Microplastics in the Desert Southwest:

Occurrence and Characterization

In Atmospheric, Aquatic, and Terrestrial Environments

by

Kanchana Chandrakanthan

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Graduate Supervisory Committee:

Pierre Herckes, Chair
Matthew Fraser
Everett Shock

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ABSTRACT

Microplastics, plastics smaller than 5 mm, are an emerging concern worldwide due to their potential adverse effects on the environment and human health. Microplastics have the potential to biomagnify through the food chain, and are prone to adsorbing organic pollutants and heavy metals. Therefore, there is an urgent need to assess the extent of microplastic contamination in different environments.

The occurrence of microplastics in the atmosphere of Tempe, AZ was investigated and results show concentrations as high as 1.1 microplastics/m^3. The most abundant identified polymer was polyvinyl chloride. However, chemical characterization is fraught with challenges, with a majority of microplastics remaining chemically unidentified. Laboratory experiments simulating weathering of microplastics revealed that Raman spectra of microplastics change over time due to weathering processes. This work also studied the spatial variation of microplastics in soil in Phoenix and the surrounding areas of the Sonoran Desert, and microplastic abundances ranged from 122 to 1299 microplastics/kg with no clear trends between different locations, and substantial total deposition of microplastics occurring in the same location with resuspension and redistribution of deposited microplastics likely contributing to unclear spatial trends. Temporal variation of soil microplastics from 2005 to 2015 show a systematic increase in the abundance of microplastics. Polyethylene was prominent in all soil samples. Further, recreational surface waters were investigated as a potential source of microplastics in aquatic environments. The temporal variation of microplastics in the Salt River, AZ over the course of one day depicted an increase of 8 times in microplastic

concentration at peak activity time of 16:00 hr compared to 8:00 hr. Concurrently, microplastic concentrations in surface water samples from apartment community swimming pools in Tempe, AZ depicted substantial variability with concentrations as high as 254,574 MPs/m^3. Polyester and Polyamide fibers were prevalent in surface water samples, indicating a release from synthetic fabrics. Finally, a method for distinguishing tire wear microplastics from soot in ambient aerosol samples was developed using Programmed Thermal Analysis, that allows for the quantification of Elemental Carbon. The method was successfully applied on urban aerosol samples with results depicting substantial fractions of tire wear in urban atmospheric environments.

DEDICATION

I would like to dedicate this thesis to my parents;

Ponnappah Chandrakanthan and Rohini Chandrakanthan,

and to all my mentors over the years

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GLOSSARY OF ABBREVIATIONS AND TERMS

CAP-LTER ..... Central Arizona Phoenix Long-Term Ecological Research Program

EC..... Elemental Carbon

ESCA..... Ecological Survey of Central Arizona

FT-IR..... Fourier Transform Infrared Spectroscopy

MP..... Microplastic

OC ..... Organic Carbon

OC-EC..... Organic Carbon Elemental Carbon

PA..... Polyamide

PE ..... Polyethylene

PES..... Polyester

PET..... Polyethylene terephthalate

PM..... Particulate Matter

PS ..... Polystyrene

PTA ..... Programmed Thermal Analysis

PVC..... Polyvinyl chloride

TOR..... Thermal Optical Reflectance

TOT ..... Thermal Optical Transmittance

CHAPTER 1

INTRODUCTION

1.1 Microplastic occurrence, sources, and environmental implications

Since large scale global production of plastics began in the 1950s, the overall production of plastics has increased from 1 million tons per year in 1960 to 350 million tons of plastics in 2017 (Barnes et al., 2009). Over time, larger plastic debris degrade to produce smaller plastics; microplastics. Microplastics are defined as plastic particles that measure smaller than 5 mm in size (Arthur et al., 2009). Microplastics have continued to receive attention over the years and have been observed frequently accumulating in different environments, largely resulting from the secondary breakdown of plastic debris (Thompson et al., 2004). Primary microplastics are intentionally manufactured at the microscopic size and are mainly derived from the direct release from products such as pre-production pellets and micro beads from personal care products (facial scrubs, cosmetics, and cleansers) (Fendall and Sewel, 2009; Hidalgo-Ruz et al., 2012). Secondary microplastics arise from the breakdown of larger plastic debris and constitute a majority of the synthetic micro-particles accumulating in the environment (Cole et al., 2011). Secondary microplastics tend to have more diverse shapes such as fibers, fragments (Figure 1.1), foams and films while primary microplastics exhibit regular and uniform shapes such as spherical beads (Hidalgo-Ruz et al., 2012).

Owing to their persistent nature and reported harmful effects on ecosystems and human health, microplastic research has attracted increasing interest over recent years (Gasperi et al., 2018;(Yang et al., 2021; Yuan et al., 2019). Microplastics are now frequently

detected in aquatic, terrestrial and atmospheric environments, depicting their pervasive nature (Zhang et al., 2020).

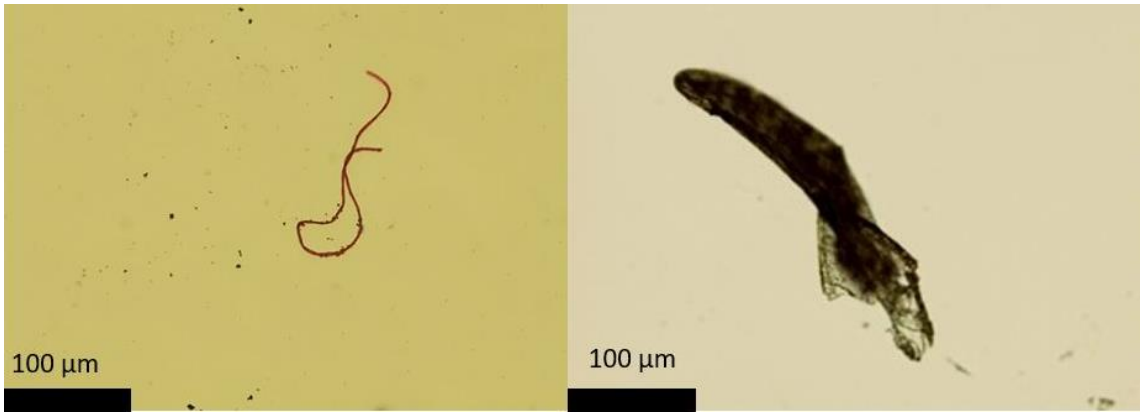

Figure 1.1 Microplastic Fiber and Fragment

1.1.1 Microplastics in aquatic environments

The presence of plastics has been reported in freshwater and marine environments, even in remote, polar regions (Barnes et al., 2009). Owing to their relatively low densities and high durability, microplastics have the ability to float and have been extensively reported in oceans and riverine ecosystems (Andrady, 2011; Bordós et al., 2019; Yuan et al., 2019; Li et al., 2020; Peller et al., 2020b). Marine based sources of microplastics include degradation of fishing and aquaculture gear, and 80% of them are generated from inland sources (Thompson et al., 2004). Sources include secondary fragmentation of larger plastic debris from rivers, tidal waves and catastrophic sea events (Watson et al., 2013). A large majority of the plastic debris reaching the oceans originate from terrestrial sources, and are transported through freshwater pathways due to the mismanagement of plastics (Wagner et al., 2014). Freshwater is in close proximity to pollution sources and has a relatively smaller waterbody area compared to oceans, and is therefore more severely affected by microplastic pollution (Andrady, 2011). Waste water treatment plant (WWTP) outlets are also important point sources of microplastics (McCormick et al., 2014). The most commonly reported microplastic shapes in the aquatic environment are fibers and fragments (Barrows et al., 2018; Rebelein et al., 2021).

In the marine environment, higher fibrous microplastic concentrations are reported in close proximity to the shore lines compared to offshore locations, which is ascribed to the anthropogenic contribution from fishing gear and nets, industrial effluent and laundry discharge (Lusher et al., 2014; Nel and Froneman, 2015; Rebelein et al., 2021). However, microplastics concentrations, particularly the contribution from the discharge of fibers, in freshwater riverine systems are rather limited in literature. Additionally, the impact of

recreational activities and the resulting microplastic fibers shed to the aquatic environment is also less studied and understood.

The ever increasing and continuous production and disposal of plastic debris into marine and freshwater media aggravate the issue of contamination of such ecosystems and microplastics have shown to provide a habitat to host microorganisms (Andrady, 2011). Microplastics can accrue and release hazardous persistent organic pollutants into water including polybrominated diphenyl ethers and other additives that are incorporated during their manufacture, thereby elevating their concentrations in water (Gonte and Balasubramanian, 2017). Owing to their small size, microplastics can be ingested by fresh water aquatic organisms that can eventually cause ecotoxicological and physiological changes (Thacharodi et al., 2024). The presence of microplastics in riverine ecosystems and marine environments of interest can also potentially reduce the feeding uptake of such aquatic organisms (Mallik et al., 2021). Microorganisms including pathogens have the potential to form biofilms (microbial 'plastisphere') on the surface of microplastics, and therefore can act as agents for infectious waterborne agents (Andrady, 2011).

1.1.2 Microplastics in terrestrial environments

Given that a majority of plastic debris is generated and discharged on land, it is surprising that microplastic research on terrestrial environments is still in its' infancy, compared to freshwater and marine environments (Kumar et al., 2020; Moller et al., 2020). Street runoff, landfills and atmospheric deposition are key input pathways of microplastics into terrestrial ecosystems, making soils an important sink for synthetic microparticles in terrestrial ecosystems (Möller et al., 2020). Additionally, plastic mulch films and soil conditioners used in agricultural amendments are potential sources of soil microplastics (Ng et al., 2018). Soils can serve as a source of atmospheric microplastics to other environmental compartments through resuspension of fugitive dust, thereby contributing to the overall microplastics transport cycle (Zhang et al., 2020). Additionally, emissions related to vehicle transport, including tire wear and brake wear are other sources of microplastics in the environment (Kole et al., 2017).

Studies have shown the negative effects of soil microplastics on the functioning of microbial communities and earthworms in soil environments (Lwanga et al., 2017; Rillig et al., 2017; Yang et al., 2018). The presence of microplastics in terrestrial environments can cause alterations in soil ecosystems affecting soil structure, porosity, plant growth and microbial activity (De Souza Machado et al., 2019). Studies predict that microplastics can degrade through microbial action as microorganisms can utilize plastic polymer chains as a carbon source for their growth (Mohanan et al., 2020; Huang et al., 2023). A study depicts how microplastics can pose an acute toxic effect on soil organisms such as nematodes (Kim et al., 2020). In addition to the direct toxic effects caused by microplastics, they can also act as carriers of other contaminants such as Persistent

Organic Pollutants (POPs) found in soils owing to their lipophilic surface characteristics (Hildebrandt et al., 2021; Hu et al., 2022).

1.1.3 Microplastics in the atmosphere

While the ubiquitous nature of microplastics in aquatic and terrestrial environments has been well documented, studies on their distribution in the air gained interest only in 2015 (Eerkes-Medrano et al., 2015). Therefore, the occurrence of microplastics in the atmosphere, is still relatively less understood. Studying the presence and distribution of airborne microplastics, as a constituent of atmospheric particulate matter, is important in understanding the effects of air pollution within a breathing zone. A recent report shows that airborne microplastics in the western United States mainly arise from secondary re-emission sources such as roads (84%), the ocean (11%), and agricultural soil dust (5%) (Brahney et al., 2021). Microplastics have been detected in quite different environments, from remote to highly densely populated areas with the ability to transport through the atmosphere (Bergmann et al., 2019; Brahney et al., 2020). Assessing the impact of microplastics on human health and the consequent impacts has gradually attracted increasing attention. A recent study demonstrated that SARS-CoV-2 aerosols have the potential to bind to microplastics, and therefore aid the entry of the virus to the human body (Amato-Lourenço et al., 2022). Microplastic fibers have been found in human lung tissue samples obtained from autopsies (Amato-Lourenço et al., 2021). Adsorbed organic chemical contaminants have the potential to get desorbed once microplastics reach lung tissues. Consumption of food products that contain microplastics can be intentionally minimized, however exposure to microplastics in the air is unavoidable (Liebezeit and

Liebezeit, 2013; Zhang et al., 2020). Owing to their small size and relatively low material densities, microplastics can be easily inhaled and have been found to be extremely durable in physiological fluid (Amato-Lourenço et al., 2021).

Among the various types of microplastics, tire microplastics that originate from synthetic tires are a significant source of microplastic contamination in the environment (Hartmann et al., 2019; Sieber et al., 2020; Luo et al., 2021). Synthetic tires consist of styrene butadiene rubber, which is formed from the monomer styrene, a precursor of polystyrene, in a mix with natural rubber and other additives (Sommer et al., 2018). However, studies on the presence of tire wear as a component of particulate matter in ambient air are limited. While larger sized tire wear particles may deposit near hotspot emission areas, relatively smaller sized particles (including $PM_{2.5}$) can undergo transport across long distances (Goßmann et al., 2023).

1.2 Chemical characterization of microplastics; Challenges in identification and weathering

In addition to studying the occurrence and distribution of microplastics in the atmosphere, it is important to identify their chemical composition as the polymer type can determine the adsorption capacities and toxicity of microplastics (Hwang et al., 2019). Chemical characterization can provide information on the nature of microplastics present in a sample and therefore provide an insight into their origin (Song et al., 2014, Hwang et al., 2019). Pyrolysis Gas Chromatography-Mass Spectrometry (Pyr GC-MS) is a thermo-analytical technique reported in microplastics literature to identify their chemical composition (Fries et al., 2013). However, this technique is destructive in nature (Araujo et al., 2018). Micro-Raman spectroscopy and micro-Fourier Transform Infrared (FTIR) spectroscopy are common non-destructive optical techniques that have been extensively used to characterize microplastics that require minimal sample preparation and small sample amounts. (Marina-Montes et al., 2022). Micro-Raman spectroscopy offers an added advantage in chemical characterization, in that it allows for a higher spatial resolution (~1 µm), compared to micro-FTIR (~20 µm). However, challenges are encountered during chemical identification of microplastics due to their alterations during weathering processes such as physical abrasion, ultraviolet (UV) oxidation, and chemical oxidation (Liu et al., 2020). Weathering can alter the physico-chemical properties of microplastics, thereby changing their environmental fate.

During chemical characterization of microplastics, Raman spectra lacking characteristic peaks for different functional groups make the chemical identification process more challenging. Weathering of microplastics in the environment is a proposed hypothesis

that could explain such the observations (Duan et al., 2021). Once released, microplastics can undergo aging in the environment, causing significant alterations in the Raman spectra that differ distinctly from those in their pristine state. Raman spectroscopy is a technique based on the inelastic scattering of light from a surface (Araujo et al., 2018). Physical abrasion from wind, stones and wave action can cause micro-scratches on the surface of the plastic (Ribeiro-Claro et al., 2017). The stray light from the abraded surface can hinder proper identification of the nature of the microplastic.

