using "chemical additives", "plastic", and "marine organisms" was performed on October 28, 2020. Resulting publications were found to include individual research articles and review articles. Publications were deemed irrelevant and excluded if they did not focus upon the marine environment (e.g. freshwater) or did not address chemicals known to be intentionally added to plastic (e.g. polychlorinated biphenyls). Additionally, we reviewed and considered relevant publications cited within resulting studies, especially review articles like Hermabessiere et al. (2017).

In total, 184 publications were selected for inclusion. From these, we extracted and recorded environmental compartment, sample collection date, location, chemical class along with concentration and units, extraction method, extraction solvent, analytical instrument, among other metadata.

B. Development of Database

Compartment, Compounds, and Concentrations. Environmental compartment was determined based on the type of samples analyzed within the method sections (i.e. plastic marine debris, seawater, sediment, or biota). All compounds and their concentrations reported in the results sections or within the supporting information documents of the publications were recorded within the database. Each compound detected was categorized by additive and chemical class based on uses described in the reviewed literature, in the "Uses" section in PubChem, and from our experience. Many compounds could not be classified as one additive type as certain compounds have multiple additive functions (organophosphates are used as a plasticizer and flame retardant). In these cases, additional resources were consulted and the primary additive use was recorded and an additional column described the secondary additive uses. Because of this complexity, the results of this meta-analysis are organized by chemical class (e.g. benzotriazole UV stabilizers) and not by additive type (e.g. heat stabilizers).

Exclusion Criteria. Some detected compounds could not be definitively categorized as plastic additives, for example, dichlorodiphenyltrichloroethane (DDT) or polychlorinated biphenyls (PCBs). These were noted as "not an additive" in the database and eliminated from the current meta-analysis. Additionally, polyfluorinated alkyl substances (PFASs) were excluded from this database, even though some could be considered plastic additives. Inorganic compounds and elements were included in this meta-analysis for only the plastic debris compartment. Inorganics (e.g. silicon dioxide) are used as fillers and elements (e.g. Cr, Ti, Mo, Zr, Hf, Pd, Fe, and Ni) are used as catalysts, heat stabilizers, antioxidants, or colorants in the production of plastics. Currently, there is no way to determine if inorganic compounds and elements detected within seawater, sediments, and marine biota originated from plastic products. Furthermore, inorganics and elements in seawater, sediments, and biota have been reviewed previously.

It is important that we acknowledge limitations of this database. This database is nearly comprehensive for all compound classes except for brominated flame retardants (BFRs). The extent of BFR research and the volume of literature was beyond the scope of this meta-analysis. Additionally, studies that assess additive concentrations in environmental samples cannot distinguish the source of the detected compounds as directly from additives that were originally in plastic products vs. chemicals that were in the environment that sorbed to plastic marine debris. This limitation does cause uncertainty about the source of detected compounds within plastic debris.

Laboratory Methods. The extraction and analytical methods were compiled by reviewing the methods section of each source. Analytical instruments utilized to identify the detected compounds were recorded. Studies that were recorded under "None" were literature reviews and did not utilize any of the analytical instruments (i.e. Teuten et al., 2009) and studies that were recorded under "Not Reported" utilized an analytical instrument for identification or quantification but did not report which instrument in their methods. Extraction methods were slightly more complicated to record. In this case, a flow chart found in Figure 1 was followed and studies were recorded based on the resulting criteria. Studies recorded with "No Extraction" did not perform an extraction method and therefore did not use an extraction solvent. Those recorded with "None" performed an extraction but did not use any solvent and those recorded with "Not Reported" did not report an extraction method or solvent in their methods.

C. Conducting a Meta-Analysis

Using Microsoft Excel, I mined the master database utilizing the PivotTable functions. A PivotChart of publication, environmental compartment and year was created. In this PivotChart, the publications were tallied by environmental compartment and year to discover time-trends in the data. If a publication analyzed more than one compartment, location, or compound class, each was counted as an individual study (i.e. Giam et al., 1978 analyzed water, biota, and sediment so it was counted once for each water, biota, and sediment). Another PivotChart of publication, compartment, and study location was created to determine where the majority of plastic additive studies are sampling from. The values in this PivotChart were converted to percentages to show the percent of studies that collected from each location (Pelagic, Indian, Europe, Asia, Antarctica, America, Africa) in each compartment. Four additional PivotCharts, one for each compartment, were created to analyze the compound class vs. which analytical instrument was utilized to identify or quantify these compounds. Similar to the location PivotChart, the number of studies using a specific analytical instrument in each compound class were converted into percentages to compare the total percent of studies using each analytical instrument. Finally, two PivotCharts, one for extraction method and one for extraction solvent were created and values were converted to percentages as stated previously.

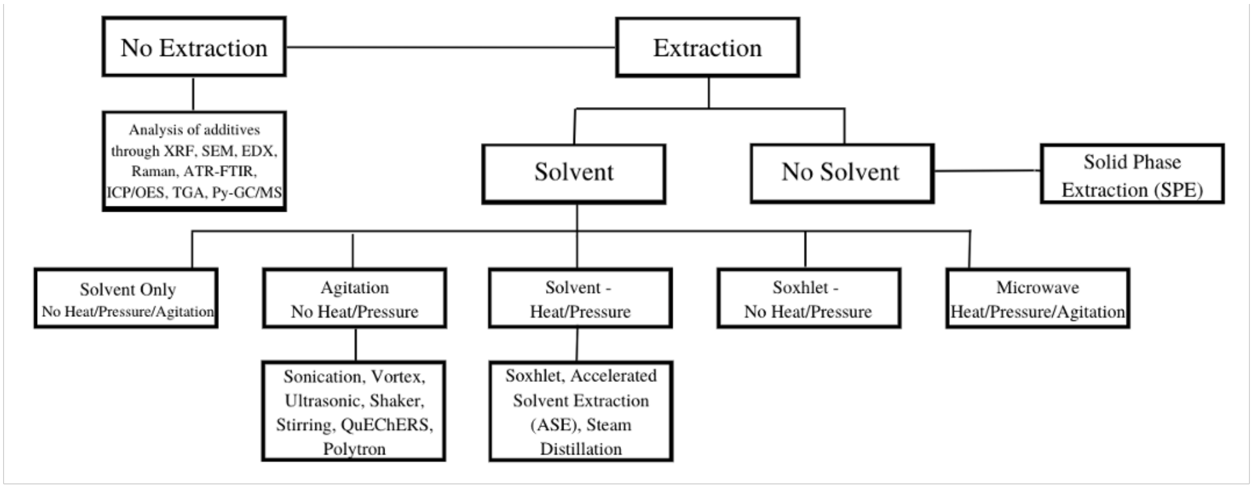

Figure 1. Flow chart of plastic additive extraction methods reported in this meta-analysis.

RESULTS AND DISCUSSION

A. Sample Collection

The 193 publications contained 38 studies on marine plastic (16.2%), 67 on seawater (28.6%), 65 on marine sediment (27.8%), and 64 on marine organism tissue samples (27.4%; Figure 2). Based on these findings, the water, sediment, and biota compartments are more frequently analyzed for plastic additives than marine plastic.

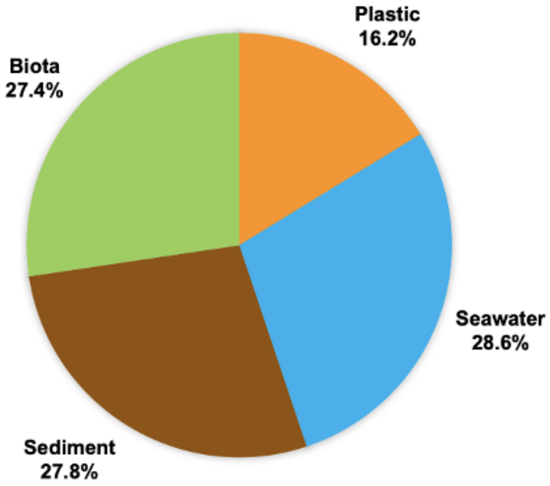

Figure 2. Percentage of publications analyzing plastic additives within each of the four environmental compartments.

Publications ranged from 1978 to 2021. The first publication found included water, sediment, and biota samples (Giam et al., 1978), whereas plastic publications were not found until the early 2000s, increasing after 2012. There is an exponential increase in the number of publications since 1978 (Figure 3), furthering the notion that plastic research, specifically plastic additive research, has become a high priority in the research community.

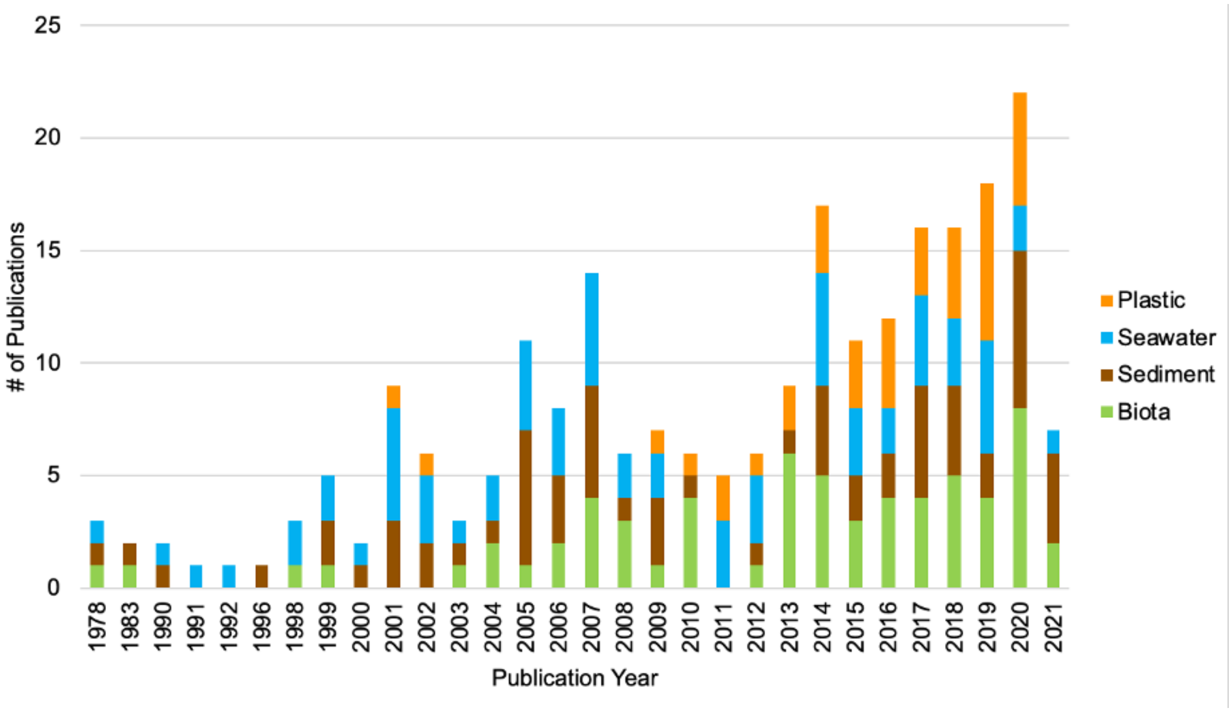

Figure 3. Number of studies measuring plastic additives within four marine environmental compartments across time.

Most studies collected samples from European and Asian regions (Figure 4). For example, within the biota compartment, over half of the studies (64%) analyzed samples from European and Asian waters with fewer collecting from the Americas (21%), Africa (6%), pelagic realms (4.5%), the Indian Ocean (3%), and Antarctica (1.5%). The biota compartment was the only compartment that collected and analyzed samples from Antarctica. Pelagic regions were mostly sampled for plastic, examples include the Great Pacific Garbage Patch in the North Pacific Ocean

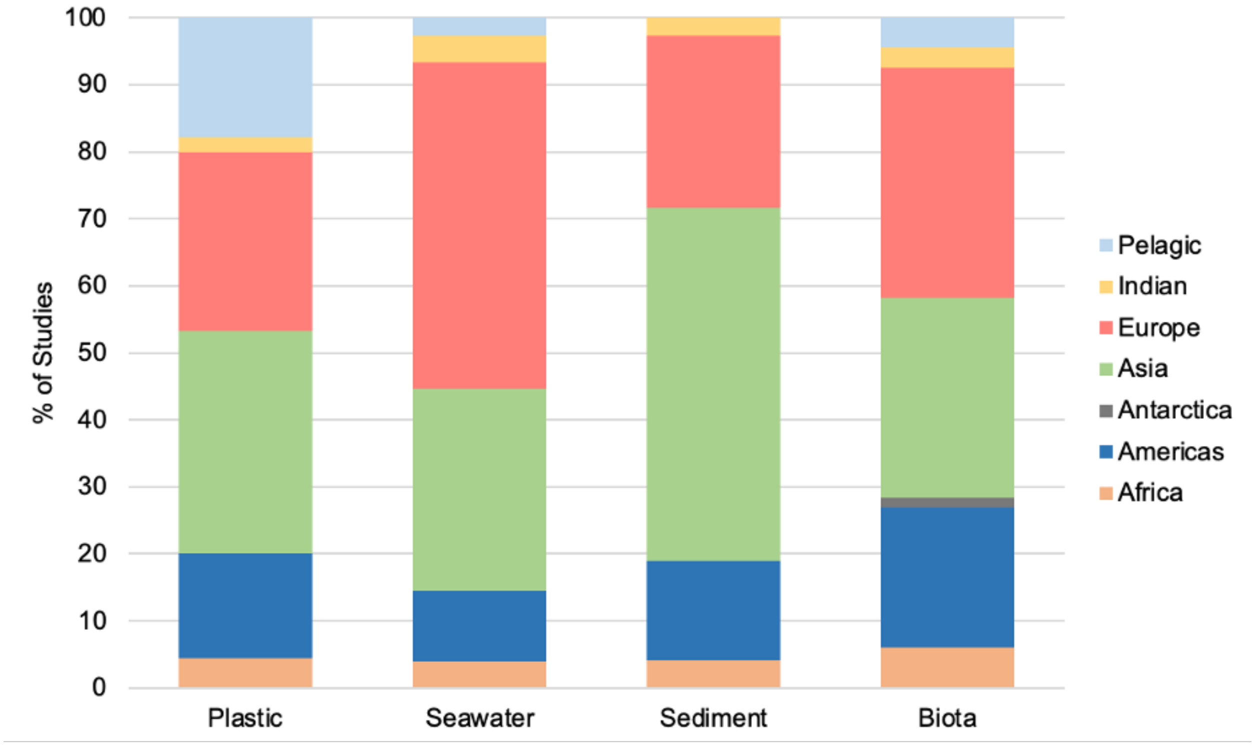

Figure 4. Percentage of studies that measured plastic additives in four marine environmental compartments across seven geographical regions.

B. Compound Class

Out of all the studies assessed in this meta-analysis, phthalates, brominated flame retardants (BFRs), bisphenol A, and alkylphenols were the most common additive classes analyzed (Figure 5). Phthalates and alkylphenols were found in equal frequency in the seawater compartment (27.6%), followed by bisphenol A (19.4%). Alkylphenols were most commonly assessed in sediments (30.9%), with 15.5% of these studies identifying phthalates, and 26.8% equally split between BFRs and alkylphenols. The biota compartment is heavily dominated in literature evaluating BFRs (27.6%), phthalates (25%), and alkylphenols (17.1%). The studies on plastic samples targeted the most diverse compound classes. All 11 additive classes considered in this meta-analysis were found within the literature assessed for the plastic compartment.

Compared to the full suite of plastic additive types (Table 1), studies in all four compartments have not commonly targeted heat stabilizers, fillers, impact modifiers, colorants, or lubricants. This is a major gap in the data that future studies should consider filling. Furthermore, plastic samples were the only compartment that evaluated and identified hindered phenolic antioxidants in their samples (e.g. Irganox®). Future plastic additive studies assessing seawater, sediment or biota should include hindered phenolic antioxidants into their target compounds as well as all types of UV stabilizers as these additive groups were highly under-represented in the literature.

The results of the meta-analysis on compound class are not surprising, Plasticizers, including alkyphenols and phthalates, are the largest group of additives in polymers with typical loadings at least three times higher than other groups of additives and 34% of the global plastic product market share (Lynch et al., 2022; Teuten et al., 2009). Additionally, flame retardants can constitute 3 % to 25 % of plastics by weight, second only to plasticizers (Lynch et al., 2022).

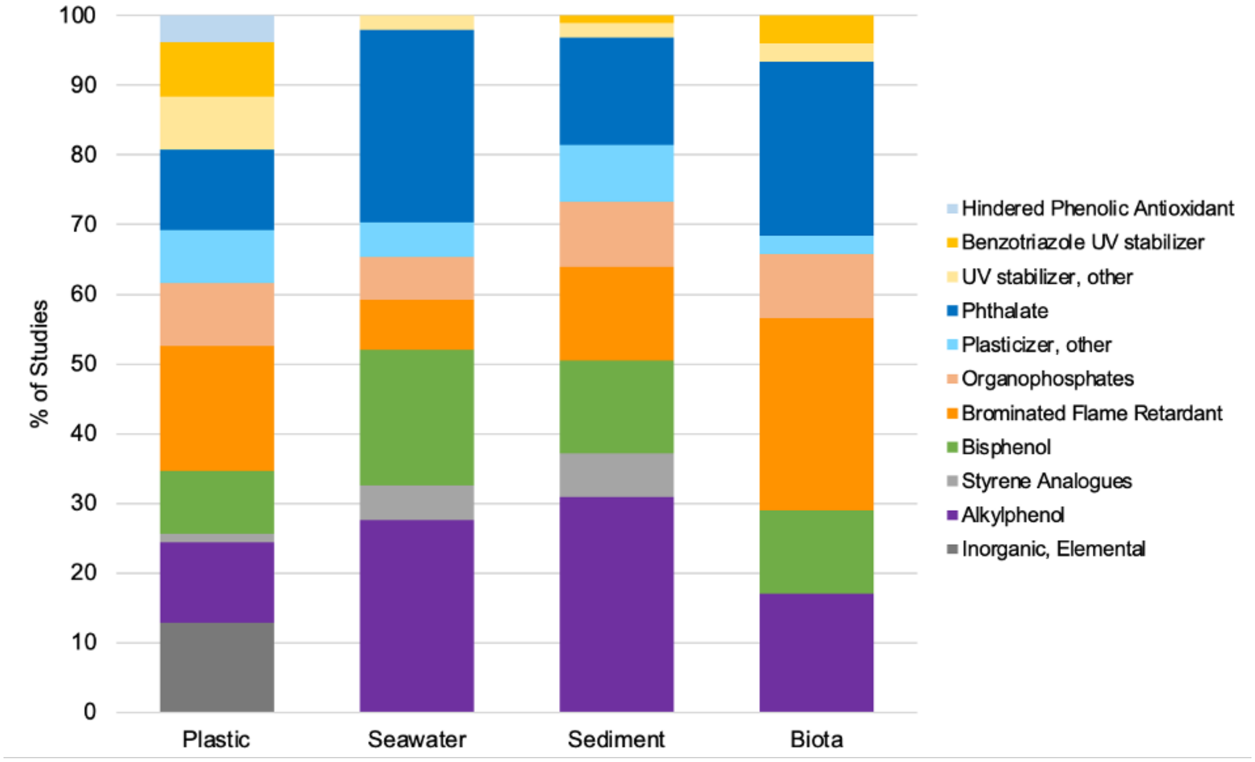

Figure 5. Percentage of studies that have assessed various chemical classes of plastic additives in samples from four marine compartments.

C. Extraction Method

Solvent extraction of compounds from the original matrix is usually a necessary first step for the detection and quantification of additives. The extraction process provides a smaller sample concentrated in the target analytes and free from the original matrix components (i.e. seawater, sediment, tissues, blood, plastic, etc.). That way there is little to no interference from non-targeted compounds (Pichon 2000). It is important to acknowledge that the extraction methods and solvents are chosen based on the original matrix components and the instrument used for detection and quantification.

Solvent - Agitation and Soxhlet - No Heat/Pressure were the dominant extraction methods in the plastic debris, sediment, and biota compartments (Figure 6). Solid phase extraction (SPE) was the most utilized method for extraction within the seawater compartment. The large number of studies that do not report solvent extraction methods in the plastic debris compartment is due to analytical methods which directly analyze the surface of the plastic debris particle and do not require a solvent extraction method to concentrate these additives. These analytical methods include inductively coupled plasma optical emission spectrometry (ICP/OES), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscope (SEM), X-ray fluorescence (XRF), and Raman spectroscopy, along with Py-GC/MS which pyrolyzes the plastic before injecting the sample onto the GC/MS.

There are not many studies using Solvent - Microwave or Solvent - Heat/Pressure extraction methods (such as ASE). The majority of studies in this meta-analysis use traditional methods of solvent extraction including Soxhlet and sonication which fall under the Solvent - No Heat/Pressure. The advantages of Soxhlet and ultrasonic or sonication extraction include extraction efficiency and their well-established, widely used protocols. These techniques are mainly used for solid samples, which explains the large number of studies in the plastic, sediment, and biota compartments that reported these techniques (Figure 6; Alcala, 2020). However, these methods are known for being extremely time consuming and utilize lots of organic solvents which can be costly. Other methods for extraction, including microwave assisted extraction, accelerated solvent extraction (ASE), and solid phase extraction (SPE), have been developed to reduce the volume of solvents, improve precision, reduce extraction time, and reduce overall costs (Heemken et al 1997).

Montano et al. (2020) states that through microwave extraction, they were able to complete the extraction with improved control over the target plastic additives and background contamination with limited use of solvent, unlike traditional extraction methods. Bridson et al. (2021) compares the extraction efficiency of two studies analyzing plastic samples. They report that extraction of PE with sequential microwave assisted extraction using dichloromethane and hexane achieved greater than 98% recovery of PBDE 209, a flame retardant (Sun et al., 2019), whereas using Soxhlet extraction with dichloromethane yielded poor extraction efficiency (< 15%) of PBDE 209 from PP (Hirai et al., 2011). Pichon (2000) reports that SPE is the method of choice for extracting and concentrating compounds in liquid solutions. SPE was developed to extract analytes from water samples as a replacement for the liquid-liquid extraction techniques that utilizes significant amounts of solvent and is more time consuming (Pichon 2000).

Traditional methods of extraction have been found to be used more in the extraction of plastic additives from marine compartments, however this does not mean they are better. Novel methods such as microwave extraction and solid phase extraction are cheaper, quicker and better at reproducibility.

