

**ADSORPTION INTERACTIONS OF UV-AGED  
MICROPLASTIC PARTICLES WITH SULFAMETHAZINE**

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at the University of Missouri – Columbia

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of the Requirements for the Degree

Master of Sciences

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By

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The undersigned, appointed by the dean of the Graduate School, have examined the  
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ADSORPTION INTERACTIONS OF UV-AGED  
MICROPLASTIC PARTICLES WITH SULFAMETHAZINE

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a candidate for the degree of Master of Science \_\_\_\_\_,

and hereby certify that, in their opinion, it is worthy of acceptance.

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## **ABSTRACT**

Due to growing plastic demand and production without proper waste management, microplastics have become common around the world throughout diverse systems. At the same time, increased detection of antibiotics in the environment has led to concerns over the spread of these antibiotics and antibiotic resistance. Evidence for microplastics' ability to adsorb and carry environmental contaminants has led to concern over the intersection of these two pollutants. Microplastic PET and recycled PET particles were UV-aged before they were used in batch adsorption tests with the antibiotic sulfamethazine. Neither the pristine condition nor the aged microplastic PET exhibit signs of adsorption with the sulfamethazine solution. Some interference was measured that may explain why adsorption was not detectable in these samples which bring up questions of leaching or desorbing compounds from microplastics that require further study.



# **Chapter 1 - Introduction**

## **1.1 - Research Background**

Plastics have become an unavoidable part of everyday life. They are commonplace as food and beverage containers, as clothing material, within household appliances, and more with global plastic waste reaching 353 million metric tons in 2019 (OECD 2022). Due to plastics resilience to complete degradation, if released into the environment they tend not to disappear but rather break down into smaller pieces that persist in the environment. Any plastics smaller than 5 millimeters are considered microplastics, which can be categorized as primary microplastics if being manufactured at a size less than 5 mm, or as secondary microplastics which originated as larger fragments but through weathering processes broke down to the microplastic size (NOAA 2022). Polyethylene terephthalate (PET) is an especially common material for food and beverage containers. Due to this popularity PET was selected for further study (PETRA 2015). Not only can microplastics alone be concerning, but they have a worrying ability to adsorb other contaminants and act as a vector for dissolved pollutants in the environment.

Release of antibiotics to the environment has also been a growing concern in recent years. Exposing organisms to antibiotics can lead to pathogens with antibiotic resistant genes in the environment which may eventually make their way to humans (Larsson and Flach 2021). Sulfamethazine is an antibiotic common to the livestock and veterinary industries and was selected for this study due to its determination as an environmental contaminant (NCBI 2022). The intersection of microplastic pollution with dissolved antibiotics in

aquatic systems has the potential to spread antibiotics this stimulate production of antibiotic resistant genes through aquatic biota as microplastics are suspended in water, deposited in sediments, or consumed by organisms.

## 1.2 - Research Objectives

The goal of this research was to investigate how microplastic particles of polyethylene terephthalate may interact with a dissolved antibiotic in the form of sulfamethazine. The literature points to these interactions changing as plastics are degraded by environmental factors, so this research also aims to account for UV-aging of microplastics and how they may change the material's sorption capacity in various environments. Because PET is a widely recycled material, some characterization of the adsorption differences between virgin and recycled PET materials was also of interest.

This thesis has been organized into six chapters. After this introductory chapter, Chapter 2 provides a review of literature on the presence of both microplastics and antibiotics as environmental contaminants and of the body of work that exists characterizing the adsorption capacities of microplastics. Chapter 3 then presents the materials and methodology utilized for this study, while Chapter 4 provides the results of testing completed with discussion of those results. Chapter 5 draws conclusions from the preceding chapters and lastly Chapter 6 provides recommendations on future work for this subject.

## **Chapter 2 - Literature Review**

### **2.1 - Prevalence of Microplastics**

Over the last several decades, plastics have become a huge part of everyday life, with plastics production reaching over 300 million metric tons as of 2014 (Crawford 2017). As these plastics enter and escape from the waste stream, the presence of microplastics in the environment has become increasingly common across freshwater, seawater, and sediment environments. An estimated 109 million metric tons of plastics had accumulated in rivers as of 2019, with 30 million metric tons also in oceans (OECD 2022).

Polyethylene terephthalate (PET) is a common plastic used in food and beverage packaging and other bottles. PET is an easily recyclable plastic, leading to a high recycling rate of 31% in the United States and 52% in Europe (PETRA 2015). Recycled PET (RPET) can be reformed into bottles or other containers as well as different fiber forms.

Significant work has been done in studying the presence of microplastics in the environment. A variety of studies have focused on different specific forms of microplastics and different plastic types in a range of environments.

#### **2.1.1 - Quantifying Microplastics in Seawater**

Microplastics have been in seawater environments around the world. Based on metrics of coastal countries' economies, population, and solid waste production an estimated 4.8 to 12.7 million metric tons of the plastic waste generated in 2010 entered the ocean, with 100

to 250 million metric tons predicted to enter the oceans in 2025 (Jambeck et al. 2015). Microplastics have been found in the Mediterranean Sea in average concentrations of 100,000 particles per km<sup>2</sup>, mainly consisting of polyethylene, polypropylene, and polystyrene (de Haan et al. 2019). Contamination of seas and oceans by microplastics has been significant enough to find microplastic particles in the gills and digestive systems of fish (Białowąs et al. 2022).

Estuary environments represent a meeting point for microplastics that have been carried by freshwater systems to enter seawater. In the Changjiang Estuary of China, polyvinyl chloride has been the most common microplastic found, believed to mainly be attributed to waste from aquaculture operations (Xu et al. 2018). In sampling estuary rivers entering the Chesapeake Bay, USA microplastics were found in nearly all samples (Yonkos et al. 2014). Microplastics concentrations in the Chesapeake Bay reached up to 560 g/km<sup>2</sup> and were able to be correlated with urban development upstream of the estuarine rivers.

### **2.1.2 - Quantifying Microplastics in Freshwater**

While microplastic levels in saltwater environments have been more fully characterized, fewer than 4% of studies concerning microplastic concentrations have studied freshwater environments (Lambert and Wagner 2018). Still, the body of work that has been completed points to microplastics being similarly common in freshwater systems and diverse in form.

Measurements taken along the Rhine River in Germany found microplastics in all samples collected using a 300 µm net across a variety of metropolitan and rural locations (Mani et al. 2015). Surface concentrations along the Rhine River averaged 892,777 microplastic

particles per km<sup>2</sup> but reached as great as 3.9 million microplastic particles per km<sup>2</sup> in urban river reaches. The plurality of microplastics collected in the study of the Rhine River were opaque spherical particles, while the next most common were microplastic fragments.

Samples collected by similar means along the North Shore Channel in Chicago Illinois found similar contamination from microplastics (McCormick et al. 2014). The average microplastic concentration in the North Shore Channel was determined to be 720,341 microplastic particles per km<sup>2</sup>. In the collection from the North Shore Channel microplastic fibers were instead the dominant type found while microplastic fragments were less common.

### **2.1.3 - Quantifying Microplastics in Treated Wastewater Effluent**

Wastewater treatment plants are of concern as they may be point sources for primary microplastics that come from beauty products washed down the sink or fibers from laundry in addition to the secondary plastics that may enter with stormwater collection. While the body of work demonstrating microplastic presence in treated wastewater is small, the findings consistently point to these plants as point sources of microplastic.

In addition to sampling typical sites upstream of a wastewater treatment plant in Chicago, Illinois' North Shore Channel, McCormick et al (2014) also collected samples directly downstream of a wastewater treatment plant to track the effluent's contribution to microplastic levels. The average microplastic surface concentration downstream of the wastewater treatment plant in this study was 6.7 million microplastic particles per km<sup>2</sup>, an order of magnitude greater than what was found upstream. The microplastics found

downstream of the North Shore Channel wastewater treatment plant were still mainly fibers and microplastic fragments, but microplastic pellets were only found downstream of the plant.

Of 17 wastewater treatment plants across the United States that were reviewed in 2014 and 2015, each one had microplastic particles in the effluent (Mason et al. 2016). Across the plants studied, an average of less than one microplastic particle was released per liter of water, though this resulted in an average of 4.3 million particles released per day when combined with average daily flow rate. The dominant microplastic types across all the treatment facilities were fibers with microplastic fragments being next most common.

#### **2.1.4 - Pharmaceuticals as Emerging Pollutants**

Pharmaceuticals are a class of pollutants of growing concern. Through release from manufacturing facilities, agricultural practices, and excretion they may enter the environment. Amongst many types of pharmaceuticals, antibiotics are of concern as exposure of pathogens to antibiotics may allow for antibiotic-resistant mutations (Larsson and Flach 2021). Sulfamethazine (SMZ) is a common veterinary and agricultural antibiotic that has been detected in the environment. SMZ has been found in effluent from animal farms as well as in pond and river water in concentrations up to the mg/L range (Kuppusamy et al. 2018). SMZ has also been found across a variety of urban drainages in concentrations in the  $\mu\text{g/L}$  range (Binh et al. 2018).

## 2.2 - Sorption Characteristics of Microplastics

The adsorption characteristics of microplastics have been of increasing interest as the persistence and scale of microplastics in the environment has become more understood. The broad range of plastic variants that can form microplastics and compounds that may be able to sorb to them have made for a wide array of differing study conditions.

Organic pollutants and heavy metals have been the focus of several studies measuring adsorption on microplastics. Polyethylene (PE) has received particular attention in these studies. As early as 2012, interactions between PE and polycyclic aromatic hydrocarbons (PAHs) were being studied (Fries and Zarfl 2012). Fries and Zarfl (2012) demonstrated a high sorption capacity for both low- and high-density PE pellets with six different PAHs. Similar research has been completed with PE to understand the sorption capacity for heavy metals including Pb(II) (Liu et al. 2022). By combining 50 mg of PE with 100 mL of Pb(II) solutions ranging in concentration from 10 mg/L to 50 mg/L adsorption capacities for PE were found between 10.28 mg/L in the pristine condition and 18.74 mg/L in the aged condition (Liu et al. 2022). This study used naturally aged PE that had been collected from the environment to compare with those in pristine condition, and microplastic samples were selected between 0.6 and 0.84 mm in diameter. Polyvinyl chloride (PVC), polypropylene (PP), and polyethylene terephthalate (PET) have all similarly shown ability to sorb Pb(II) and other heavy metals in separate study (Yu et al. 2019).