1.3 Tire- wear microplastics and soot: Challenges in identification of tire wear in environmental samples and differentiation from interfering soot

Tire wear microplastics refer to the particles that are generated through mechanical abrasion caused by the friction between tires and road surfaces, leading to the release of smaller particles to the environment (Wik and Dave, 2009; Panko et al., 2018). The released tire wear particles contribute towards a non-negligible fraction of microplastics in the environment (Sommer et al., 2018). A previous study that analyzed non-exhaust particulate matter in highly frequented roads in Germany reports that 54% (v/v) of the traffic-related particles were associated with tire wear (Sommer et al., 2018). However, research on the presence of tire wear particles in ambient air is sparsely reported in microplastic literature. This could possibly be ascribed to limitations encountered in separating and identifying tire wear microplastics using conventional and established techniques in microplastic research. An underlying challenge in characterizing tire wear microplastics is inherent to their black color; black samples strongly absorb laser radiation during micro-Raman analyses, eventually heating up and producing intense background emissions (Araujo et al., 2018; Gillibert et al., 2022). Additionally, tire wear

is typically encrusted with mineral matter and bitumen, which increases its overall density, and therefore conventional separation techniques based on density may not account for the heterogeneity (Järlskog et al., 2022). Moreover, the Raman spectroscopic fingerprint for carbon may not be specific and provide information on the origin the particle (e.g. vehicle tire or vehicle exhaust) (Sharma et al., 2016; Gillibert et al., 2022). Therefore, an alternative method to assess and identify tire wear contamination in the ambient air is needed.

Tire wear particles are heterogenous composites that consist of copolymers with additives including Carbon Black, that is added as a reinforcing filler commonly used in tire manufacturing (Panko et al., 2018). Carbon Black constitutes a substantial portion of tires, and improves the mechanical properties of the rubber polymers in tires, improving durability and strength (Zafarmehrabian et al., 2012; Sugatri et al., 2018). Carbon Black also acts as a protective barrier against Ultraviolet (UV) radiation from the sun and helps minimize premature aging (Ghasemi-Kahrizsangi et al., 2015). It also serves an aesthetic purpose in tires, as it is added during their processing stage as a coloring pigment to achieve the desired characteristic black hue (Sugatri et al., 2018). Greater than 97% of Carbon Blacks are composed of EC arranged in graphite layers to form primary particles (Watson & Valberg, 2001). Therefore, a novel technique that is able to distinguish and identify the refractory EC of, specifically tire wear, in ambient aerosol samples would successfully overcome the limitations set by conventional separatory methods employed in microplastic literature.

1.4 Objectives

This work focuses on investigating the distribution of microplastics in the diverse environments of Phoenix, Arizona (aquatic, terrestrial and atmospheric) with the latter part focusing on developing an approach to differentiate tire wear microplastics from other interfering constituents (soot) in ambient aerosol samples.

Chapter 2 initially addresses the research question of whether the air in Tempe, AZ is contaminated with microplastics. This chapter investigates the occurrence of microplastics in atmospheric suspended particulate matter over a one-year period in Tempe, Arizona (2021-2021). Next the study aims to study if the observed concentrations correlate with meteorological data (Average wind speed and Maximum wind speed). Chapter 2 also employs micro-Raman spectroscopy to better understand polymer identities of microplastics and thereby predict possible sources. Finally, this chapter aims to study if weathering of microplastics in the environment impact our ability to identify their chemical nature using micro-Raman spectroscopy. Laboratory experiments simulating weathering of microplastics are performed to observe how microplastics are altered under representative weathering processes (physical abrasion, chemical oxidation, and UV exposure).

Chapter 3 aims to investigate if the terrestrial environment, soil, in Phoenix, AZ, metropolitan area and the surrounding areas of the Sonoran Desert is contaminated with microplastics. To answer the aforementioned research question, the study utilizes samples from the Ecological Survey of Central Arizona (ESCA) performed by the Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER), which is a large-scale

field survey that is conducted in the CAP-LTER study area characterizing the urbanized, suburbanized, and agricultural areas of metropolitan Phoenix and the surrounding Sonoran Desert. Next the chapter seeks to investigate the temporal change of soil microplastics from 2005 to 2015. The temporal data in soils were supplemented with the collection of atmospheric deposition fluxes of microplastics in the same locality within the area (Tempe, AZ) for a period of one year (Oct 5th, 2020 to Sept 22nd, 2021). All soil and deposition samples were processed using established methodologies and quantitative information including morphology was obtained using optical microscopy. Chemical characterization of microplastics were performed by micro-Raman spectroscopy to understand their chemical composition.

Chapter 4 aims to investigate the impact of recreational activities on the microplastic concentrations in a riverine system; the Salt River in Arizona. The river is a source of drinking water for the Phoenix metropolitan area and witnesses substantial crowds for recreational activities during the summer. Water samples were collected from Goldfield recreation area in the Salt River on July 1st, 2023 over the course of 8 hours in one day at a single location. To compare and contrast, water samples were collected for microplastic analyses during October in the absence all summer recreational activities. During the months of July and October, water samples will be collected from 7 apartment community swimming pools in Tempe, AZ to investigate for the occurrence of microplastics. Optical microscopy was used to obtain numerical and morphological information of their presence and distribution in water. Chemical characterization of microplastics was performed by micro-Raman spectroscopy to identify their polymer constituents.

Chapter 5 seeks to investigate if Programmed Thermal Analysis (PTA) can identify tire wear in ambient air and differentiate it from soot. It aims to understand if tire wear potentially contributes to the atmospheric refractory carbon (EC). This chapter employs PTA that allows for the differentiation of EC from Organic Carbon (OC) based on the thermal optical transmittance in the Organic Carbon-Elemental Carbon (OC-EC) analyzer. The method utilizes the thermal refractivity of EC which does not volatilize at temperatures of approximately 700 ˚C in an inert atmosphere. Tire wear samples (n=8) were cryo-milled and subsequently analyzed using the OC-EC Analyzer. Commercial grade Carbon Black used in tires and recovered Carbon Black from waste tires were used in the study. Soot samples from the tail pipes of trucks (n=4) and incomplete combustion of candle wax were used to compare and contrast with tire wear samples in the OC-EC analyzer. The size effect of the tire wear particle on the position where the high temperature thermal residue of carbon (EC) appears in the thermogram was tested using PM_{10} samples of tire wear. Aerosol samples collected from roads and urban areas typically contain a mixture of soot and tire wear particles, therefore the method was applied on aerosol samples collected at a parking structure in Tempe, AZ and inside two tunnels located in the São Paulo Metropolitan Area, Brazil.

Chapter 6 is a summary of results and findings, and presents an outlook for future research.

Figure 1.2 Overview of research projects of the dissertation

CHAPTER 2

AIRBORNE MICROPLASTICS IN A SUBURBAN LOCATION IN THE DESERT SOUTHWEST: OCCURRENCE AND IDENTIFICATION CHALLENGES

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2.1 Abstract

Microplastics are rapidly emerging anthropogenic stressors that pose a potential threat to ecosystems and human health. While the ubiquitous nature of microplastics in water has been well documented, studies on their distribution in the air are limited. Measuring microplastics, as a component of atmospheric particulate matter, is important in assessing air pollution impacts within a breathing zone. Here we investigate and present results for the occurrence of microplastics in suspended particulate matter in Tempe, a suburban location in Arizona. Samples were collected from Oct 28th, 2020, to Nov 1st, 2021, on quartz fiber filters using a high-volume air sampler, and processed with microplastics

counted under an optical microscope to obtain quantitative information of their presence and distribution in the atmosphere. Microplastics were present in all collected suspended particulate samples ranging from between 0.02 to 1.1 microplastics/m^3 (average concentration of 0.2 microplastics/m^3) with the size range of (5-5000) µm. Fibrous microplastics were the most prevalent accounting for a large majority (≥82 %) of the microplastics suspended in air in all samples. To characterize the type of microplastics present, micro-Raman spectroscopy was used to identify the chemical composition of microplastics. Chemical characterization results revealed an array of polymers for the airborne microplastics. The most abundant identified polymer was polyvinyl chloride (19%). However, many micro-Raman spectra lacked characteristic peaks, making the chemical identification process more challenging. Laboratory experiments simulating weathering of microplastics were performed to understand how microplastics change under weathering processes; these experiments revealed that Raman spectra of microplastics change over time due to weathering processes.

2.2 Introduction

Plastics, integral materials today, are projected to reach a global production accumulation of 25 billion metric tons by 2050 (Geyer et al., 2017). Plastics materials are widely used owing to their durability and versatility. As a result, large amounts of plastic waste are generated due to mismanagement. Larger plastic debris entering the environment accumulates and persist in ecosystems, eventually breaking down into smaller plastics. The National Oceanic and Atmospheric Administration (NOAA) in 2008 defined microplastics as plastic particles smaller than 5 mm in size (Arthur et al., 2009). Microplastics are classified as either primary, intentionally manufactured at a microscopic size, or secondary, resulting from the fragmentation of larger plastic particles (Jenner et al., 2021; Wright et al., 2020). Primary microplastics can enter the environment by exfoliants in personal care products such as facial cleansers. As they are intentionally manufactured, primary microplastics typically have more regular shapes like beads or spheres, whereas secondary microplastics can have diverse shapes like fibers and fragments (Hidalgo-Ruz et al., 2012; Khatmullina and Isachenko, 2017).

While the ubiquitous nature of microplastics in water has been well documented, their abundance in the air has gained interest only since 2015 (Chu et al., 2022; Karapanagioti and Kalavrouziotis, 2022; Loganathan and Kizhakedathil, 2023; Mu et al., 2022; Yusuf et al., 2022; Dris et al., 2016, 2015; Evangeliou et al., 2022). Therefore, the distribution of microplastics in the immediate environment above land and water, that is in the atmosphere, is still poorly understood. A recent study suggests that atmospheric microplastics in the western United States are mainly derived from secondary re-emission sources such as roads (84%), the ocean (11%), and agricultural soil dust (5%) (Brahney et

al., 2021). Microplastics have been found in quite diverse environments, from remote to highly densely populated areas with the ability to transport through the atmosphere across long distances(Bergmann et al., 2019; Brahney et al., 2020) .

Assessing the impact of microplastics on human health and the consequent impacts has gradually attracted increasing attention. A recent study demonstrated that SARS-CoV-2 aerosols have the potential to bind to microplastics, and therefore aid the entry of the virus to the human body (Amato-Lourenço et al., 2022).Microplastics have also been found to be present in human lung tissue samples obtained from autopsies (Amato-Lourenço et al., 2021).Consumption of food products that contain microplastics can be deliberately minimized, but exposure to microplastic contaminated air is unavoidable (Kosuth et al., 2018; Kutralam-Muniasamy et al., 2020; Liebezeit and Liebezeit, 2013; Zhang et al., 2020). Owing to their small size and low material density, microplastics can be easily inhaled and pose a potential threat on humans. Since our current understanding of the impacts of airborne microplastics on the environment and human health is in its infancy, it becomes particularly important to study the atmospheric compartment as a potential vector of microplastics.

In addition to the abundance of microplastics in the atmosphere, it is important to understand their chemical composition as the polymer type is important for toxicity assessment (Hwang et al., 2019). Chemical characterization can yield information on the nature of microplastics present and therefore provide an insight into their origin, as well as determine their toxicity (Song et al., 2014). Micro-Raman spectroscopy has been

extensively used to characterize microplastics since it is a relatively simple method (Marina-Montes et al., 2022). However, an underlying challenge towards correct chemical identification of microplastics is posed by weathering processes such as physical abrasion, exposure to ultraviolet (UV) radiation, and chemical oxidation (Andrady, 2011; Liu et al., 2020). Weathering can change the physical and chemical properties of microplastics, thereby changing their environmental behavior.

Here we present results on the occurrence of microplastics in atmospheric suspended particulate matter over a one-year period in Tempe, Arizona. Filter samples were collected, processed and microplastics were counted under an optical microscope to obtain quantitative information of their presence and distribution in the atmosphere. Meteorological data (Average wind speed and Maximum wind speed) were investigated to understand meteorological impacts on observed airborne microplastic presence. Chemical characterization of microplastics was performed by micro-Raman spectroscopy to understand their chemical make-up and possible sources. Finally, laboratory experiments simulating weathering of microplastics were performed to understand how microplastics are altered under representative weathering processes.

2.3 Materials and methods

2.3.1 Sampling of microplastics suspended in air

Total Suspended Particulate matter (TSP) samples were collected from the observation deck of the Interdisciplinary Science and Technology building #4 on the Tempe campus of Arizona State University (33.4179° N, 111.9284° W) (Figure A1). The suburban location is bordered by the cities of Phoenix to the west and Scottsdale to the north, and suburban areas to the east and south. TSP samples were collected using a high-volume air sampler (Tisch Environmental Inc, OH, USA) by drawing air through pre-fired (650 °C, overnight) quartz fiber filters (Whatman QM-A, Sigma Aldrich, MO, USA) at a rate of 1.13 m^3/min for 24 hours, on a 1 in 6-day schedule from Oct 28th, 2020 to Nov 1st, 2021. The collected samples were covered with aluminum foil to avoid contamination and frozen until further sample processing.

2.3.2 Sample processing

TSP filter samples were extracted using ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) in a sonicating bath (Branson 5510, USA). The NOAA method for elimination of natural organic matter in water and beach sediment samples was applied and adapted as appropriate for the smaller sample amounts of the atmospheric microplastics, with lower volumes of reagents (same volume ratios), shorter oxidative time periods and lower applied temperatures (Marine Debris Program, 2015). In brief, a 10 mL aqueous 0.05 M Fe (II) solution prepared from $FeSO_4.7H_2O$ (Sigma Aldrich, MO, USA) and 10mL of 30% hydrogen peroxide (Sigma Aldrich, MO, USA) were added separately to the aqueous extracts to eliminate natural organic matter. The mixtures were left to stand for five minutes on a lab bench at room temperature and thereafter heated to 60°C on a hot

plate (Fischer Scientific, NH, USA). The solutions were vacuum filtered through baked glass microfiber filters (Whatman GF/A, Sigma Aldrich, MO, USA). The filters were oven-dried at 80°C until complete dryness in a Muffle furnace (Vulcan 3-1750, CA, USA). Three 2×2 $in.^2$ sections of the filter were analyzed for microplastics. Running blanks is important to account for background contamination during sampling, laboratory procedures, quantification and characterization of microplastics (Dawson et al., 2023; Prata et al., 2021). A field blank was run by allowing the high-volume sampler (lid closed) run with pre-fired quartz filters for one minute to account for possible contaminants from the pump. A procedural blank was run during all stages of sample handling and treatment. The procedural blank was made to undergo all stages of sample processing, including digestion. A test to assess recovery through matrix spikes was performed with a known number of microplastics (5 µm-5000 µm). Sample treatment was performed under a laminar flow hood. Glass and metal equipment were used during all stages of field sampling and sample treatment. All glassware was cleaned and baked prior to sample analysis. Glassware was soaked/washed with a detergent and rinsed three times with ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA). The clean equipment was covered from the field or laboratory environment due to potential contamination from microplastics through deposition. All working surfaces were cleaned prior to use by ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) and isopropyl alcohol (Fischer Scientific, MA, USA). Samples and working solutions were covered with watch glasses during analysis.

The usage of synthetic textiles was avoided as much as possible. Clothes were cleaned with a lint roller to remove any loose fibers. A fiber was drawn from the lab coat during

each day of laboratory analysis and analyzed under the optical microscope to check for fibers with similar appearance in samples.

Additionally, steps were taken to promptly close samples and reagent lids when pausing or at the end of sample analyses. Samples were covered with a watch glass during digestion.

2.3.3 Optical microscopy

Filters were examined under a digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software. The size range of interest was selected as 5 µm-5000 µm to provide an overview of the size distribution of microplastics and the morphology of microplastics present. The lower size limit of 5 µm was limited by the smallest possible size resolution of the digital microscope. As there is no standard definition for the distinction between a fiber and a fragment in microplastics literature, in the current study we used an operational definition for the observed shapes of microplastics. A fiber was recognized to be cylindrical in shape with an aspect ratio (length/ diameter) ≥ 3, while a fragment was recognized to be shard-like and flattened. Microplastics were sized along their largest dimension using the software program ImageJ (version 1.5, National Institute of Health, USA, http://imagej.nih.gov/i).