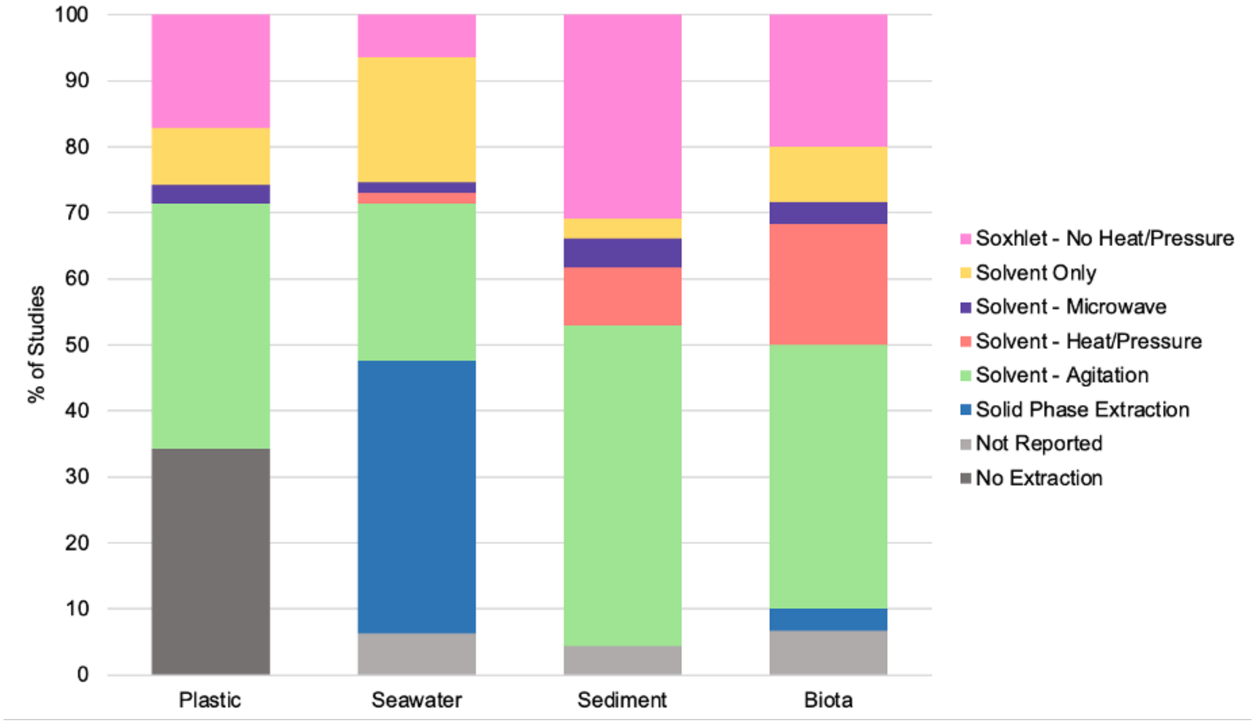

Figure 6. Percentage of studies that performed specific extraction methods to analyze plastic additives based on environmental compartment.

Dichloromethane (DCM) was the dominant solvent for chemical extraction in the plastic debris, seawater, and sediment compartments. In the biota compartment, DCM and mixtures of solvents including DCM were utilized the most, however, acetonitrile, acetone:hexane mixture, and other solvent mixtures were also heavily reported as a chemical extraction solvent. DCM mixtures included DCM:hexane, DCM:acetone, DCM:methanol, and DCM:hexane:acetone. The large number of studies in the plastic compartment falling under "No Extraction" is due to analytical instruments that do not require solvent extraction, similarly to what was stated previously.

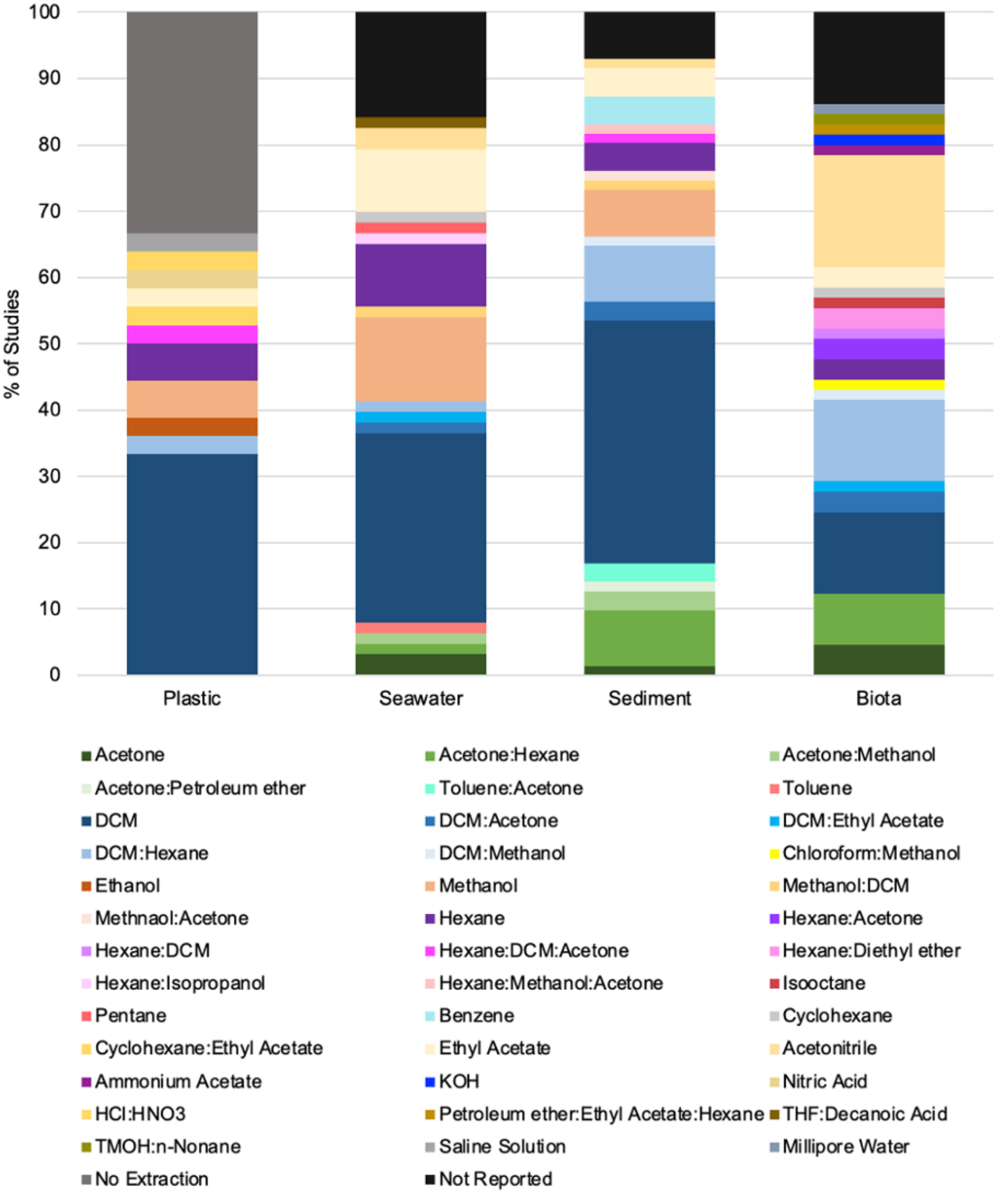
100
90
80
70
60
50
40
30
20
10
0
% of Studies
Plastic
Seawater
Sediment
Biota
Acetone
Acetone:Hexane
Acetone:Methanol
Acetone:Petroleum ether
Toluene:Acetone
Toluene
DCM
DCM:Acetone
DCM:Ethyl Acetate
DCM:Hexane
DCM:Methanol
Chloroform:Methanol
Ethanol
Methanol
Methanol:DCM
Methnaol:Acetone
Hexane
Hexane:Acetone
Hexane:DCM
Hexane:DCM:Acetone
Hexane:Diethyl ether
Hexane:Isopropanol
Hexane:Methanol:Acetone
Isooctane
Pentane
Benzene
Cyclohexane
Cyclohexane:Ethyl Acetate
Ethyl Acetate
Acetonitrile
Ammonium Acetate
KOH
Nitric Acid
HCl:HNO3
Petroleum ether:Ethyl Acetate:Hexane
THF:Decanoic Acid
TMOH:n-Nonane
Saline Solution
Millipore Water
No Extraction
Not Reported

Figure 7. Percentage of studies utilizing specific chemical solvents to extract plastic additives based on the compartment. Solvent mixtures are organized based on greater concentration:lower concentration.

D. Analytical Method

The detection and quantification of additives in marine environmental samples was dominated by gas chromatography coupled to mass spectrometry (GC/MS), followed by liquid chromatography coupled to tandem mass spectrometry (LC/MS/MS) (Figure 8). Within the plastic compartment, 44.7% of studies reported utilizing GC/MS along with 66.7% of studies within the seawater compartment, 59.7% of studies within the sediment compartment and 46.9% in the biota compartment. LC/MS/MS was utilized in 23.6% of plastic debris studies, 8.7% of seawater studies, 13.4% of sediment studies and 29.7% of biota studies. The least common methods were gas chromatography coupled to flame ionization detector (GC/FID), gas chromatography coupled with an electron capture detector (GC/ECD), and gas chromatography coupled with an atomic emission detector (GC/AED) with less than 5% of the studies utilizing these methods.

The marine plastic debris compartment was the most diverse in methods. This is due to the presence of inorganic and elemental additives identified in this compartment. Inorganic and elemental additives were identified through additional methods including inductively coupled plasma mass spectrometry (ICP/MS), inductively coupled plasma optical emission spectrometry (ICP/OES), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscope (SEM), X-ray fluorescence (XRF), and Raman spectroscopy (Figure 8).

For benzotriazole UV stabilizers, brominated flame retardants, bisphenols, and other UV stabilizers; one method did not seem to dominate another (Figure 8). For styrene monomers and oligomers, only GC/MS was used. Other plasticizers were mainly identified through GC/MS/MS.

Methods for measuring phthalates varied greatly with GC/MS dominating, but also LC/MS and LC/MS/MS, pyrolysis GC/MS (Py-GC/MS), gas chromatography flame ionization detection (GC/FID), gas chromatography electron capture detection (GC/ECD) and thermogravimetric analysis (TGA; only in plastic compartment). For organophosphate-based additives, GC/MS only was used to analyze plastic, but GC/MS and LC/MS/MS were used for water, sediment, and biota. GC/MS was the predominant method used to analyze alkylphenols, especially in the water and sediment compartments.

Non-target screening techniques are utilized to complement targeted analysis in gas chromatography and liquid chromatography. Although these screenings are qualitative and not quantitative, they prove useful to identify the hundreds of plastic additives present in the marine environment. Kuhn et al. (2018), Rani et al. (2015), and Gauquie et al. (2015) performed non-targeted studies on plastic debris using GC/MS in full scan mode with compound identifications made with the National Institute of Standards and Technology (NIST) Mass Spectral Library. These studies found 22, 40, and 75 plastic-related compounds, respectively. A benefit of the non-targeted approach includes the detection of surprise chemicals from multiple and diverse additive classes that are rarely investigated by targeted analysis, including heat stabilizers, fillers, impact modifiers, colorants (especially inks and chemicals used in ink coatings), or lubricants.

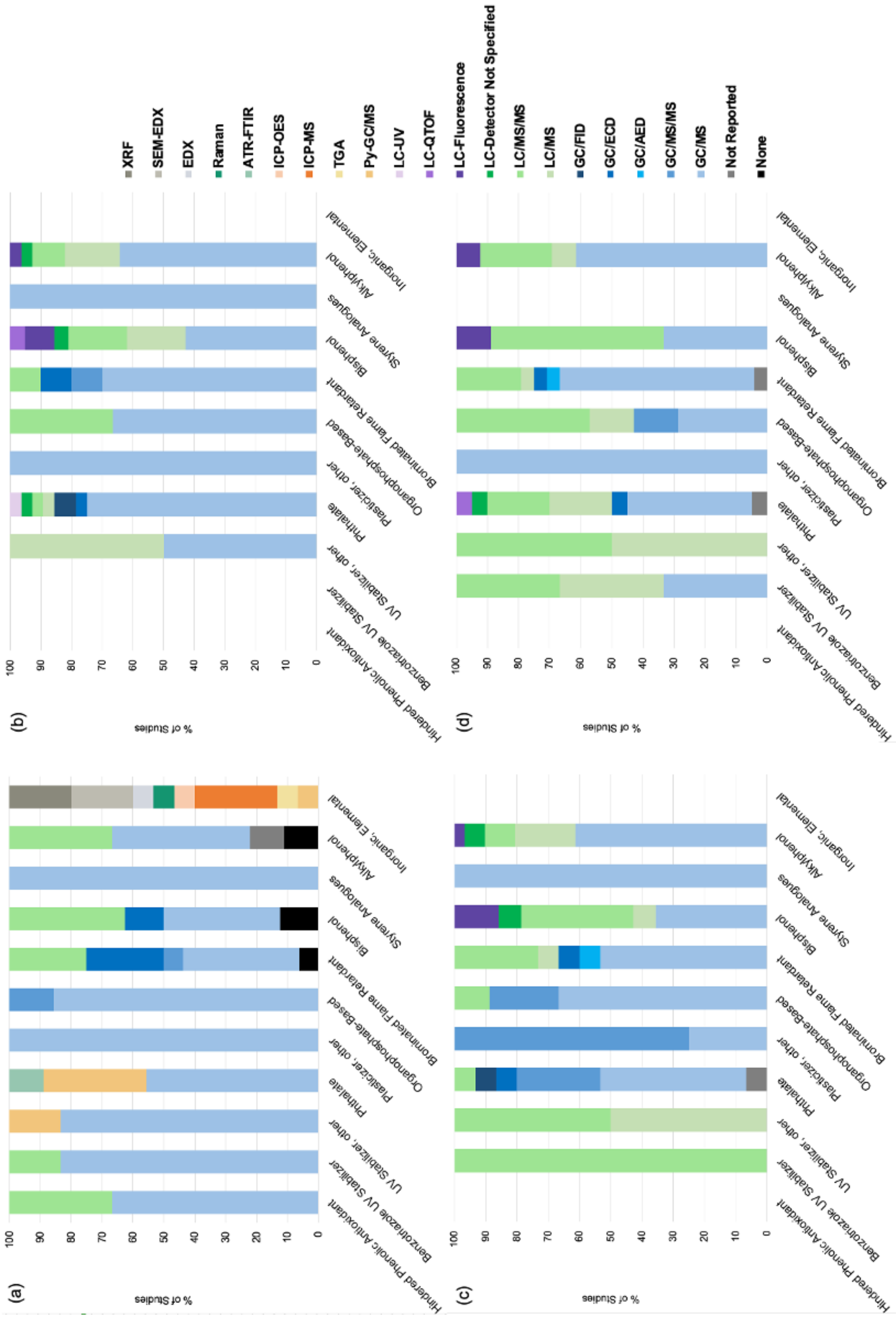
(a)
(b)
(c)
(d)
% of Studies
100
90
80
70
60
50
40
30
20
10
0
Hindered Phenolic Antioxidant
Benzotriazole UV Stabilizer
UV Stabilizer, other
Phthalate
Plasticizer, other
Organophosphate-Based
Brominated Flame Retardant
Bisphenol
Styrene Analogues
Alkylphenol
Inorganic, Elemental
XRF
SEM-EDX
EDX
Raman
ATR-FTIR
ICP-OES
ICP-MS
TGA
Py-GC/MS
LC-UV
LC-QTOF
LC-Fluorescence
LC-Detector Not Specified
LC/MS/MS
LC/MS
GC/FID
GC/ECD
GC/AED
GC/MS/MS
GC/MS
Not Reported
None

Figure 8. Analytical method utilized to identify and/or quantify plastic additive chemical class in each compartment: (a) plastic compartment, (b) seawater compartment, (c) sediment compartment, and (d) biota compartment.

CONCLUSIONS

Overall, there are many data gaps within plastic additive research that need to be filled in order to fully understand the scope of the potential threats these compounds pose to the marine environment. Additionally, there is a strong urge for standardization and consistency within the plastic research community.

There is no definitive conclusion as to which method is the most accurate or precise way to extract or identify plastic additives. There is a lack of studies comparing methodology in terms of time, cost, and yield. It has been shown that one technique is not able to measure all compounds in a particular additive class or across different classes. A combination of analytical methods will yield the best results of identification and quantification but, this can result in inconsistent findings, incomparable data, and lack of cohesion within the field. Time, cost, and availability of resources can also significantly affect the techniques used. Standardization procedures across analysis techniques will increase the accuracy and comparability of results.

This review's suggestions for enhancing methods and for the future of plastic additive analysis are aimed at widening the scope of literature assessing all additive classes (especially those indicated as under-represented in this meta-analysis), reducing inconsistencies with methodology across studies, encouraging the performance of additional studies to continue to compare extraction and analytical methods so a consensus can be reached as to which method will prove to be the most viable for plastic additive studies.

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CHAPTER 2

Semi-quantitative analysis of plastic additives within marine derelict fishing gear and post-industrial plastic compatibilized for use in asphalt

INTRODUCTION

A circular economy closes the loop of the product stream, collecting materials at the end of their life and reusing or repurposing them to continue the use of the material in the supply chain. As concerns for job security, resource preservation, and climate change from the emission of greenhouse gasses continue to rise, nations such as the United States, South Korea, and many in Europe have begun to foster research initiatives for a more circular economy (Stahel, 2016). The growing interest of politicians, businesses and environmentalists for the circular economy initiative has resulted in calls for circular economy proposals with the European Commission submitting a Circular Economy Package to the European Parliament in recent years. The circular economy approach will allow for the increase of industrial workforces due to the necessity of new job openings, preservation of natural resources through the reuse of products already in the consumer market, reduction in global greenhouse gas emissions, reduction of the need and space for landfills due to the limitation of waste, and the reduction of mismanagement of waste and therefore the reduction of plastics and their associated additives entering the marine environment (Stahel, 2016).

Since the beginning of production in the 1950s, plastic has become a universal and highly versatile material in the consumer market. Currently, the American economy is mostly linear where plastic products are discarded as waste. In this end-of-life scenario, plastics end up in landfills (75.5%), incinerated (15.6%), or disposed of improperly more than they are reused or recycled (8.6%; EPA, 2022), even though reuse and mechanical recycling are known to be the most sustainable option for plastic waste management due to lower emissions of greenhouse gasses (GHGs) which contribute to climate change and the prevention of possible mismanagement of the waste plastic (Andrady, 2015). Mismanaged plastic products have become a serious global concern due to associated negative economical, environmental, and human health impacts. Research and reviews have highlighted the threat of microplastics and plastic additives leaching from landfill runoff (Teuten et al., 2009), the emission of greenhouse and toxic gasses when plastic is incinerated (i.e. carbon monoxide from the polymer and bromide/heavy metals from the additives; Verma et al., 2016), and the pollution of waterways (Jambeck et al., 2015; Law et al., 2020). Approximately 31.6 million metric tons (MT) of plastic waste generated by coastal populations (within 50 kilometers of a coast) was classified as mismanaged in 2015, which we can only assume has increased due to the continual rise in plastic production and use (Jambeck et al., 2015). Of this 31.6 million MT of mismanaged plastic waste, 4.8 to 12 MT was calculated to have entered the ocean (Jambeck et al., 2015).

The US generates the largest amount of plastic waste of all countries. In 2016, the US was estimated to have produced 42.0 MT of plastic waste (Law et al., 2020). However, the US has been shipping plastic waste to other countries for decades despite having the proper waste management infrastructure. In the past, China was the major importer of recycled goods from the US due to their global lead in recycling, but China introduced a ban on waste import in 2018. This ban caused the diversion of plastic waste to other Asian countries, such as Vietnam, Malaysia, or Indonesia, which lack proper recycling facilities or technologies. In 2016, approximately 88% of properly managed plastic waste in the US was exported to countries with greater than 20% mismanaged waste rates (Law et al., 2020). From this estimate, the US contributes an additional 0.15 to 0.99 MT of plastic waste likely entering the environment through other countries.

The countries with high waste mismanagement rates receiving the US plastic waste are major sources of plastic pollution to the marine environment. The island chain of Hawai'i is located south of the Subtropical Convergence Zone (STCZ) and southwest of the Eastern North Pacific

Garbage Patch. The wind-driven convergence in this area causes extremely high concentrations of floating plastic debris to accumulate and deposit onto reefs or beaches (Brignac et al., 2019). Additionally, derelict fishing gear (DFG) is a prevalent issue in this area and can account for as much as 52% of floating plastic debris in the oceans by mass (Lebreton et al., 2018). The DFG affecting Hawai‘i includes large, conglomerated masses of fishing nets and lines that weigh hundreds of pounds and cause damage to coral reefs. This form of marine debris (DFG) consists mostly of plastic, makes up approximately 80% of the mass of marine debris in Hawaii, and is most likely coming from countries with large plastic pollution problems and a lack of proper waste management systems (Lynch et al., in preparation).

Piquing the interest of both environmentalists and the asphalt industry, and in line with the circular economy initiative, utilizing post-consumer recycled plastics in asphalt binder has become a new area of research (Willis et al., 2022). Currently on the island of O’ahu, it is mandated for public roads and airports to be paved with State PMA IV Mix asphalt containing approximately 95% aggregate (i.e. rocks/stones, etc.) and about 5% polymer-modified binder. Polymer-modified binder (PMA) is utilized to improve the performance and extend the life of asphalt pavements. Styrene-butadiene-styrene (SBS), a class of plastic polymer consisting of polystyrene and polybutadiene (Kraton, 2019), has been the preferred polymer-modifier of choice by the asphalt and roadway industry on O’ahu. The replacement of virgin SBS polymers within the binder with post-industrial plastic and post-consumer plastic will prevent the plastic products from ending up in landfills, being incinerated, shipped off to other countries, or discarded in the natural environment. Utilizing DFG as a replacement of a fraction of the binder, promotes the removal of these large conglomerates in and around the Hawai’i archipelago and prevents the further destruction of reefs and entanglement of marine organisms (McElwee et al. 2012, Therriault et al., 2018). Furthermore, asphalt mixed with recycled polyethylene-modified binder has been shown to result in lower global warming potential than styrene-butadiene-styrene-modified binder (Rangelov et al. 2021).

Although recycling plastic and marine debris into roadways can be beneficial to reduce environmental pollution and greenhouse gas emissions, it could have engineering repercussions in terms of performance and other environmental effects, such as the leaching of toxic plastic additives into stormwater or into the ocean. Plastic additives within post-consumer plastic and DFG are not chemically bonded to the polymer matrix, allowing them to migrate freely within the resin and between the resin and the environment (Weisenger et al., 2021). Many of these additives have the potential to leach out of the plastic and into the environment (Lynch et al, 2022). Furthermore, some additives are known toxicants and can produce a range of negative effects in organisms if exposure exceeds the toxic threshold (e.g. endocrine disruption, carcinogenic effects, immunosuppression, acute aquatic toxicity, and in specific cases, mortality; Lynch et al., 2022; Tian et al., 2022).

The growing concern of the migration of additives and absorbed chemicals from plastic products to the environment makes it important to evaluate their role as environmental contaminants. Here, I present the results of a preliminary study evaluating the polymer identification and the semi-quantitative analysis of plastic additives associated with pelletized post-industrial and post-consumer recycled plastic and DFG compatibilized for addition into asphalt roadways. This study is the first of its kind to analyze potential plastic additives leachates from roadways due to addition of post-recycled plastics. Highlighted in this study are (1) the plastic polymer identification through attenuated total reflectance Fourier-Transform Infrared spectroscopy and differential scanning calorimetry, (2) the development of a polymer reference library on a Thermo Nicolet iN10 MX micro-FTIR, (3) development of standardized methods for the extraction and analysis of a suite of plastic additive classes, and (4) the identification and semi-quantification of plastic additives within the plastic pellets compatibilized for roadways. The results of this study will be used to inform future research by providing the expected polymers and plastic additives or potential compounds of concern to target in the analysis of stormwater runoff from asphalt paved with post-recycled plastics and water samples from mechanical laboratory tests of asphalt samples mixed with post-recycled plastics.

METHODS

A. Plastic Products

Five plastic products were the focus of analysis in this study. The Center for Marine Debris Research (Waimanalo, HI, USA) supplied the company AltiSora with previously polymer identified high-density polyethylene (HDPE) derelict fishing nets removed from the surrounding waters of the Hawaiian Archipelago. AltiSora created two products from these nets: (1) AltiSora XB23-H consisting of strictly pelletized marine DFG and (2) AltiSora XB24-H consisting of pelletized marine DFG that has been compatibilized for addition into asphalt roadways (Figure 1). The third product, NewRoad, was sourced from Pacific GeoSource (Drain, Oregon, USA) and is a formulation of post-industrial recycled plastic compatibilized for addition into asphalt roadways. The NewRoad pellets analyzed here were from the same lot that was used during the repaving of Fort Weaver Road in Ewa Beach in October 2022. GreenMantra (Brantford, ON, Canada) formulates post-consumer recycled plastic compatibilized for addition into asphalt roadways; a small trial batch of this material was obtained during early discussions between GreenMantra and

Hawai'i Department of Transportation. The fifth product, standard virgin styrene-butadiene-styrene (SBS), was given to this project by Asphalt Hawai'i (Honolulu, HI, USA).