How microplastic aging relates to sorption mechanisms and capacities is an important factor as microplastics in the environment may be exposed to UV irradiation or high ionic

strength from saltwater. For polystyrene (PS), exposure to UV light can lead to increases in oxygen-containing functional groups as C-H bonds are broken (Mao et al. 2020). Mao et al (2020) made this determination by examining PS after 3 months of aging under 340 nm wavelength UV lamps in air, distilled water, and seawater using FTIR. Batch experiments were then performed to determine the sorption capacity of the aged PS versus pristine PS with heavy metals, which showed increased sorption capacity with increased aging time (Mao et al. 2020). Samples of 180  $\mu\text{m}$  PET aged directly in air, in freshwater, and in saltwater by exposure to high temperatures have also showed increased sorption capacity with Cu(II) (Wang et al. 2022). Temperature-aged PET developed cracks and fissures that increased the topography of samples under SEM.

#### **2.2.1 - Antibiotic Adsorption with Microplastics**

Batch experiments have also been an important tool in understanding adsorption interactions between microplastics and antibiotics. Batch experiments have been conducted with aged PE fibers and polystyrene (PS) foam particles collected from the East China Sea and Yellow Sea to show sorption capabilities with sulfamethazine and other antibiotics (Guo and Wang 2019). Pristine and UV-aged polyurethane (PU) have shown some ability to adsorb the antibiotic oxytetracycline (OTC), with sorption capacity for this antibiotic increasing with age and exhibiting pseudo second order adsorption kinetics (Xue et al. 2021). These samples of PU were UV-aged under a 254 nm wavelength lamp for a period of 10 days and reached a maximum adsorption capacity of 1.113 mg/L with OTC when 100 mg of plastics were combined with 30 mL of solution in concentrations from 2.5 to 50 mg/L.



The specific sorption interactions between sulfamethazine and PET microplastics have been studied before, showing that PET does have sorption capacity for SMZ (Guo et al. 2019). Guo et al (2019) were able to develop an adsorption isotherm for PET between SMZ concentrations of 0.5 and 12 mg/L by combining 20 mg of plastics with 10 mL of solution, finding a maximum adsorption capacity for PET of approximately 0.25 mg/g. This testing was carried out with pristine virgin PET (there was no aging component to the study) and utilized PET particles with sizes from 100 – 150  $\mu\text{m}$ . The isotherm developed indicated SMZ adsorption to PET was pseudo second order and it was concluded that because SMZ is hydrophilic, there would be limited interaction due to hydrophobicity of plastics but instead interaction would be from electrostatic and Van der Waals forces (Guo et al. 2019).

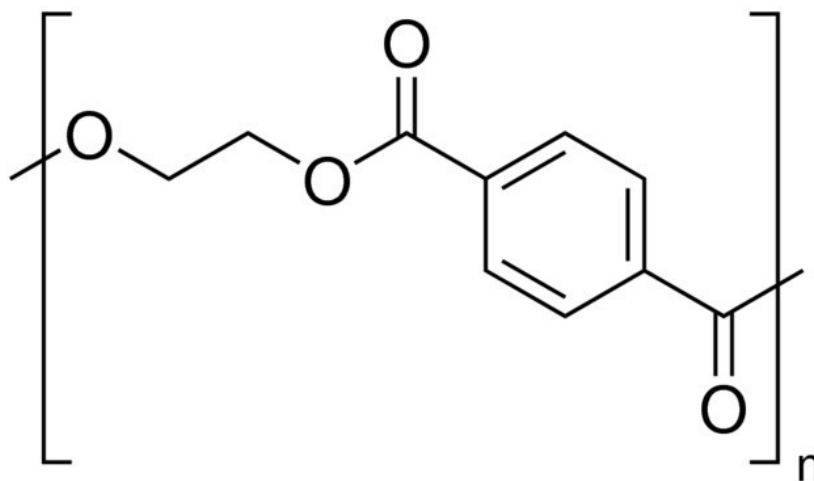
### **2.3 - Hypotheses**

This study is aimed at determining the adsorption capacity of microplastic PET across a variety of degradation conditions. Microplastic samples were exposed to differing durations of exposure to UV light to replicate a natural aging process. Once aged, their sorption capacity was tested with sulfamethazine antibiotic. The primary hypothesis of this study is that microplastic PET will show increasing sorption capacity as the material is exposed to increased UV-aging. It is also expected that recycled PET will have greater adsorption capacity than the virgin materials and will behave similar to virgin PET that has undergone some UV-aging due to the recycling process. Microplastics aged in solutions with high ionic strength are expected to appear more degraded in analysis than their counterparts aged in distilled water or in air.

## Chapter 3 - Materials and Methods

### 3.1 - Plastics and Preparation

Polyethylene terephthalate (PET) is well regarded by the plastics industry for its strength, chemical resistance, and thermal resistance (Omnexus 2022). PET has a glass transition temperature, at which the plastic will change from a glassier form to one that is more malleable, of approximately 80 °C, and the maximum service temperature for PET is typically in the range of 80 – 140 °C (Crawford 2017). PET has the chemical formula  $(C_{10}H_8O_4)_n$  and its structure is shown below in *Figure 3-1*. It is generally classified as a hydrophobic polymer (Sigma-Aldrich 2022).



*Figure 3-1: Chemical structure of PET (Sigma-Aldrich 2022)*

Virgin PET was purchased from Sigma-Aldrich (St Louis, MO, USA) lab supply as short segments of filament in 3-5 mm cylindrical granules. Recycled PET (RPET) was sourced from Phoenix Technologies, Inc. which specializes in the manufacture of RPET resin pellets (Phoenix Technologies 2021). The recycled sample arrived as elliptical granules in similar sizes to the virgin material. Samples of the plastics in their as-received condition can be seen below in *Figure 3-2*. While these plastics were less than 5 mm in at least one dimension and could therefore be considered microplastics, being at the large end of what are considered microplastics meant they had relatively low surface area per unit weight. To increase the surface area of these plastics so that their ability to act as an adsorbent would increase, their size was reduced with an electric blade grinder (Sunbeam Products Inc, USA).



*Figure 3-2: As-received PET granules (left) and RPET granules (right).*

Plastic granules were processed through the electric blade grinder in batches of approximately 5 to 10 grams, to bring them to a coarse-powder consistency. The plastics were ground for approximately 20 second intervals to prevent excessive heat buildup until the particle size appeared sufficiently reduced. In order to provide consistency in the materials, they were then sieved using Number 20 and Number 100 sieves, limiting the range of plastic particles to 150 to 850 micrometers ( $\mu\text{m}$ ). Plastic granules that were too large to pass the Number 20 sieve were saved to be reprocessed through the electric grinder and sieved again. Plastic granules that were small enough to pass through the Number 100 sieve were saved for possible use in later study.

The buildup of static electricity during the plastic grinding process became a challenge as particles would cling to the grinder, sieves, and storage bottles. To reduce the buildup of static on the plastics, less than 1 milliliter of DI water was added to the electric grinder with batches of plastic exhibiting increased static cling.

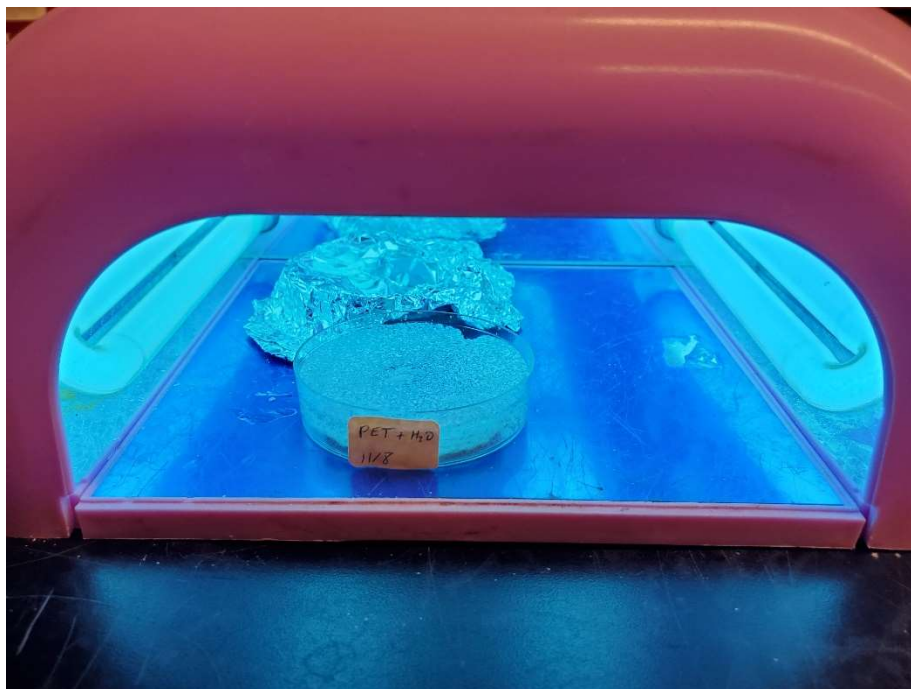
### **3.2 - UV Treatment of Plastics**

To model a variety of environmental conditions in which microplastic PET may be found, PET and RPET samples were aged under UV lamps at 365 nm in three different environments as shown in *Table 3-1* below. UV lamps were turned on for 8 hours a day, with treatment periods of 2-days, 7-days, 20-days, and 30-days to create a range of degradation levels.