The following criteria are used to identify microplastics (Hidalgo-Ruz et al., 2012).

1. No Cellular or Organic Structures Visible.

2. Fibers should be equally thick throughout their entire length. This is generally true for fibers. However, sometimes splitting or fraying of fibers is observed. The fiber should depict 3-dimensional bending.

3. Particles should exhibit clear and homogeneous color throughout.

Exceptions- Some plastics are not entirely homogenous in color, with patterns and stripes. Biofouling can potentially alter color, or part of the fiber may be bleached. Weathered microplastics may exhibit loss of color towards the edges.

2.3.4 Statistical analysis and comparisons to meteorological data

Wind parameters were obtained from the weather station located at the sampling site (Earth Networks Inc., an AEM company, https://www.earthnetworks.com/). Regression analysis ($p \leq 0.05$) was performed using Microsoft Excel to check for a possible relationship between airborne microplastics, average wind speed and maximum wind speed.

2.3.5 Chemical characterization using Micro-Raman spectroscopy

Micro-Raman spectroscopy was used to determine the chemical composition of the microplastics. All microplastics counted under the optical microscope were analyzed under the micro-Raman spectrometer. In the case where an unclear spectrum was obtained for a microplastic, Raman spectra was obtained for two additional locations on the same microplastic. Raman data was collected from 50-3800 cm^{-1} using a custom-built microscope and a Mitutoyo M Plan Apo 50X/0.42 (Mitutoyo Corporation, Japan) objective. An Acton Research monochromator (SpectraPro-300i, Acton Corporation, MA) utilizing a 600 g/mm grating and coupled to a CCD (model LN/CCD 1340/100-

EB/1, Roper Scientific Inc, MA) recorded the signal. A Coherent Sapphire solid state cw (continuous wave) laser emitting 532 nm served as the excitation source and the data was calibrated using cyclohexane with known peak positions. The micro-Raman spectrometer has a spatial resolution of 1 µm and a spectral resolution of $1cm^{-1}$.

2.3.6 Laboratory simulations for weathering of microplastics to examine the impact on Raman spectra

Based on the largest manufactured volumes of plastic materials, Polyethylene terephthalate, Polyethylene, Polypropylene, Polystyrene and Polyvinyl chloride were selected to examine changes caused by weathering in Raman spectra of pristine plastics. Water bottles for Polyethylene terephthalate (PET), grocery bags for Polyethylene (PE), straws for Polypropylene (PP), coffee cup lids for Polystyrene (PS), and raincoats for Polyvinyl chloride (PVC) were utililized to simulate artificial weathering. The microplastics were of $1mm^2$ size with the thickness of these products ranging from 100 µm to 950 µm.

2.3.6.1 Physical abrasion

To simulate physical abrasion, sand samples were collected from a local roadway in Tempe. The samples were combusted at 450°C in a muffle furnace (Vulcan 3-1750, NJ, USA) for 4 hrs to remove organic matter. Plastic contaminants in the soil samples were removed by density separation using NaCl (Sigma Aldrich, MO, USA) as the flotation agent. The fresh plastic samples were placed in glass amber bottles with the pretreated soil (50 g) and were continuously rotated on a rotary shaker (Southwest STB1500, NJ, USA) to simulate physical abrasion. The microplastic samples were continuously treated

according to the above procedure for different time periods in days (14, 28, 42, 56, 70, 84 and 98 days) at room temperature. Thereafter the weathered microplastics were chemically characterized using micro-Raman spectroscopy. Five microplastics were analyzed under the micro-Raman spectrometer for each time step/period and composite spectra were obtained. The surface average roughness of pristine microplastics and physically abraded microplastics was measured using an optical profilometer (Zygo Zescope, CT, USA).

2.3.6.2 Chemical oxidation

Chemical oxidation was simulated by investigating the weathering of microplastics by heat- activated $K_2S_2O_8$ (Sigma Aldrich, MO, USA) treatments. Microplastic samples were introduced to 20 mL of 100 mM $K_2S_2O_8$ solution. Equal volumes of $K_2S_2O_8$ were added to the mixture every 3 days to replace consumed oxidant. The microplastic samples were continuously treated according to the above procedure for different time periods in days (14, 28, 42, 56, 70, 84, and 98 days) to observe a possible gradual change in the Raman spectra over time. The artificially weathered microplastics were chemically characterized using micro-Raman spectroscopy. Five microplastics were analyzed under the micro-Raman spectrometer for each time step/period and composite spectra were obtained.

2.3.6.3 UV exposure

Fresh microplastics samples in glass petri dishes were exposed to UV C and UV A/B light (200 to 400 nm) (Coospider, Paris, France) in a custom-made UV chamber for different time periods in days to simulate artificial aging from UV exposure. A powered fan (Wathai, China) was installed in the unit was used to prevent excess heat from building up in the UV Chamber. The microplastic samples were continuously treated according to the above procedure for different time periods in days (14, 28, 42, 56, 70, 84 and 98 days). Thereafter the weathered microplastics were chemically characterized using micro-Raman spectroscopy. Five microplastics were analyzed under the micro-Raman spectrometer for each time step/period and composite spectra were obtained.

2.4 Results and discussion

2.4.1 Microplastics suspended in air

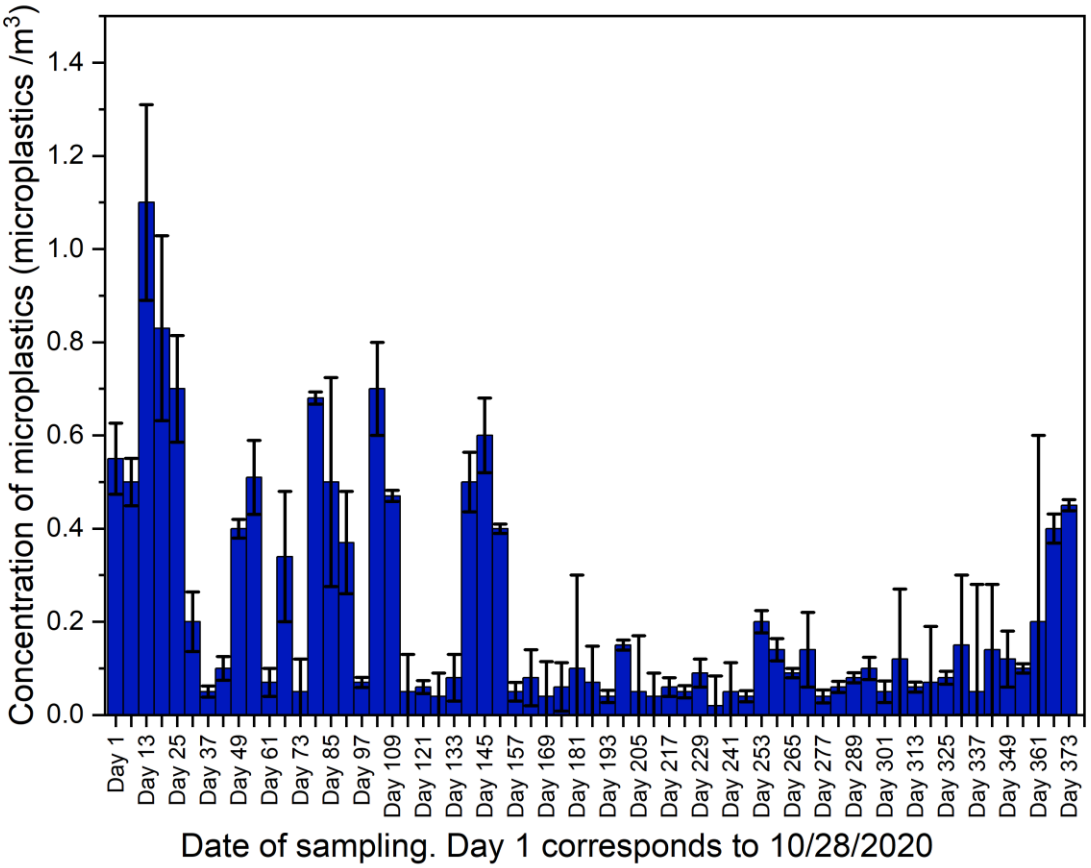

Figure 2.1 Microplastics in suspended particulate matter in Tempe, AZ, USA. Each error bar represents the standard deviation of the mean obtained from three replicate measurements.

Microplastics were present in all collected samples, thereby indicating the ubiquitous presence of microplastics in the local atmospheric environment. Microplastics were found to range between 0.02 to 1.1 microplastics/m^3 with an average concentration of 0.2 microplastics/m^3 and a median of 0.1 microplastics/m^3. Three replicates were analyzed for each sampling period throughout the period of one year. A total average of 1020 microplastics were counted under the optical microscope in all samples (average of three replicates). The blank filters identified microplastics through contamination and were

found to range between 2 to 7 microplastics/filter with an average of 3 microplastics/filter. Matrix spikes of microplastics (5 µm -5000 µm) to assess for recovery of microplastics showed a recovery percentage of 94%. Microplastics concentrations were calculated as Table A1.

Each bar in Figure 2.2 represents the average microplastics concentration over the course of 24 hours (one sampling period). The error bar in Figure 2.2 depicts the standard deviation of the average obtained from three replicate measurements. To put microplastics concentrations into context, it is necessary to compare with other existing research studies (Table 2.1). The following is not an exhaustive comparison. The average concentration of microplastics in the local atmosphere in Tempe, USA is lower than what has been previously reported in Shanghai, China (approximately 6 times) and Paris France (approximately 4 times) (Dris et al., 2017; Liu et al., 2019a). The author attributes the high concentrations in Shanghai, China to the density of buildings and a common customary practice of drying clothes in natural sunlight in the study location. The higher microplastics concentration in Paris, France is attributed to the higher population density and industrial activities. The average concentration in Tempe is one order of magnitude higher than what has been published in the atmosphere over the West Pacific Ocean (Liu et al., 2019b). The sampling location over the West Pacific Ocean is reasonably away from point locations and hence could explain the lower concentrations over the ocean. The average concentration in Tempe is higher than what is reported in Ahvaz City, Iran (approximately 40 times)(Abbasi et al., 2023).The size range of interest in the study at Ahvaz City was ≤ 10 µm and is attributed by the author as the reason for observing lower concentrations at the study site. A relatively higher airborne

microplastics concentration was reported in Beijing where SEM coupled with Energy Dispersive X-ray Detecting (EDX) was used (Li et al., 2020). However, it should be noted that the analyzed size ranges differ across published studies, with different processing and chemical characterization techniques. Therefore, comparing microplastic concentrations is fraught with difficulties.

Table 2.1 Summary of airborne microplastics reported in previous studies.

Location	Microplastics/m^3	Size range/ µm	References
Wenzhou, Eastern China	188.7 ± 84.8	5–1794	Liao et al., 2021
Ahvaz City,Iran	0-0.017	<10	Abbasi et al., 2023
Beijing, China	4500–7200	5–200	Li et al., 2020
Paris, France	0.3–1.5	50-1650	Dris et al., 2017
Shanghai, China	1.42 ± 1.42	23-9555	Liu et al., 2019
Surabaya, Indonesia	55.93–174.97	< 500–5000	Syafei et al.,2019
West Pacific Ocean	0-1.37	16–2087	Liu et al., 2019b
Tempe, USA	0.2 (0.02-1.1)	5-5000	Current study

Fibrous microplastics accounted for the large majority (≥82 %) of the microplastics suspended in air in all samples (Figure A2). Fibers are likely to enter the environment as secondary microplastics. Fragments were observed as the only other morphology present and could originate possibly from thicker plastic products (Figure A2). No spherical pellets and beads were observed in the samples. Studies have reported shape-dependent health effects, and shape can be considered a key indicator for the degradation and decomposition of microplastics (Andrady, 2011; Bergmann et al., 2015; Ebrahimi et al., 2022). The shape of microplastics can also be used to predict their origin because certain shapes, such as fibers, may shed from synthetic textiles, carpets, and upholstery (Liu et al., 2019).

2.4.2 Particle Size

A normalized size distribution of microplastics present during all sampling periods of the current study was analyzed (Figure 2.2). The highest count for microplastics was observed between 5 µm-100 µm during all sampling periods.

The higher counts of microplastics in the smaller size classes can be explained by the atmospheric residence time of particles. Smaller particles generally have a larger surface area to mass ratio, and therefore have longer atmospheric residence times when compared to that of larger particles. Hence it is not surprising that the smaller particles investigated are also the most abundant.

Considering the hypothetical degradation of a large microplastic, a cubic millimeter microplastic can give rise to 1000 particles of 1 µm. Therefore, one would expect the presence of a large number of smaller microplastics in the environment when compared to larger microplastics. The contribution to $PM_{2.5}$ is not known as the current study examines microplastics larger than 5 µm in size. Smaller plastic particles in the atmosphere have the potential to scatter and absorb light and thereby could change the earth's effective radiative forcing.

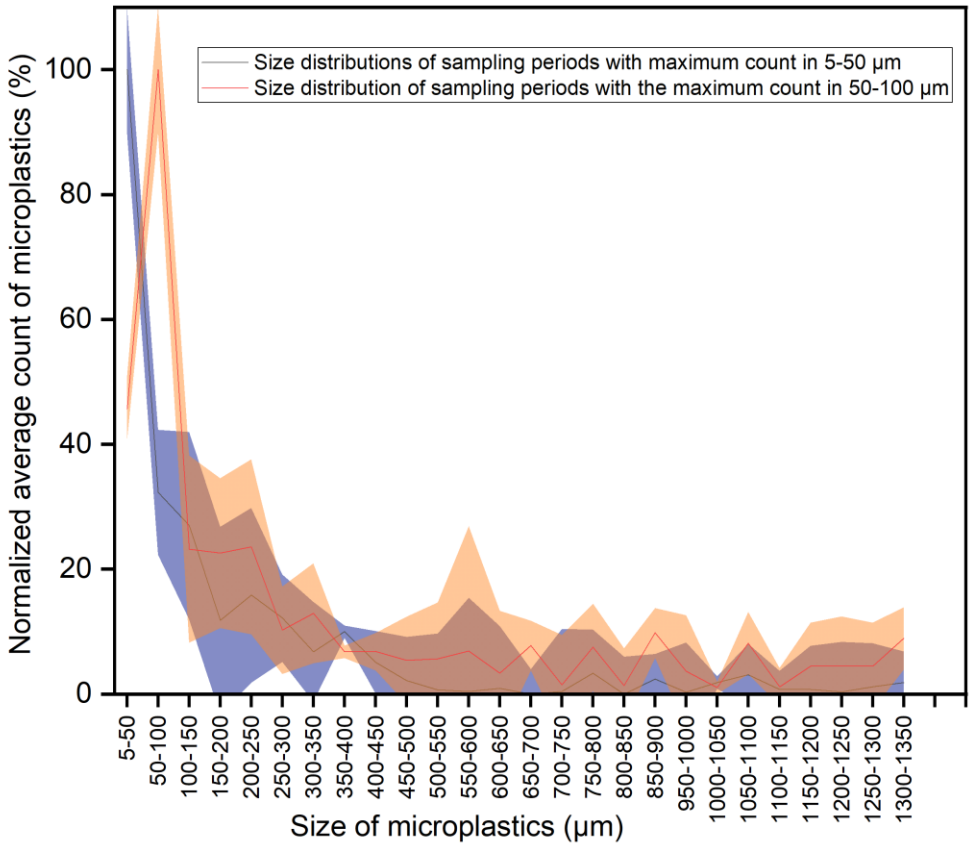

Figure 2.2 Normalized percent size distributions of microplastics in suspended particulate matter. Shaded error bars represent the standard deviation of the mean

2.4.3 Microplastics suspended in air compared to meteorological data

Regression analysis for airborne microplastics and average wind speed ($r^2 = 0.022$, $p = 0.24$), maximum wind speed ($r^2 = 0.023$, $p=0.0014$) indicate no correlation between the variables (Figure A3 and Figure A4). This suggests that weather parameters such as wind speed may not solely govern the distribution of airborne microplastics and so the airborne concentrations do not appear to be purely a function of airborne re-entrainment of deposited material.