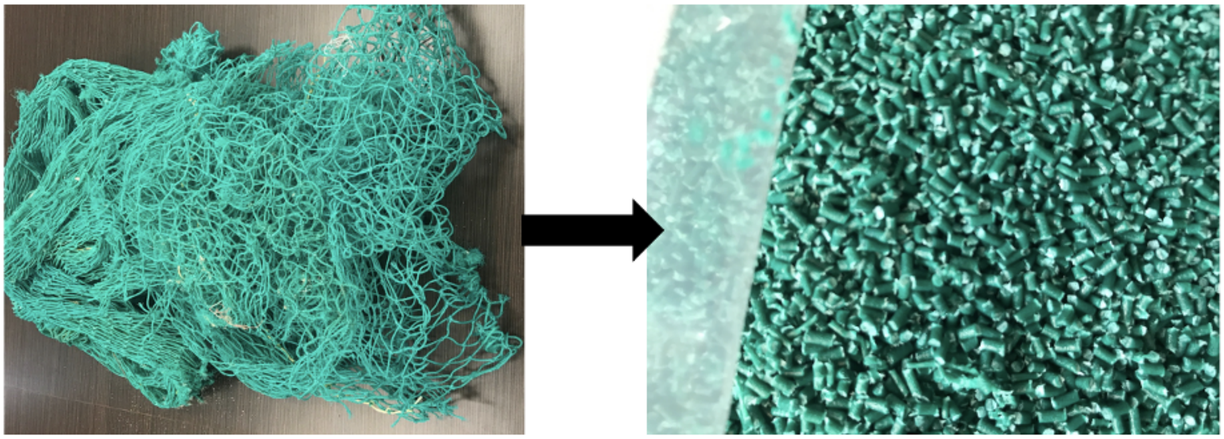


Figure 1. Picture of example HDPE derelict fishing nets and the pellets made from the HDPE fishing nets.

B. Polymer Identification

Plastic pellet products consisting of AltiSora XB23-H (AS23; n = 3), AltiSora XB24-H (AS24; n = 3), NewRoad (NR; n = 9), GreenMantra (GM; n = 3 flat pellets and n = 3 round pellets), and SBS (n = 3) were analyzed for polymer identification. The polymer identification was performed to ensure the two AltiSora products were not contaminated during the pelletization process and to identify what polymer or polymers the NR and GM products consisted of as these were unknowns. Polymer identification was performed in two steps. The first consisted of using Attenuated Total Reflectance Fourier-Transform Infrared (ATR FTIR) spectroscopy to acquire spectra of the polymers on the Thermo Scientific Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific). The methods outlined in Jung et al. (2018) were followed to capture three spectra per pellet, two distinctly separate outside spots and one inside after the pellet was cut with a razor blade cleaned with isopropanol. Briefly, the ATR FTIR diamond crystal was cleaned with 70%

isopropanol and a background spectrum was taken before each spectrum was collected. Spectra were collected from 4000 to 650 cm^{-1} with 32 accumulations. If plastic pellets crumbled, the powder was analyzed and only one spectrum was obtained. Spectra were polymer identified visually by comparing spectra to the results of Jung et al. (2018) and matching the four largest or most distinct absorption bands. A reference library search consisting of 507 library spectra from the libraries "Aldrich Polymers" and "CMDR Library" was performed to confirm manual polymer identification (full list of polymers in library search found in the Supplementary Information). Library match and match percent were recorded.

ATR FTIR can only identify general plastic polymers and cannot distinguish between different types of polyethylene (PE), such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE), or determine the percentage in blends of polymers such as polypropylene/polyethylene. Therefore, the second step in polymer identification consisted of analyzing the pellets on a TA Discovery Series 250 differential scanning calorimeter (DSC; TA Instruments). Plastic pellets were cut with a clean razor blade to a mass between 3.000 and 5.000 mg using a Sartorius Micro M3P balance with a 0.000 mg resolution. The subsample was crimped into a TA Tzero pan with a TA Tzero lid, and the pan was placed into a numbered position in the loading tray of the DSC. Each new day, a cell burn out and indium calibration were performed prior to sample runs to ensure the quality of the data. The following heat-cool-heat method was used: equilibrate at 50 °C, hold isothermal for 1 min, ramp 10 °C min^{-1} to 200 °C or 300 °C, hold isothermal for 5 min, ramp 10 °C min^{-1} to 50 °C, hold isothermal for 1 min, and ramp 10 °C min^{-1} to 200 °C or 300 °C. The two melting curves and single cooling curve produced by the DSC were integrated within the program TRIOS using the TA peak integration function. Curves were integrated from 60 °C to where the curve settles into the baseline after the melting or cooling peak. The second melt curve peak temperature - Tm (°C) - was utilized to determine the final polymer identification based on the melting ranges that distinguish HDPE (above 126.5 °C) from LDPE (below 114.2 °C; Lynch et al., in preparation). The second melt curve is used to determine the true melting temperature of the polymer because the sample has melted once previously in the run, eliminating any influence of the thermal history of the sample that could be seen in the first melt curve. The Tm and final polymer identification were recorded.

C. Creation of Micro-FTIR Library

Plastic pellets product consisting of AltiSora XB23-H (n = 3), AltiSora XB24-H (n = 3), NewRoad (n = 9), GreenMantra (n = 3), and styrene butadiene-styrene (n = 3) were analyzed on the Thermo Nicolet iN10 MX microscope FTIR (Thermo Fisher Scientific) with a 15x objective to create a library for future reference. Spectra were collected in reflectance mode with a cooled detector and 64 scans and 8 cm^{-1} resolution from 675 cm^{-1} to 4000 cm^{-1}. Spectra were collected by focusing on the surface of the sample. Three spectra per pellet (two distinctly separate outside spots and one inside after the pellet was cut with a razor blade cleaned with isopropanol) were captured and searched against an in-house reflectance “Cara’s Thesis iN10 Library" (full list of polymers in library search found in the Supplementary Information). Match names and percentages were recorded. All spectra collected were added to an in-house library for future microplastic analysis.

D. Development of Plastic Additive Methods

Generally, only one or two additive classes (e.g., phthalates or flame retardants) are targeted in studies evaluating plastic additives in marine environmental compartments and extraction and analytical methods utilized in the analysis of plastic additives lack standardization (see Chapter 1). One of the goals of my study was to create a standardized method to extract and identify multiple plastic additive classes in a single injection through a targeted analysis by gas chromatography mass spectroscopy (GC/MS).

Targeted Plastic Additives. To determine the plastic additives targeted in this study, a database of studies developed by Lynch et al. (2022) of plastic additive concentrations identified in marine environmental samples was mined to determine the most commonly reported compounds of the following additive classes: phthalates, other plasticizers, brominated flame retardants (BFRs), organophosphate flame retardants, antioxidants, UV stabilizers, alkylphenols, and bisphenol A. In addition, commercially available high purity plastic additive standards were added to the targeted compounds to expand upon the range of compounds searched for within the additive classes, plasticizers, flame retardants, and antioxidants. The full list of targeted plastic additives is shown in Table 1 and includes 78 plastic additive compounds. Additional information about the target plastic additives is found in the supplementary information.

Table 1. Full list of target plastic additives and chemicals of concern with the associated additive class, compound class, compound subclass, abbreviation, and full chemical name. Matching internal standards are listed.

Additive Class	Compound Class	Compound Subclass	Additive Abbreviation	Full Chemical Name	Internal Standards
Antioxidant			BHT	2,6-di-tert-butyl-4-methylphenol	2,6-Di(tert-butyl)-4-methyl-phenol (D21, 98%)
Antioxidant			Kemamide® E ultra	Erucamide	-
Antioxidant			Vitamin E	-	-
Antioxidant	Hindered Phenolic		Irgafos® 168	Tris(2,4-di-tert-butylphenyl) phosphite	-

Antioxidant	Hindered Phenolic		Irganox® 3114	-	-
Antioxidant	Hindered Phenolic		Irganox® 1010	-	-
Antioxidant	Hindered Phenolic		Irganox® 1076	-	-
Antioxidant			Antioxidant S (Naugard$^{\text{TM}}$ PS-30)	-	-
Antioxidant			BHA	Butylated hydroxyanisole	-
UV Stabilizer			UV Tinuvin® 326	2-tert-Butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol	2-Benzotriazol-2-yl-4,6-bis-(1,1-dimethyl-propyl)-phenol-d4 (UV-328-d4)
UV Stabilizer			UV Tinuvin® 327	2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol	-
UV Stabilizer			UV Tinuvin® 328	2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol	-
UV Stabilizer			UV Tinuvin® 329	2-(2-Hydroxy-5-tert-octylphenyl)benzotriazole	-
Alkylphenols	Nonylphenol		Nonylphenol	-	-
Alkylphenols	Nonylphenol		Nonylphenol monoethoxylate	-	-
Alkylphenols	Nonylphenol		Nonylphenol diethoxylate (tech)	-	Bisphenol A (Ring-13C12, 99%)
Alkylphenols	Nonylphenol		4-tert-Octylphenol	-	p-n-nonylphenol (Ring-13C6, 99%)
Alkylphenols		Bisphenol	Bisphenol A (BPA)	-	-
Alkylphenols	Nonylphenol		4-Nonylphenol	-	Dimethyl Phthalate-3,4,5,6-d4
Alkylphenols	Nonylphenol		4-Nonylphenol monoethoxylate	-	Diethyl Phthalate-3,4,5,6-d4
Plasticizer	Phthalate		DMP	Dimethylphthalate	Di-n-butyl phthalate-d4
Plasticizer	Phthalate		DEP	Diethylphthalate	-
Plasticizer	Phthalate		DnBP	Di-n-butylphthalate	Bis(2-ethylhexyl) Phthalate-3,4,5,6-d4
Plasticizer	Phthalate		BBP	Benzylbutylphthalate	Di-n-octyl Phthalate-3,4,5,6-d4

Plasticizer	Phthalate		DEHP	Bis(2-ethylhexyl) phthalate	Bis(2-ethylhexyl)Adipate (Adipate-13C6, 99%)
Plasticizer	Phthalate		DnOP	Di-n-octylphthalate	Tris(2-Chloroethyl)phosphate (D12, 98%)
Plasticizer	Adipate		DEHA	Bis(2-ethylhexyl) adipate or Di(2-ethylhexyl) adipate	Tri-n-Butyl Phosphate (D27, 98-99%)
Plasticizer/Flame Retardant	Phosphate-Based		TCEP	Tris(2-Chloroethyl) Phosphate	-
Plasticizer/Flame Retardant	Phosphate-Based		TBP	Tributylphosphate	Triphenyl phosphate (D15, 98%)
Plasticizer/Flame Retardant	Phosphate-Based		TEHP	Tris(2-Ethylhexyl) Phosphate	-
Plasticizer/Flame Retardant	Phosphate-Based		TPP	Triphenylphosphate	-
Flame Retardant	BFR	PBDE	PBDE 17	(2,2',4-Tribromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 25	(2,3',4-Tribromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 28	(2,4,4'-Tribromodipenyl ether)	6-Flouro-2,2',4,4'-Tetrabromodiphenyl ether
Flame Retardant	BFR	PBDE	PBDE 30	(2,4,6-Tribromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 47	(2,2',4,4'-Tetrabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 49	(2,2',4,5'-Tetrabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 66	(2,3',4,4'-Tetrabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 71	(2,3',4',6-Tetrabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 74	(2,4,4',5-Tetrabromodiphenyl ether)	-

Flame Retardant	BFR	PBDE	PBDE 75	(2,4,4',6-Tetrabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 85	(2,2',3,4,4'-Pentabromodiphenyl ether	-
Flame Retardant	BFR	PBDE	PBDE 97	(2,2',3',4,5-Pentabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 118	(2,3',4,4',5-Pentabromodiphenyl ether)	2,2',4,6,6'-Pentabromodiphenyl Ether (PBDE 104)
Flame Retardant	BFR	PBDE	PBDE 99	(2,2',4,4',5-Pentabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 100	(2,2',4,4',6-Pentabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 101	(2,2',4,5,5'-Pentabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 116	(2,3,4,5,6-Pentabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 119	(2,3',4,4',6-Pentabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 138	(2,2',3,4,4',5'-Hexabromodiphenyl ether	4-Flouro-2,3,3',4,5,6-Hexabromodiphenyl Ether (BDE 160)
Flame Retardant	BFR	PBDE	PBDE 139	(2,2',3,4.4',6-Hexabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 153	(2,2',4,4',5,5'-Hexabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 154	(2,2',4,4',5,6'-Hexabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 155	(2,2',4,4',6,6'-Hexabromodiphenyl ether)	-

Flame Retardant	BFR	PBDE	PBDE 156	(2,3,3',4,4',5-Hexabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 173	(2,2',3,3',4,5,6-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 190	(2,3,3',4,4',5,6-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 181	(2,2',3,4,4',5,6-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 182	(2,2',3,4,4',5,6'-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 183	(2,2',3,4,4'5',6-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 185	(2,2',3,4,5,5',6-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 191	(2,3,3',4,4',5',6-Heptabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 196	(2,2',3,3',4,4',5,6'-Octabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 197	(2,2',3,3',4,4',6,6'-Octabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 204	(2,2',3,4,4',5,6,6'-Octabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 198	(2,2',3,3',4,5,5',6-Octabromodiphenyl ether)	-
Flame Retardant	BFR	PBDE	PBDE 203	(2,2',3,3',4,5,5',6-Octabromodiphenyl ether)	4-Fluoro-2,2',3,3',4,5,5',6,6'-nonabromodiethyl ether
Flame Retardant	BFR	PBDE	PBDE 206	(2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether)	DecaBDE (BDE-209) (13C12, 99%)
Flame Retardant	BFR	PBDE	PBDE 208	(2,2',3,3',4,5,5',6,6'-Nonabromodiphenyl ether)	Hexabromocyclododecane (unequal mix; 13C12, 99%)

Flame Retardant	BFR	PBDE	PBDE 209	Decabromodiphenyl Ether	1,2-Bis(2,4,6-tribromo[13C6]phenoxy)ethane
Flame Retardant	BFR	HBCD	HBCD	alpha, beta, gamma Hexabromocyclododecane	Hexabromo[13C6]benzene
Flame Retardant	BFR	Other	BTBPE	Bis(2,4,6-tribromophenoxy)ethane	-
Flame Retardant	BFR	Other	HBB	Hexabromobenzene	Decabromodiphenylethane[13C14]
Flame Retardant	BFR	Other	PBEB	Pentabromoethylbenzene	2-Ethylhexyl-d17-2345-tetrabromo[13C6]benzoate
Flame Retardant	BFR	Other	DBDPE	Decabromodiphenyl ethane	Bis(2-ethylhexyl-d17)tetrabromo[13C6]phthalate
Flame Retardant	BFR	Other	TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate	-
Flame Retardant	BFR	Other	TBPH	Bis (2-ethylhexyl) tetrabromophthalate	-
Flame Retardant	BFR	Other	Dechlorane Plus	-	-

Additional compounds of concern associated with asphalt roadways were identified and added to the target compounds. Polycyclic aromatic hydrocarbons (PAHs) stem from the bitumen binder as well as combustion of oils and gasoline (Muller et al., 2020). Sixteen of these compounds have been listed by the US-Environmental Protection Act (EPA) as they are known carcinogens and are associated with adverse human and environmental health effects (Fuchte et al., 2022). Tian et al. (2022) identified a toxic chemical, 6-p-phenylenediamine-quinone (6PPD-Q), that causes acute mortality to coho salmon. Since the publication of the Tian et al. study, 6-PPD-Q has become a popular compound in roadway and stormwater analysis, therefore, I added this compound to the target chemicals of concern. Table 2 highlights the full list of target chemicals of concern.

Table 2. Full list of target chemicals of concern with the associated asphalt roadways including compound class, abbreviation, and full chemical name. Matching internal standards are listed.

Compound Class	Additive Abbreviation	Full Chemical Name	Internal Standard
Antiozonant	6-PPD	6-p-phenylenediamine	-
Antiozonant	6-PPD-Q	6-p-phenylenediamine-quinone	6PPD-Quinone (95% CP) (Ring-13C12, 99%)
PAH		Naphthalene	Naphthalene-d8
PAH		Biphenyl	Biphenyl-d10
PAH		Acenaphthylene	-
PAH		Acenaphthene	Acenaphthene-d10
PAH		Fluorene	-
PAH		Dibenzothiophene	-
PAH		Phenanthrene	Phenanthrene-d10
PAH		Anthracene	-
PAH		4H-Cyclopenta[def]phenanthrene	-
PAH		Fluranthene	Flouranthene-d10
PAH		Pyrene	Pyrene-d10
PAH		Benzo[ghi]fluoranthene	-
PAH		Cyclopenta[cd]pyrene	-
PAH		Benzo[c]phenanthrene	-
PAH		Benz[a]anthracene	Benz[a]anthracene-d12
PAH		Chrysene	-
PAH		Triphenylene	-
PAH		Benzo[b]fluoranthene	-
PAH		Benzo[j]fluoranthene	
PAH		Benzo[k]fluoranthene	-
PAH		Benzo[a]fluoranthene	-
PAH		Benzo[e]pyrene	-
PAH		Benzo[a]pyrene	Benzo[a]pyrene-d12

PAH		Perylene	Perylene-d12
PAH		Indeno[1,2,3-cd]pyrene	-
PAH		Benzo[ghi]perylene	Benzo[ghi]perylene-d12
PAH		Dibenz[a,h]anthracene	Dibenz[a,h]anthracene-d14
PAH		Dibenz[a,c]anthracene	-
PAH		Dibenz[a,j]anthracene	-
PAH		Picene	-
PAH		Benzo[b]chrysene	-
PAH		Anthanthrene	-
PAH		Coronene	-
PAH		Dibenzo[b,k]fluoranthene	-
PAH		Dibenzo[a,e]pyrene	-
Alkylated PAH		1-Methylnaphthalene	-
Alkylated PAH		2-Methylnaphthalene	-
Alkylated PAH		1,2-Dimethylnaphthalene	-
Alkylated PAH		1,6-Dimethylnaphthalene	-
Alkylated PAH		2,6-Dimethylnaphthalene	-
Alkylated PAH		1-Methylphenanthrene	-
Alkylated PAH		2-Methylphenanthrene	-
Alkylated PAH		3-Methylphenanthrene	-
Alkylated PAH		9-Methylphenanthrene	-
Alkylated PAH		2-Methylanthracene	-
Alkylated PAH		1,7-Dimethylphenanthrene	-
Alkylated PAH		1-Methylfluoranthene	-
Alkylated PAH		3-Methylfluoranthene	-
Alkylated PAH		1-Methylpyrene	-
Alkylated PAH		4-Methylpyrene	-
Alkylated PAH		Retene	-
Alkylated PAH		3-Methylchrysene	-
Alkylated PAH		6-Methylchrysene	-

Extraction Method Development. To develop a method to extract the plastic additive identified above from the plastic pellets analyzed in this study, I utilized the meta-analysis I performed in Chapter 1. In the previous chapter, I reported on the most common methods utilized for extraction of plastic additives in four separate marine compartments: marine plastic debris, seawater, sediment, and biota. As the marine plastic debris compartment is the most relevant to this study, I focused my method development on the results from this compartment. The most common methods for extraction of additives from marine debris were Soxhlet extraction and extraction with agitation, specifically sonication, but based on the shorter extraction times and lower solvent volumes microwave extraction requires, this was determined as the ideal extraction method for this study.

The protocol for extraction was developed by consulting previous literature assessing microwave extraction efficiencies. Two previous studies evaluating different extraction times, temperatures, and solvents to analyze a similar array of plastic additives in plastic polymers were consulted (Camacho et al., 2001; Cui et al., 2021). The method with the highest extraction efficiency along with additions to the methods based on knowledge of solvent extraction formed the protocol utilized in this study.

Internal Standards. To determine relative retention times of plastic additives as well as to determine the appropriate solvent delay on the GC/MS, plastic additive mass-labelled standards, either isotopically labelled through deuteration or carbon-13 were analyzed.

Mass-labelled standards consisting of di-n-butyl phthalate-d4 (DnBP-d4), diethyl phthalate-3,4,5,6-d4 (DEP-d4), dimethyl phthalate-3,4,5,6-d4 (DMP-d4), di-n-propyl phthalate-3,4,5,6-d4 (DnPP-d4), di-n-octyl phthalate-3,4,5,6-d4 (DnOP-d4), bis(2-ethylhexyl) phthalate-3,4,5,6-d4 (DEHP-d4), and 2,2',4,6,6'-pentabromodiphenyl ether (PBDE 104) were purchased from AccuStandard, Inc. (New Haven, CT, USA). Mass labeled 6PPD-quinone (Ring- 13C12, 99%), 2,6-di(tert-butyl)-4-methyl-phenol (D21, 98%), bis(2-ethylhexyl) adipate (13C6, 99%), tris(2-chloroethyl)phosphate (D12, 98%), tri-n-butyl phosphate (D27, 98-99%), triphenyl phosphate (D15, 98%), bisphenol A (Ring-13C12, 99%), and p-n-nonylphenol (Ring-13C6, 99%) were purchased from Cambridge Isotope Laboratories (MA, USA). 6-flouro-2,2',4,4'-tetrabromodiphenyl ether (6-F-BDE 47), 4-flouro-2,3,3',4,5,6- hexabromodiphenyl ether (4’-F-BDE 160), and 4-fluoro-2,2',3,3',4,5,5',6,6'- nonabromodiethyl ether (4’-F-BDE 208) was supplied by Chiron AS (Trondheim, Norway). Hexabromobenzene (unequal mix of alpha, beta, gamma, 13C12, 99%), decabromodiphenylethane[13C14], 2-ethylhexyl-d17-2,3,4,5-tetrabromo[13C6]benzoate, and bis(2-ethylhexyl-d17)tetrabromo- [13C6]phthalate were supplied by Wellington Laboratories (Guelph, ON, Canada). 2-Benzotriazol-2-yl-4,6-bis-(1,1-dimethyl-propyl)-phenol- d4 (UV-328-d4) was purchased from ASCA GmbH Angewandte Synthesechemie Adlershof. Polycyclic aromatic hydrocarbon (PAH) mass labeled standards were included in Standard Reference Material (SRM) 2269 and SRM 2270 supplied from the National Institute of Standards and Technology (NIST).

A plastic additive internal standard solution called “PA IS” in acetone (Honeywell B&J GM2 Lot#: DU031-US) was created on 5 December 2022 consisting of 100 ng L^{-1} of each plastic additive standard . A second solution, called “PAH IS”, in acetone (Honeywell B&J GM2 Lot#: DU031-US) was created on 6 December 2022 consisting of 120 ng L^{-1} of each PAH standard. These concentrations were chosen to represent concentrations of plastic additives and PAHs in stormwater reported in previous literature (Awonaike et al., 2021; Gasperi et al., 2014; Birch et al., 2011; Tian et al., 2022; Erikksen et al., 2007; Sanchez-Avila et al., 2011). All stock solutions were created gravimetrically. Gravimetric addition of the standards was performed by weighing the Hamilton syringe utilized to collect the target volume of standard from the original ampoule before and after addition into the stock solution. The amount of standard added to the stock solution depended on the original concentration of the standard in the ampoule. Certain standards went through a series of gravimetric dilutions before the final target concentration was reached and the standard could be added to the stock solution. Both internal standard solutions were stored in a -20 ºC freezer for use in future experiments.