*Table 3-1: Environments for UV-Aging*

Dry
Freshwater - 20 mL DI Water
Saltwater - 20 mL NaCl Solution (35mg/L)

For each UV-aging environment approximately 2.5 g of PET or RPET was placed into a plastic petri dish to be left under the UV lamps. Every aging environment and treatment duration had a control condition treated at the same time. The control samples were placed in the same environment but covered with aluminum foil to block UV. This would allow for examination of potential heat effects from the lamps as well as how the high ionic strength of the NaCl solution would affect the plastics. Samples and their controls being treated under the UV lamp can be seen in *Figure 3-3*. Samples aged with water and NaCl solution were checked approximately once every 48 hours to ensure they had not dried out. DI water was added to each as needed to maintain a consistent level of water or NaCl solution throughout the treatment.



*Figure 3-3: UV treatment of microplastic samples*

Following their UV treatment, samples that had been aged in DI water were passed through a vacuum filtration system and then oven-dried at 80 °C to remove any moisture. Samples that had been aged in the NaCl solution were filtered, and then rinsed with DI water. To rinse them, microplastic samples were placed into centrifuge tubes and shaken with 20 mL of clean DI water for 1-minute. The water was drained using vacuum filtration and a second rinse was completed using the same method and duration. Once the microplastic samples aged in NaCl solution were rinsed twice, they were oven dried to remove moisture.

### **3.3 - Analysis of Microplastic Surface Properties**

#### **3.3.1 - Optical Microscopy**

An optical microscope (Revelation III, LW Scientific, USA) was used to examine microplastic particles before and after the UV-aging. The microscope focus was set using a calibration slide and an image of this slide was captured at the start of each session to set the scale for the samples that followed. Microplastics were photographed through the microscope before being examined in ImageJ software (National Institutes of Health, USA).

#### **3.3.2 - Scanning Electron Microscopy (SEM)**

Microplastic samples were analyzed using a Scanning Electron Microscope (FEI Quanta 600F, Thermo-Fisher, USA) to see how detailed surface structures may change with UV-Aging. Samples of the pristine PET and RPET, as well as samples of PET and RPET that had undergone the 30-day UV aging in NaCl solution were used for SEM analysis. These samples were chosen as they represented the two extremes in treatments with the pristine samples receiving no treatment and the samples UV-aged for 30 days with NaCl being exposed to both the UV degradation and potential degradation from high ionic strength.

In preparation for SEM work, samples of microplastic were attached to a double-sided carbon tape. The plastics were arranged on the tape in order to create a single layer, with minimal stacking of particles on top of each other. Once placed on carbon tape, SEM samples were sputter coated with a 25 nm platinum coating to provide necessary

conductivity. The SEM was conducted at 2.00 kV to emphasize surface texture using magnifications between 100x and 1,000x.

### 3.3.3 - FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy (Nicolet 4700, Thermo Electron Corporation, USA) with mid-IR ( $400 - 4000 \text{ cm}^{-1}$ ) was used to examine the surface groups on microplastic samples in pristine and UV-aged conditions. FTIR testing involved irradiating samples with infrared light at known wavelengths, then by measuring how much light was absorbed by a sample at particular wavelengths, FTIR can indicate the presence of functional groups in the sample. The objective of investigation with FTIR was to determine if bonds on the surface of the aged plastics were shifting and morphing into different bonds or being destroyed. The Attenuated Total Reflectance (ATR) method of FTIR was used so that plastics could be tested in their microplastic form without making any modifications to the material. For mid-IR use with ATR, a germanium (Ge) crystal was used in the FTIR device.

The experiment setup in OMNIC™ software for ATR-FTIR utilized 32 scans at a resolution of  $4 \text{ cm}^{-1}$ , the final format was absorbance, no correction was applied, and a new background was to be collected every 100 minutes. The initial step in the ATR-FTIR testing was collecting a background reading to account for ambient conditions. The background collection was taken after the Ge crystal was cleaned with isopropanol and non-woven wipes to ensure no residue was left behind from previous testing. Once the isopropanol dried, the background reading was taken.



After taking a background reading, the sample collection process was started by placing just enough microplastic on the instrument to completely cover the crystal element. The anvil was then lowered to contact the sample and was tightened to torque markings of between 8 and 10. This operation can be seen below in *Figure 3-4*. The collection could then be run in the OMNIC™ software. After which the anvil was raised and cleaned with isopropanol on a non-woven wipe, the crystal element was removed, and the microplastic sample disposed of. Between each sample the crystal was then cleaned with isopropanol on a non-woven wipe and then isopropanol on a microfiber cloth. Once the crystal was dry the process was repeated for the next sample.



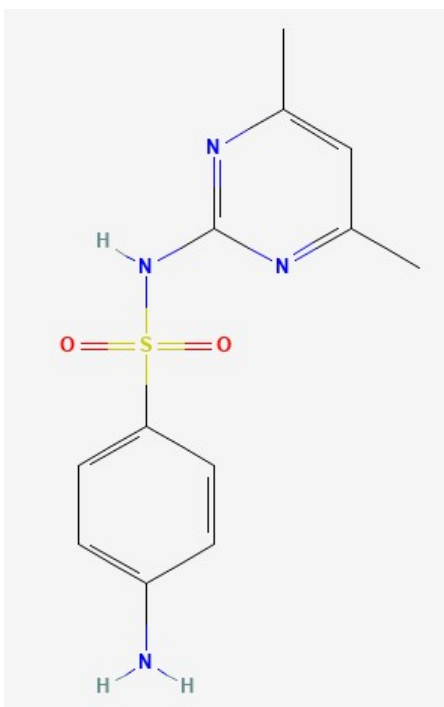
*Figure 3-4: ATR-FTIR assembly with microplastic sample*

After FTIR collection was completed, the Automatic Baseline Correct tool from the OMNIC™ software was applied to each sample to correct for air conditions that may have had effect on the spectra. Then the Advanced ATR Correction tool was applied to correct

for spectra shifts from the ATR crystal (Thermo 2006). The correction used was for the Ge crystal with the default options for Angle of Incidence, Number of Bounces, and Sample Refractive Index.

### 3.4 - Sulfamethazine Adsorption Testing

Adsorption tests were performed by mixing a known volume of sulfamethazine (SMZ) solution at a known initial concentration, with a known mass of microplastic. SMZ has the chemical formula  $C_{12}H_{14}N_4O_2S$  and the chemical structure of SMZ is shown in *Figure 3-5* (NCBI 2022). SMZ has two dissociation constants a  $pK_{a1}$  of 2.65 and a  $pK_{a2}$  of 7.65, testing was accordingly conducted at neutral pH to examine the neutral speciation of SMZ (Tolls 2001).



*Figure 3-5: Chemical structure of sulfamethazine (NCBI 2022)*

From kinetics testing conducted, an equilibrium time of 24 h was used for the sorption of SMZ to PET though occasional tests were run longer to ensure no further sorption occurred after 24 h. The mass of SMZ adsorbed onto the microplastic could then be calculated according to the mass balance in *Equation 3-1*:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

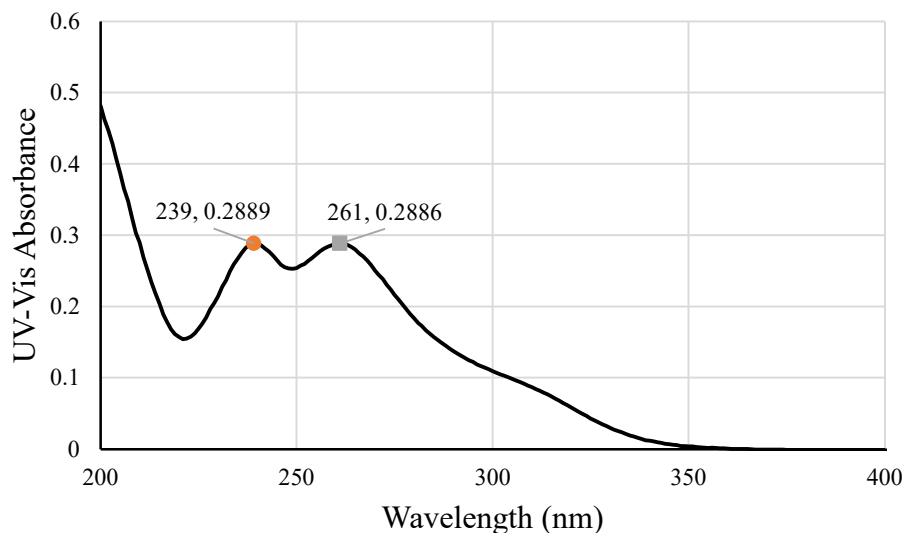
*Equation 3-1: Adsorption equilibrium mass balance (Benjamin and Lawler 2013)*

Equation 3-1 expresses the equilibrium mass of SMZ sorbed onto the microplastic,  $q_e$ , as milligram SMZ per gram plastic, where  $C_0$  is the initial solution concentration in milligram per liter,  $C_e$  is the final solution concentration in milligram per liter,  $V$  is solution volume in liters, and  $m$  is the mass of microplastic added to the solution in grams. The initial solution concentration, volume of solution, and mass of microplastic added to the solution were all variables that could be controlled and were known input values. The equilibrium concentration in the solution was measured using the spectrophotometry techniques below so that the mass sorbed onto the microplastic could be calculated.