Although not included in Figure 2.1 (1 in 6 schedule sampling), suspended particulate matter was sampled continuously during the months of the North American monsoon season. During the North American monsoon season, Phoenix, Arizona routinely experiences dust storms (Eagar et al., 2017). During the monsoon season, opportunistic samples, outside of the regular monitoring, were collected during only the storm impacted times (i.e., just before the storm started the sampler was manually started and stopped when the storm dissipated). In one such dust storm on July 9, 2021, microplastics were measured at 1.9 MPs/m^3. This suggests that local dust storms can affect the concentration of microplastics in the air.

2.4.4 Chemical characterization of microplastics

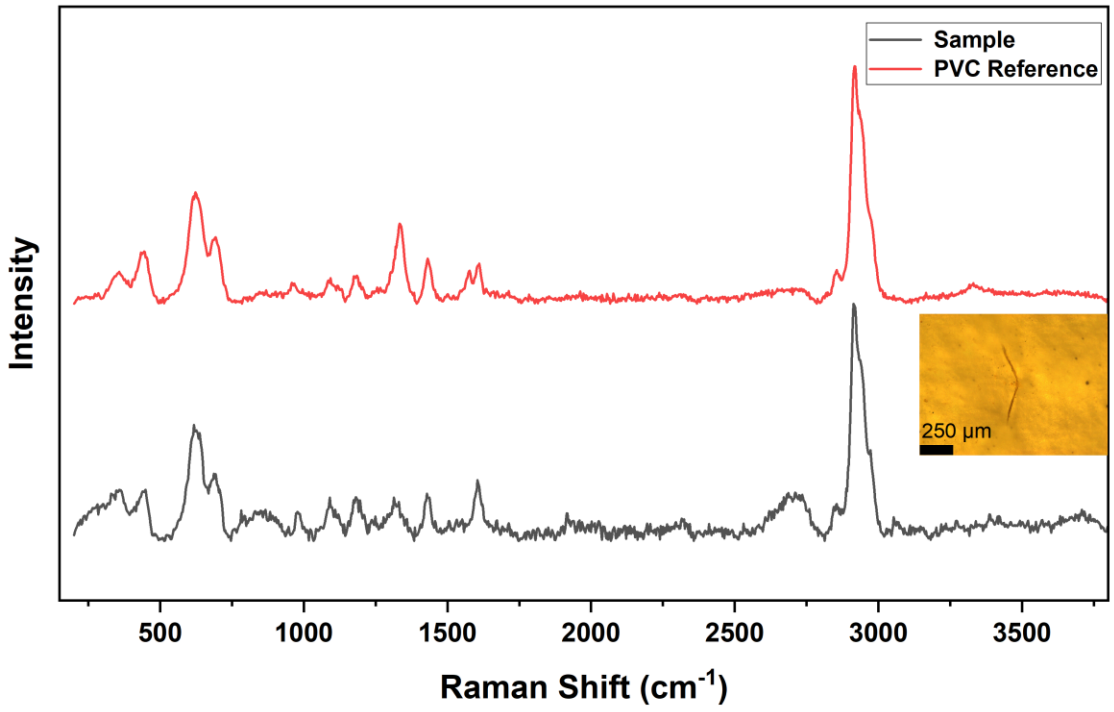

Figure 2.3 Micro Raman spectrum and the corresponding image of a sample verified as PVC

Micro-Raman spectroscopy was used to identify the nature of the microplastics suspended in air. Chemical characterization revealed that the most abundant identified polymer was polyvinyl chloride (19%) (Figure 2.3) followed by polyester (15%) (Figure A5), polystyrene (7%) (Figure A6) and polyethylene (1%) (Figure A7). A large majority of microplastics (58%) remain unidentifiable in our study. Polyethylene and polystyrene fragments could possibly originate from the fragmentation and weathering of packaging and insulating material. Textiles are a possible source for polyvinyl chloride and polyester; polyester ranks first in the list of the most popular man-made fibers in the world (Prata et al., 2020). A recent study shows that the secondary emission of polyester

microfibers per person per year to the air is of a similar order of magnitude compared to that released to wastewater by laundering (De Falco et al., 2020).

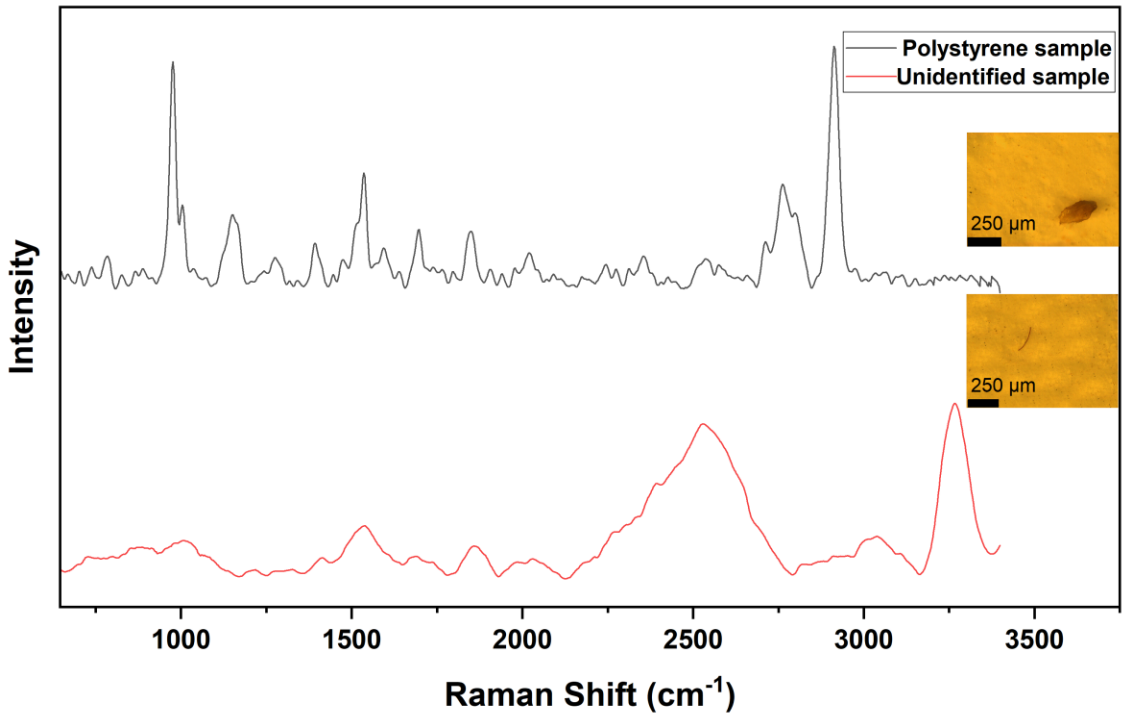

Figure 2.4 Comparison of an unidentifiable and polystyrene micro-Raman spectra

Spectra lacking characteristic peaks were obtained during micro-Raman spectroscopic analysis, thereby making the chemical identification process more challenging. Figure 2.4 depicts a typical example of a spectrum lacking sharp identifiable Raman peaks compared to an identified polystyrene sample. Here we hypothesize that weathering of microplastics is a possible explanation for the observations. Microplastics undergo aging in the environment, causing the Raman spectra to distinctly change from that of pristine plastics over time. While micro-Raman spectroscopy has gradually emerged to be a popular technique for chemical characterization of microplastics during recent years,

there also exists a major challenge during chemical identification. Once released from point sources, microplastics can undergo various weathering processes, including physical abrasion, exposure to ultraviolet (UV) radiation, and chemical oxidation (Andrady, 2011; Liu et al., 2020). Raman spectroscopy is a surface characterization technique. These weathering processes could change the physical (surface) and chemical properties of microplastics, thereby rendering them unidentifiable using a characterization technique and changing their environmental behavior.

2.4.5 Impact on Raman spectra of microplastics by laboratory simulations of weathering processes

2.4.5.1 Physical Abrasion

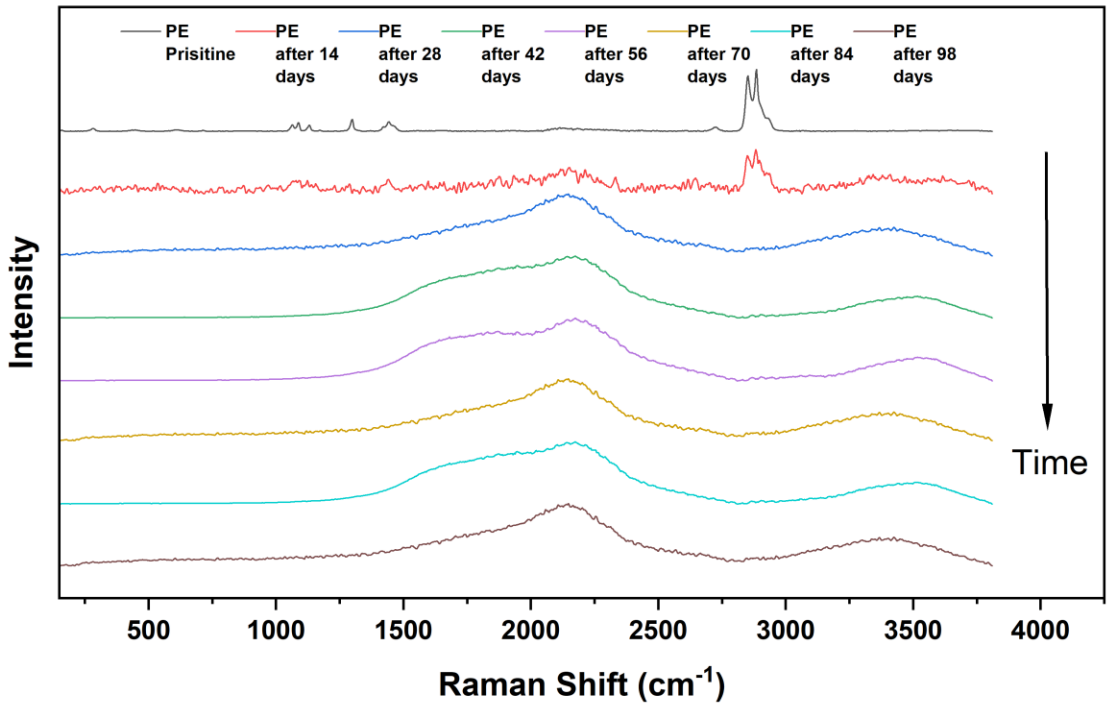

Figure 2.5 Raman spectra of polyethylene exposed to weathering by physical abrasion over time

Raman spectra of a physically abraded polyethylene microplastic appeared to be distinctly different from that of pristine polyethylene (Figure 2.5). Similar Raman spectra lacking characteristic identifiable peaks were observed for microplastics in samples. Raman spectroscopy is based on the inelastic scattering of light on a surface. Physical abrasion can cause micro-scratches on the surface of the plastic, thereby due to stray light can hinder the correct identification of the nature of the microplastic. Surface average roughness measurements for pristine microplastics (0.66 µm) compared to microplastics

physically abraded for 14 weeks (2.66 µm) depicted a substantial increase in the roughness of the surface. They ranged from 99.2 to 949.8 µm in thickness. However, a large change in the Raman spectra was not observed for the remaining pristine microplastics (PS, PVC, PET, PP) (Figure A8, A9, A10, A11). This suggests that the nature of the plastic can be factor that determines the extent it undergoes weathering.

2.4.5.2 Chemical Oxidation

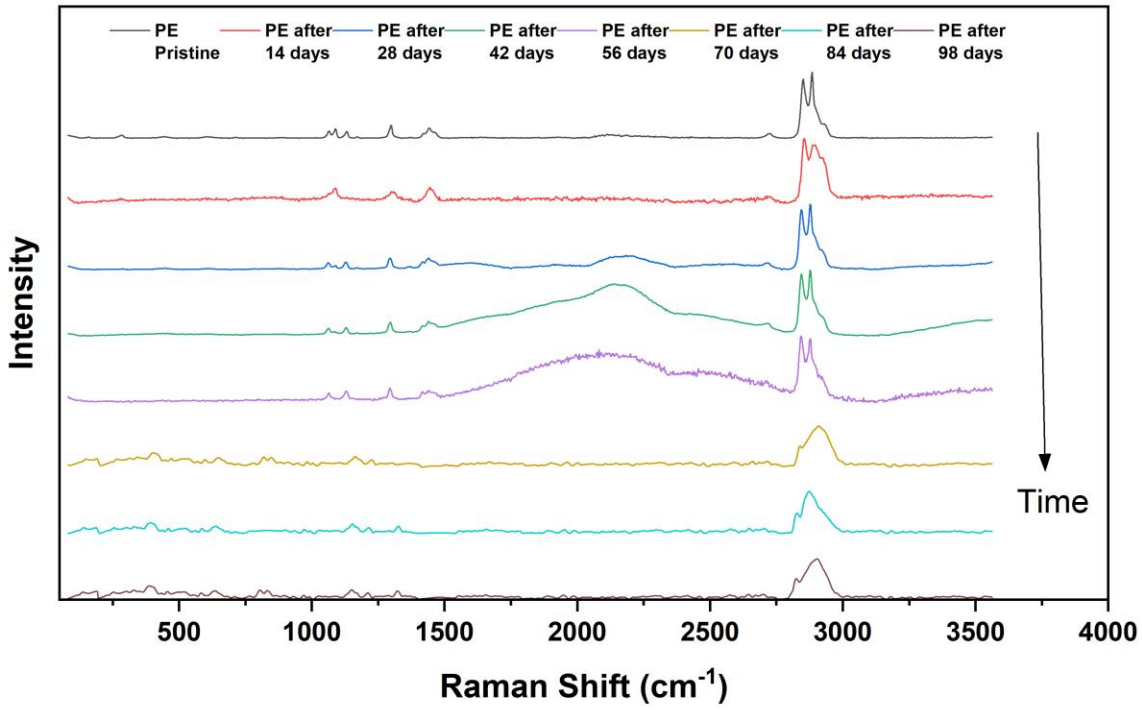

Figure 2.6 Raman spectra of polyethylene exposed to weathering by chemical oxidation over time

Raman Spectra of a polyethylene microplastic weathered through chemical oxidation did not depict a distinct change over the course of time (Figure 2.6). This suggests that to observe a significant change in Raman spectra, oxidative weathering simulations must be performed over a longer period. However, the CH_2 peak around 2900 cm^{-1} appears to be

less intense as time progresses. Raman spectra for the remaining pristine microplastics (PS, PVC, PET, PP) did not depict a clear change over time (Figure A12, A13, A14, A15).