The original ampoules containing the mass labeled standards or SRMs were rinsed three times with isooctane (Honeywell B&J GM2 Lot# DL203) and the rinses were transferred with a Hamilton syringe to individually labeled ASVs for injection on the GC/MS. A 2 uL aliquot of each mass labeled standard or SRM was injected on-column using the Agilent Model 6890N GC System with Agilent Model 5975B MSD. The GC and MS acquisition methods and oven temperature program as shown in Table 3 was utilized, except this method had a 6 min solvent delay. If the standard could be seen within the chromatogram, then no further action was required. If the standard was not found, either a selected ion monitoring (SIM) method was applied to the MS or an earlier solvent delay was utilized and the sample was reinjected. Once all standards that could be found had a suitable chromatogram, the retention times and ion masses of the compounds were recorded.

E. Extraction and Identification of Plastic Additive Compounds

Plastic pellets (n = 3 of each plastic product) were cut with either a razor blade or a pill cutter cleaned with isopropanol into 2 mm by 2 mm pieces. Pieces were combined until reaching a mass of approximately 0.10000 g using a calibrated Sartorius MC210S balance. For extraction, the samples were placed into labeled 10 mL baked glass open-focused microwave (OFM) vials (CEM Corporation, Charlotte, NC, USA), along with a solvent-cleaned Teflon-coated magnetic stir bar, 1.8 mL of a 1:1 dichloromethane:methanol (DCM:MeOH v:v) solution (DCM: Honeywell B&J GM2 Lot# DU142-US; MeOH: Honeywell B&J GM2 Lot# DI827), and 0.2 mL of an internal standard solution measured gravimetrically using a new solvent-cleaned and dried Hamilton syringes for each sample. The internal standard solution created on 9 February 2023, consisted of 5000 ng mL^{-1} mass-labeled di-n-propyl phthalate-d4 in acetone (Honeywell B&J GM2 Lot#: DU031-US). The OFM vials were capped with the corresponding solvent-rinsed silicone cap with teflon insert (CEM Corporation). Three laboratory blanks were prepared with the same methods and solutions as the samples. Vessels were swirled by hand and extracted with the method "Cara Megill" on the Discover SP open focused microwave (CEM Corporation). Briefly, samples were heated to 80 °C and held at steady temperature for 20 min. Parameters included maximum power at 250-watt, maximum pressure at 250 psi, PowerMax on, and stirring at medium. Extracts were transferred to a muffled 2 mL amber auto-sampler vial (ASV) with a glass pipette and solvent-exchanged with toluene under a steady stream of nitrogen in a Biotage TurboVap (0.5 L min^{-1} nitrogen flow rate; 35 °C water bath). The ASV vials were then capped with solvent-rinsed ASV vial caps with a Teflon-lined insert and centrifuged at 1300 rpm for 10 min using a LW Scientific C5 centrifuge (Lawrenceville, GA, USA). The top 1.0 mL of the sample was transferred with a glass pipette to a new ASV vial and placed in a numbered position in the gas chromatograph mass spectrometer (GC/MS) autosampler tray.

A 2 uL aliquot of each extract was analyzed using a Agilent Model 6890N GC System with Agilent Model 5975B mass spectrometer (Agilent Technologies, Palo Alto, CA) in electron ionization (EI) mode with hydrogen as a carrier gas supplied by a Precision SL Hydrogen Generator (Peak Scientific, Scotland, UK). Injection was performed on-column with a 5 uL gold standard syringe (Agilent Technologies). Details of the GC acquisition method and oven temperature program along with the MS acquisition methods are shown in Table 3.

Table 3. GC/MS settings and methods.

Gas Chromatograph	**Agilent Model 6890N**
Carrier Gas	Hydrogen
Injection mode	On-Column
Solvent Delay	3.0 min
Oven Temperature	70 ºC → 170 ºC at 25 ºC min^{-1} → 270 ºC at 2 ºC min^{-1} → 325 ºC at 25 ºC (10 min)
Run Time	66.2 min
Carrier Gas Flow Rate	0.7 mL min^{-1}
Guard Column	Restek Siltek: 5 m x 0.25 mm (Bellefonte, PA)
Capillary Column	Agilent DB-5MS: 30 m x 0.18 mm x 0.18 μm

Mass Spectrometer	**Agilent Model 5975B**
MS Source Temperature	250 ºC
MS Quadruple Temperature	150 ºC
Detection Type	Scanning ion mode
Scan Range	50 - 650 m/z
Scan Rate	1562 u s^{-1}
Ionization Energy	70 eV

Peaks were identified through a visual inspection. Any peak at least three times the abundance of the baseline was analyzed. Retention time, the three greatest intensity ions, and the greatest mass ion were recorded for each peak. A search against the NIST Mass Spectral Library was performed and compound match name, match number, and match probability were recorded. The NIST MS Library was found to not accurately identify hydrocarbons, so the highest mass ion was utilized to manually distinguish between these compounds. Peaks were integrated in the program MassHunter Quantitative Analysis to quantify peak area. The peak area of each compound was then divided by the peak area of the internal standard to calculate a ratio per compound that could be compared across the plastic products.

F. Statistics

To test if the ratios of relative area of each compound differed among pellet products, JMP 14 software was used. All data was tested for normality using a Shapiro-Wilk test and homogeneity of variance using a Bartlett's test. When assumptions were met, an analysis of variance (ANOVA) was performed followed by a Tukey Post-Hoc test. When they were not met, a Wilcoxon followed by a Steel-Dwass multiple comparison test was performed. The reported statistics ignored all assumptions and were based on the results from the ANOVA and Tukey Post-Hoc test. A p-value of less than 0.05 was determined to be statistically significant.

G. Glassware

All glassware including OFM vials, ASV vials, and glass pipettes were cleaned in a Thermolyne F30438CM furnace (Thermo Fisher Scientific) to prevent any contamination from prior use. The oven cycle was as follows: heat to 450 ºC and hold at steady temperature for 4 hours. The glassware was wrapped in aluminum foil before baking to prevent additional particle or chemical contamination while in or once removed from the furnace. To prevent additive chemical contamination, the magnetic stir bars were solvent cleaned three times by sonication for 5 min with acetone (Honeywell B&J GM2 Lot# DM724) and again with hexane (Honeywell B&J GM Lot# DM620, DU167-US, EF140US). The OFM Teflon caps and inserts along with the ASV caps and inserts were solvent-rinsed by swirling in a muffled beaker three times for 30 sec with acetone (Honeywell B&J GM2 Lot# DM724) and again with hexane (Honeywell B&J GM Lot# DM620, DU167-US, EF140US). The Hamilton syringes used to spike the samples with the internal standard solution were cleaned under a vacuum 3 x acetone (Honeywell B&J GM2 Lot# DM724), 3 x DCM (Honeywell B&J GM2 Lot# DU142-US), and 3 x hexane (Honeywell B&J GM Lot# DM620, DU167-US, EF140US). The syringe tips were solvent cleaned by rinsing with the same acetone, DCM, hexane from Teflon squirt bottles.

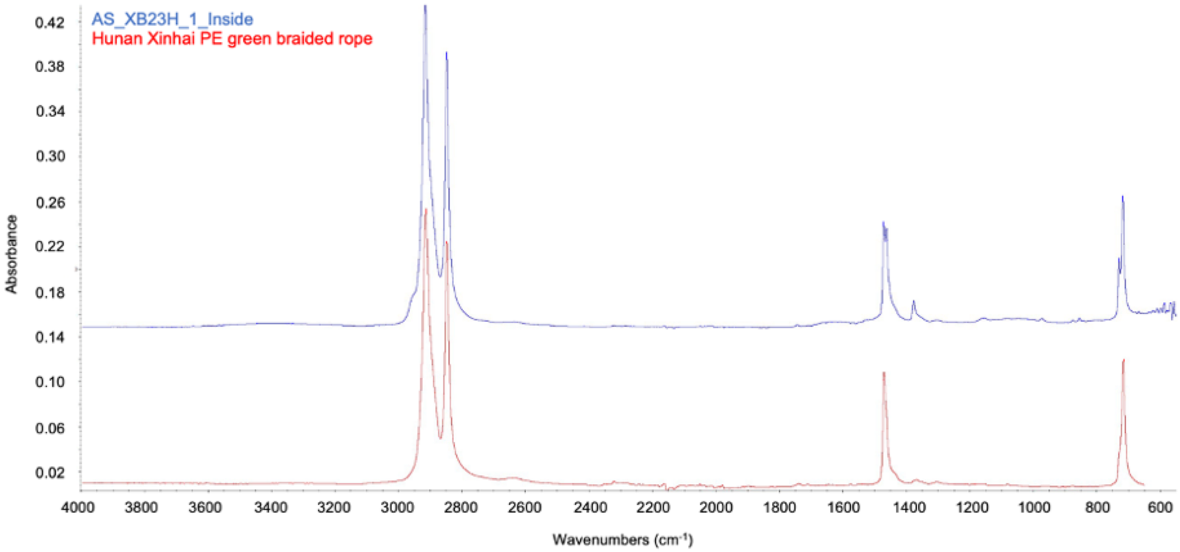
All glassware utilized in the making of the standard stock solutions and injection on the GC/MS were muffled prior to use under the same parameters defined previously in the methods. The Hamilton syringes used to transfer the standards into the stock solutions were solvent cleaned and dried utilizing the same cleaning protocol defined in the methods above.

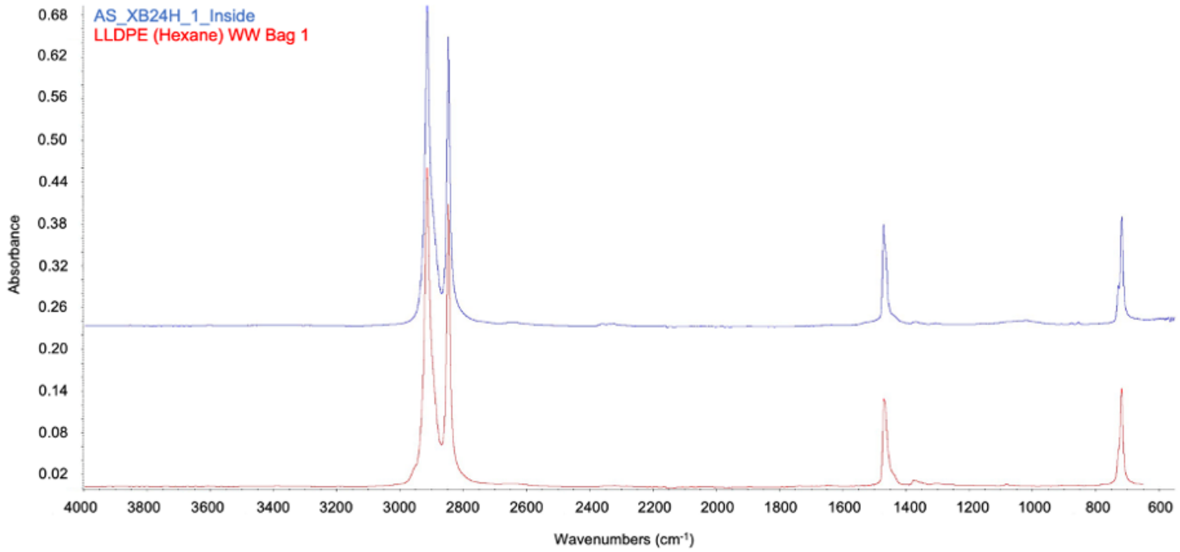
RESULTS

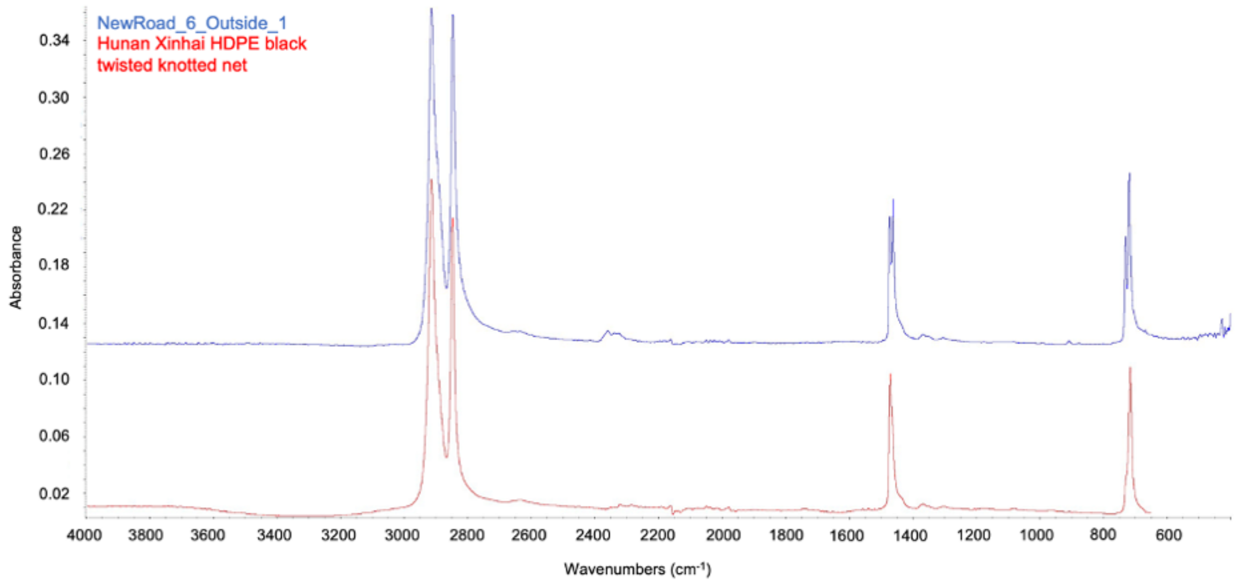
A. Polymer Identification

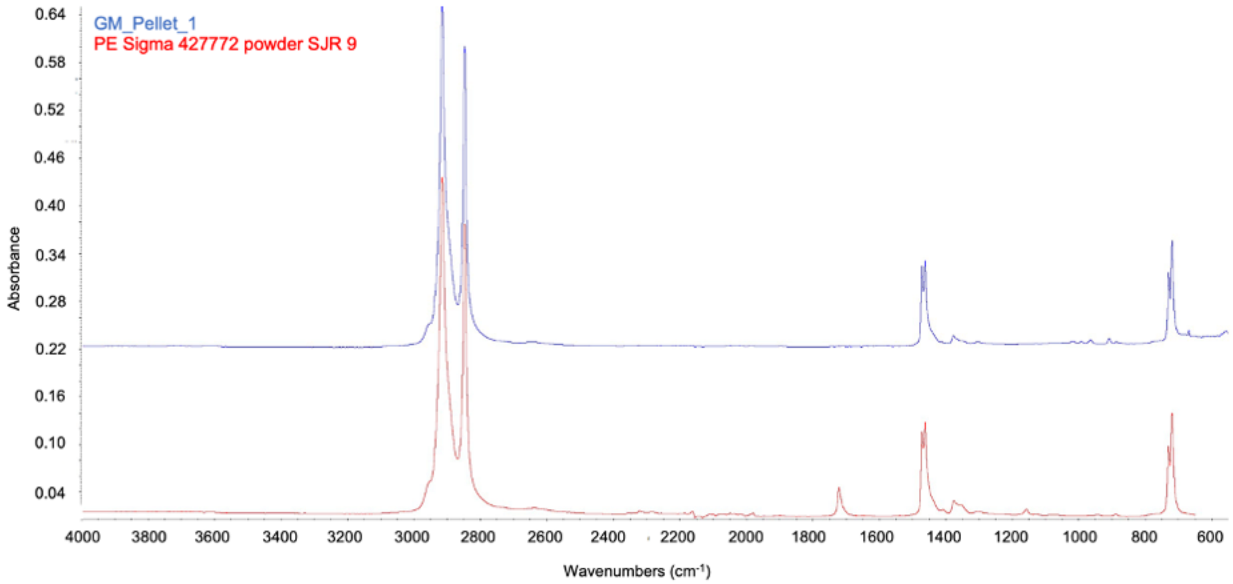
Four plastic pellet types (AltiSora XB23-H, AltiSora XB24-H, NewRoad, and GreenMantra) were identified as polyethylene (PE) based on manual inspection of ATR FTIR spectra and matches to a library search. All spectra of these four plastic pellet types had peaks around the 2915 cm^{-1}, 2845 cm^{-1}, 1472 cm^{-1}, 1462 cm^{-1}, 730 cm^{-1}, and 717 cm^{-1} wavelengths which are characteristic of PE (Figure 2; Jung et al., 2018). All spectra taken of these four pellet types yielded library matches to various materials all known to be made with PE stored in the spectral library and all matches were greater than 91.58% (Table 4). Based on these two criteria, there is high confidence that the polymer identification of these pellets is PE. Identifying the density or type of PE should not be performed using the ATR FTIR match results. A more detailed look into particular spectral peaks or another chemical technique, like DSC, are needed (Jung et al., 2018). The SBS pellets were matched to poly(butadiene) or polystyrene butadiene with lower match percentages (62.15% to 76.30%; Table 4). The lower library match percentages are because the library utilized does not contain SBS spectra, but the functional groups in SBS are the same as functional groups in the two matched materials. The new spectra taken in this study of SBS will be added to the "CMDR Library" as reference spectra for future use.

Interestingly, the inside spectra of the AltiSora products and the SBS pellets were slightly different from the outside spectra. The differences are compared in Figure 3. The AltiSora outside spectra produces an additional broad peak around a wavelength of 1000 cm^{-1} to 1200 cm^{-1} possibly due to the original oxidation of the DFG or the oxidation of the pellets themselves. The outside of the SBS pellet produced a peak around 3670 cm^{-1} not seen in the inside spectra. Further analysis will need to be performed to determine if a free alcohol is the cause of this extra peak. Additionally, in the range of 600 cm^{-1} to 1200 cm^{-1} the peaks are more defined in the inside spectra of the SBS pellets than the outside.


AS_XB23H_1_Inside
Hunan Xinhai PE green braided rope
Absorbance
0.42
0.38
0.34
0.30
0.26
0.22
0.18
0.14
0.10
0.06
0.02
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)


AS_XB24H_1_Inside
LLDPE (Hexane) WW Bag 1
Absorbance
0.68
0.62
0.56
0.50
0.44
0.38
0.32
0.26
0.20
0.14
0.08
0.02
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)


NewRoad_6_Outside_1
Hunan Xinhai HDPE black twisted knotted net
Absorbance
0.34
0.30
0.26
0.22
0.18
0.14
0.10
0.06
0.02
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)


GM_Pellet_1
PE Sigma 427772 powder SJR 9
Absorbance
0.64
0.58
0.52
0.46
0.40
0.34
0.28
0.22
0.16
0.10
0.04
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)

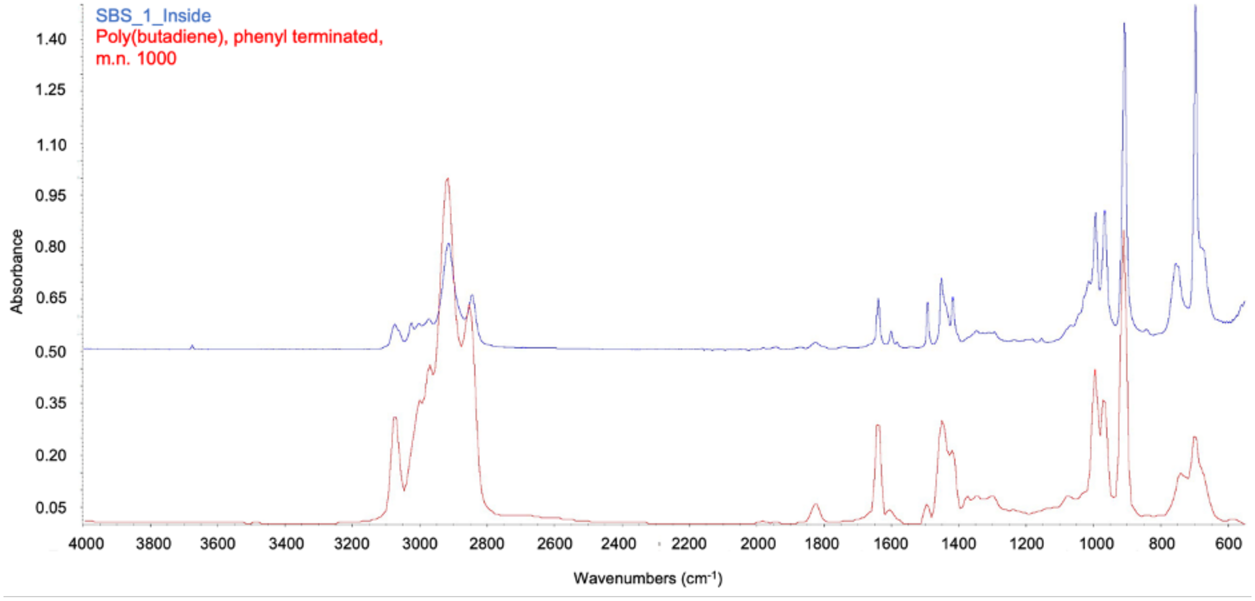


Figure 2. ATR FTIR spectra of the five plastic pellet types along with matching reference spectra. Each spectra is representative of the other spectrum collected within that plastic type, except for differences in the inside and outside spectra of the two AltiSora products and SBS which is shown in Figure 3.