#### 3.4.1 - UV-Vis Spectrophotometry

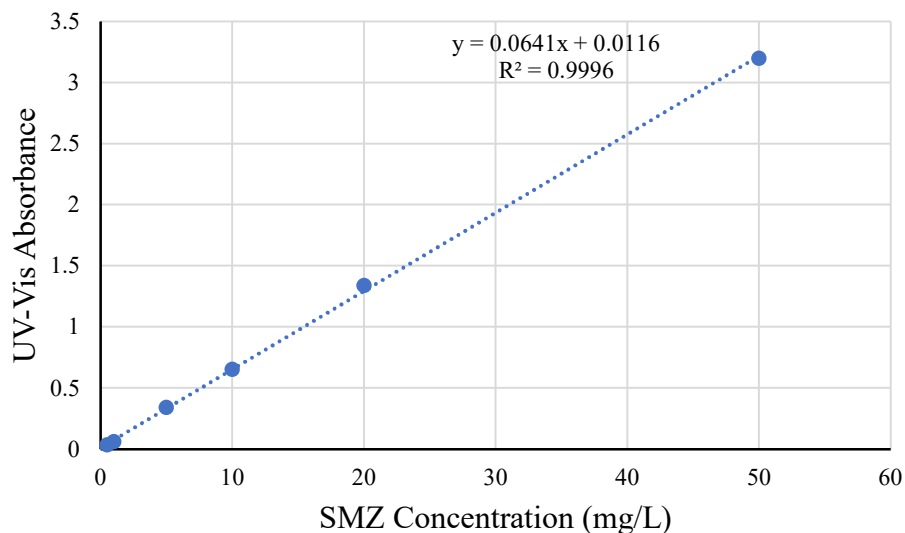
UV-Vis spectrophotometry (Cary 60, Agilent Technologies, USA) was used to measure concentrations in the SMZ solutions. UV-Vis was operated on the principle that chemical

compounds have specific interactions with UV light that allows different UV absorbance at certain wavelengths. By finding the wavelength at which a chemical of interest shows the most UV absorbance, measuring changes in UV absorbance could be used to measure changes in chemical concentration. The Cary 60 double beam spectrophotometer was used first to investigate what wavelength of UV light achieved the highest absorbance from SMZ. From reference spectra that measured the UV-Vis absorbance of SMZ in a methanol solution, it was determined the peak absorbance would likely be less than 300 nm (SpectraBase 2022). This knowledge meant that a quartz cuvette was used for the UV-Vis testing as quartz has a usable range of approximately 160 – 380 nm (Barron and Raja 2021). In order to find the analysis wavelength to be used for further testing, a preliminary scan was completed with UV-Vis which collected absorbance at wavelengths from 200 nm to 800 nm. A 5 mg/L SMZ solution exhibited absorbance peaks at 239 nm and 261 nm as shown below in *Figure 3-6*. The absorbance at 239 nm was slightly greater so this was selected as the analysis wavelength to be used in the remainder of UV-Vis testing.



*Figure 3-6: UV-Vis wavelength scan for 5 mg/L sulfamethazine*

Once the analysis wavelength was found, a calibration curve was built for SMZ using a series of solutions with known concentration. For each UV-Vis test, the quartz cuvette was first cleaned with delicate task wipes and the spectrophotometer was zeroed at the 239 nm analysis wavelength using 3 mL of DI water in the quartz cuvette. The cuvette was subsequently emptied and dried before it was filled with 3 mL of the sample to be tested. Each sample was scanned three times, each for a period of 1 second, and the average was used for analysis. Between samples the cuvette was emptied, rinsed with DI water, and dried. Samples were tested from lowest concentration to highest concentration to minimize chances of cross-contamination between samples. A range of solution standards for calibration were selected to include two orders of magnitude (0, 0.5, 1, 5, 20, 50 mg/L), with the curve shown in *Figure 3-7*.



*Figure 3-7: UV-Vis calibration curve for sulfamethazine*

To use UV-Vis to read sulfamethazine concentrations before and after adsorption testing, the same procedures were applied. Absorbance readings were then used to calculate the unknown sulfamethazine concentrations using *Equation 3-2* taken from the calibration curve.

$$\text{Concentration} = (\text{Absorbance} - 0.0116)/0.0641$$

*Equation 3-2: Sulfamethazine concentration equation from UV-Vis absorbance*

### 3.4.2 - HPLC Spectrophotometry

High Performance Liquid Chromatography (LC- 2010A, Shimadzu, Japan) was also used to measure SMZ solution concentrations to confirm the results of the UV-Vis spectrophotometry. High Performance Liquid Chromatography (HPLC) separates

compounds so they could be noted by their different retention times. This was a useful advantage over UV-Vis spectrophotometry as the SMZ solutions from adsorption testing could be examined for other compounds in the case that anything was leaching from the microplastics. However, due to the lengthy sample preparation process and since HPLC testing requires much more time for each sample, it was not the primary method of analysis.

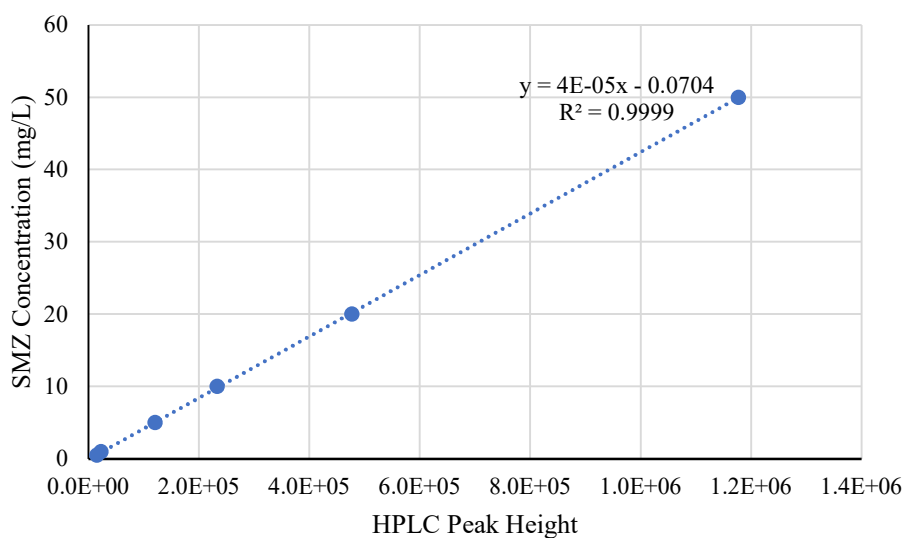
The HPLC was used with a C18 reversed-phase column (4.6 mm x 100 mm, Phenomenex, USA) and used a diode array detector (DAD) at a detection wavelength of 254 nm (Numaan 2021). The column temperature for testing was set at 40°C and the injection volume used was 20 µL, using the gradient conditions in *Table 3-2*.

*Table 3-2: Gradient conditions for HPLC (Numaan 2021)*

Time (min.)	Acetonitrile
0 - 0.5	2%
0.5 - 7	2% - 80% (Linear)
7 - 9	80% - 98% (Linear)
9 - 10	98% - 2% (Linear)
10 - 15	2%

HPLC samples were prepared by filtering with 0.22 µm nylon membrane filters. Samples were arranged in the HPLC trays from lowest concentration to greatest concentration. The first and last samples were always blanks consisting only of DI water, with more blank samples placed as every fifth sample. The mobile phases for HPLC consisted of 0.1%

phosphoric acid and 100% acetonitrile at a flow rate of 0.5 mL/min. Before any HPLC test the mobile phases were all sonicated for at least 1-hour until no bubbles were seen. The calibration curve shown in *Figure 3-8* was developed with the same SMZ standards as used for the UV-Vis calibration but could be used to calculate SMZ concentration from HPLC peak heights using *Equation 3-3*. The retention time for SMZ detection with HPLC used for sample analysis was 7.05 min.



*Figure 3-8: HPLC calibration curve for sulfamethazine*

$$SMZ\ Concentration = 4E^{-05}(HPLC\ Peak) - 0.0704$$

*Equation 3-3: HPLC concentration equation from HPLC peak height*

The same methods of sample, HPLC machine, and HPLC column preparation were used for testing the rest of the samples used with HPLC.