2.4.5.3 UV Exposure

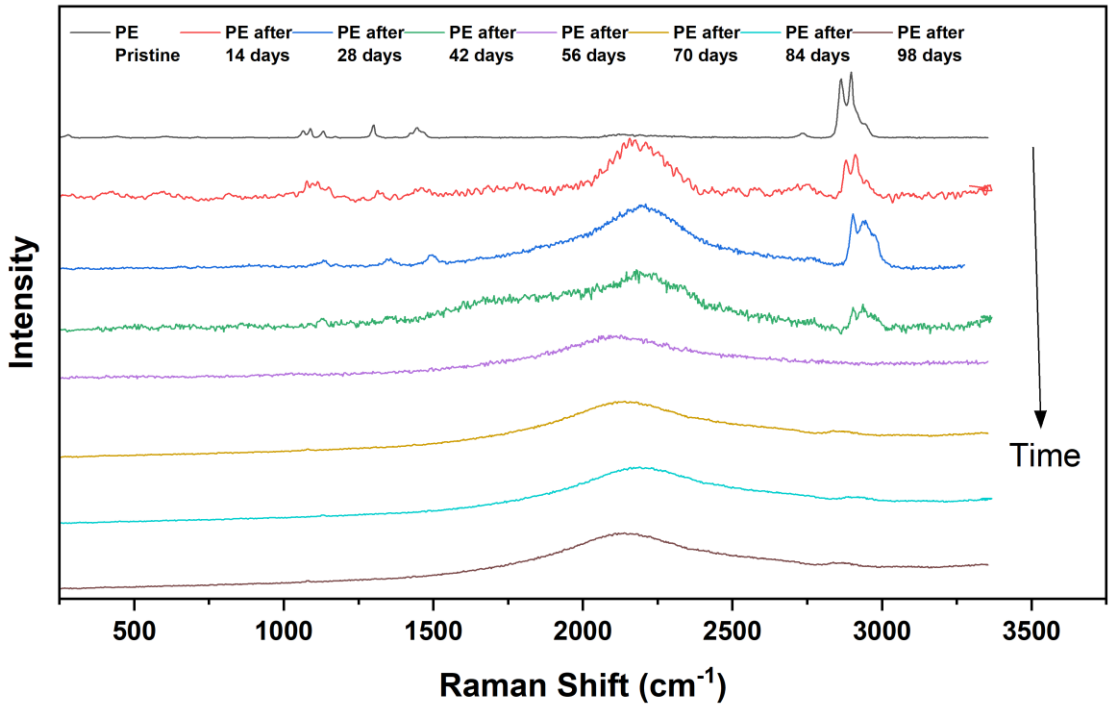

Figure 2.7 Raman spectra of polyethylene exposed to weathering by UV Exposure over time

Raman spectra of a PE microplastic weathered by UV exposure shows a distinct change as time progresses (Figure 2.7), thereby indicating how weathering can alter the chemical composition of the plastic. Raman spectra for the remaining pristine microplastics (PS, PVC, PET, PP) did not depict a clear change over time (Figure A16, A17, A18, A19).

2.5 Conclusions

The results of the current study measured microplastics in total suspended particulate matter in Tempe, Arizona. Microplastics were present in all collected samples, indicating their ubiquitous presence in the atmosphere. The majority of microplastics were fibers (≥82%), with the predominant particles present in smaller size classes (5 µm-100 µm). Microplastics concentrations were not correlated with $PM_{2.5}$, PM_{10}, average wind speed and maximum wind speed. However, it was observed that microplastics concentration can be affected by episodic influences such as local dust storms.

A large majority of sampled microplastics remain chemically unidentifiable. Spectral matching with reference microplastics becomes increasingly challenging due to possible weathering processes undergone by microplastics. Laboratory simulations of weathering processes for pristine plastics depicted that microplastics can undergo significant physical and chemical changes, thereby rendering aged microplastics collected from the environment as chemically unidentifiable. Further, this physical and chemical alteration could potentially impact how these microplastics behave in the environment. Weathering could modify surface polarity thereby increasing their interaction with polar compounds in the environment.

2.6 Acknowledgements

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CHAPTER 3

MICROPLASTICS ARE UBIQUITOUS AND INCREASING IN SOIL OF A SPRAWLING URBAN AREA, PHOENIX (ARIZONA)

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3.1 Abstract

Microplastics are environmental contaminants that have been extensively studied in marine and aquatic environments; terrestrial ecosystems, where most microplastics originate and have the potential to accumulate, typically receive less attention. This study aims to investigate the spatial and temporal soil concentrations of microplastics in a large desert metropolitan area, the Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER) area. Soil samples from the Ecological Survey of Central Arizona (ESCA) surveys (2005 and 2015) were leveraged to study spatial distributions and the temporal change of microplastic abundances. The temporal soil microplastics data were supplemented by microplastics deposition fluxes in a central location within the area (Tempe, AZ) for a period of one year (Oct 5th, 2020 to Sept 22nd, 2021). Samples were processed and microplastics were counted under an optical microscope to obtain

quantitative information of their distribution in soil. Results for the spatial variation of the microplastic abundances in soil samples in Phoenix and the surrounding areas of the Sonoran Desert from 2015 depict microplastics as ubiquitous and abundant in soils (122 to 1299 microplastics/kg) with no clear trends between different locations. Microplastics deposition fluxes show substantial deposition in the local area (71 to 389 microplastics/m^2/day with an average deposition flux of 178 microplastics/m^2/day) but the role of resuspension and redistribution by dust storms to deposition may contribute to the unclear spatial trends. Comparison between the 2005 and 2015 surveys show a systematic increase in the abundance of microplastics and a decrease in microplastics size. Micro-Raman spectroscopy identified a variety of plastics including PE, PS, PVC, PA, PES and PP. However, a majority of microplastics remained chemically unidentifiable. Polyethylene was present in 75% of the sampling sites and was the most abundant polymer on average in all soil samples.

3.2 Introduction

Microplastics are a growing concern as pervasive environmental pollutants. They are mostly secondary in nature and result from the breakdown of larger plastics over time into microplastics, generally defined as plastic particles less than 5 mm in size (Arthur et al., 2009). Primary microplastics are purposefully manufactured at this small size, tend to have uniform shapes including spherical microbeads, and originate from sources such as personal care and abrasive cleaning products (Revell et al., 2021). Secondary microplastics generally exhibit more diverse shapes.

Existing research shows that microplastics are found in interconnected environments; from the Artic to Antarctica, including the depths of oceans, freshwater bodies, atmospheric deposition and soil environments (Patil et al., 2022; Li et al., 2023; Zhao et al., 2023). While numerous studies have investigated the occurrence and abundance of microplastics in marine and freshwater environments (Andrady, 2011; Eriksen et al., 2013; Horton et al., 2017; Bergmann et al., 2017; Klein and Fischer, 2019; Chandrakanthan et al., 2023) research in terrestrial ecosystems remains less well developed despite the fact that a majority of the plastic debris reaching the oceans has originated on land (Lebreton et al., 2022).

A review study has estimated that the annual release of plastic waste to land is 4-23 times greater than that released to the oceans (Horton et al., 2017). Although soil microplastics were first reported in 2016 (Ding et al., 2022), microplastics research in terrestrial ecosystems remains underrepresented and accounts for only about 5% of the research on microplastics (Ding et al., 2022). Street runoff, landfills and atmospheric

deposition are potential input pathways of microplastics into terrestrial ecosystems, making soils a significant sink for synthetic microparticles in terrestrial ecosystems (Möller et al., 2020). Moreover, plastic mulch films and soil conditioners used in agricultural amendments are potential sources of soil microplastics (Ng et al., 2018). Soils can also act as a source of atmospheric microplastics to other environmental reservoirs through resuspension of fugitive dust, thereby contributing to the global microplastics transport cycle (Zhang et al., 2020).

Microplastics in terrestrial environments can cause changes in soil ecosystems affecting soil structure, plant growth and microbial activity (De Souza Machado et al., 2019). A meta-analysis in agricultural soils in China revealed that microplastics affect soil enzymes including fluorescein diacetate hydrolase and urease, influence the bulk density of soil, and interfere crop growth (Hu et al., 2022). Furthermore, plants and crops are likely to uptake microplastics present in soil, subsequently becoming a source of microplastics present in plant-derived food used for human consumption (Liang et al., 2023). In soil environments, microplastics can degrade through microbial action as microorganisms can utilize the carbon in plastic polymer chains for their growth (Mohanan et al., 2020; Huang et al., 2023). Owing to the low organic matter in dryland soils (Marusenko et al., 2011), soil microbes in these locations may resort to metabolize anthropogenic carbon sources such as microplastics. Studies have shown microplastics to have an acute toxic effect on soil organisms such as nematodes (Kim et al., 2020). In addition to the direct toxic effects caused by microplastics, they can also act as vectors of other contaminants such as Polycyclic Aromatic Hydrocarbons (PAHs) and metals found in soils (Hildebrandt et al., 2021; Hu et al., 2022).

This study investigates soil concentrations and deposition fluxes of microplastics in the Phoenix, AZ, metropolitan area. The study area is vast (6400 km^2) and is a rapidly growing urban metropolis that has been intensively studied for urban ecology for over 20 years (Grimm and Redman, 2004). Our study utilizes samples from the Ecological Survey of Central Arizona (ESCA) performed by the Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER), a large-scale field survey that is conducted in the CAP-LTER study area characterizing the urbanized, suburbanized, and agricultural areas of metropolitan Phoenix and the surrounding Sonoran Desert (Grimm and Redman, 2004). Previous studies have investigated various key ecological indicators and contaminants, including soot black carbon concentrations and isotopic compositions, PAHs and lead concentrations in soils (Marusenko et al., 2011; Zhuo et al., 2012; Hamilton and Hartnett, 2013). We leveraged the Ecological Survey of Central Arizona (ESCA) 200-point survey (2005 and 2015) to study spatial distributions and the temporal change of microplastic abundances. We supplement the temporal data in soils with the collection of atmospheric deposition fluxes of microplastics in a central location within the area (Tempe, AZ) for a period of one year (Oct 5th, 2020 to Sept 22nd, 2021). All soil and deposition samples were processed and characterized using an optical microscope to obtain quantitative information of the distribution of microplastics. Chemical characterization of microplastics was performed by micro-Raman spectroscopy to understand their chemical composition.

3.3 Materials and methods

3.3.1 Sampling of microplastics

3.3.1.1 Sampling of microplastics in soil

Soil samples used in the study were collected by CAP-LTER from the ESCA 200-point survey (2005 and 2015). CAP-LTER program is one of twenty-eight LTER sites funded by the National Science Foundation and is one of the two LTER sites that specifically study urban ecology (Grimm and Redman, 2004). CAP-LTER studies how human activities alter the functioning of ecosystems, and subsequently urban sustainability, in Central Arizona and metropolitan Phoenix where two tributaries of the Colorado River, the Salt and Gila Rivers, merge (Grimm et al., 2013). The ESCA 200-point survey is a field survey that is conducted every 5 years at approximately 200 sample plots randomly located in the urbanized, suburbanized, and agricultural areas of metropolitan Phoenix, and the surrounding Sonoran Desert (Figure B1) (Grimm and Redman, 2004). The sampling plots (30m x 30m) are randomly located using a tessellation-stratified dual-density sampling scheme. Forty-eight samples from 2015 were selected to study the spatial variation aspect, while fourteen samples from 2005 and 2015 were analyzed for the temporal variation of microplastics. Topsoil samples (2 cm depth) were used for this study as this range could be expected to have the highest abundance of microplastics accumulated over time by direct input from terrestrial sources and atmospheric deposition. Top soil samples from the same study area were sampled and analyzed in a previous study for other environmental contaminants, such as PAHs (Marusenko et al., 2011). The soils analyzed in this study are desert soil samples, mainly from urban and suburban areas of metropolitan Phoenix and remote areas in the surrounding areas of the

Sonoran Desert. According to the United States Department of Agriculture – National Resource Conservation Service (USDA-NRCS, http://soils.usda.gov/), soils in Central Arizona are classified as aridisols (too dry for the growth of mesophytic plant life) and entisols (little to no evidence of developing pedogenic horizons) (Bohn et al.,2001; Hamilton and Hartnett, 2013).

3.3.1.2 Sampling of microplastics in air

Total atmospheric fallout (dry and wet deposition) samples were collected by means of glass funnels in 4L glass bottles (Figure B2) on the observation deck of the Interdisciplinary Science & Technology Building #4 on the Tempe campus of Arizona State University (33.4179° N, 111.9284° W). Samples were collected for 14 days each, from Oct 5th, 2020 to Sept 22nd, 2021. The suburban location is located in the city of Tempe, Arizona, approximately eight miles east of downtown Phoenix. Once collected, the samples were covered with aluminum foil to prevent contamination.

3.3.2 Sample processing

The soil samples were weighed (60g) and sieved (8"-FH-SS-SS-US-#3-1/2, Hogentogler & Co.Inc., MD, USA) to remove material larger than 5.6 mm. The following approach was based on the methods manual from the National Oceanic and Atmospheric Administration (NOAA) for microplastics analyses in water and beach sediment samples and adapted as appropriate to process the soil samples (Masura et al., 2015; Chandrakanthan et al., 2023). First, sieved samples were subjected to wet peroxide oxidation to remove natural organic matter. A 10 mL aqueous 0.05 M Fe (II) solution prepared from $FeSO_4.7H_2O$ (Sigma Aldrich, MO, USA) and 10mL of 30% hydrogen peroxide (Sigma Aldrich, MO, USA) were added to samples for 5 minutes at room temperature and subsequently heated to 60°C on a hot plate (Fischer Scientific, NH, USA) to remove naturally occurring organic matter. Samples were subsequently made to undergo a density separation step using a 1.8 g cm^{-3} NaI solution prepared from NaI (Sigma Aldrich, MO, USA). The saturated NaI solution allows the separation of

microplastics, including relatively denser plastics such as PVC (≤1.58 g cm^{-3}) from the sample (Nuelle et al., 2014; Zhang and Liu, 2018). After allowing solids to settle, the floating microplastics were filtered through pre-fired glass microfiber filters (Whatman GF/A, Sigma Aldrich, MO, USA). The filters were oven-dried at 80°C until complete dryness in a Muffle furnace (Vulcan 3-1750, CA, USA).

The sample collectors for total atmospheric fallout (funnel and bottle) were thoroughly rinsed thrice with ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) to ensure that all microplastics adhering to the glass surface were recovered. Samples were processed similar to an approach adopted in a recent study reporting microplastics suspended in air in Tempe, AZ (Chandrakanthan et al., 2023). The aqueous extracts were obtained and subjected to wet peroxide oxidation to eliminate natural organic matter. The solutions were vacuum filtered through baked glass fiber filters (Whatman GF/A, Sigma Aldrich, MO, USA). The filters were then oven-dried at 80 °C to complete dryness in a Muffle furnace (Vulcan 3–1750, CA, USA).