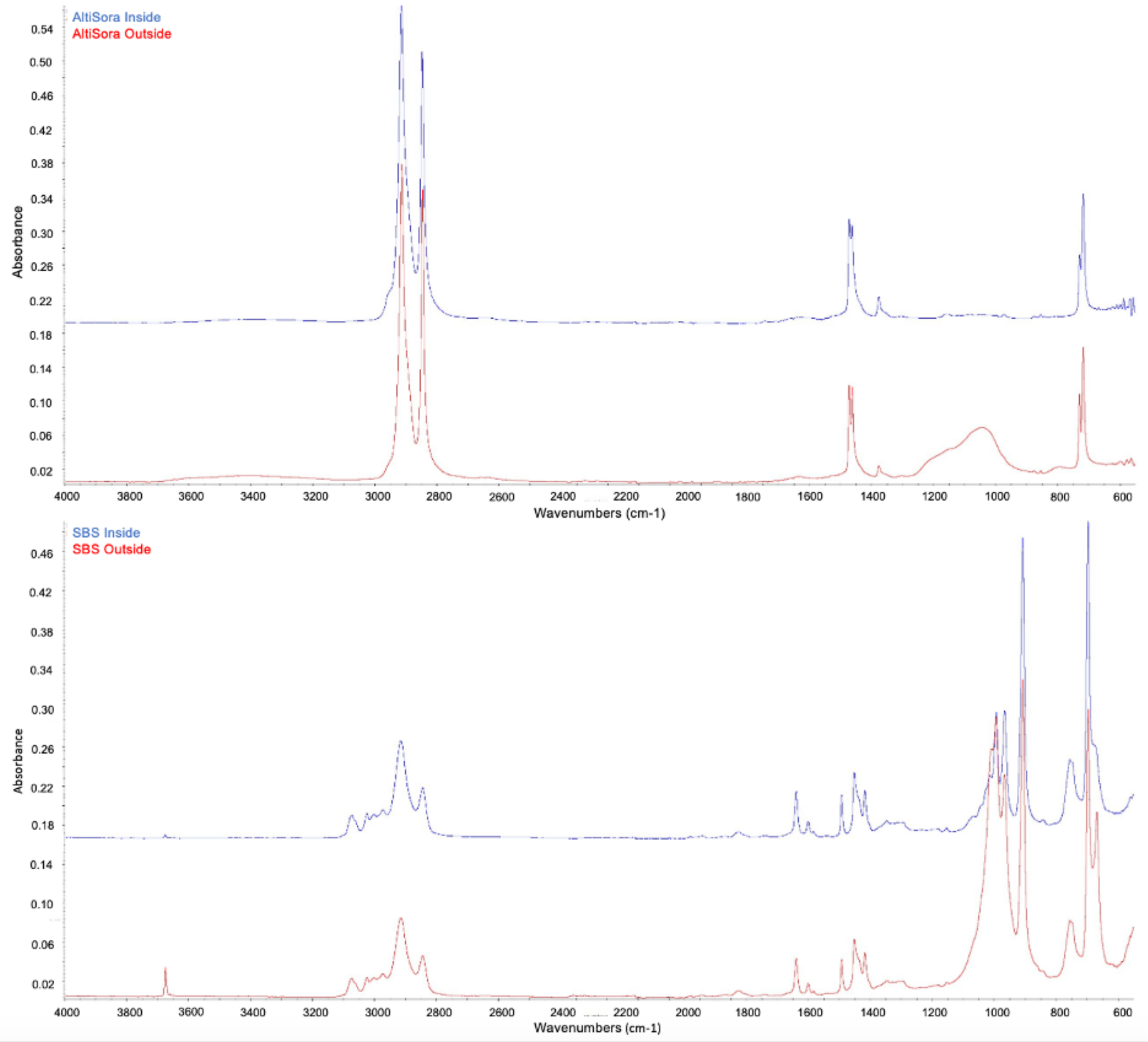
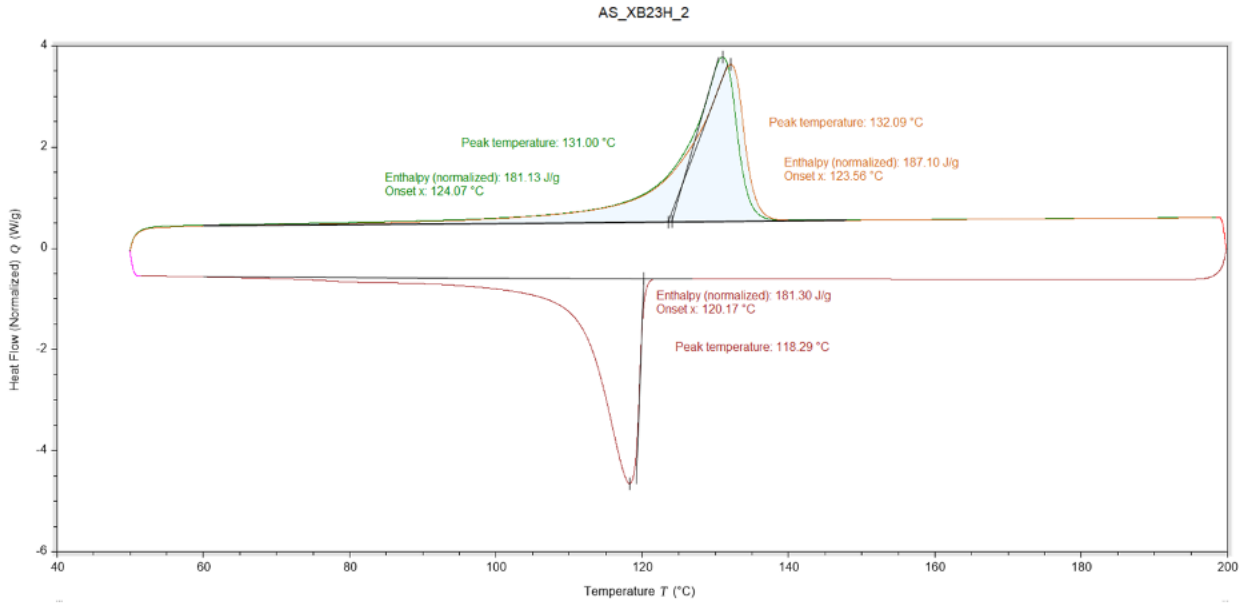
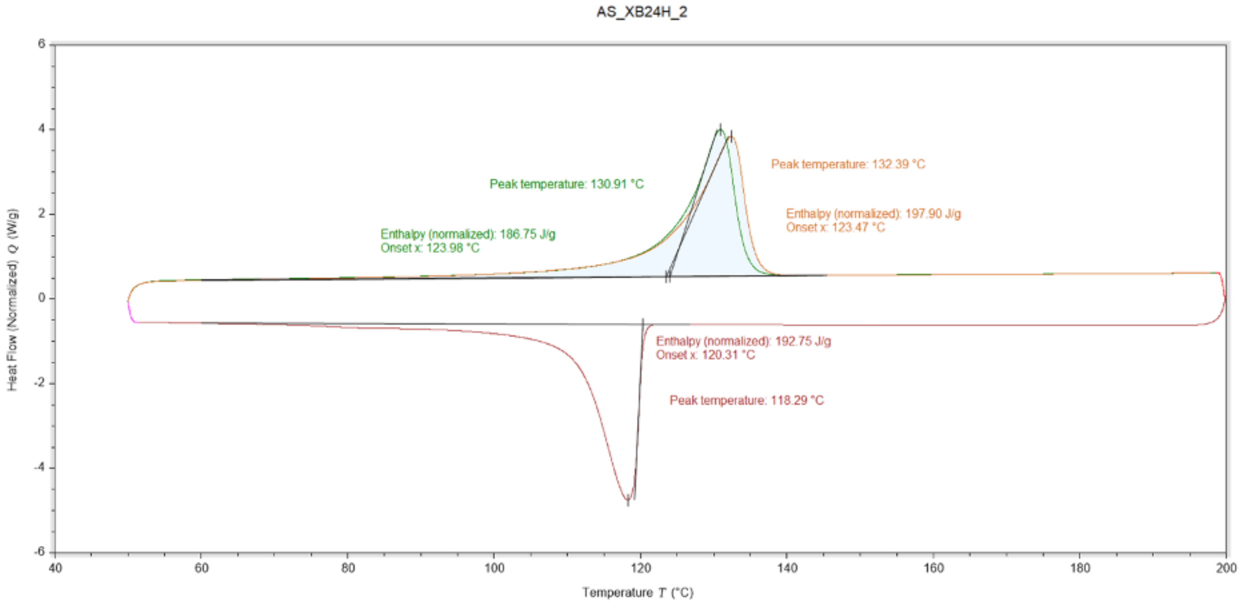


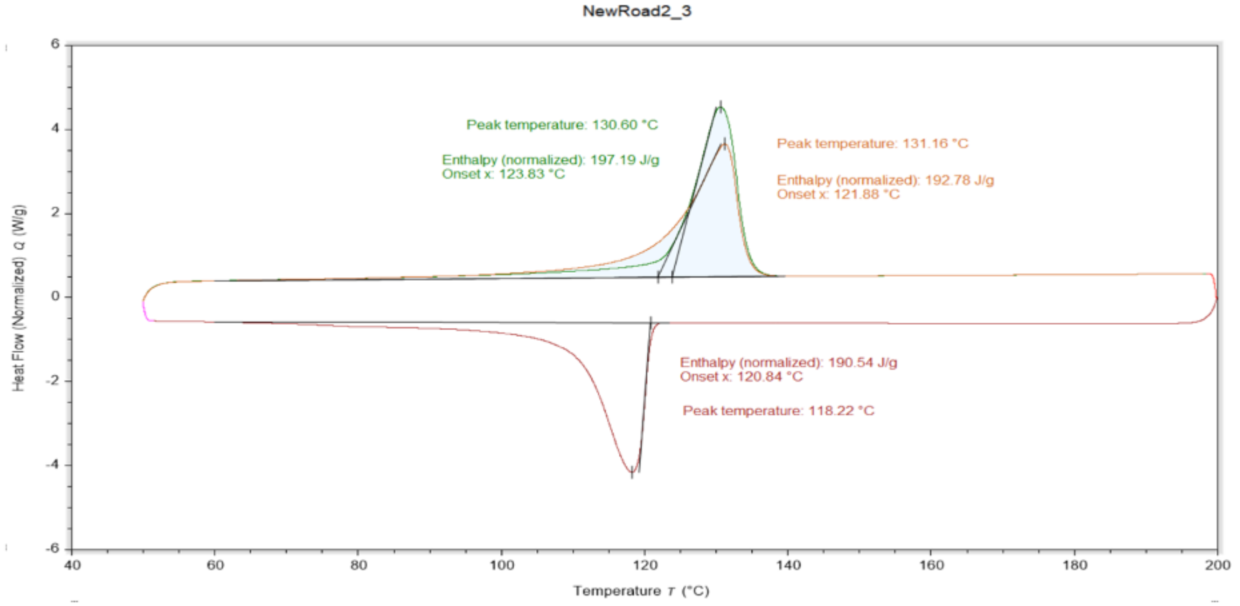
Figure 3. Comparison of AltiSora and SBS inside and outside spectra from ATR FTIR. These two spectra comparisons are representative of all inside and outside spectra taken of the samples of these products.

Tm values of the products were as follows: AltiSora XB23-H (132.02 +/- 0.15; mean +/- s.d.), AltiSora XB24-H (132.23 +/- 0.46), NewRoad (131.34 +/- 0.27), and GreenMantra (flat 112.64 +/- 1.20.; pellet 113.39 +/- 1.04). Based on the melting ranges developed by Lynch et al.

(in preparation), I was able to distinguish the different densities of the samples identified as PE as well as determine that none of the products were made from a blend of polymers due to the presence of only a single melting peak in all of the melting curves produced. Examples of the integrated thermograms are shown in Figure 4. AltiSora XB23-H and AltiSora XB24-H were within the melting range of HDPE, as expected since previously identified HDPE nets were converted into these pellets by AltiSora. Results confirm that the pellets made from the DFG were not contaminated from additional plastic polymers during the conversion process. The unknown samples of NewRoad showed no blends of polymers as there was a single melting peak in all nine samples and the peak melting temperature of all samples was within the range of HDPE, validating that this product is made completely from HDPE post-industrial plastic. The six samples of GreenMantra provided different results with the peak melting temperature in the range of LDPE, validating that these samples are made from LDPE post-consumer plastic. All peak melting temperatures and final polymer ID are shown in Table 4.




AS_XB24H_2
Peak temperature: 130.91 °C
Peak temperature: 132.39 °C
Enthalpy (normalized): 197.90 J/g
Onset x: 123.47 °C
Enthalpy (normalized): 186.75 J/g
Onset x: 123.98 °C
Enthalpy (normalized): 192.75 J/g
Onset x: 120.31 °C
Peak temperature: 118.29 °C
Heat Flow (Normalized) Q (W/g)
6
4
2
0
-2
-4
-6
40
60
80
100
120
140
160
180
200
Temperature T (°C)


NewRoad2_3
Peak temperature: 130.60 °C
Enthalpy (normalized): 197.19 J/g
Onset x: 123.83 °C
Peak temperature: 131.16 °C
Enthalpy (normalized): 192.78 J/g
Onset x: 121.88 °C
Enthalpy (normalized): 190.54 J/g
Onset x: 120.84 °C
Peak temperature: 118.22 °C
Heat Flow (Normalized) Q (W/g)
6
4
2
0
-2
-4
-6
40
60
80
100
120
140
160
180
200
Temperature T (°C)

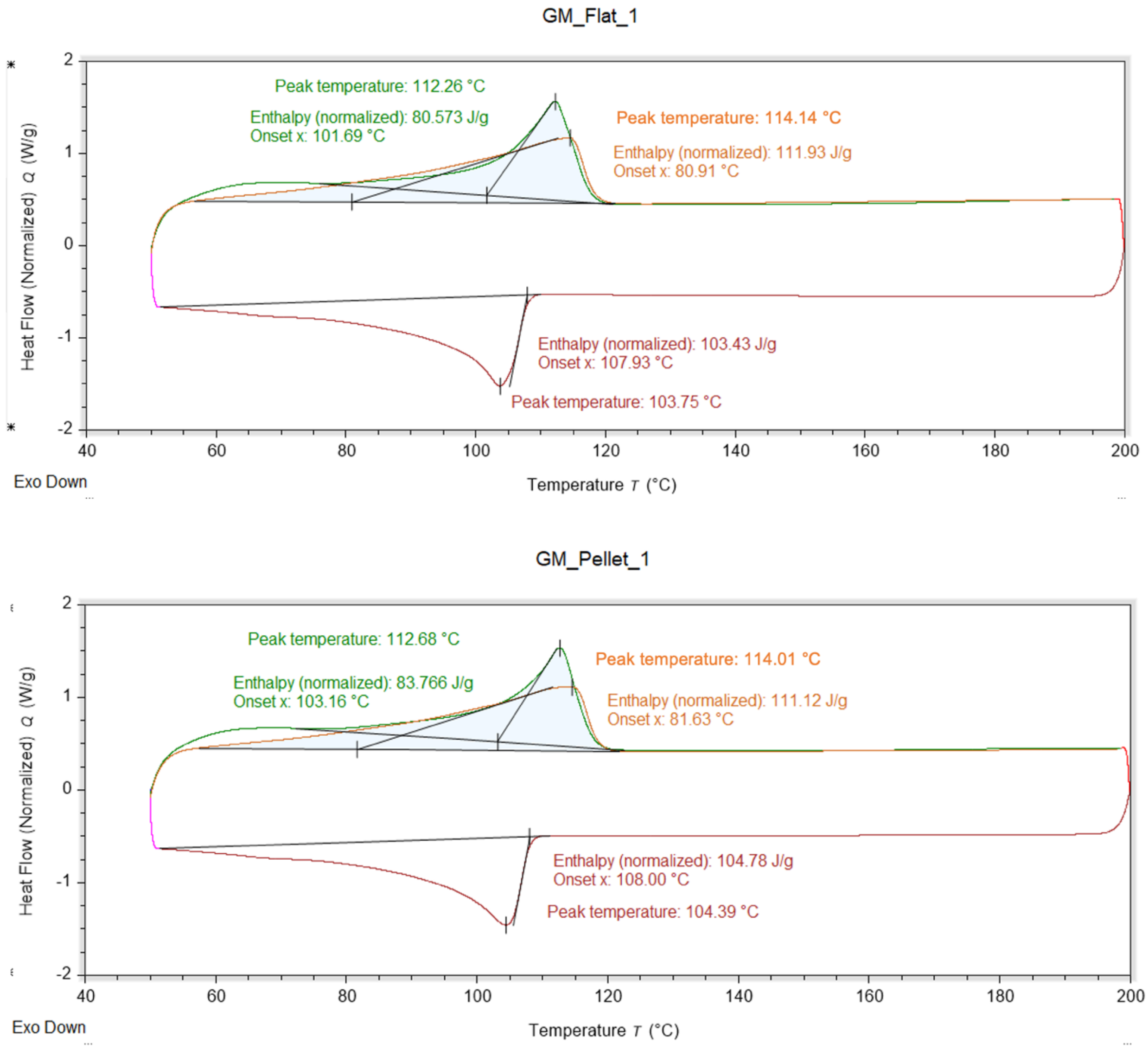


Figure 4. Integrated DSC thermograms of each plastic pellet product. Each curve is representative of the others collected within that product.

Table 4. ATR FTIR polymer library match with match percentage along with DSC melt temperature and final polymer ID.

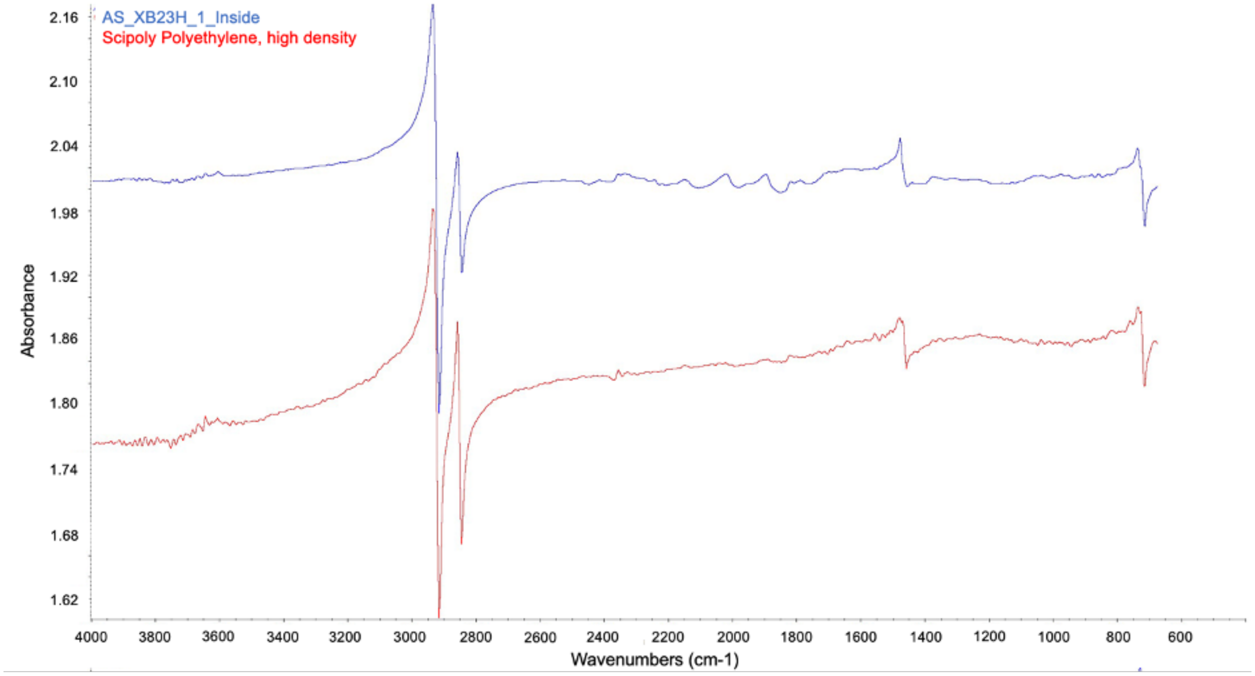
Product	Sample	Side	ATR FTIR Top Library Match	% Match	DSC Second Melt - Tm (oC)	Polymer ID
AltiSora	ASXB23H-1	Outside	LDPE 25% recycle Amazon bag	98.88	131.85	HDPE
AltiSora	ASXB23H-1	Outside	LDPE 25% recycle Amazon bag	98.59		
AltiSora	ASXB23H-1	Inside	Hunan Xinhai PE green braided rope	98.62		
AltiSora	ASXB23H-2	Outside	HDPE TS bag MJ 2.3	98.25	132.09	HPDE
AltiSora	ASXB23H-2	Outside	HDPE TS bag MJ 2.3	98.67		
AltiSora	ASXB23H-2	Inside	PE Sigma 427772 powder SJR 9	98.31		
AltiSora	ASXB23H-3	Outside	HDPE TS bag MJ 2.3	98.39	132.12	HPDE
AltiSora	ASXB23H-3	Outside	HDPE TS bag MJ 2.3	98.74		
AltiSora	ASXB23H-3	Inside	Hunan Xinhai PE green twine	98.44		
AltiSora	ASXB24H-1	Outside	LDPE >40% recycled Patagonia bag	99.17	131.71	HPDE
AltiSora	ASXB24H-1	Outside	LDPE >40% recycled Patagonia bag	99.30		
AltiSora	ASXB24H-1	Inside	LLDPE (Hexene) WW Bag 1	99.13		
AltiSora	ASXB24H-2	Outside	LDPE >40% recycled Patagonia bag	99.20	132.39	HDPE
AltiSora	ASXB24H-2	Outside	LDPE 25% recycle Amazon bag	99.25		
AltiSora	ASXB24H-2	Inside	Hunan Xinhai PE green twine	98.61		
AltiSora	ASXB24H-3	Outside	LDPE 25% recycle Amazon bag	98.76	132.58	HDPE
AltiSora	ASXB24H-3	Outside	LDPE 25% recycle Amazon bag	98.53		
AltiSora	ASXB24H-3	Inside	HDPE 0.9510	98.38		
NewRoad	NR-1	Outside	HDPE TS bag MJ 2.3	95.59	131.18	HDPE
NewRoad	NR-1	Outside	HDPE TS bag MJ 2.3	95.92		
NewRoad	NR-1	Inside	Hunan Xinhai HDPE Black Twisted Knotted Net	97.88		

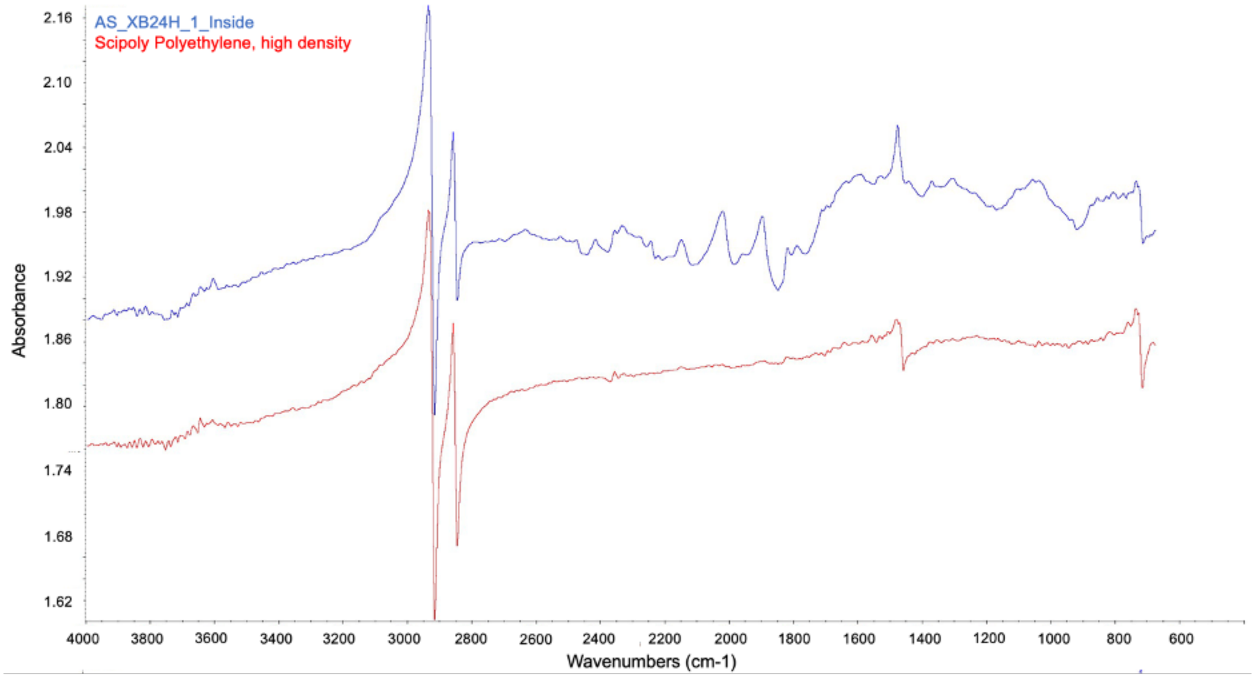
NewRoad	NR-2	Outside	HDPE TS bag MJ 2.3	96.37	131.21	HDPE
NewRoad	NR-2	Outside	HDPE TS bag MJ 2.3	96.24		
NewRoad	NR-2	Inside	PE SRM 1474B	99.16		
NewRoad	NR-3	Outside	HDPE TS bag MJ 2.3	96.48	131.16	HDPE
NewRoad	NR-3	Outside	Hunan Xinhai HDPE Black Twisted Knotted Net	95.28		
NewRoad	NR-3	Inside	Hunan Xinhai HDPE Black Twisted Knotted Net	98.64		
NewRoad	NR-4	Outside	Hunan Xinhai HDPE Black Twisted Knotted Net	94.74	131.14	HDPE
NewRoad	NR-4	Outside	HDPE TS bag MJ 2.3	96.62		
NewRoad	NR-4	Inside	Hunan Xinhai HDPE Black Twisted Knotted Net	96.04		
NewRoad	NR-5	Outside	HDPE TS bag MJ 2.3	94.71	131.16	HDPE
NewRoad	NR-5	Outside	HDPE TS bag MJ 2.3	96.84		
NewRoad	NR-5	Inside	LLDPE GnT bag	97.00		
NewRoad	NR-6	Outside	Hunan Xinhai HDPE Black Twisted Knotted Net	94.04	131.50	HDPE
NewRoad	NR-6	Outside	14895494 DYNEEMA Line	96.21		
NewRoad	NR-6	Inside	LLDPE GnT bag	96.87		
NewRoad	NR-7	Outside	Hunan Xinhai HDPE Black Twisted Knotted Net	91.58	131.87	HDPE
NewRoad	NR-7	Outside	14895494 DYNEEMA Line	92.52		
NewRoad	NR-7	Inside	HunanXinhai HDPEHapuNet	97.17		
NewRoad	NR-8	Outside	HDPE TS bag MJ 2.3	94.37	131.66	HDPE
NewRoad	NR-8	Outside	Hunan Xinhai HDPE Black Twisted Knotted Net	92.11		
NewRoad	NR-8	Inside	14895494 DYNEEMA Line	92.44		
NewRoad	NR-9	Outside	HDPE TS bag MJ 2.3	96.25	131.22	HDPE
NewRoad	NR-9	Outside	HDPE TS bag MJ 2.3	94.50		
NewRoad	NR-9	Inside	Hunan Xinhai HDPE Black Twisted Knotted Net	97.41		
Green Mantra	GM_Flat_1	-	PE Sigma 427772 powder SJR 9	99.00	114.14	LDPE
Green Mantra	GM_Flat_2	-	PE Sigma 427772 powder SJR 9	97.86	112.09	LDPE