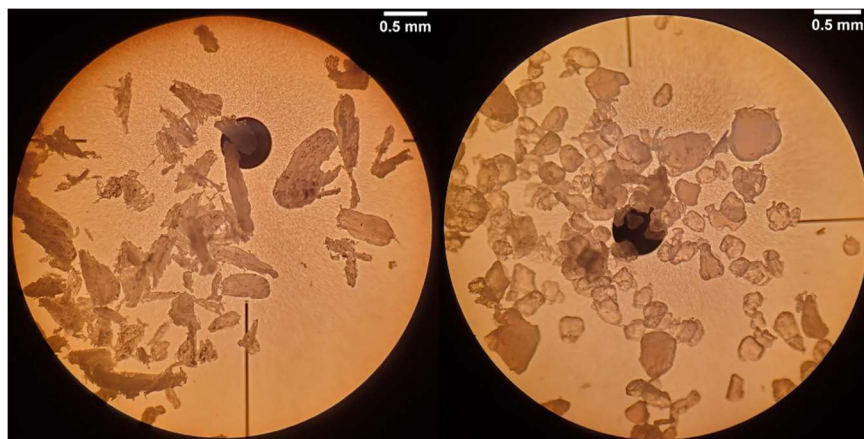


## Chapter 4 - Results and Discussion

### 4.1 - Results of Microplastic Surface Analysis

#### 4.1.1 - Optical Microscopy Results

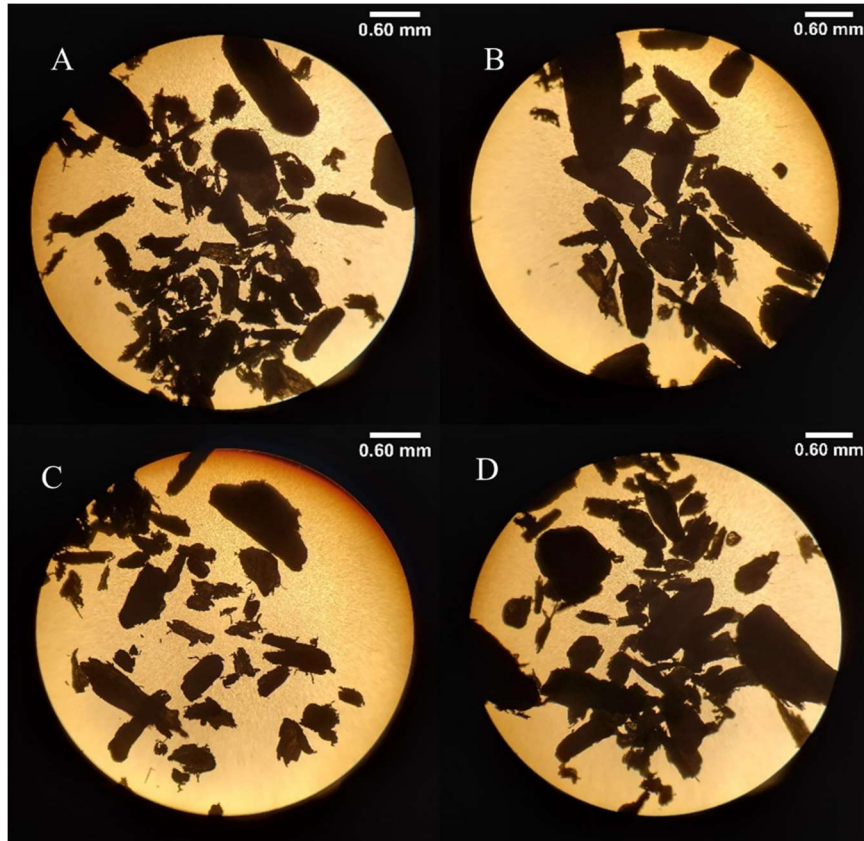
Under the optical microscope, different morphologies could be seen between the virgin and recycled PET material (*Figure 4-1*). Virgin material tended to be more oblong with a typical aspect ratio of approximately 2.6:1. The recycled materials were generally rounder and evenly sized showing average aspect ratios of approximately 1.27:1. Both materials had similar average widths across their shortest dimension indicating similar distribution between the sieves used to select these sizes.



*Figure 4-1: Optical microscope view of pristine virgin PET (left) and pristine recycled PET (right)*

When UV-aged samples were examined with the optical microscope, differences were not visible (*Figure 4-2*). The general shape and size of the particles remained the same. Surface

detail could not be seen well enough to get any indication of surface texture differences across the aging periods compared.

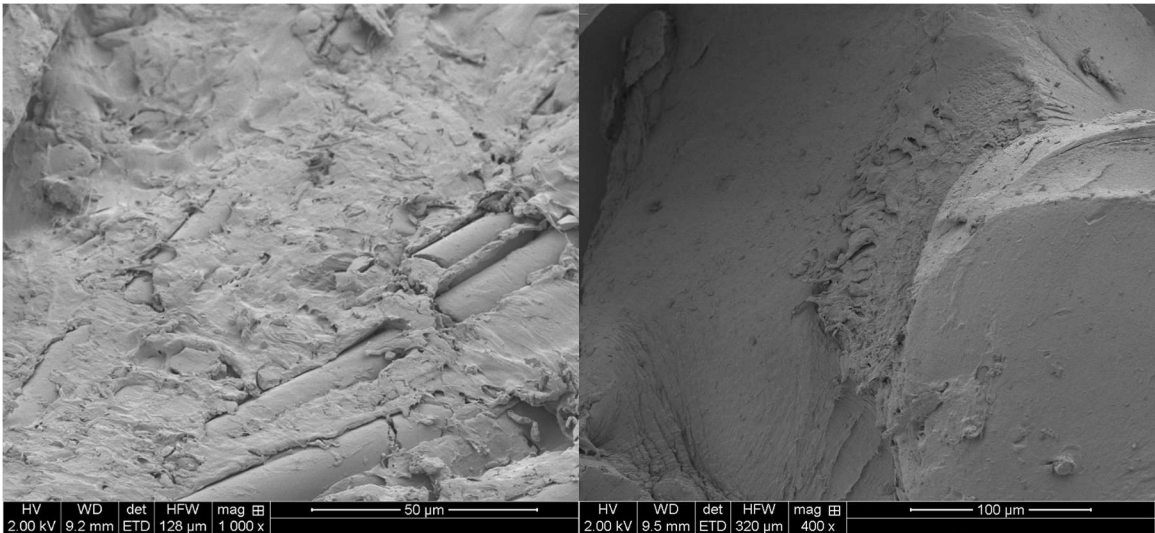


*Figure 4-2: Optical microscope images of PET UV-treated with freshwater for 2 days (A), 7 days (B), 20 days (C), and 30 days (D)*

#### 4.1.2 - Scanning Electron Microscopy Results

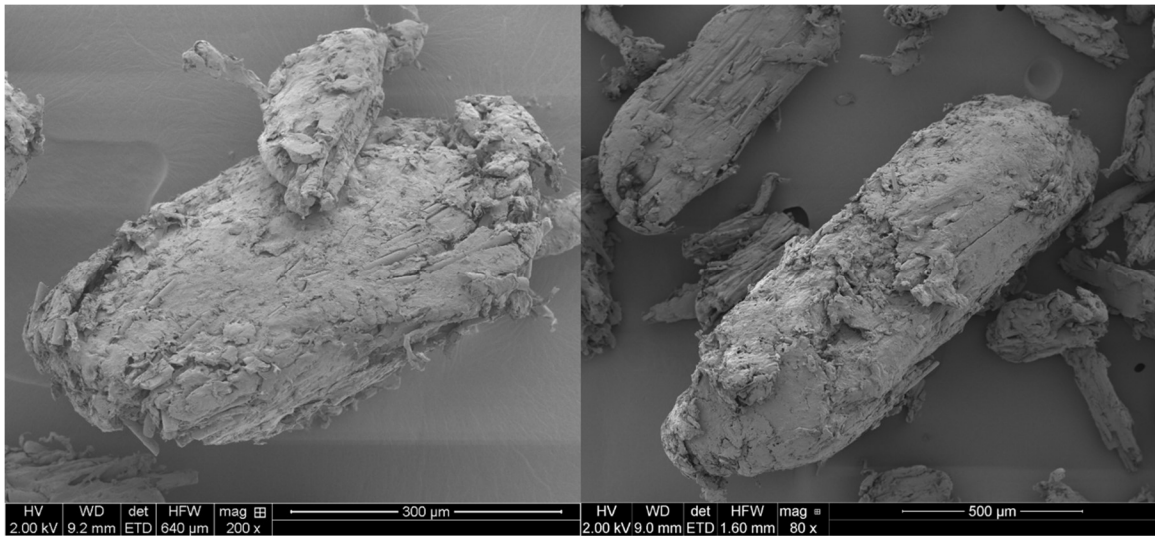
SEM images were able to be collected at close enough scale to see detailed surface texture. The difference in surface texture between pristine samples of the virgin PET and recycled PET material can be seen below in *Figure 4-3*. In addition to the differences in shape that could be seen from the optical microscope, the SEM shows the presence of a distinct

material at the surface of the PET samples. The lab supply grade of PET contains 30% glass reinforcer, which is likely what these cylindrical structures are (Sigma-Aldrich 2022). The RPET samples photographed under SEM do not show any similar cylindrical structure and generally appear smoother than the virgin material.

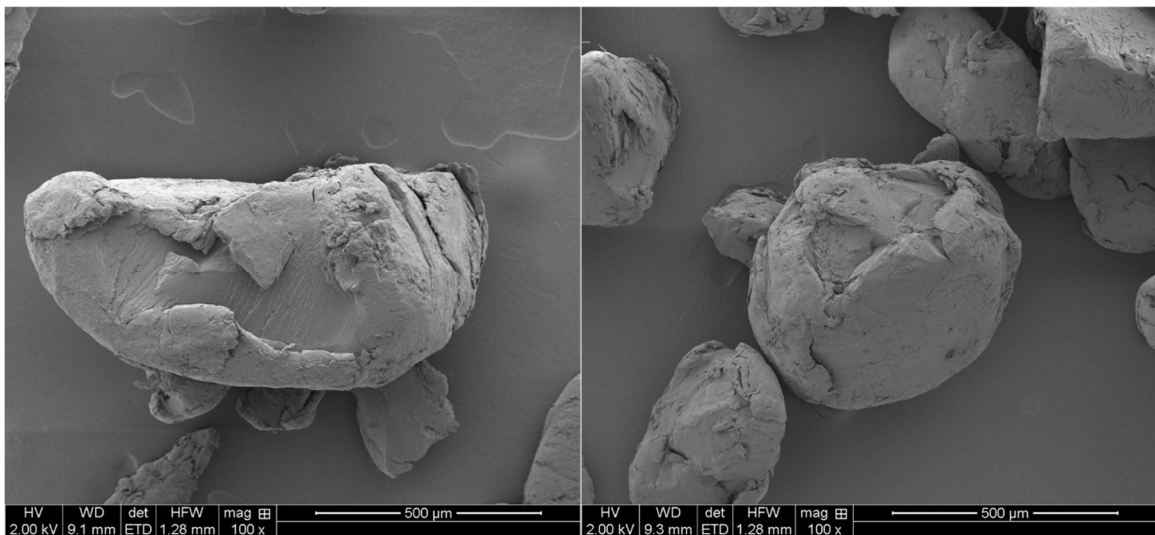


*Figure 4-3: SEM view of surface texture on pristine virgin PET (left) and RPET (right)*

A comparison of the pristine PET material and the UV-aged PET (30-days in saltwater solution) can be found in *Figure 4-4*. The two samples showed similar surface texture, appearing generally rough with the surface containing many small cracks, fissures, and inconsistencies. *Figure 4-5* shows the comparison of pristine RPET and the RPET that underwent 30 days of UV aging in the saltwater condition. The RPET samples also show little variation in surface texture between the pristine and aged condition. The two RPET particles shown have similar surface topography and have no major differences in features that distinguish them.