Preventive measures to minimize background contamination during microplastics analyses is important to produce reliable results (Prata et al., 2021; Shanmugam et al., 2022; Hidalgo et al., 2023). A procedural blank was run during all stages of sample processing including wet peroxide oxidation, density separation and subsequent analyses. Glassware washed with a detergent and rinsed three times with ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) were subsequently baked and used during all stages of sample processing and analyses. The clean equipment was covered to minimize potential airborne microplastics contamination. Working surfaces were cleaned with ultrapure

water (>18.4 MΩ cm, Purelab Flex, IL, USA) and isopropyl alcohol (Fischer Scientific, MA, USA) prior to sample analyses. The usage of synthetic textiles was minimized, and a fiber was drawn from the lab coat during each day of laboratory analysis and observed under the optical microscope to check for fibers with similar appearance in samples. The recovery percentage of microplastics from filters was assessed through matrix spikes with a known number of microplastics (5 µm-5000 µm). A soil sample (60g) sourced from the ESCA 200-point survey in 2015 was spiked with a known number of microplastics (n=60). The microplastics were photographed and sized using a digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software prior to spiking, and were distinctive of color and shape. The artificially incorporated microplastics included Polyethylene (PE), Polypropylene (PP), Polyvinyl Chloride (PVC), Polystyrene (PS) and Polyethylene terephthalate (PET) ranging in size from 5 µm - 5000 µm. The spiked soil sample was subjected to wet peroxide oxidation and subsequently density separation similar to the approach in Section 2.2. The spiked microplastics were observed on a filter under the digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software. The recovery test showed a recovery of 95% of spiked microplastics.

3.3.3 Optical microscopy

Filters were examined under a digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software. The size range of interest was selected as 5 µm - 5000 µm; both the size and the morphology of each microplastic was noted to characterize each sample. The lower size limit is 5 µm due to the smallest possible size resolution of the digital microscope. As there is no standard definition for the distinction between a fiber and a fragment in the microplastics literature, we used an operational definition for the observed shapes of microplastics where a fiber was recognized to be cylindrical in shape with an aspect ratio (length/diameter) ≥ 3, while a fragment was recognized to be shard-like and flattened. Microplastics were sized along their largest dimension using the software program ImageJ (version 1.5, National Institute of Health, USA, http://imagej.nih.gov/i).

The following criteria were used to identify microplastics under the optical microscope (Hidalgo-Ruz et al., 2012; Chandrakanthan et al., 2023). Only objects that did not display cellular or organic structures were identified as microplastics. Further, only fibers that were generally equally thick through their entire length exhibiting 3-dimensional bending were identified as microplastics with further accounting for fiber splitting which can occur in microplastic fibers. Finally, particles that exhibit clear and homogenous color throughout their entire structure were identified as microplastics with the exception of the appearance of bleaching, biofouling and weathering which could cause patterns or stripes.

3.3.4 Statistical Analysis of the temporal variation of soil microplastics (2005 and 2015)

A Mann-Whitney Test ($p \leq 0.05$) was performed using OriginPro, Version 2023 (Origin Lab Corporation, Northampton, MA, USA) to compare differences between the soil microplastic abundances in 2005 and 2015.

3.3.5 Chemical characterization using Micro-Raman spectroscopy

Micro-Raman spectroscopy was used to provide chemical characterization of the polymers in identified microplastics. All microplastics counted under the optical microscope were analyzed under the micro-Raman spectrometer. Raman data was collected from 50-3800 cm^{-1} using a custom-built microscope and a Mitutoyo M Plan Apo 50X/0.42 objective. An Acton Research monochromator (SpectraPro-300i) utilizing a 600 g/mm grating and coupled to a Roper Scientific CCD (model LN/CCD 1340/100-EB/1) recorded the signal. A Coherent Sapphire solid state cw laser emitting 532 nm served as the excitation source and the data was calibrated using cyclohexane with known peak positions. The spatial and spectral resolutions of the micro-Raman spectrometer were 1 µm and $1cm^{-1}$ respectively.

3.4 Results and Discussion

3.4.1 Spatial Variation of microplastics

Microplastics were found in all soil samples, thereby indicating their ubiquitous presence in soil environments in Phoenix and surrounding areas of the Sonoran Desert (Figure B3). The microplastic abundance in soil samples from 2015 ranged from 122 to 1399 microplastics/kg with a heterogeneous spatial distribution depicting no clear spatial trends (Figure 3.1). Three replicates sampled were analyzed for each sampling location (Table B1). The relative standard deviation of the measurements was on average 6%. The highest microplastic abundance was found at Site 14 which is located in a residential area within the city of Phoenix, AZ. The lowest microplastic abundance was observed at sampling Site 8; a residential location within the city of Peoria, AZ.

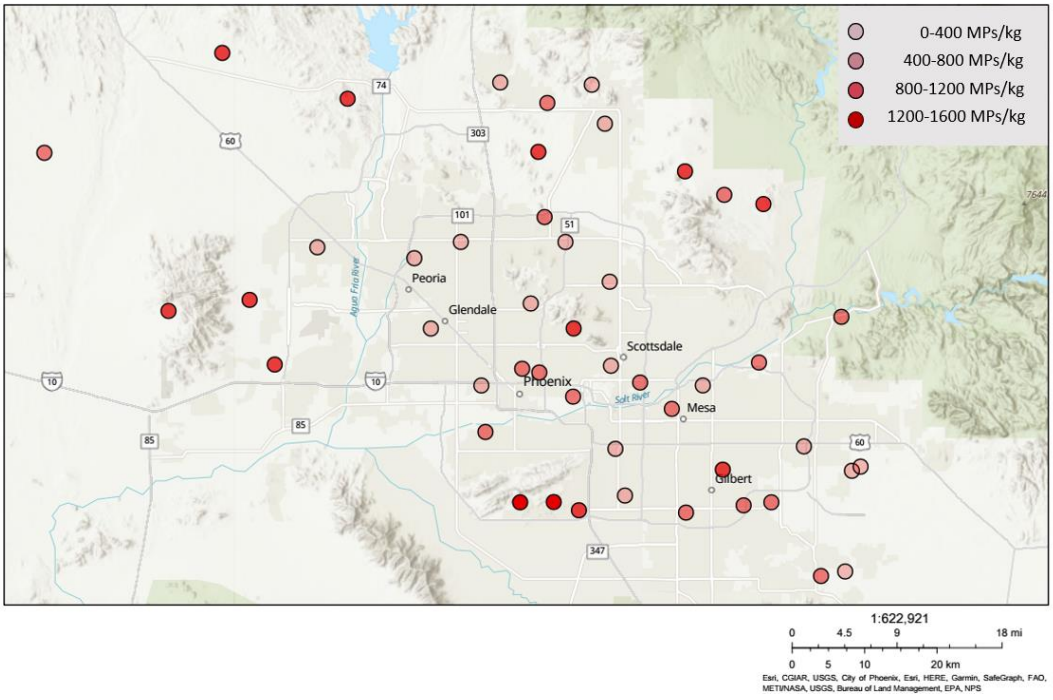

Figure 3.1 Spatial distribution of microplastics in soil samples from 2015

Sampling sites K6, I14, L14, U21, AB19 had higher microplastics abundances compared to other sampling locations and were in the vicinity of roadsides or public alleyways.

Comparing the observed microplastic abundances with those reported in literature is not straightforward due to the discrepancies in sampling approaches, sample processing, microplastics identification, operational definitions of microplastics and instrument detection limits. However, it can be useful to put microplastic abundances in soil into context by comparing with other existing studies (Table 3.3.3). A recent review reported that microplastics in soil globally range from 0.36 to 160,000 microplastics/kg, where a majority of the reported studies are from China (Zhang et al., 2022). Microplastic abundances reported in Lut and Kavir Deserts in Iran, Northeast Tibetan Plateau in China, Swiss Flood plain soils and Badain Jaran Desert in China are 1-2 orders of magnitude lower than that observed in the current study (Scheurer and Bigalke, 2018; Feng et al., 2020; Abbasi et al., 2021; Li et al., 2022). This could be attributed to the relatively higher lower size limits of interest in the aforementioned studies (≤ 100 µm, 20 µm, 125 µm and 40 µm) when compared to that of the current study (5 µm) as this study observed a greater number of microplastics in the smaller size categories (Section 3.3.3). The observed differences in microplastic abundance could also be attributed to the differences in microplastics input via dry and wet deposition, resuspension and dilution by mobile dust/sand particles, and environmental conditions that can weather microplastics to sizes that evade identification by the analytical techniques used in each study (e.g. make particles smaller). The microplastic abundances in the current study is an order of magnitude lower than that reported in Lahore, Pakistan (Rafique et al., 2020);

note this study specifically links the high measured microplastics abundance to high population density in the study area.

Table 3.1 Summary of soil microplastics reported in previous studies.

Location	Microplastics/kg	Size range/μm	References
Lut and Kavir Deserts, Iran	20 (0-83)	≤100-500	(Abbasi et al., 2021)
Northeast Tibetan Plateau, China	47 (20-110)	20-5000	(Feng et al., 2020)
Swiss Flood plain soils	≤593	125-5000	(Scheurer and Bigalke, 2018)
Northern Germany farmland soils	4 ± 12	1000-5000	(Harms et al.,2021)
Shanghai, China farmland soils	78 ± 13	30-5000	(Liu et al.,2018)
Shaanxi Province, China	1430-3410	Dominant <500	(Ding et al.,2020)
Southwestern China	18760 (7100 - 42960)	Dominant (50-1000)	(Zhang & Liu, 2018)
Taklamakan desert, China	119-7292	Dominant <500	(Li et al., 2022)
Mu Us Desert, China	2696 (1360-4960)	0-5000	(Ding et al., 2021)
Lahore, Pakistan	4483 (1750-12200)	50-5000	(Rafique et al., 2020)
Fars province, South Central Iran	Field 1; 380 (40-830) Field 2; 510 (200-1100)	≤100-5000	(Rezaei et al., 2022)
Badain Jaran Desert, China	6 (1-12)	40-5000	(Wang et al., 2021)
Phoenix and the surrounding areas of the Sonoran Desert	122- 1399	5-5000	Current Study

Substantial variability was observed spatially for microplastics abundance across the study area. A previous study investigating the density of plastic trash in the Sonoran Desert, AZ states the occurrence of passively-dispersed plastic trash in the desert did not appear to dissipate with distance from potential sources of origin and were independent

of road proximity (Zylstra, 2013). Prior work suggests a majority of the microplastics in the environment originate from secondary degradation of larger plastics (Kasmuri et al., 2022). As such, it is not surprising that higher microplastics abundances were observed in relatively remote areas in our study as environmental transport and degradation can lead to secondary microplastics. An additional source such as atmospheric deposition of microplastics could be a contributing factor for microplastics in soil.

Three previous studies addressed the spatial variation of soil contaminants within the CAP-LTER area (Marusenko et al., 2011; Zhuo et al., 2012; Hamilton and Hartnett, 2013). PAHs were reported to be present in surface soils along major highways in the Phoenix, AZ metropolitan area in a previous study (Marusenko et al., 2011). A previous study reporting soot black carbon concentrations did not observe a strong correlation between soot black carbon concentrations and distance to the urban core (Hamilton and Hartnett, 2013). A study in 2012 investigated the distribution of trace elements in soil samples as part of the Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER) from the Ecological Survey of Central Arizona (ESCA) 200-point survey in 2005. A majority of trace elements depicted higher concentrations above their crustal averages. The author attributes the accumulation of elements to other additional sources such as atmospheric deposition (Zhuo et al., 2012). Consistent with these other studies, the measured microplastics in the current study also show no clear pattern relative to land use, anthropogenic activities or proximity to urban core.

A recent study investigating the spatial distribution of soil microplastics in Hainan Island, China reports a heterogenous distribution with high variability between sampling sites

(Khan et al., 2023). Also, a previous study investigating the microplastics distribution in a Central Asian Desert (an enclosed area with almost no human activity) attributes the source of microplastics to atmospheric transport and airborne microplastics deposition (Wang et al., 2021). The distribution of soil microplastics in arid and semi-arid environments in Fars province, south-central Iran, was reported to be heterogenous between fields and sampling locations with no clear trend (Rezaei et al., 2022). This study suggests that the region experiences significant dust storms, which is a similar occurrence in the region of interest in our study (Eagar et al., 2017). Eagar and coworkers estimated that haboob dust storms alone might account for 75% of the dust deposition locally (Eagar et al., 2017). Wind-blown dust is an important factor for the transport of anthropogenic contaminants such as microplastics in arid and semi-arid regions (Ashrafi et al., 2014). A recent study in the metropolis of Shiraz, Iran estimated that a majority of microplastics (>90%) in deposited dust were derived from outside of the city during an intense dust storm event in May 2018 (Abbasi et al., 2022). This suggests that dust storms could affect the local site-specific soil microplastic abundances through both deposition and resuspension, and hence environmental processes would redistribute microplastics throughout the region.

3.4.2 Deposition fluxes of microplastics

The deposition fluxes (collected as 2-week averages) of microplastics in Tempe, AZ for a one-year period ranged from 71 to 389 microplastics/m^2/day with an average deposition flux of 178 microplastics/m^2/day (Figure3. 2). Microplastics were identified in all

deposition samples collected through the one-year period. Higher deposition fluxes were observed during (Nov 2nd- Nov 15th, 2020) and (Jan 11th-Jan 24th, 2021) compared to other biweekly sampling periods. Rainfall was not observed and recorded from the weather station located at the sampling site (Earth Networks Inc., an AEM company, https://www.earthnetworks.com/) during the aforementioned two bi-weekly periods. Since Tempe, AZ received very limited rainfall during the sampling periods, it was not possible to perform a correlation analysis between microplastics deposition fluxes and precipitation events. The lowest deposition flux was observed during (July 1st – July 14th, 2021). Wind-rose diagrams did not show any correlation between microplastics deposition fluxes and wind speed/direction. A recent study investigating suspended airborne microplastics in Tempe, AZ during the same period reports a similar observation with no clear seasonal and meteorological influence on microplastics concentrations and is consistent with the observations in the current study (Chandrakanthan et al., 2023). Deposition fluxes measured in Tempe show substantially higher, but variable, rates and may not directly govern the distribution of soil microplastics abundances. Windblown dust storms common in arid regions (Eagar et al., 2017; Abbasi et al., 2022) result in re-entrainment and further degradation of microplastics captured by deposition studies. These types of processes likely impact incorporation of microplastics into local soil deposits and may explain discrepancies between prior deposition studies and the current measurements.

The deposition flux in the current study is approximately three times higher when compared to that reported in a recent study at a Southern China metropolis (Yuan et al., 2023). This maybe be attributed to the differences in the lower size limits for

quantification of microplastics between the two studies (Table 3.2). The mean deposition fluxes reported at Hamburg in Germany, Lanzhou City in China and Central London, UK are approximately 1.5, 2, and 4 times higher than that in our study (Klein & Fischer, 2019; Wright et al., 2020; Liu et al., 2022). The authors attribute the relatively higher deposition fluxes observed in Lanzhou City, China to local sources including a local waste recycling site. The high deposition fluxes in Central London, UK is attributed to the higher density population in the study area of interest.