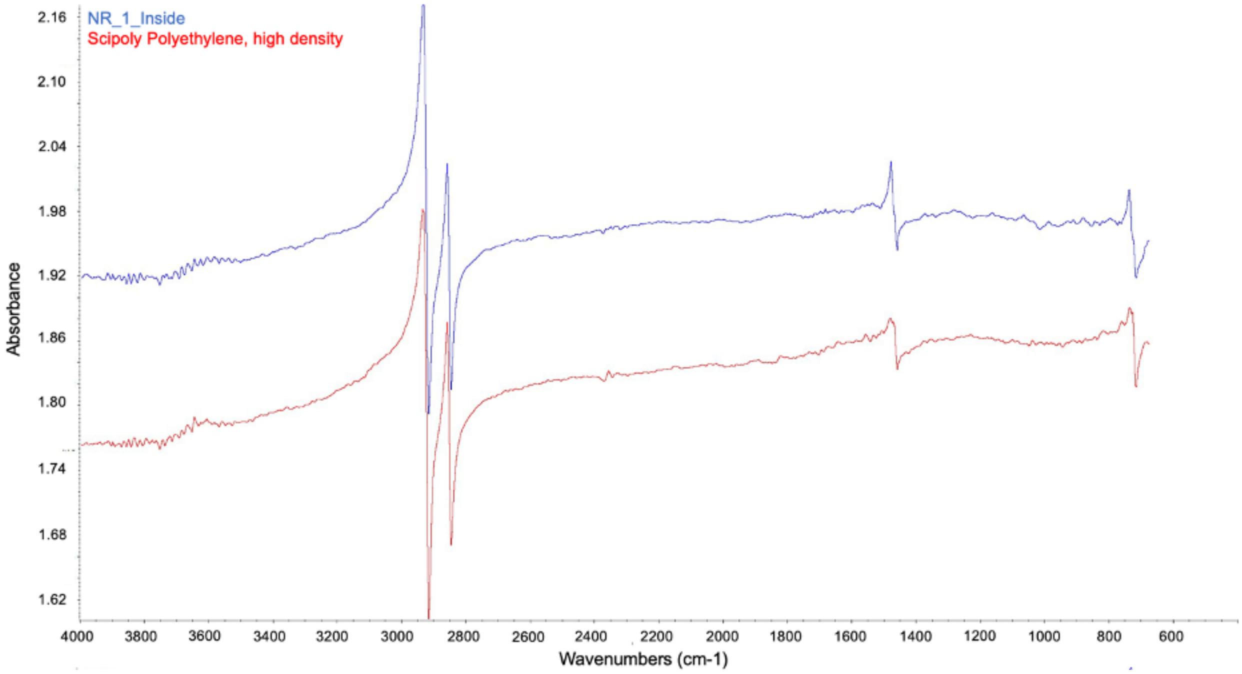
Green Mantra	GM_Flat_3	-	PE Sigma 427772 powder SJR 9	97.57	111.81	LDPE
Green Mantra	GM_Pellet_1	-	PE Sigma 427772 powder SJR 9	98.88	114.01	LDPE
Green Mantra	GM_Pellet_2	-	PE Sigma 427772 powder SJR 9	98.96	114.08	LDPE
Green Mantra	GM_Pellet_3	-	PE Sigma 427772 powder SJR 9	98.88	113.90	LDPE
SBS-Polymer	SBS-1	Outside	Poly(butadiene), phenyl terminated, m.n. 1000	71.93		
SBS-Polymer	SBS-1	Outside	Poly(butadiene), phenyl terminated, m.n. 1000	72.67		
SBS-Polymer	SBS-1	Inside	PolystyreneButadiene WW	76.07		
SBS-Polymer	SBS-2	Outside	Poly(butadiene), phenyl terminated, m.n. 1000	65.89		
SBS-Polymer	SBS-2	Outside	Poly(butadiene), phenyl terminated, m.n. 1000	68.44		
SBS-Polymer	SBS-2	Inside	PolystyreneButadiene WW	76.44		
SBS-Polymer	SBS-3	Outside	Poly(butadiene), phenyl terminated, m.n. 1000	62.15		
SBS-Polymer	SBS-3	Outside	Poly(butadiene), phenyl terminated, m.n. 1000	69.84		
SBS-Polymer	SBS-3	Inside	PolystyreneButadiene WW	76.30		

Similarly to the ATR FTIR results, the AltiSora XB23-H, AltiSora XB24-H, NewRoad, and GreenMantra pellets all yielded reflectance spectra on the microscope FTIR that matched to a type of polyethylene in the library search. The SBS spectra matched to a variety of spectra including Scipoly Styrene/Butadiene ABA block copolymer, GPPS pellets Polykit 2020, and PS JAF soft pellet SS12, often with lower match scores. Difficulty in identifying the SBS product exemplifies the need for spectral libraries to contain the polymers that are expected in samples, so they can be distinguished and identified in unknown samples. Examples of these spectra can be found in Figure 5 and the list of matches with the match percent can be found in Table 5. Differences in the inside and outside spectra of the two AltiSora products and SBS were seen.

These differences are shown in Figure 6 including greater definition of peaks from outside spectra of the AltiSora products and greater peaks from the inside spectra of SBS. From these spectra, a reflectance library called “HDOT Static Library” was created for use in future microplastic testing of stormwater runoff and laboratory water samples of asphalt mixtures created with these plastic products.




AS_XB24H_1_Inside
Scipoly Polyethylene, high density
Absorbance
2.16
2.10
2.04
1.98
1.92
1.86
1.80
1.74
1.68
1.62
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)


NR_1_Inside
Scipoly Polyethylene, high density
Absorbance
2.16
2.10
2.04
1.98
1.92
1.86
1.80
1.74
1.68
1.62
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)

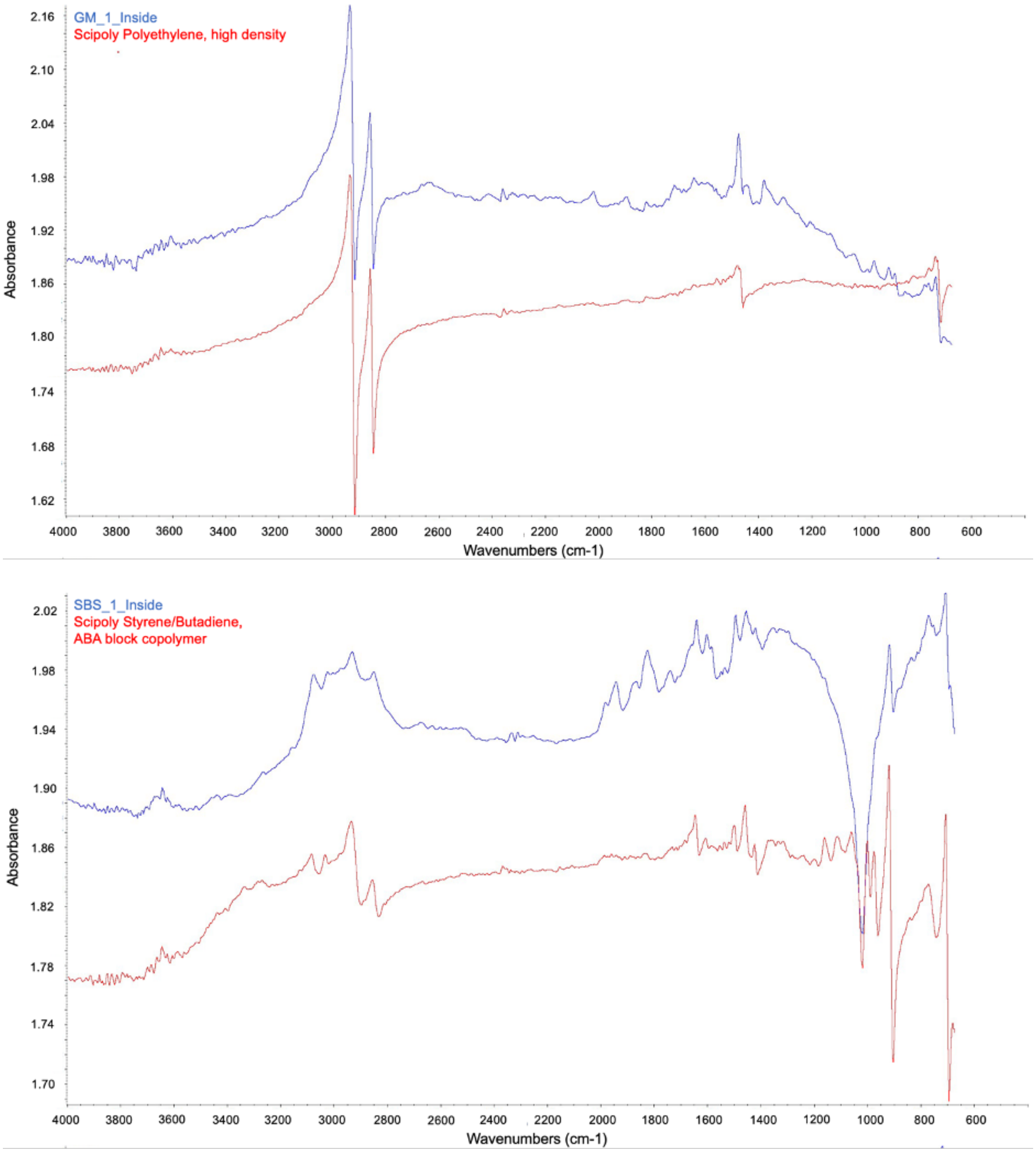


Figure 5. Microscope FTIR reflectance spectra of the five plastic pellet products along with matching reference spectra. Each spectra is representative of the other spectrum collected within that plastic product, except for differences in the inside and outside spectra of the two AltiSora products and SBS which is shown in Figure 5.

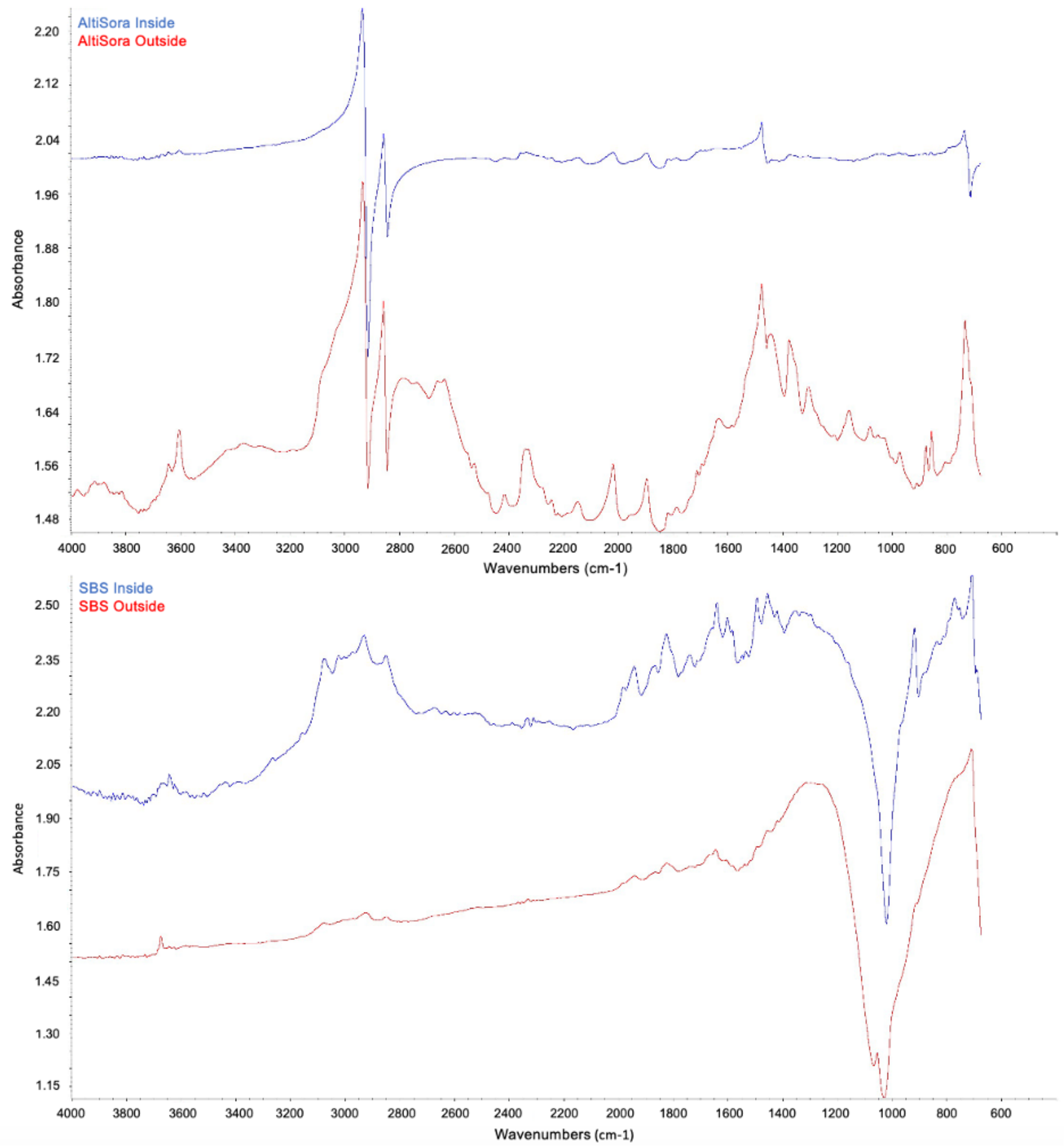


Figure 6. Comparison of AltiSora and SBS inside and outside reflectance spectra from the microscope FTIR. These two spectra comparisons are representative of all inside and outside spectra taken of the samples of these products.

Table 5. Microscope FTIR polymer library match with match percentage.

Product	Sample	Side	Library Match	% Match
AltiSora	ASXB23H-1	Outside	Scipoly Polyethylene, high density	84.61
AltiSora	ASXB23H-1	Outside	Scipoly Polyethylene, high density	94.92
AltiSora	ASXB23H-1	Inside	LDPE pellets Polykit 2020	97.13
AltiSora	ASXB23H-2	Outside	Scipoly Polyethylene, high density	93.24
AltiSora	ASXB23H-2	Outside	Scipoly Polyethylene, high density	97.34
AltiSora	ASXB23H-2	Inside	Scipoly Polyethylene, high density	94.61
AltiSora	ASXB23H-3	Outside	Scipoly Polyethylene, high density	88.00
AltiSora	ASXB23H-3	Outside	Scipoly Polyethylene, high density	94.98
AltiSora	ASXB23H-3	Inside	LDPE pellets Polykit 2020	96.66
AltiSora	ASXB24H-1	Outside	Scipoly Polyethylene, high density	97.14
AltiSora	ASXB24H-1	Outside	Scipoly Polyethylene, high density	97.45
AltiSora	ASXB24H-1	Inside	Scipoly Polyethylene, high density	95.04
AltiSora	ASXB24H-2	Outside	Scipoly Polyethylene, high density	97.27
AltiSora	ASXB24H-2	Outside	Scipoly Polyethylene, high density	97.72
AltiSora	ASXB24H-2	Inside	Scipoly Polyethylene, high density	93.85
AltiSora	ASXB24H-3	Outside	Scipoly Polyethylene, high density	97.26
AltiSora	ASXB24H-3	Outside	Scipoly Polyethylene, high density	96.87
AltiSora	ASXB24H-3	Inside	Scipoly Polyethylene, high density	96.99
NewRoad	NR-1	Outside	Scipoly Polyethylene, high density	96.37
NewRoad	NR-1	Outside	Scipoly Polyethylene, high density	98.34
NewRoad	NR-1	Inside	Scipoly Polyethylene, high density	96.87
NewRoad	NR-2	Outside	Scipoly Polyethylene, high density	96.66
NewRoad	NR-2	Outside	Scipoly Polyethylene, high density	95.87
NewRoad	NR-2	Inside	LDPE pellets Polykit 2020	97.14
NewRoad	NR-3	Outside	Scipoly Polyethylene, high density	96.23
NewRoad	NR-3	Outside	Scipoly Polyethylene, high density	96.96
NewRoad	NR-3	Inside	LDPE pellets Polykit 2020	97.20
NewRoad	NR-4	Outside	Scipoly Polyethylene, high density	97.26

NewRoad	NR-4	Outside	Scipoly Polyethylene, high density	96.82
NewRoad	NR-4	Inside	LDPE pellets Polykit 2020	97.48
NewRoad	NR-5	Outside	Scipoly Polyethylene, high density	96.76
NewRoad	NR-5	Outside	Scipoly Polyethylene, high density	96.19
NewRoad	NR-5	Inside	LDPE pellets Polykit 2020	97.31
NewRoad	NR-6	Outside	Scipoly Polyethylene, high density	96.78
NewRoad	NR-6	Outside	Scipoly Polyethylene, high density	97.80
NewRoad	NR-6	Inside	Scipoly Polyethylene, high density	97.08
NewRoad	NR-7	Outside	Scipoly Polyethylene, high density	97.18
NewRoad	NR-7	Outside	Scipoly Polyethylene, high density	97.11
NewRoad	NR-7	Inside	LDPE pellets Polykit 2020	97.40
NewRoad	NR-8	Outside	Scipoly Polyethylene, high density	96.59
NewRoad	NR-8	Outside	Scipoly Polyethylene, high density	97.00
NewRoad	NR-8	Inside	LDPE pellets Polykit 2020	97.39
NewRoad	NR-9	Outside	Scipoly Polyethylene, high density	96.47
NewRoad	NR-9	Outside	Scipoly Polyethylene, high density	96.54
NewRoad	NR-9	Inside	LDPE pellets Polykit 2020	97.05
Green Mantra	GM-1	Outside	Scipoly Polyethylene, high density	96.90
Green Mantra	GM-1	Outside	Scipoly Polyethylene, high density	97.33
Green Mantra	GM-1	Inside	Scipoly Polyethylene, high density	94.17
Green Mantra	GM-2	Outside	Scipoly Polyethylene, high density	97.34
Green Mantra	GM-2	Outside	Scipoly Polyethylene, high density	96.38
Green Mantra	GM-2	Inside	ULDPE pellets Polykit 2020	90.51
Green Mantra	GM-3	Outside	Scipoly Polyethylene, high density	96.85
Green Mantra	GM-3	Outside	Scipoly Polyethylene, high density	96.77
Green Mantra	GM-3	Inside	ULDPE pellets Polykit 2020	81.26
SBS-Polymer	SBS-1	Outside	SBS Polymer	37.85
SBS-Polymer	SBS-1	Outside	Poly(vinyl formal)	36.49
SBS-Polymer	SBS-1	Inside	SBS Polymer	63.21
SBS-Polymer	SBS-2	Outside	Poly(vinyl formal)	35.09

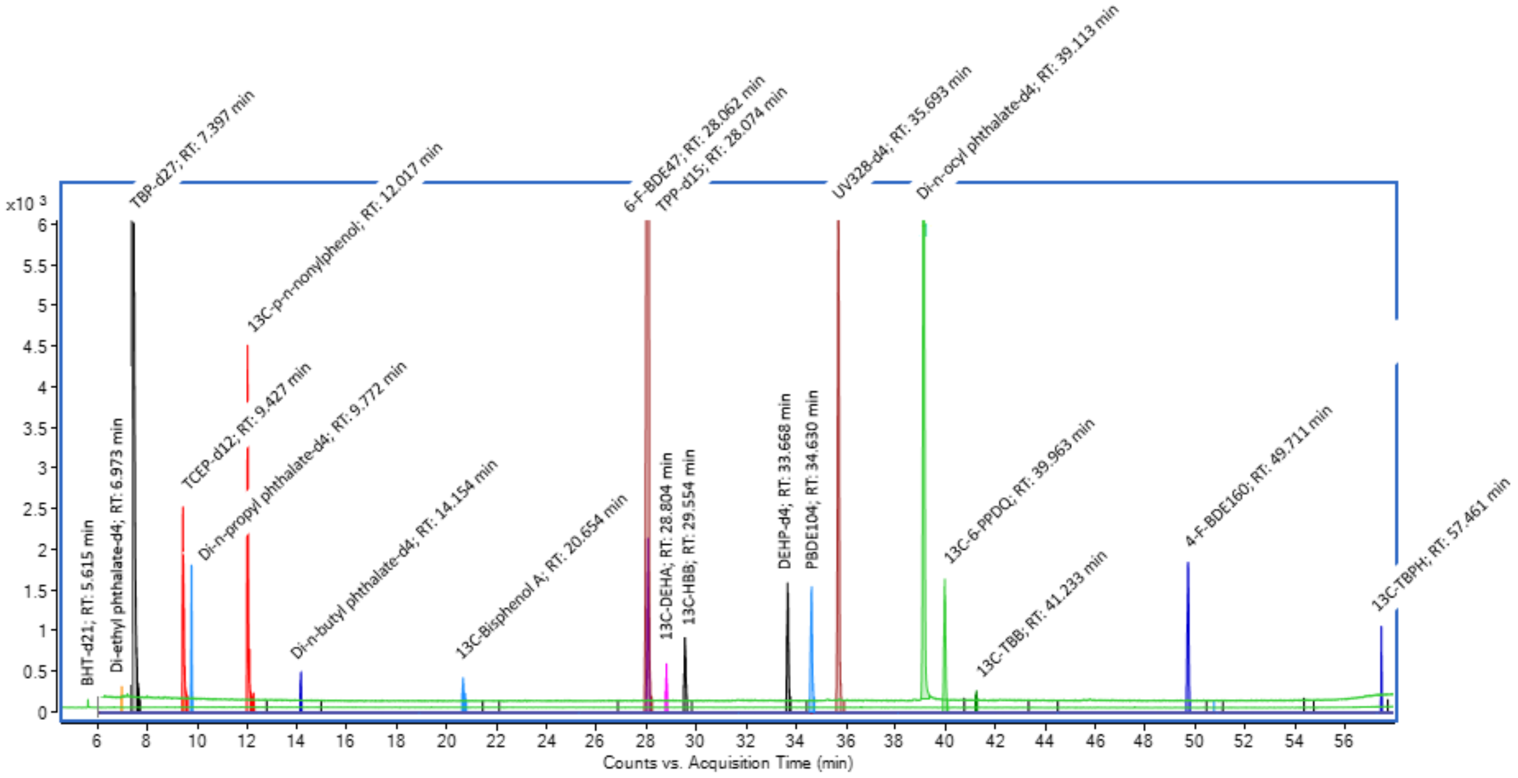
SBS-Polymer	SBS-2	Outside	Poly(vinyl formal)	32.12
SBS-Polymer	SBS-2	Inside	Alginic acid, sodium salt	33.53
SBS-Polymer	SBS-3	Outside	Alginic acid, sodium salt	32.00
SBS-Polymer	SBS-3	Outside	Hydroxypropyl methyl cellulose	33.72
SBS-Polymer	SBS-3	Inside	SBS Polymer	97.44

B. Internal Standards

A GC/MS chromatogram puzzled together with plastic additive and PAH internal standards is shown in Figure 7 with each compound name and retention time labeled. This chromatogram will aid in the identification of plastic additives and PAHs in unknown samples by utilizing the known retention times of the mass labeled compounds and comparing them to peaks of unknown compounds.