*Figure 4-4: SEM images of pristine PET (left) and PET UV-aged for 30 days in saltwater (right)*



*Figure 4-5: SEM images of pristine RPET (left) and RPET UV-aged for 30 days in saltwater (right)*

### 4.1.3 - FTIR Results

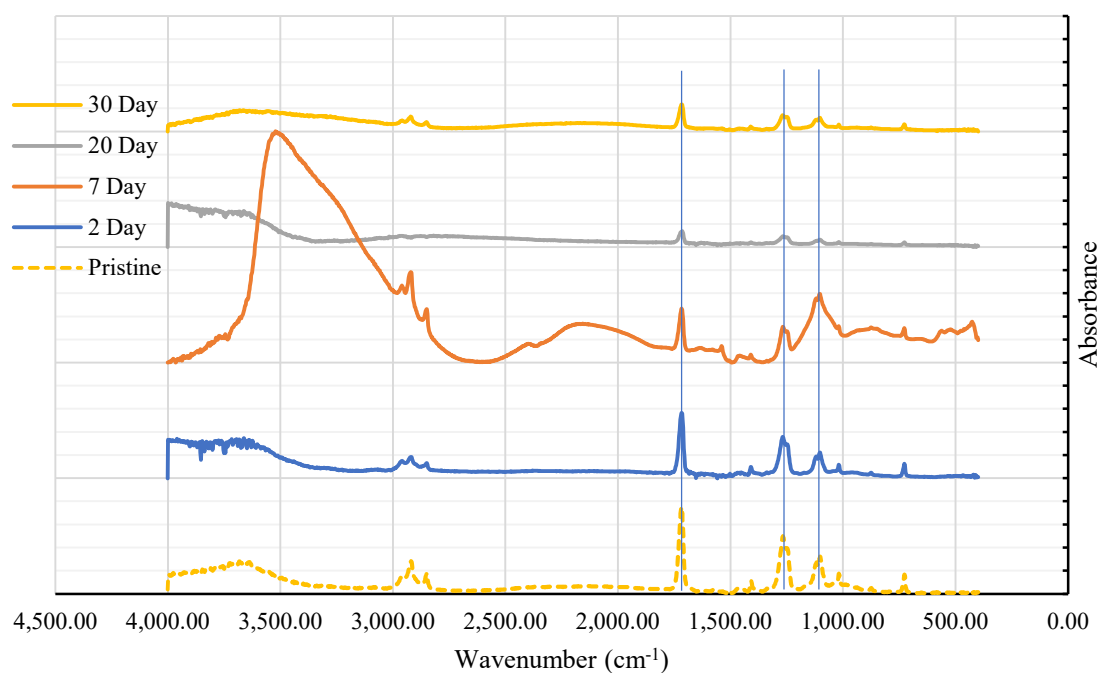
Scans from the FTIR were grouped together by treatment conditions to show how response changed as UV-aging time increased for the dry, freshwater, and saltwater conditions. While little quantitative analysis can be performed with the results of FTIR scans, examining how peak bands changed with treatment can provide some qualitative insight into the aging mechanisms. The characteristic peak absorbance bands for PET are shown below in *Table 4-1*.

*Table 4-1: Characteristic FTIR response for PET (Socrates 2004)*

Functional Group	Characteristic Response Wavelength (cm <sup>-1</sup> )
Out-of-plane Bending	730
Aromatic Esters, C-O-C	1,130
	1,260
Carbonyl, C=O	1,740
Carboxyl, COOH	3,260
Hydroxyl, OH	3,450

*Figures 4-6, 4-7, and 4-8* show the FTIR responses of PET samples aged in dry, freshwater, and saltwater, respectively. With increased exposure to UV, the samples tend to show less response in the characteristic bands for PET, suggesting some loss of those functional groups at the surface of the plastic. These trends are especially visible in the samples aged in the dry conditions, for the carbonyl group at approximately 1,700 cm<sup>-1</sup>, and for the

aromatic esters at approximately  $1,130\text{ cm}^{-1}$  and  $1,260\text{ cm}^{-1}$  (where these groups are marked by vertical lines in the plots). With the hydroxyl and carboxyl groups, at  $3,450\text{ cm}^{-1}$  and  $3,260\text{ cm}^{-1}$ , respectively, it is generally difficult to see the response due to humidity effects (Socrates 2004). These humidity effects are thought to account for the outlier portion of the response for the dry conditions aged for 7 days and the freshwater conditions aged for 2 days, as both show large outlier response at approximately  $3,500\text{ cm}^{-1}$ .



*Figure 4-6: FTIR response from PET aged in dry conditions*

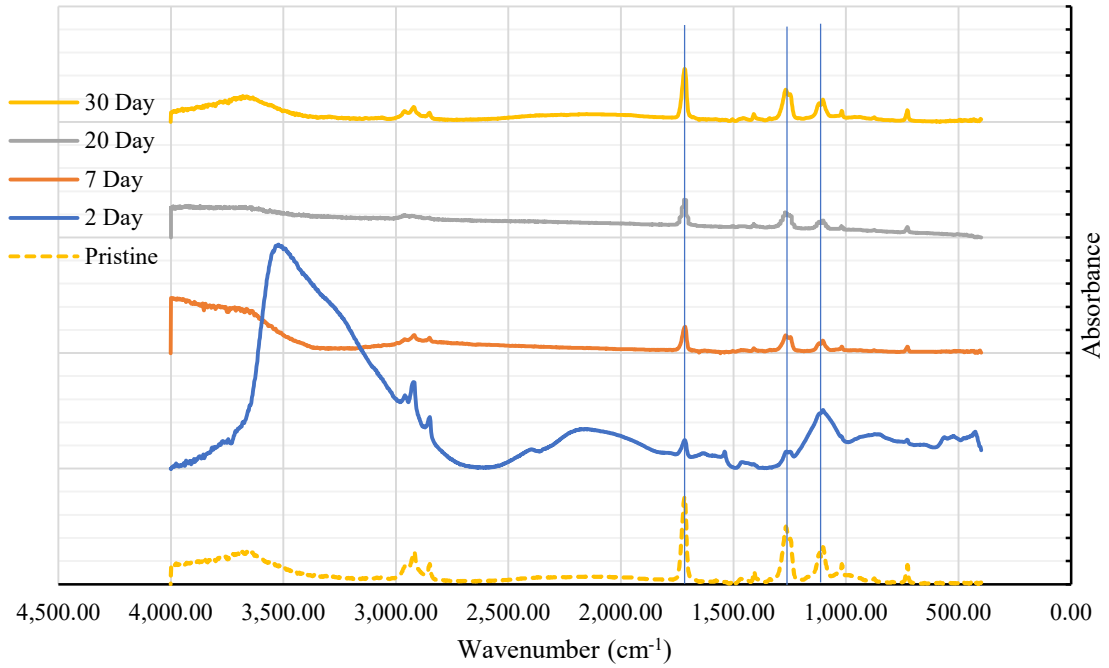


Figure 4-7: FTIR response from PET aged in freshwater conditions

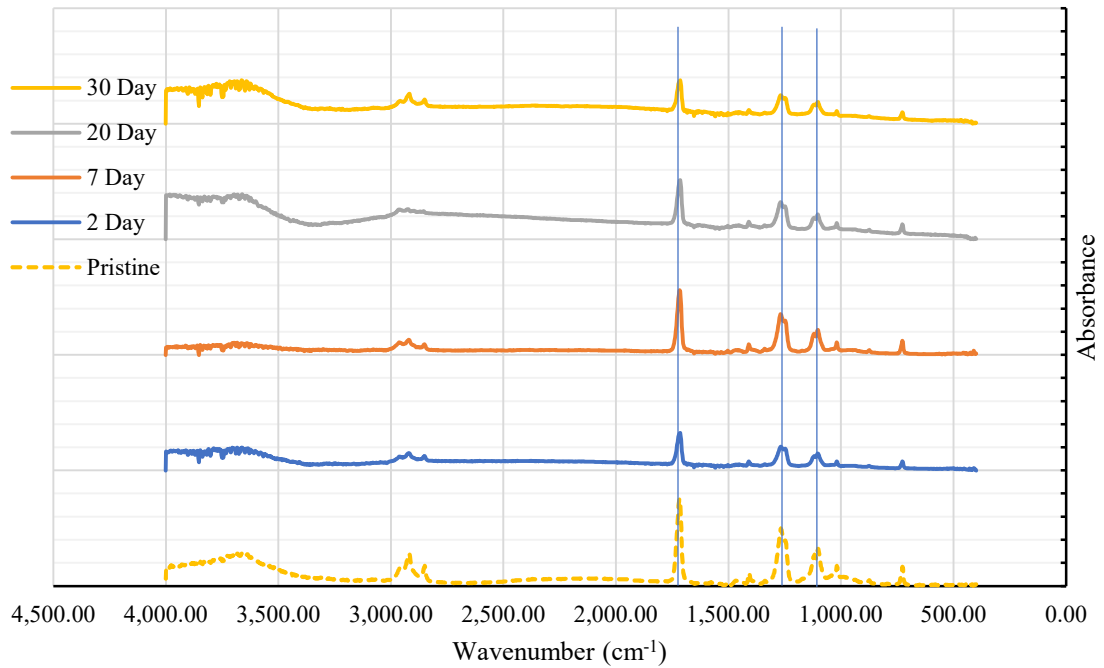
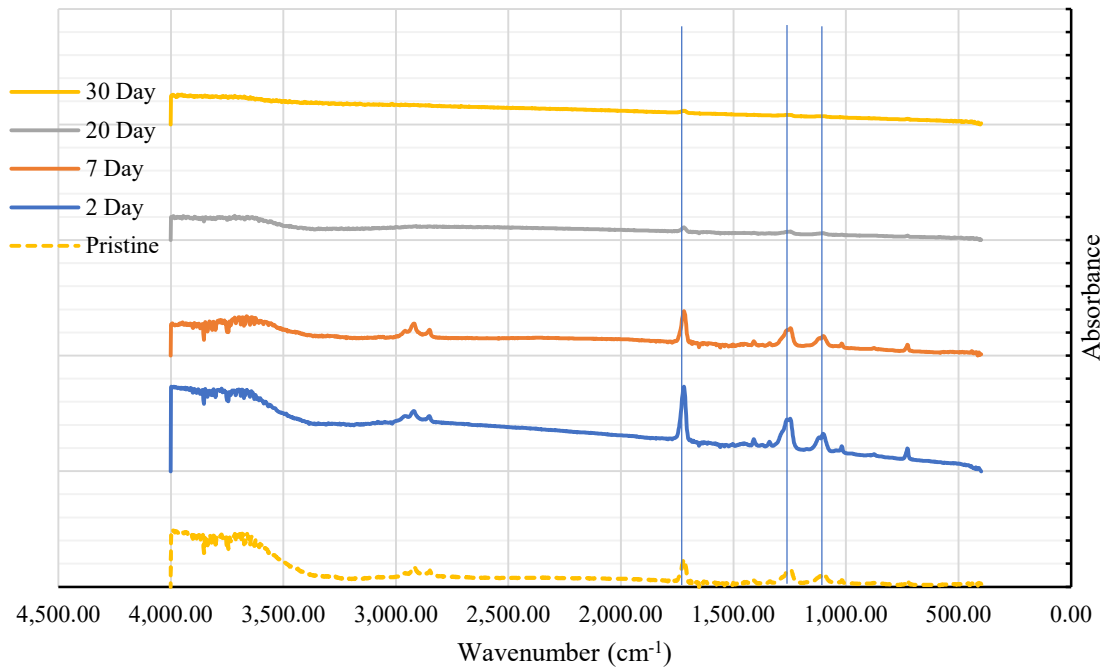