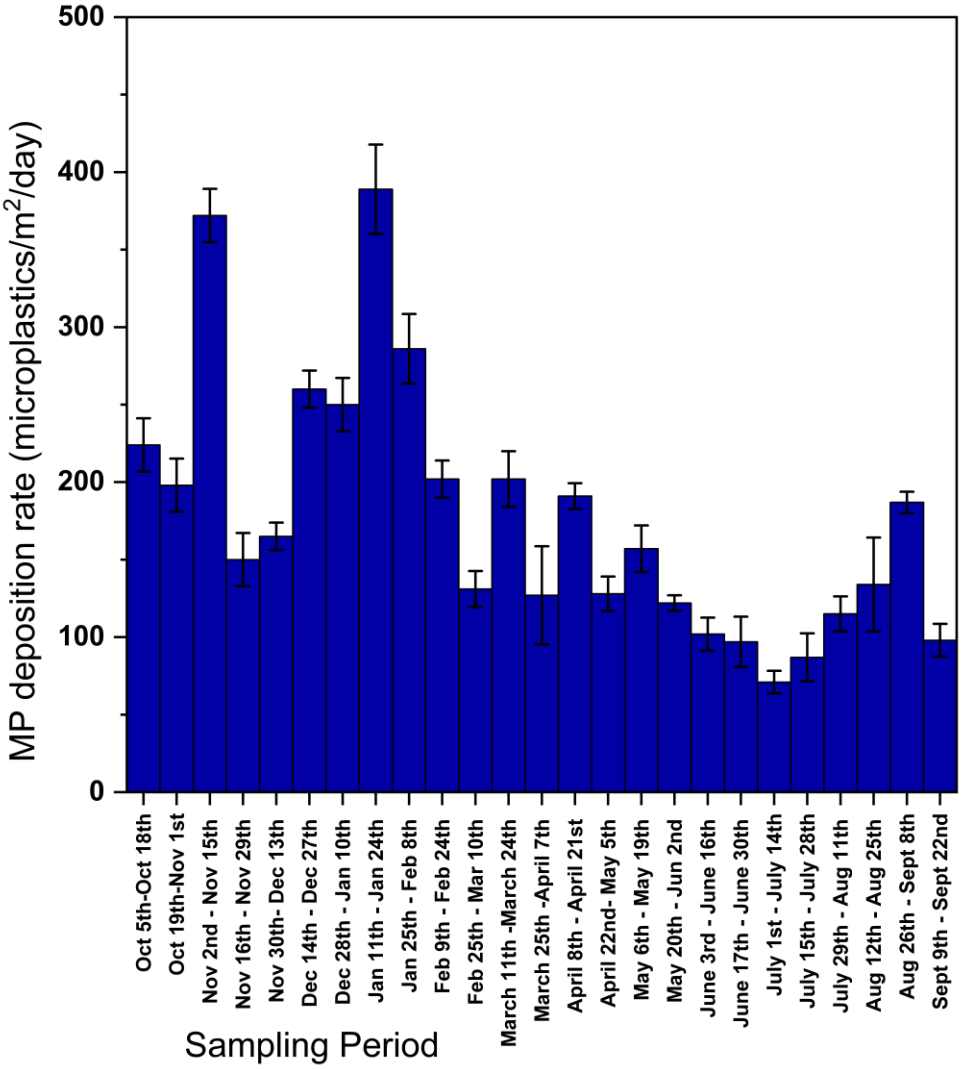

Figure 3.2 The deposition flux of microplastics (MP) in Tempe, AZ. The error bars represent the standard deviation of the mean obtained from three replicate measurements.

Table 3.2 Summary of microplastic deposition fluxes reported in previous studies.

Location	Microplastics/m^2/day	Size range/µm	References
Lanzhou City, China	354 (57-689)	50-5000	(Liu et al., 2022)
Hamburg, Germany	275 (136-512)	< 63 - < 300	(Klein and Fischer, 2019)
Central London, UK	712 (575-1008)	20-5000	(Wright et al., 2020)
Pyrenees mountains, France	365	< 25-5000	(Allen et al., 2019)
São Paulo megacity, Brazil	123 ± 48	Dominant (100-200)	(Amato-Lourenço et al., 2022)
South Central Ontario, Canada	7 (4-9)	20-5000	(Welsh et al., 2022)
Ho Chi Minh City, Vietnam	71-917	300-5000	(Truong et al., 2021)
Haizhu Districts, Southern China	66 ± 8 (21 - 109)	13 - 334	(Yuan et al., 2023)
Tropical sites in Malaysia	114-689	≤5-5000	(Hee et al., 2023)
Jakarta, Indonesia	15 (3-40)	358-925	(Purwiyanto et al., 2022)
Tempe, USA	178 (71-389)	5-5000	Current Study

3.4.3 Temporal variation of microplastics

Results for the temporal variability of microplastics in soil indicate a systematic increase in the abundance of microplastics from 2005 to 2015 at all the studied sampling sites (Figure 3.3). The microplastics abundances are 1.3 to 5.2 times higher in 2015 compared to 2005. Results of a Mann-Whitney Test ($p \leq 0.05$) performed indicated a statistically significant difference between the microplastics abundances in 2005 and 2015 ($p=0.006$). A study investigating the temporal variation of microplastics in sediment samples from the Chucki Sea over 5 years reports an increase in microplastics over time (Fang et al., 2022). While the temporal variations of microplastics in aquatic systems have been relatively well reported (Kobayashi et al., 2021; Munari et al., 2021; Talbot et al., 2022), studies on their temporal variation in terrestrial arid environments are limited.

Microplastics enter the environment mostly through secondary degradative processes of large plastics (Wong et al., 2020). Therefore, increasing amounts of plastics in the environment can give rise to increasing numbers of microplastics in the environment over time. A similar observation is reported in a study that investigated the microplastics abundances in sediment samples from the Chucki Sea over 5 years (Fang et al., 2022). The authors attributed this increase in smaller microplastics over time to the breakdown of large plastics during long-range transport. The substantial atmospheric deposition of microplastics occurring in the region could also be a contributing factor to the observed increase of microplastics after the lapse of 10 years in the current study (Section 3.1.1).

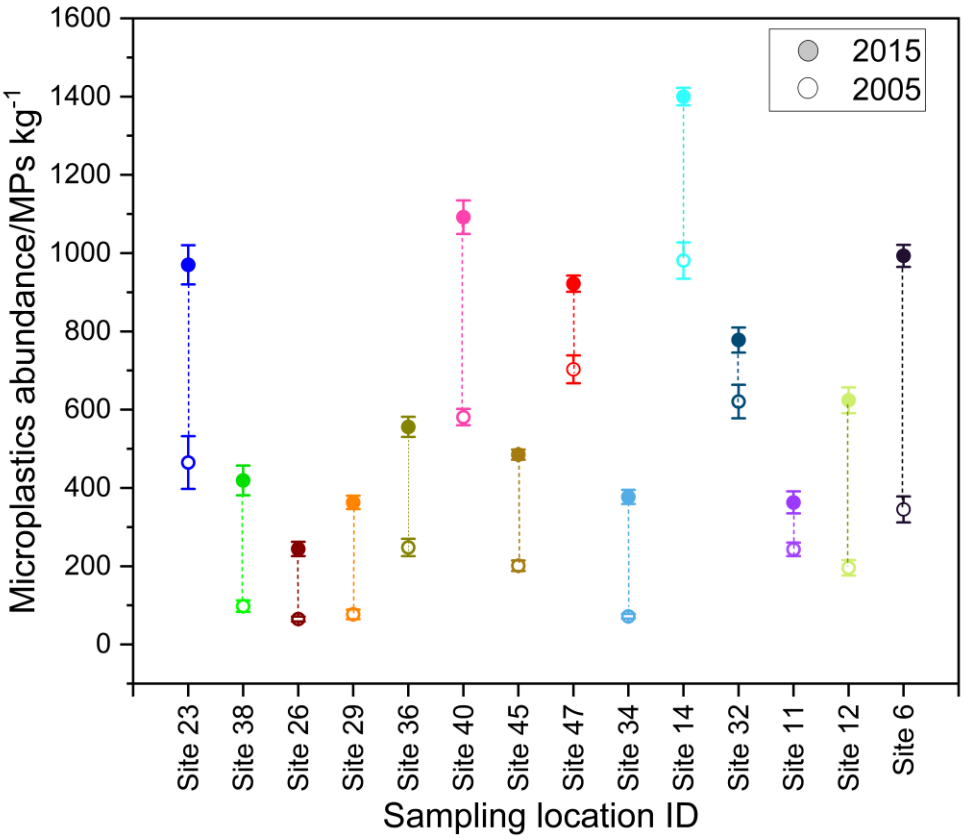

Figure 3.3 Temporal changes in microplastics in soil samples from 2005 and 2015. Each error bar represents the standard deviation of the mean obtained from three replicate measurements. Sampling location IDs were randomly assigned.

The size distributions of microplastics in soil samples from 2005 and 2015 were analyzed to compare sizes of microplastics over time. Normalized size distributions of microplastics present in all soil samples collected in 2005 and 2015 were analyzed (Figure 3.4) to understand which size classes of the microplastics were most prevalent in the two years. The size distributions represent the averages of all normalized size distributions of samples (Figure 3.4).

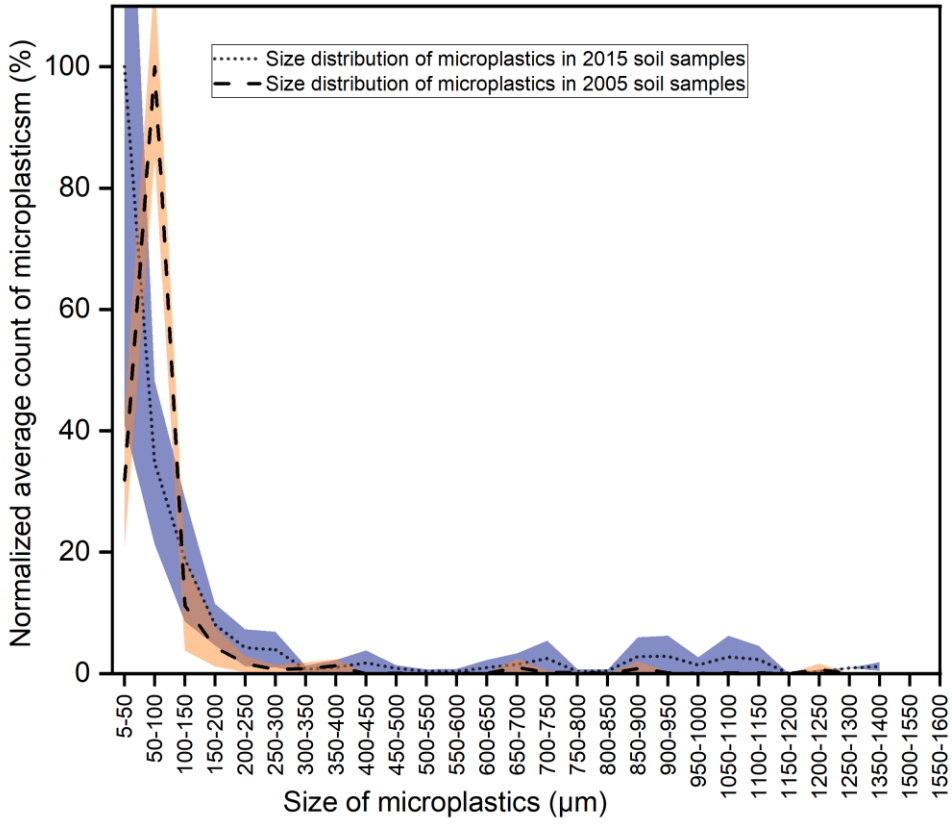

Figure 3.4 Normalized percent size distributions of microplastics in soil samples from 2005 and 2015. Shaded error bars represent the standard deviation of the mean.

The highest count for microplastics on average was observed between 5 µm -50 µm in soil samples from 2015. Contrary to this observation from 2015, microplastics were

predominantly found between 50 µm - 100 µm on average in soil samples from 2005. This finding is consistent with microplastics entering the environment through secondary formation with various weathering processes, including physical abrasion, resulting in more, smaller microplastics over time. This can result in their degradation to even smaller sized microplastics as time progresses during long range-transport (Fang et al., 2022). A study exposing millimeter sized polyethylene and polypropylene pellets to UV radiation and mechanical abrasive forces at temperatures typical of a dry (beach) environment report the production of smaller microplastics, of which the abundances increased with decreasing size (Song et al., 2017). Therefore, it is not surprising that significant degradation and weathering of microplastics can occur to produce smaller sized microplastics over longer time scales under relatively dry, high-temperature conditions in the Sonoran Desert. Our results on size distribution patterns are an indication of breakdown processes of microplastics that could occur over the span of ten years in this location.

Fibrous microplastics accounted for the majority (≥87 % in 2005 and ≥98% in 2015) of the microplastics in soil samples. The overall increase in relatively smaller sized fibers in 2015 soil samples are likely an indication of the degradation of larger fibrous microplastics to produce smaller fibers over time. Fragments were observed as the only other morphology present and no spherical pellets and beads were observed in the samples.

3.4.4 Chemical characterization of microplastics in soil

Micro-Raman spectroscopy was used to identify the chemical composition of polymers contained in the microplastics. Raman characterization for microplastics in 2005 and 2015 soil samples revealed an array of polymers including PE, PS, PVC, Polyamide (PA), Polyester (PES), PP depicting a variety of polymers. A majority of microplastics remain chemically unidentified (Figure 3.5 and Figure B4). This observation is consistent with the chemical characterization results of airborne microplastics in Tempe, AZ reported in a recent study (Chandrakanthan et al., 2023). The aforementioned study conducted lab experiments and postulated that weathering of microplastics over time could potentially alter surface properties thereby rendering them unidentifiable using µ-Raman spectroscopy. Polyethylene was present in 75% of the sampling sites and was the most abundantly identified polymer on average in all soil samples. A previous study investigating the density of plastic trash in the Sonoran Desert, AZ during 2005-2006, states polyethylene bags were found in substantial numbers during field crew surveys (Zylstra, 2013). This is reflective of the high overall global production of polyethylene which is the most produced thermoplastic worldwide (Nerland et al., 2014.; Zhong et al., 2018) and mismanagement of plastic bags in landfills and waste streams is widely reported. Previous studies reporting the occurrence and chemical characterization of microplastics in terrestrial environments also showed polyethylene as one of the most prevalent polymers found in samples (Scheurer and Bigalke, 2018; Ding et al., 2021; Khan et al., 2023). The types of identified polymers have not changed from 2005 to 2015 for soil microplastics. Additionally, there is no substantial increase in the abundance of each identified polymer from 2005 to 2015. This could possibly be due to the large

fractions of microplastics that are chemically unidentifiable in soil samples. Weathering of microplastics by complex degradative processes in the environment can cause significant alteration rendering them chemically unidentifiable (Chandrakanthan et al., 2023). A large majority of microplastics were chemically unidentifiable in all sites, ranging from 8% to as high as 95% of total microplastics with an average of 54% in 2015 soil samples. The average of chemically unidentified microplastics was even higher in 2005 (67%).

The observed differences for abundances of each polymer in soil samples may possibly be due to the differences in their inherent resistances to weathering mechanisms in the environment (Abbasi et al., 2021). Mechanical and oxidative weathering can degrade less strong polymeric materials with relatively lower tensile strengths. Accordingly, PP that has a relatively lower tensile strength of 40 MPa was observed in only 29% (in 2015) and 21% (in 2005) of the sampling sites. Polyamide with a relatively higher tensile strength (70 MPa) was dominant in Site 24, chemically amounting to as high as 77% of the total microplastics in the soil sample.

A recent study deployed sediment traps in an arid region in Sarakhs, Iran to investigate the entrainment of microplastics in sediments at different heights from the ground (Abbasi et al., 2023). The chemical characterization results of the aforementioned study are consistent with the findings of the current study where PE (a relatively low-density polymer; <1 g cm^{-3}) was the most abundant polymer present in samples with fibers as the most dominant shape of microplastics.