DnOP-d4 required a reinjection of the standard with a SIM method on the GC/MS targeting the mass ion 153.0 m/z. With this more sensitive method I was able to identify a peak in the chromatogram. BHT-d12, SRM 2269, and SRM 2270 required a reinjection of the standards with an earlier solvent delay of 3 min. With the earlier solvent delay, I was able to identify BHT-d12 and the peaks of naphthalene-d8, acenaphthene-d10, and biphenyl-d10 in the SRMs, which were not seen with a 6 min solvent delay. This determined the solvent delay for the GC/MS methods of the plastic pellet analysis.

All internal standards except DMP-d4, 4’F PBDE 208, and 13C-DBDPE were able to be identified in their resulting chromatograms. The 30 m capillary column is not an appropriate length to be able to identify the 4’F PBDE 208 and 13C-DBDPE as these compounds are too large for this analysis. Shorter columns have been shown to be more successful in identifying brominated flame retardants (Stapleton et al., 2009). I searched for DMP-d4 using a SIM method as well as a shorter solvent delay and no peak was detected. Future research will attempt a greater concentration of this compound in order to produce a chromatogram peak to identify the retention time.


x10 3
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
BHT-d21; RT: 5.615 min
Di-ethyl phthalate-d4; RT: 6.973 min
TBP-d27; RT: 7.397 min
TCEP-d12; RT: 9.427 min
Di-n-propyl phthalate-d4; RT: 9.772 min
13C-p-n-nonylphenol; RT: 12.017 min
Di-n-butyl phthalate-d4; RT: 14.154 min
13C-Bisphenol A; RT: 20.654 min
6-F-BDE47; RT: 28.062 min
TPP-d15; RT: 28.074 min
13C-DEHA; RT: 28.804 min
13C-HBB; RT: 29.554 min
DEHP-d4; RT: 33.668 min
PBDE104; RT: 34.630 min
UV328-d4; RT: 35.693 min
Di-n-ocyl phthalate-d4; RT: 39.113 min
13C-6-PPDQ; RT: 39.963 min
13C-TBB; RT: 41.233 min
4-F-BDE160; RT: 49.711 min
13C-TBPH; RT: 57.461 min
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
Counts vs. Acquisition Time (min)

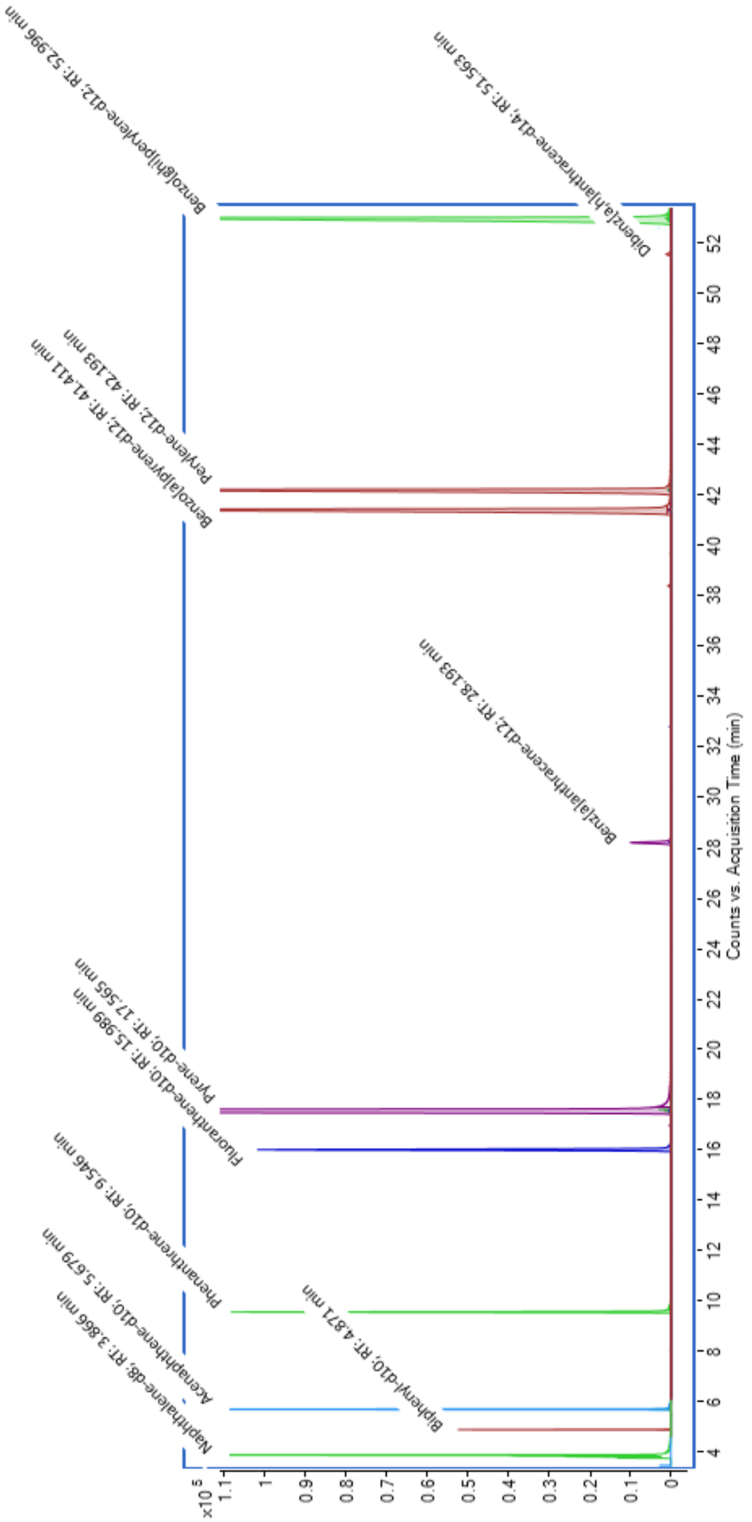
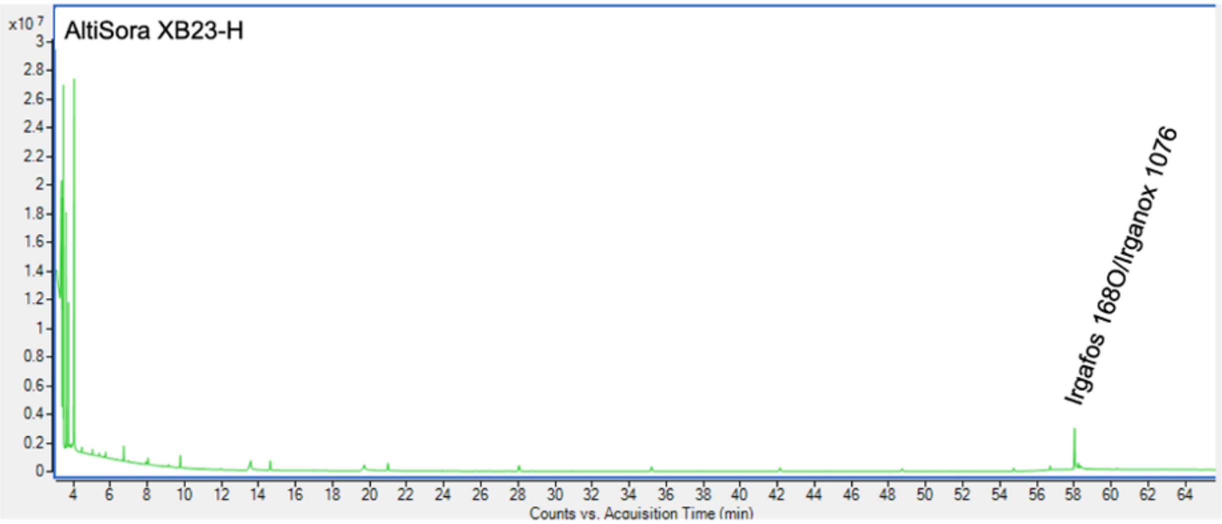
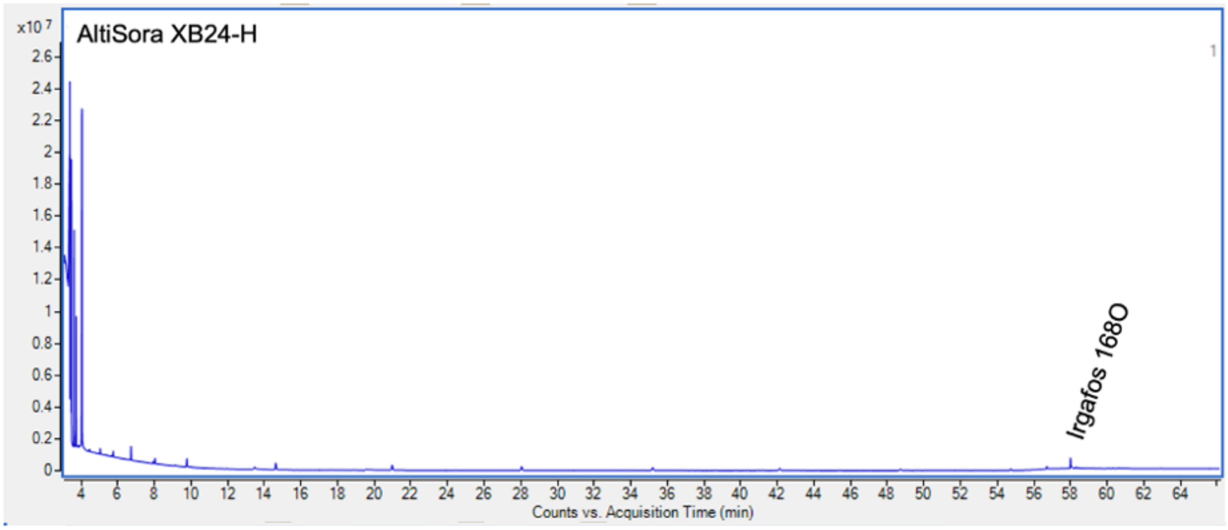

Naphthalene-d8, RT: 3.866 min
Acenaphthene-d10, RT: 5.679 min
Biphenyl-d10, RT: 4.871 min
Phenanthrene-d10, RT: 9.546 min
Fluoranthene-d10, RT: 15.989 min
Pyrene-d10, RT: 17.565 min
Benz[a]anthracene-d12, RT: 28.193 min
Benzo[a]pyrene-d12, RT: 41.411 min
Perylene-d12, RT: 42.193 min
Dibenz[a,h]anthracene-d14, RT: 51.563 min
Benzo[ghi]perylene-d12, RT: 52.996 min
x10^5
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
Counts vs. Acquisition Time (min)

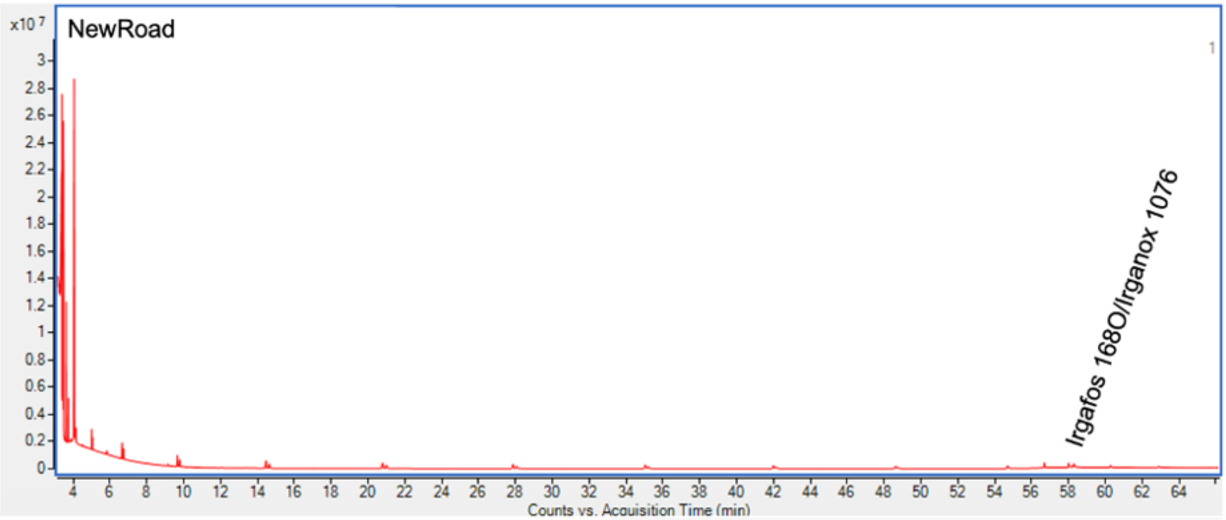
Figure 7. GC/MS chromatograms of internal standard peaks labeled with specific compound names and retention times, (a) mass-labeled plastic additives and (b) mass-labeled polycyclic aromatic hydrocarbons in NIST SRMs.

C. Plastic Additives

Examples of gas chromatograms of AltiSora XB23-H, AltiSora XB24-H, NewRoad, GreenMantra, and SBS are shown in Figure 8. A total of 97 compounds were identified from the visible peaks by searches against the NIST Mass Spectral Library (n = 2 plastic additives, n = 45 hydrocarbons, n = 30 isomers of various compounds, n = 19 miscellaneous compounds, and n = 1 unknown compound). This was challenging, specifically for the hydrocarbon compounds, as the NIST Mass Spectral Library identified separate peaks as the same compound. In these cases, the highest mass ion (m/z) produced by the mass spectrum was used to distinguish between the hydrocarbons. The full list of compounds identified with their respective peak area ratios are shown in Table 6 and more information on the NIST Spectral Library Match and the mass ions produced is found in the supplementary information. The peak area ratios of eight compounds [(Benzyloxy)(methyl)amine or Urea, (phenylmethoxy)-; isomer 1 of hexadecane; thiocarbamic acid; isomer of octasiloxane or W-18 2; .psi.,.psi.-Carotene, 1,1',2,2'-tetrahydro-1,1'-dimethoxy-; isomer 3 of octasiloxane; and isomer of Bufa-20,22-dienolide or .psi.,.psi.-Carotene] were not significantly different between any pellet and the laboratory blank samples. Since this indicated that the blanks were contaminated with these compounds, they were excluded from further statistical analysis.


AltiSora XB23-H
x10 7
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64
Counts vs. Acquisition Time (min)
Irgafos 168O/Irganox 1076


AltiSora XB24-H
1
x10 7
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64
Counts vs. Acquisition Time (min)
Irgafos 168O


NewRoad
1
x10 7
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64
Counts vs. Acquisition Time (min)
Irgafos 168O/Irganox 1076

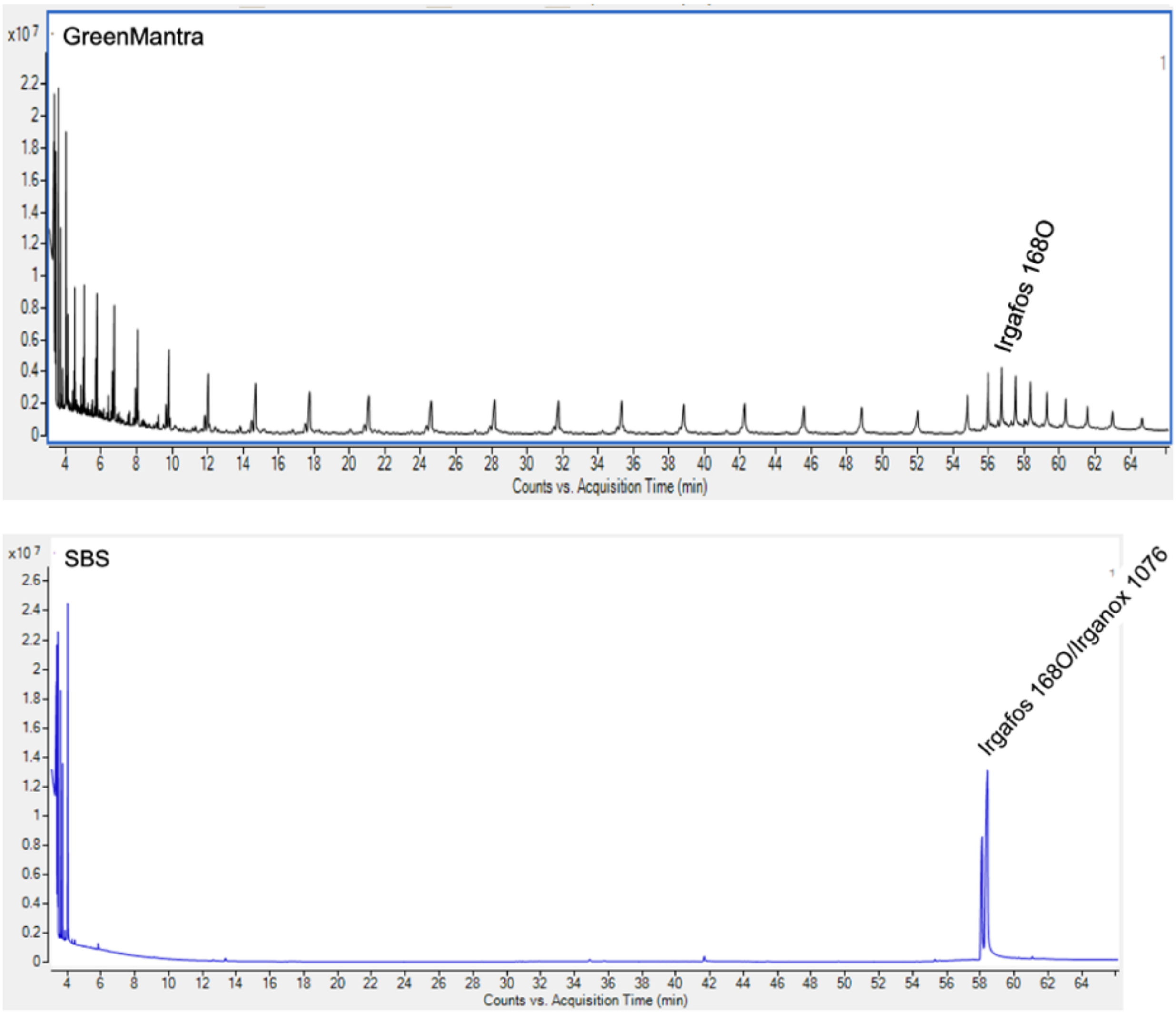


Figure 8. Total ion chromatograms representative of all samples for AltiSora XB23-H, AltiSora XB24-H, NewRoad, GreenMantra, and SBS. The plastic additives Irgafos 168-O and Irganox 1076 are indicated on each chromatogram.

Two plastic additives, oxidized Irgafos® 168 (Irgafos® 168O) and Irganox® 1076, were detected in most of the pellet types, both compounds are antioxidants (Figure 9). Irgafos® 168O was identified in all five pellet types. Mean peak area ratios in SBS (64.137 +/- 3.358, mean +/- s.d.) were significantly greater than those found in AltiSora XB23-H (5.612 +/- 0.354), AltiSora

XB24-H (1.138 +/- 0.052), NewRoad (0.361 +/- 0.102), and GreenMantra (0.402 +/- 0.105; $p < 0.001$; full statistical analysis provided in Supplementary Information). The mean peak area ratios of Irgafos® 168O in AltiSora XB23-H was significantly different from AltiSora XB24-H, NewRoad, and GreenMantra ($p < 0.05$). Irganox® 1076 was detected in AltiSora XB23-H, NewRoad, and SBS. Mean peak area ratios in SBS (94.495 +/- 2.118) was significantly greater ($p < 0.0001$) than AltiSora XB23[1] [2] -H (0.227 +/- 0.023) and NewRoad (0.067 +/- 0.018) which were not significantly different from AltiSora XB24-H and GreenMantra that had non-detected peak areas of Irganox® 1076. Overall, SBS had greater peak area ratios of Irgafos® 168O and Irganox® 1076 than the recycled pellets.

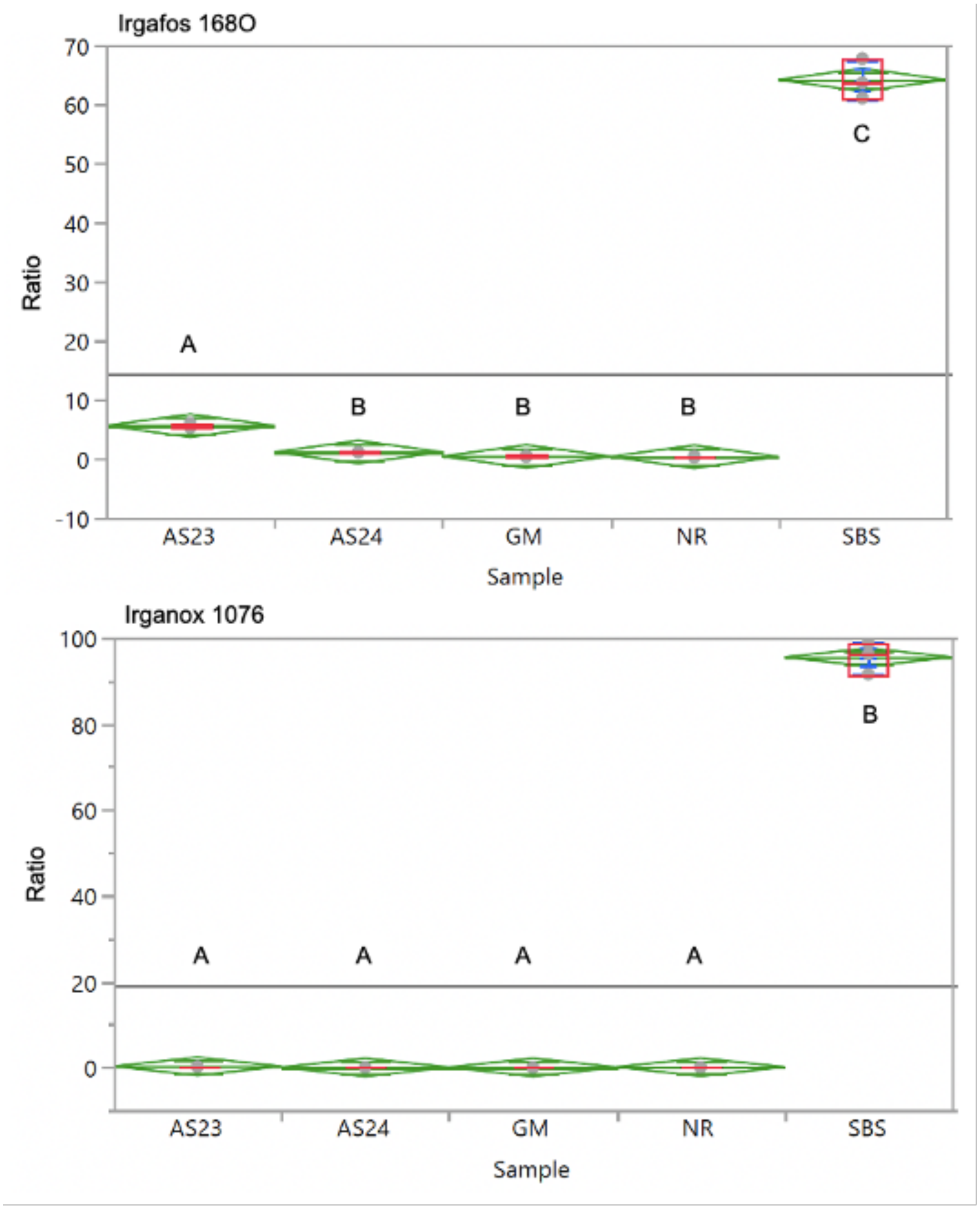


Figure 9. Peak area ratios of Irgafos® 168O and Irganox® 1076 measured via GC/MS from five plastic pellets manufactured for asphalt pavement applications. Grey points show the distribution of sample values. Blue bars represent one standard deviation and red boxes represent the 25th and 75th percentiles and mean values .