Figure 4-8: FTIR response from PET aged in saltwater conditions

Similar results were found for the FTIR responses of RPET samples across different UV exposure lengths for the dry, freshwater, and saltwater treatments, as shown in *Figures 4-9, 4-10, and 4-11* respectively. In the RPET samples, the FTIR response appears most related to UV exposure time for the dry and freshwater conditions, while results for the saltwater conditions appear less correlated with UV treatment time.



*Figure 4-9: FTIR response from RPET aged in dry conditions*



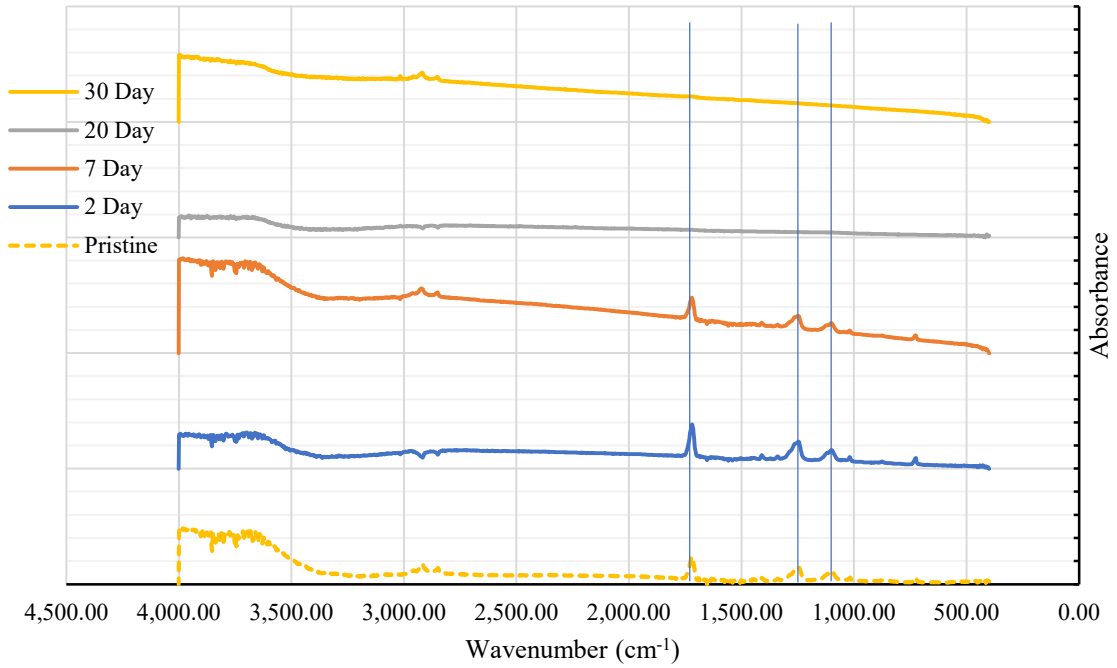


Figure 4-10: FTIR response from RPET aged in freshwater conditions

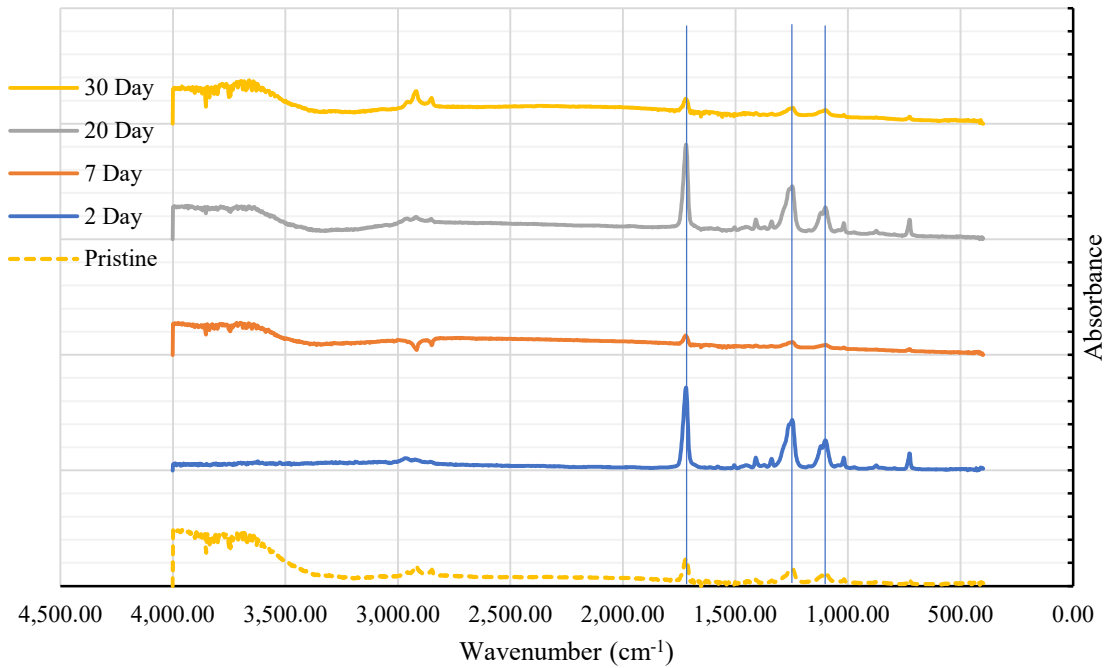


Figure 4-11: FTIR response for RPET aged in saltwater conditions

The changes in magnitude shown by FTIR scans seem to indicate decreases in the corresponding functional groups. For RPET samples aged in saltwater, the 2- and 20-day aging periods seem to break this trend for unknown reason. Because no mixing periods were included over the course of the UV-aging, it is possible that the microplastics used from these treatments for FTIR were shielded from UV by other particles. None of the peak bands showed any shifting in the wavelength that elicited response, so it is unlikely that surface groups are changing as a result of UV aging, but rather decreasing in number. This may occur as a result of photo-reactive groups present in the plastics whose bonds can be broken by exposure to UV-light (Crawford 2017). The loss of these carbonyl (C=O) and ester (C-O-C) surface groups may have some implications for sorption capacity. Loss of these polar groups may be changing the hydrophobicity of the plastics although with a hydrophilic adsorbate such as SMZ this should not be of great impact (Guo et al. 2019). Increased hydrophobicity in the plastics would result in decreased driving force for SMZ adsorption. However, if the dissolved pollutant were more hydrophobic, there may be an increased driving force as both compounds would be trying to escape the solution.

## **4.2 - Sulfamethazine Adsorption Results**

### **4.2.1 - UV-Vis Spectrophotometry Results**

Analysis of adsorption test samples with UV-Vis consistently showed no changes in concentration of the bulk solution, suggesting no adsorption was occurring on the plastics. Some adsorption was seen in early testing with the plastics in the as-received condition, but the results could not be replicated and so are not included here. Adsorption

characteristics for the pristine, un-aged microplastics are shown below in *Error! Reference source not found.*

*Table 4-2: Pristine microplastics average adsorption characteristics*

	PET	RPET
Mass of Adsorbent, m (g)	0.20	0.20
Solution Volume (L)	0.05	0.05
Initial Solution Concentration, $C_0$ (mg/L)	18.15	20.03
Final Solution Concentration, $C_e$ (mg/L)	18.31	20.16
Equilibrium Adsorption Concentration, $q_e$ (mg/g)	-0.04	-0.03

The UV-Vis collected sorption equilibrium results for microplastics UV-aged for 30 days are shown below in *Table 4-3*, with the results for microplastics that were UV-aged for 20 days shown in *Table 4-4*. The equilibrium concentrations that were sorbed to the plastics are generally very small, less than 0.1 mg/g, and across the averaged results there was a tendency for negative sorbed concentrations.

Table 4-3: Adsorption equilibrium results for microplastics with 30-day aging

Microplastic Treatment	Avg Equilibrium Solution Concentration, $C_e$ (mg/L)	Avg Equilibrium Adsorbed Concentration, $q_e$ (mg/g)
Dry PET	20.32	-0.02
Freshwater PET	20.31	-0.02
Saltwater PET	20.68	-0.11
Dry RPET	20.16	-0.03
Freshwater RPET	20.56	-0.08
Saltwater RPET	20.26	-0.05

Table 4-4: Adsorption equilibrium results for microplastics with 20-day UV aging

Microplastic Treatment	AVG Equilibrium Solution Concentration, $C_e$ (mg/L)	AVG Equilibrium Adsorbed Concentration, $q_e$ (mg/g)
Dry PET	20.16	-0.02
Freshwater PET	20.40	-0.08
Saltwater PET	20.39	-0.08
Dry RPET	20.36	-0.08
Freshwater RPET	20.37	-0.08
Saltwater RPET	20.11	-0.02

The negative adsorbed concentration values shown by UV-Vis tested samples indicated the possibility of desorption or leaching of some unknown compounds from the microplastics during mixing with the SMZ solutions. This possibility was examined further with HPLC testing so that compounds could be separated by retention time.