An array of hydrocarbons were identified in the AltiSora products, NewRoad, and GreenMantra pellets. No hydrocarbons were found to be present in the SBS samples. Generally, even-chain hydrocarbons of higher mass were present in the HDPE products (AltiSora and NewRoad) whereas both even- and odd-chain hydrocarbons of higher mass were identified in the LDPE GreenMantra product. For the majority of hydrocarbons, the peak area ratios of GreenMantra were significantly greater than the rest of the products.

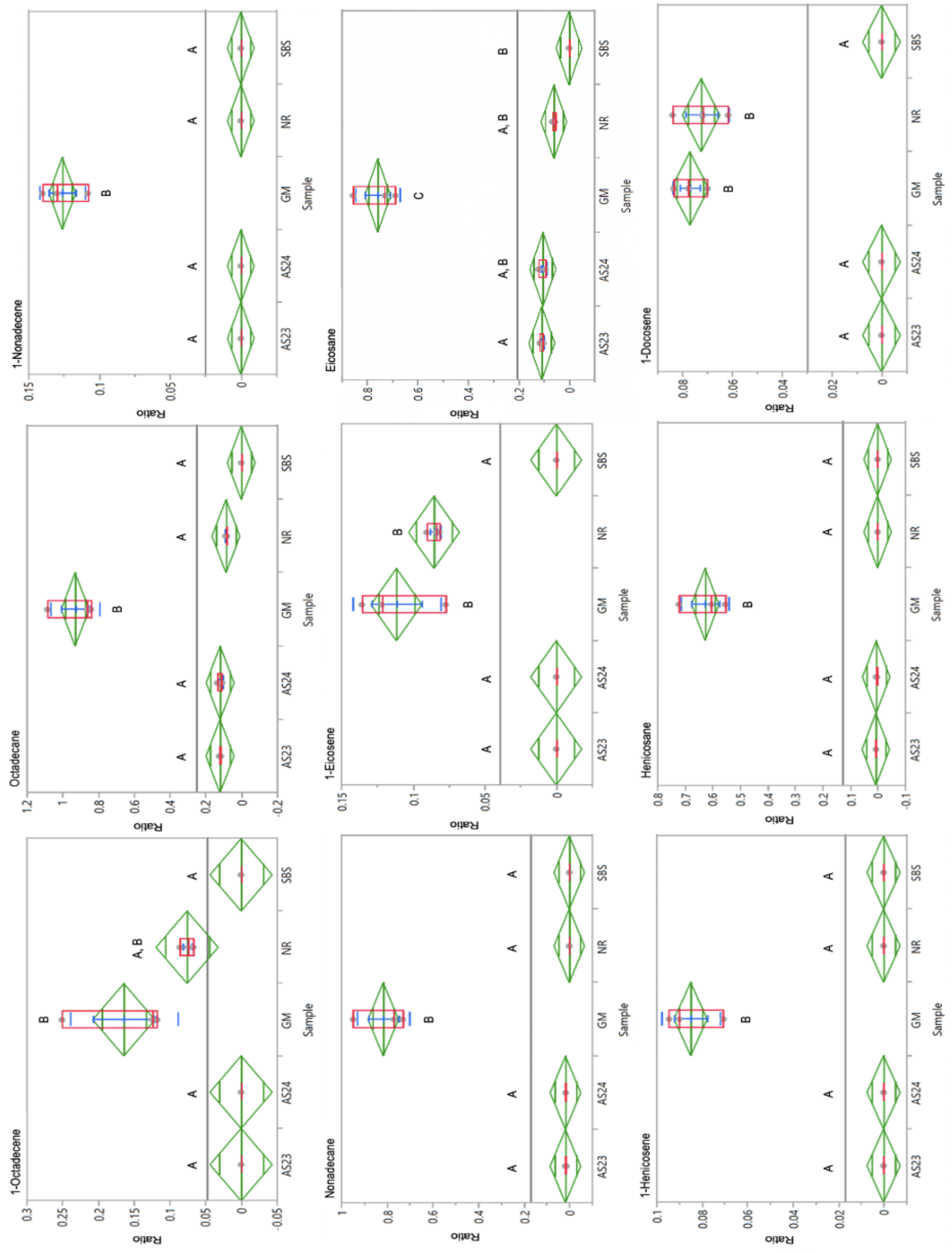

1-Octadecene
B
A, B
A
Octadecane
B
A
1-Nonadecene
B
A
Nonadecane
B
A
1-Eicosene
B
A
Eicosane
C
A, B
A
B
1-Henicosene
B
A
Henicosane
B
A
1-Docosene
B
A
Ratio
Sample
AS23
AS24
GM
NR
SBS

Figure 10. Mean ratio values of a sample of hydrocarbons. Grey points show the distribution of sample values. Blue bars represent the standard deviations and red boxes represent the 25th and 75th percentiles with the mean value.

Table 6. Mean ratio values of all compounds detected in respective products.

Compound	Lab Blank	AltiSora XB23-H	AltiSora XB24-H	NewRoad	GreenMantra	SBS
Irgafos® 168O		5.612	1.138	0.361	0.402	64.137
Irganox® 1076		0.227		0.067		95.495
Dodecane				0.195	0.434	
Tridecane				0.013	0.602	
1-Tetradecene				0.078		
Tetradecane				0.160	0.747	
1-Pentadecene					0.207	
Pentadecane					0.882	
1-Hexadecene				0.066	0.082	
Hexadecane		0.108	0.128	0.108	0.968	
1-Heptadecene					0.198	
Heptadecane		0.051	0.056	0.012	0.952	
1-Octadecene				0.075	0.164	
Octadecane		0.119	0.118	0.086	0.929	
1-Nonadecene					0.126	
Nonadecane		0.017	0.017		0.816	
1-Eicosene				0.085	0.112	
Eicosane		0.108	0.103	0.060	0.757	

1-Henicosene					0.085	
Heneicosane		0.006	0.005	0.000	0.626	
1-Docosene				0.072	0.077	
Docosene		0.076	0.071	0.040	0.571	
Docosane, 9-octyl-					0.027	
1-Dodecanol, 3,7,11-trimethyl-		0.002				
9-Tricosene, (Z)-					0.077	
Tricosane					0.462	
1-Tetracosene				0.053	0.067	
Tetracosane		0.049	0.045	0.026	0.423	
1-Pentacoene					0.052	
Pentacosane					0.340	
1-Hexacosene				0.038	0.064	
Hexacosane		0.030	0.028	0.014	0.304	
1-Heptacosene					0.089	
Heptacosane					0.234	
1-Octacosene				0.022	0.105	
Octacosane		0.018	0.015	0.005	0.206	
1-Nonacosene					0.075	
Nonacosane					0.158	
1-Triacontene				0.011		
Triacontane		0.009	0.006	0.001	0.136	
Hentriacontane					0.105	
1-Dotriacontane				0.007		
Dotriacontane		0.004	0.004	0.001	0.102	
Tritriacontane					0.093	

Tetratriacontane		0.003	0.003		0.085	
Heptatriacontane					0.093	
Octatriacontane					0.070	
Tetratetracontane					0.001	
Octadecanoic acid		0.351	0.069			
Hexatriacontane					0.183	
n-Hecadecanoic acid		0.504				
Oleic Acid			0.108			
W-18						0.031
Benzenepropanoic acid						0.152
(Benzyloxy)(methyl)amine or Urea, (phenylmethoxy)-	4.457	5.147	0.128	5.905	3.031	6.540
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-, didehydro deriv.				0.013		
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione				0.009		
.psi.,.psi.-Carotene, 1,1',2,2'-tetrahydro-1,1'-dimethoxy-		0.020	0.039			0.031
.psi.,.psi.-Carotene, 1,1',2,2'-tetrahydro-1,1'-dimethoxy- 2						0.010
7,8-Epoxylanostan-11-ol, 3-acetoxy		0.005	0.013			
Thiocarbamic acid, N,N-dimethyl, S-1,3-diphenyl-2-butenyl ester						0.009
(R)-(1-Cyclopentylpropane-1,3-diyl)dibenzene						0.178
Benzeneacetic acid, 4-tetradecyl ester						0.052
Methyl 9,11-octadecadiynoate						0.049

2-(2-Fluoro-6a,8a,10,10-tetramethyl-4-oxo-7-(2,2,2-trifluoroacetoxy)-2,4,5,6,6a,6b,7,8,8a,8b,11a,12,12a,12b-tetradecahydro-1H-naphtho[2',1':4,5]indeno[1,2-d][1,3]dioxol-8b-yl)-2-oxoethyl 2,2,2-trifluoroacetate						0.259
(3aR,10aR)-3a-Phenyl-2,3,3a,4,5,6-hexahydro-8H-naphtho[8a,1-b]furan-8-one						0.568
Isomer of Octasiloxane or W-18		0.010				
Isomer of Octasiloxane or W-18 2			0.003			
Isomer of Bufa-20,22-dienolide		0.026	0.031	0.000		0.024
Isomer of Bufa-20,22-dienolide or .psi.,.psi.-Carotene	0.007	0.017	0.015	0.028		0.022
Isomer 3 of Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-						0.065
Isomer 4 of Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-						0.037
Isomer 2 of Octadecane, 3-ethyl-5-(2-ethylbutyl)-		0.036	0.047	0.134		
Isomer 3 of Octadecane, 3-ethyl-5-(2-ethylbutyl)-		0.000	0.000			
Isomer 1 of Hexadecane					0.010	
Isomer 2 of Hexadecane					0.003	
Isomer 1 of Tetracyclo[5.2.1.0(2,6).0(3,5)]non-8-ene, 4-methyl-4-phenyl-, exo-				0.001		
Isomer 2 of Tetracyclo[5.2.1.0(2,6).0(3,5)]non-8-ene, 4-methyl-4-phenyl-, exo-				0.002		
Isomer 3 of Tetracyclo[5.2.1.0(2,6).0(3				0.029		

,5)]non-8-ene, 4-methyl-4-phenyl-, exo-						
Isomer 1 of 17-Pentatriacontene					0.043	
Isomer 2 of 17-Pentatriacontene					0.036	
Isomer 3 of 17-Pentatriacontene					0.050	
Isomer 4 of 17-Pentatriacontene					0.120	
Isomer 5 of 17-Pentatriacontene				0.002		
Isomer 1 of Octatriacontyl pentafluoropropionate				0.012		
Isomer 2 of Octatriacontyl pentafluoropropionate				0.002		
Isomer 1 of Octasiloxane						0.014
Isomer 2 of Octasiloxane						0.022
Isomer 3 of Octasiloxane						0.003
Isomer 4 of Octasiloxane		0.003				
Isomer 6 of Octasiloxane		0.001	0.002			
Isomer 7 of Octasiloxane		0.001	0.001	0.001		
Isomer 1 of Pentatriacontane					0.063	
Isomer 2 of Pentatriacontane					0.284	
Isomer 1 of Tritetracontane					0.062	
Isomer 2 of Tritetracontane					0.050	
Unknown Compound						0.078

DISCUSSION

This chapter has prepared the Center for Marine Debris Research (CMDR) for the undertaking of a research project funded by the Hawai'i Department of Transportation (HDOT) to detect microplastics and plastic additives in water samples from mechanical performance testing performed at the University of Hawaii's Asphalt Testing Laboratory and from simulated stormwater runoff on a trial roadway section paved with the NewRoad post-industrial recycled plastics. The results from this study predict the expected types of plastic polymers and plastic additives potentially present in the stormwater and water collected from the mechanical testing. Furthermore, this study developed the first methods to extract and analyze plastic additives through gas chromatography mass spectrometry utilized by the CMDR.

Ongoing analyses of water samples from the mechanical performance testing are evaluating the microplastic particle release from the asphalt. The polymer identification performed in this preliminary study was imperative for this analysis in order to target specific polymers. From this study, the microplastics research team will target HDPE and SBS. Additionally, the in-house library on the iN10 MX microscope FTIR resulting from this study, will allow for the spectra of unknown particles found in the water samples to be compared and/or matched to reference spectra of the plastic polymers evaluated in this study. Spectra of unknown microplastic particles that match to the spectra of the NewRoad pellets or the SBS pellets are determined to be from the asphalt samples.

Out of the 133 plastic additives and other compounds of concern targeted in this study, Irgafos® 168O and Irganox® 1076 were the only two target compounds found in the plastic polymers analyzed. Plasticizers, flame retardants, organophosphate-based, UV stabilizers, other antioxidants, alkylphenols, PAHs, and 6-PPD/6-PPD-Q were not found within the plastic pellets.

Furthermore, the polymer routinely added to asphalt binder, SBS, was found to contain higher values of the antioxidants Irgafos® 168O and Irganox® 1076 than recycled plastics and marine DFG. In the United States, Irgafos 168® and Irganox® 1076 are regulated additives for food contact safety. Irgafos® 168 and Irganox® 1076 have been deemed safe for use in plastic food contact articles as there are no safety concerns and their degradation products (e.g., Irgafos® 168O) show no risk of neurotoxicity (Markley et al., 2021). The presence of Irgafos® 168O confirms what previous studies have shown that Irgafos® 168 transforms to Irgafos® 168O under ultraviolet (UV) radiation, heat, and water contact (Shi et al., 2020; Hammond et al., 2014).

Previous studies evaluating plastic additives in marine DFG, show that PE fishing nets contain the lowest concentration of additives out of an array of fishing gear evaluated for additives. A study performed by Jang et al. (2022) analyzed plastic additives within PE fishing nets and rope, PP fishing nets and rope, PVC fishing nets and rope, and PE, PP, and polyurethane (PU) buoys. Their results found that PVC fishing nets and ropes contain the highest concentrations of phthalates, flame retardants, antioxidants, and UV stabilizers whereas PE nets and ropes had the lowest concentrations of additives. The buoys were found to have high concentrations of antioxidants and phthalates compared to other additives. The results of my study, show that the HDPE DFG sourced from in and around the Hawaiian Islands do not contain multiple additive classes and the results from the Jang et al. (2022) study show that recycling HDPE derelict fishing nets into roadways has less of an environmental threat in terms of plastic additives than other types of fishing gear and fishing gear of other polymers.

An additional interesting point of discussion from this study is the extraction of hydrocarbon compounds from LDPE vs HDPE. LDPE produces a greater diversity of hydrocarbons than the extraction of HDPE. The structures of the two polymers are very different and therefore different hydrocarbon compounds are extracted. The two chemical structures of LDPE and HDPE are shown in Figure 11. LDPE has a short chain branched chemical structure whereas HDPE has a longer chain linear structure. I hypothesize that more hydrocarbons are extracted from the LDPE samples as the oligomers are breaking apart due to its branched structure. We generally only see even hydrocarbons from the HDPE samples as this structure is in segments of ethylene, containing two carbons which explains the even hydrocarbon trend.

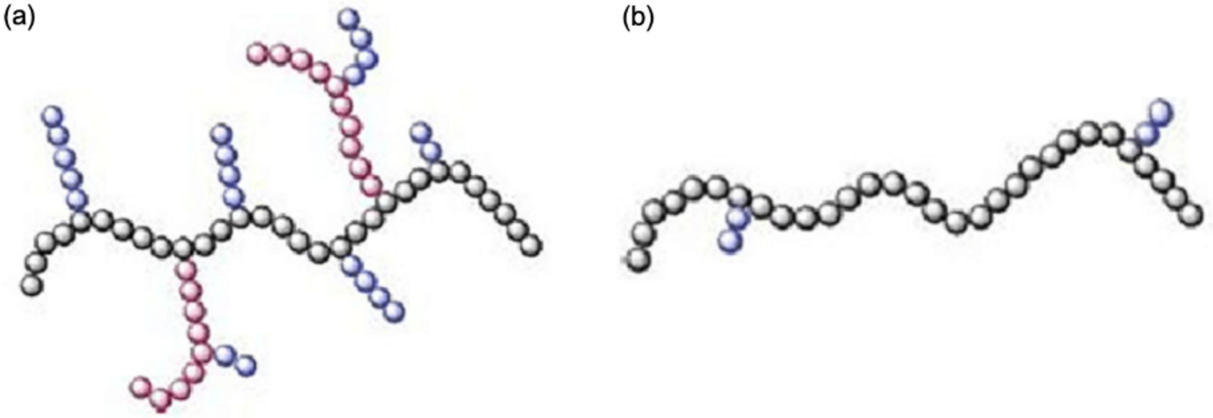


Figure 11. (a) chemical structure of LDPE, (b) chemical structure of HDPE (figure modified from Graziano et al., 2018).

The methods utilized in this preliminary study were not sensitive enough to detect low level plastic additives within the samples. I will continue to target other plastic additives within the six previously identified additive classes that were below the limit of detection and therefore not detected in this study. In order to improve the limit of detection on the GC/MS to detect these compounds in the samples, I plan to evaporate the extracts to reduce the amount of solvent and increase the concentrations of additives within the sample. Then, I will reinject the samples and re-perform the analysis in this study, searching for new peaks in the chromatogram that correspond to any low-level plastic additives I did not detect in this study.

Future analyses will quantify the concentrations of additives within the polymers and the water samples. Quantification and identification of potentially toxic plastic additives is important for environmental and human health (Rani et al., 2015). In this case, we want to quantify the concentrations of the antioxidants within the polymer to compare with the concentrations found in the water samples in future analysis to determine if they are leaching out of the asphalt binder and into the environment. Additionally, the toxicities of the plastic additives identified in this study will be determined through research performed in previous literature. The toxicity values determine the level of threat the plastic additives can have to marine organisms and are important to acknowledge in the future studies.

The CMDR will continue the DFG removal efforts and collaboration with HDOT to bring recycling capabilities to Hawai'i and to move towards the circular economy initiative. Overall, the results of my study set in motion a new direction for the Hawai'i Department of Transportation and the Center for Marine Debris Research by providing the first analysis of plastic additives within post-recycled plastics compatibilized for addition in asphalt mixed and by developing the methods in order to perform this analysis.

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SUPPLEMENTARY INFORMATION

ATR FTIR Polymer Library Search - List of compounds in Library Search

https://docs.google.com/spreadsheets/d/1JOfiyoeIov5-tavCP45011Jrfo3W90QDscCmMckNI6s/edit#gid=0

uFTIR Polymer Library Search - List of compounds in Library Search

https://docs.google.com/spreadsheets/d/10TR9RsrCdkEugME9nJw_FrYIzpXk61SbpVG6mOV1sfw/edit#gid=0

HDOT Target Plastic Additives - List of target plastic additives and their associated internal standards

https://docs.google.com/spreadsheets/d/1V-44_XuJs0XFVtffQkIBCqdjyyQlFmnWBcIUi4-EahM/edit#gid=0

HDOT Plastic Pellet Sample Data - master database for logging information and results from ATR FTIR, DSC, and GC/MS found in tabs “Cara’s Thesis” and “Extract+GCMS Data”

https://docs.google.com/spreadsheets/d/1SzECrHmmuzAiGttAyE3oroETbY2ibJP6ZpyRQkc0vAE/edit#gid=290131317

Plastic Additive Data - data recorded from GC/MS chromatograms found in tabs “Compound Search Sheet” and “Ratio Tables”

https://docs.google.com/spreadsheets/d/1FVIA0V078o4Wg2gMCdxZaFfDuEvpp02DDjd36ZuiTBY/edit#gid=0

Statistical Analysis - link to PDFs of full statistical analysis

https://drive.google.com/drive/u/2/folders/1irbz5JZNy9k9hlPBoF82aBbbkgZd8j1m

CHAPTER 3

Reflections

This chapter contains my personal reflections on the process of developing this study, collecting the data, and putting together Chapters 1 and 2.

Chapter 1:

- In the process of developing my first chapter, I learned so much about plastic additives and their analytical methods. Although I have an interest in chemistry and polymer science, coming into this project I had very little knowledge on the subject.
- While reviewing the methods section of the studies analyzed in the meta-analysis, I was able to learn all the different types of extraction techniques and analytical methods used to identify plastic additives in different matrices.
- My advisor, Jenn Lynch, as well as Katy Shaw and Meredith Seeley aided significantly in my learning of this new subject matter.
- We hope to publish the meta-analysis found in Chapter 1, as it will help to inform the methods of future studies.
    - I have presented the preliminary data of this chapter at the Ocean Sciences Meeting 2022 and at the 7th International Marine Debris Conference. At these two conferences my data has drawn a lot of interest from the plastic research community and they want the database published for their own viewing. I believe that this publication will be a valuable resource for other researchers.

Chapter 2:

- This chapter allowed me to apply my knowledge of plastic additive identification in the ocean to a study of my own.

- Utilizing the information learned from my meta-analysis and my newfound expertise in the extraction and identification of plastic additives in marine plastic samples, I was able to select previous publications that I believed contained the best methods to replicate for this study.
- Conducting this research was exciting at every step of the process. My interests lie in marine plastic pollution, chemistry, and engineering which this project combines all three of those subjects. I truly feel like this project could make a significant impact in the state of Hawai'i, changing the way we process our waste and aiding in cleaning up the waters surrounding the islands.
- Obviously these results are just preliminary data, but they present a good argument to replace standard SBS with post-recycled plastics due to the reduction of plastic additives present in the post-recycled polymers.

Future Directions:

- The next steps of this project involve analyzing the simulated stormwater and water from the mechanical tests. I am eager to see these results to know what plastic additives and at what concentration are these compounds leaching into the water.
- We have already performed the mechanical testing, collected and processed the water samples from the Moisture Induced Sensitivity Test (MIST) and the Hamburg Wheel Tracking tests for the asphalt mixed with the NewRoad polymer and PMA (SBS-modified binder) as well as the control asphalt mixed with PMA. The next steps involve completing the rest of the MIST and Hamburg Wheel Tracking tests for the NewRoad and neat asphalt mix (NewRoad with non-polymer-modified binder).

- Additionally, at the 9 month time point, we will be testing the simulated stormwater runoff for the trial roadway.