#### 4.2.2 - HPLC Results

HPLC was used to verify the results of the UV-Vis testing by selecting a series of solutions that had been exposed to microplastic in an adsorption test and comparing them with the initial solution that had not been exposed to microplastics. Comparison of the adsorbed concentrations at equilibrium are shown in *Table 4-5*. The concentrations are in the same order of magnitude and are as consistently negative as values collected by UV-Vis. Comparisons of the chromatograph plots for HPLC are shown below in ***Error! Reference source not found.***, with a vertical line marking the position of the SMZ peak at retention time 7.05 minutes.

*Table 4-5: HPLC-measured equilibrium concentrations adsorbed to microplastics*

Microplastic Treatment	Adsorbed Equilibrium Concentration, $q_e$ (mg/g)
Dry PET 30d	-0.08
CTRL Dry PET 30d	-0.10
Freshwater PET 30d	-0.07
CTRL Freshwater PET 30d	-0.10

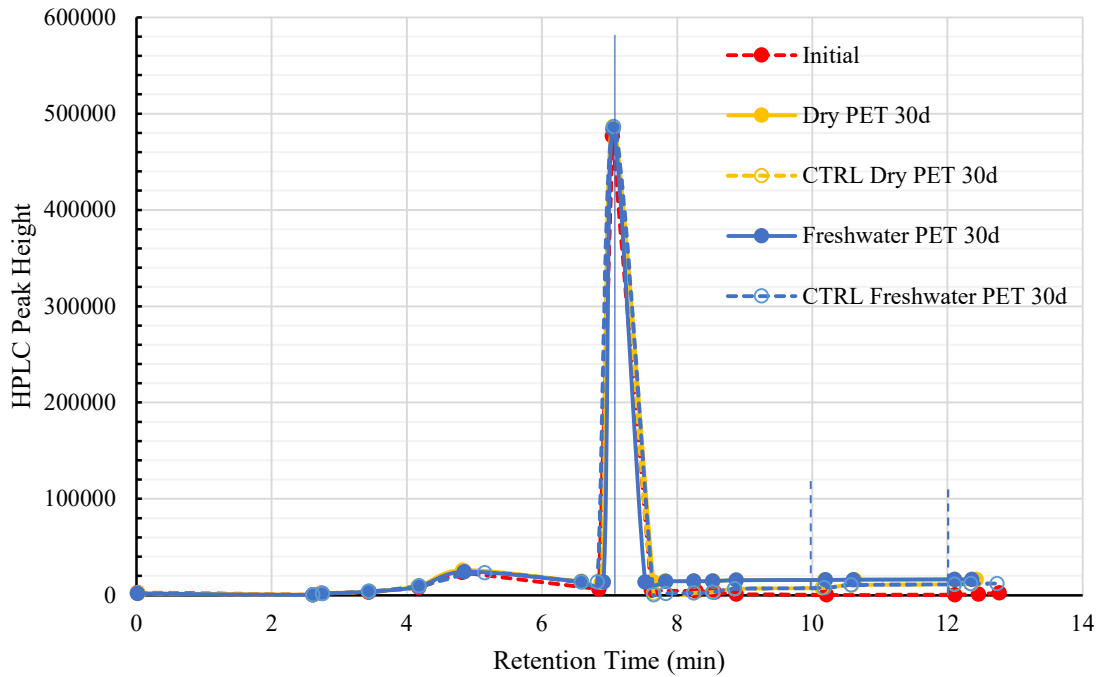


Figure 4-12: HPLC chromatograph comparisons

The peak height at this SMZ retention time points to a similar result as the UV-Vis tests produced, as the peaks show some noise from each other, without major differences. However, after the peak at 7.05 minutes, and especially between retention times of 10 and 12 minutes (bounded by vertical dashed lines), there was some response from the adsorption test solutions that was not present in the initial solution (*Error! Reference source not found.*). Here the responses differ between the sample that was not exposed to microplastics, the control samples where the plastics were not exposed to UV, and the UV-aged samples.

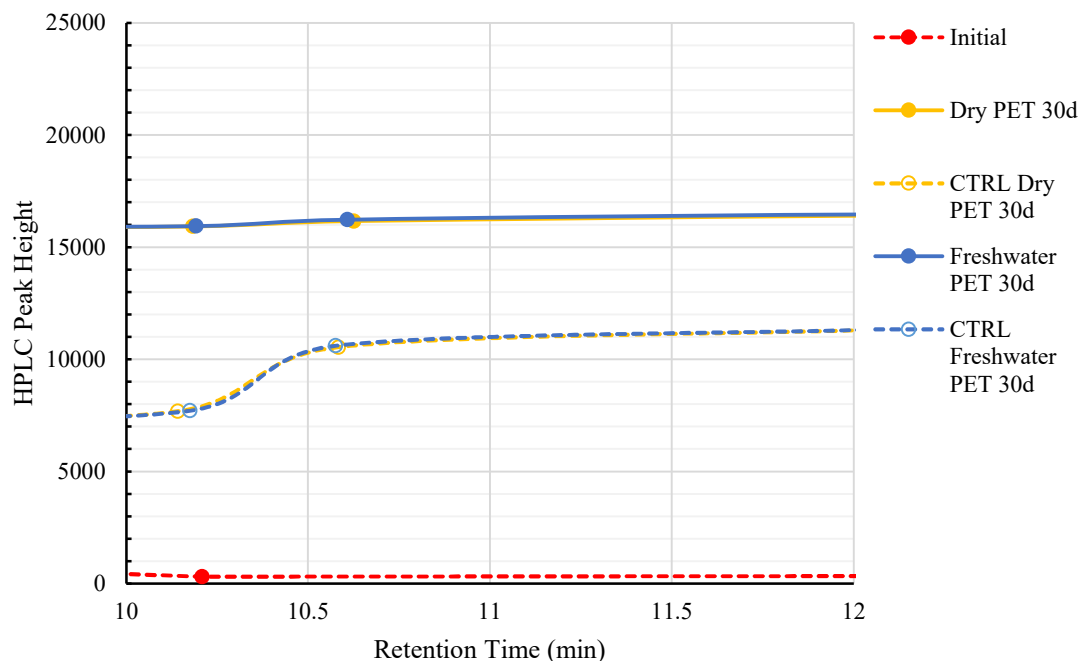


Figure 4-13: HPLC chromatograph detail comparison view

This difference across conditions between detection times of 10 – 12 min seems to indicate the potential presence of a compound other than SMZ present that was released from the microplastics during adsorption experiments. This interference at longer retention times could not be identified but is an interesting point of discussion as there is a trend towards greater presence of this potential substance across greater exposure to UV. The use of additives in plastics manufacturing is a common method of altering plastic properties for specific uses such as coloring, heat or UV stabilization, or as fillers, these additives may be responsible for the appearance of leaching from the materials.

## Chapter 5 - Conclusions

A growing body of literature has shown both microplastic pollution and antibiotic pollution to be widespread environmental concerns that have become ubiquitous across many environments, and that the two may interact as antibiotics adsorb to microplastics. Through analysis of adsorption solution samples with UV-Vis and HPLC, this study was not able to detect adsorption of sulfamethazine to microplastic PET. Samples of PET and RPET were aged under 365 nm wavelength UV lamps 8 hours a day for 2, 7, 20, and 30 days. Aging was completed in dry conditions, in freshwater conditions, and in saltwater conditions. For the pristine and aged microplastics, adsorption could not be shown as results consistently produced minute and negative values of concentration adsorbed to the plastics. However, changes in the HPLC response between SMZ solutions exposed to microplastics and those not exposed to microplastics suggest that some leaching or desorption of unknown compounds from the plastics may have occurred that interfered with adsorption measurements. The aging process did not produce changes to the plastics that were visible with optical microscopy or SEM analysis. Changes to surface groups on the PET and RPET plastics were seen with FTIR scans of the particles, which suggest that sorption properties were potentially changed in the plastics that received the longest UV-exposure but does not provide quantitative measure of how they changed. The functional groups that appeared degraded in FTIR scans may have had some impact on the hydrophobicity of the plastics that could use further analysis.



## Chapter 6 - Future Recommendations

Research characterizing the adsorption capabilities of microplastics should be continued to gain a more complete understanding of these processes. This work should be continued towards the goal of full adsorption isotherms for virgin PET, recycled PET, and aged samples of each. Addition of a regular mixing process during the UV-aging treatment in future study would help ensure that all microplastics in a sample receive the same treatment and that no particles are shielded from UV by other particles. Because PET plastics are so commonly recycled, further work should be completed to examine what relevant chemical differences may exist between virgin and recycled plastics. Brunauer-Emmett-Teller (BET) surface area testing should be applied to pristine and aged microplastic samples if readings can be obtained, as UV degradation may have the potential to increase surface area as the plastics age, allowing for increased surface sites for sorption. If the specific surface area is too low for BET to measure, further measurements could instead be collected with SEM analysis. Specific study of the hydrophobicity of microplastics will also be useful in understanding the mechanisms of adsorption to microplastics and how the adsorption processes may change depending on the plastic adsorbent and the adsorbate of concern. Indications of increased hydrophobicity meant less sorption with hydrophilic pharmaceuticals, but this likely is not the same result that would be found with less polar adsorbates. Combination of further HPLC analysis with other chromatography should be utilized to characterize the desorption or leaching possibilities of manufacturing additives from microplastics. Understanding these traits may expand water quality concerns where

microplastic contamination exists and increase the justification for containing microplastic pollutants.

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