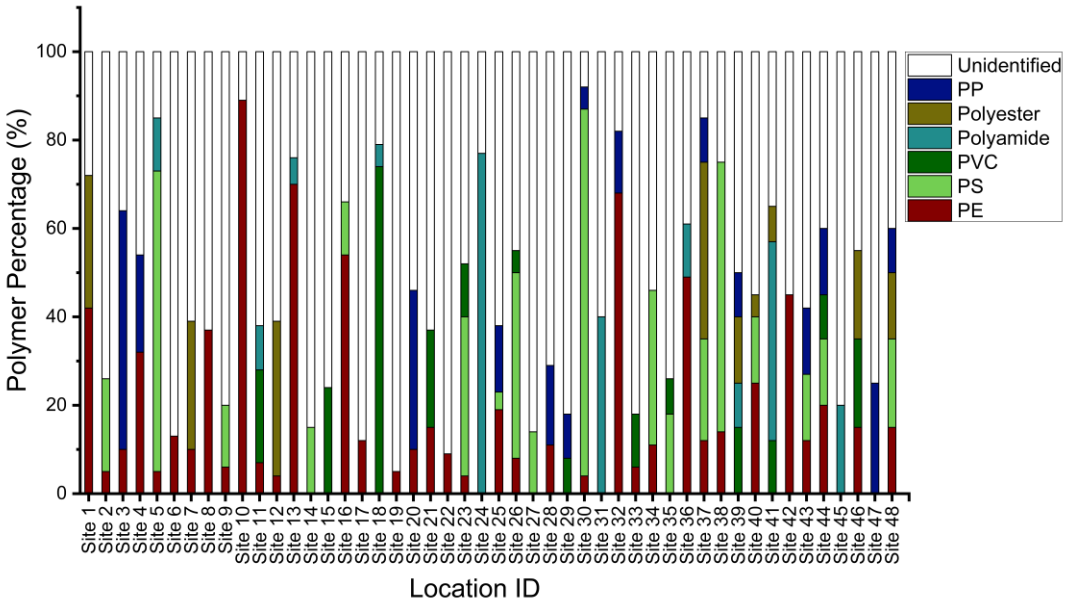

Figure 3.5 Raman Characterization of microplastics of soil samples from 2015.

3.5 Conclusions

Microplastics were ubiquitous in the soils of Phoenix and the surrounding areas of the Sonoran Desert. In 2015 soils samples, microplastics concentrations varied an order of magnitude with a spatially heterogeneous distribution with no clear spatial trends. The results for microplastics deposition fluxes show substantial microplastics deposition occurring in Tempe, AZ and this route may influence the unclear spatial trend for the abundance of soil microplastics as local dust storms could even continually redistribute microplastics from the surface.

The Ecological Survey of Central Arizona (ESCA) performed by the Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER) allowed for a temporal comparison between 2005 and 2015. At the same sampling locations over a 10-year span, all samples showed a statistically significant increase in microplastics indicative of the increasing amounts of microplastic accumulation in the environment. The deposition fluxes can account for part of this and could be enhanced by the degradation of larger plastics into smaller microplastics over time. The size class depicting the average highest count for microplastics was noticeably smaller in soil samples from 2015 while microplastics measured by our protocol were concentrated in relatively larger sizes on average in soil samples from 2005. This implies that secondary degradative processes of microplastics can be a larger contributive factor towards the temporal increase in microplastics. Raman characterization for microplastics in 2005 and 2015 soil samples revealed an array of polymers including PE, PS, PVC, PA, PES and PP. A large majority of the microplastics remain chemically unidentified. Weathering of microplastics over time could potentially change them thereby rendering them unidentifiable using μ-Raman

spectroscopy. Polyethylene was dominantly present in a majority of the sampling sites and was the most abundantly identified polymer on average in all soil samples indicative of the large production of polyethylene on a global scale.

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CHAPTER 4

MONITORING MICROPLASTICS IN RECREATIONAL SURFACE WATERS: TEMPORAL VARIATION IN THE SALT RIVER AND OCCURRENCE IN SWIMMING POOLS

4.1 Introduction

Plastic pollution has become a growing concern in recent years, with microplastics, in particular, gaining increasing attention for their ubiquitous presence in all environments (Geyer et al., 2017). Microplastics; plastic particles measuring less than 5 mm in size in the longest dimension, are released to the environment from secondary pathways or are intentionally manufactured at uniform shapes as microbeads and pre- production pellets (Arthur et al., 2009; Tran et al., 2023). Secondary microplastics generated through photolysis and mechanical abrasion usually depict diverse shapes such as fibers and fragments (Peller et al., 2020) further compound the issue of microplastic pollution.

The occurrence of microplastics in aquatic environments (Andrady, 2011; Bordós et al., 2019; Yuan et al., 2019; Li et al., 2020; Peller et al., 2020) has been extensively documented while atmospheric (Prata, 2018; Chandrakanthan et al., 2023; Zhao et al., 2023) and terrestrial ecosystems (Scheurer & Bigalke, 2018; Zhang & Liu, 2018; Chandrakanthan et al., 2024) have received less attention. While the presence of microplastics in marine environments is widely studied, less than 4% of microplastics related research is focused on freshwaters (Wagner & Lambert, 2018). Freshwater environments, many of which are sources of drinking water, are typically in close proximity to the sources of microplastics compared to marine environments, and the

resulting microplastic load to water and river sediments can be larger depending on the human population density proximal to the water body (Eerkes-Medrano et al., 2015). Sewage treatment plants, urban waste, agricultural runoff, fishing activities and recreational activities are major input pathways of microplastics into freshwater ecosystems, making riverine environments a significant sink for synthetic microparticles (Gatidou et al., 2019; Schell et al., 2022). Microplastics, once released into water, can exhibit remarkable resilience and can get transported in aquatic environments through diverse pathways, floating on surface waters, and interacting with aquatic life (Koelmans et al., 2019). Recreational beach environments suffer from serious microplastic pollution and have been well documented over the years (Claessens et al., 2011; Stolte et al., 2015; Karthik et al., 2018). However, literature on the occurrence and distribution of microplastics in recreational freshwater bodies including rivers and swimming pools is sparse and limited.

Fibers are the most commonly identified microplastic morphology reported in the gastrointestinal tracts of biota at all trophic levels (Barboza et al., 2018; Catarino et al., 2018; O'Brien et al., 2020). Despite their environmental prevalence and high research importance, little information is known about the emission sources of fibrous microplastics. A research study reports that hundreds of fibers were released per gram of polyester textile, to hundred thousand fibers after 2 months of artificial weathering simulated in the laboratory (Pinlova & Nowack, 2023). Previous studies report substantial micro-fiber emissions from swimwear and synthetic fabrics during laundering (O'Loughlin., 2018; Rathinamoorthy et al., 2023). To date, there have been few studies that establish the importance of clothing as a source of microplastic fibers to the

environment. Therefore, investigating recreational surface waters as a significant potential point of contamination, particularly for fibrous microplastics, is of paramount importance. The first reported study of microplastic ingestion by an array of invertebrates in freshwater reveal that organisms across different habitats and trophic levels ingest the synthetic micro-particles (Imhof et al., 2013). Freshwater invertebrates such as gammarid amphipods play important roles in the breakdown of particulate organic matter (D'avignon et al., 2022) and therefore could similarly digest microplastics. In addition to their direct toxic effects, microplastics can illicit synergistic effects with adhering persistent organic pollutants in the environment (Koelmans et al., 2016). The additives of micro-fibers can have a detrimental impact on aquatic organisms and must be accounted as part of the microplastic fiber pollution problem. Co-exposure to dyes and additives leaching from micro-fibers is a potential risk faced by aquatic organisms. Owing to their small size, microplastics are ingested by a range of fresh water aquatic organisms that can eventually cause ecotoxicological and physiological changes (Thacharodi et al., 2024). The Salt River in Arizona is home to fish species including the *Castostomus insignis*, *Gila robusta*, *Rhinichthys osculus*, and the *Catostomus clarkii*, and the presence of microplastics in the riverine ecosystem of interest in our current study can potentially reduce the feeding uptake of such aquatic organisms (Mallik et al., 2021).

Owing to the frequent use of plastics during swimming and leisure activities, swimming pools are recreational water systems where microplastics can accumulate and are likely hotspots for direct human exposure to microplastics and associated pathogens (Schets et al., 2011). Pathogens including E. coli, Cryptosporidium, and Giardia are present in such aquatic environments owing to human clustering (Ramírez-Castillo et al., 2015).

Microplastics can harbor such aforementioned pathogens, thereby resulting in a non-negligible indirect route of exposure of infectious agents to humans.

This study investigates the temporal variation of the occurrence of microplastics in heavily used recreational surface waters in the Salt River, Arizona. The Salt River is located within the Tonto National Forest, Arizona and contains four storage reservoirs northeast of Phoenix, Arizona that form a series of lakes nearly 96 km long (Metcalfe et al., 2023). The river is a source of drinking water for the Phoenix metropolitan area and is a popular destination for recreational activities in the summer. The study area has been studied in the past for various key ecological indicators and anthropogenic contaminants such as engineered nanomaterials, pharmaceuticals, Ti-containing particles, and additives in sunscreens (oxybenzone) (Chiu et al., 2009; Banville & Bateman, 2012; Yang et al., 2017; Venkatesan et al., 2018). Water samples were collected from a single location in the Salt River during recreational activities on July 1st, 2023. To compare and contrast, water samples were collected for microplastic analyses on October 13th in the absence of swimmers and tubers. During the same months of July and October, water samples were collected in 7 apartment community swimming pools in Tempe, AZ to investigate for the occurrence of microplastics in swimming pools. Samples were processed and microplastics were counted under an optical microscope to obtain quantitative information of their presence and distribution in water. Chemical characterization of microplastics was performed by micro-Raman spectroscopy to understand their chemical make-up and possible sources.

4.2 Materials and methods

4.2.1 Sampling of microplastics

Surface water samples (1 L) were collected at one single location in the lower Salt River, Goldfield Recreation Area (33.5544˚ N, 111.6236˚ W), by means of pre-cleaned and pre-baked (450˚ C) amber glass bottles from 8:00 to 16:00 (24-hr format) on July 1st, 2023 (in the presence of tubers) and October, 13th, 2023 (in the absence of tubers). The pre-cleaned bottles were rinsed three times with river water prior to sampling, and the discard was poured downstream of the sampling location. The Goldfield Recreation area, located in the city of Mesa, Arizona is a popular river-access point (RAP) for tubers and rafters floating the Lower Salt River, and witnesses substantial crowds during the months of June-September (Figure C1).

Water samples were collected similarly by means of pre-cleaned and pre-baked (450˚ C) amber glass bottles from apartment community swimming pools (n=7) in Tempe, AZ in July, 2023 (Figure C2) and October, 2023. Swimming pools were sampled in October to contrast with July, as a higher swimming activity is observed during the summer months. The collected water samples were stored on ice during transportation to the laboratory and refrigerated at 4˚ C until further sample processing.

4.2.2 Conductivity measurements of surface water samples from swimming pools

The conductivity of the water samples was measured using a conductivity meter (A222, Thermo Scientific, Waltham, MA, USA) after being transported to the laboratory. The conductivity and temperature of the samples were noted.

4.2.3 Sample processing

The surface water samples were first passed through a sieve (8"-FH-SS-SS-US-#3-1/2, Hogentogler & Co. Inc., MD, USA) to remove material larger than 5.6 mm. The sample bottles were thoroughly rinsed thrice with ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) to ensure that all microplastics adhering to the glass surface were recovered. The following approach was based on the methods manual from the National Oceanic and Atmospheric Administration (NOAA) for microplastics analyses in water and beach sediment samples and adapted as appropriate to process the water samples (Masura et al., 2015; Chandrakanthan et al., 2023). First, sieved water samples were subjected to wet peroxide oxidation to remove natural organic matter. A 10 mL aqueous 0.05 M Fe (II) solution prepared from $FeSO_4.7H_2O$ (Sigma Aldrich, MO, USA) and 10mL of 30% hydrogen peroxide (Sigma Aldrich, MO, USA) were added to samples for 5 minutes at room temperature and subsequently heated to 60°C on a hot plate (Fischer Scientific, NH, USA) to remove naturally occurring organic matter. The solutions were vacuum filtered through a pre-fired glass microfiber filters (Whatman GF/A, Sigma Aldrich, MO, USA). The filters were oven-dried at 60°C until complete dryness in a Muffle furnace (Vulcan 3-1750, CA, USA).

Preventive measures to minimize background contamination during microplastics analyses are crucial in producing reliable results (Prata et al., 2021; Shanmugam et al., 2022; Dawson et al., 2023). A procedural blank was run during all stages of sample processing including wet peroxide oxidation and subsequent analyses. Glassware washed with a detergent and rinsed three times with ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) was subsequently baked and used during all stages of sample processing and analyses. The clean equipment was covered to minimize potential airborne microplastics contamination. Working surfaces were cleaned with ultrapure water (>18.4 MΩ cm, Purelab Flex, IL, USA) and isopropyl alcohol (Fischer Scientific, MA, USA) prior to sample analyses. The usage of synthetic textiles was minimized, and a fiber was drawn from the lab coat during each day of laboratory analysis and observed under the optical microscope to check for fibers with similar appearance in samples. The recovery percentage of microplastics from filters was assessed through matrix spikes with a known number of microplastics (5 µm-5000 µm). Recovery tests showed a recovery of 93% of spiked microplastics.

4.2.4 Optical microscopy

Filters were examined under a digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software. The size range of interest was selected as 5 µm-5000 µm to provide an overview of the size distribution of microplastics and the morphology of microplastics present. The lower size limit of 5 µm was due to the smallest possible size resolution of the digital microscope. As there is no standard definition for the distinction between a fiber and a

fragment in microplastics literature, in the current study we used an operational definition for the observed shapes of microplastics. A fiber was recognized to be cylindrical in shape with an aspect ratio (length/ diameter) ≥ 3, while a fragment was recognized to be shard-like and flattened. Microplastics were sized along their largest dimension using the software program ImageJ (version 1.5, National Institute of Health, USA, http://imagej.nih.gov/i).

The following criteria are used to identify microplastics (Hidalgo-Ruz et al., 2012).

1. No Cellular or Organic Structures Visible.

2. Fibers should be equally thick throughout their entire length. This is generally true for fibers. However, sometimes splitting or fraying of fibers is observed. The fiber should depict 3-dimensional bending.

3. Particles should exhibit clear and homogeneous color throughout.

Exceptions- Some plastics are not entirely homogenous in color, with patterns and stripes. Biofouling can potentially alter color, or part of the fiber may be bleached. Weathered microplastics may exhibit loss of color towards the edges.

4.2.5 Chemical characterization using Micro-Raman spectroscopy

Micro-Raman spectroscopy is a vibrational spectroscopy technique based on the inelastic scattering of light and was used to provide chemical characterization of the polymers in identified microplastics. Raman data was collected from 50-3800 cm^{-1} using a custom-built microscope and a Mitutoyo M Plan Apo 50X/0.42 objective. An Acton Research

monochromator (SpectraPro-300i) utilizing a 600 g/mm grating and coupled to a Roper Scientific CCD (model LN/CCD 1340/100-EB/1) recorded the signal. A Coherent Sapphire solid state cw laser emitting 532 nm served as the excitation source and the data was calibrated using cyclohexane with known peak positions. The spatial and spectral resolutions of the micro-Raman spectrometer were 1 μm and 1cm^{-1} respectively.

4.3 Results and Discussion

4.3.1 Temporal Variation of microplastics in recreational surface waters of the Salt River

Microplastics were found in all surface water samples collected during recreational activities (8:00 hr through 16:00 hr) and showed a systematic increase in concentrations over the course of 8 hours on July 1st, 2023 (Figure 4.1). The microplastic concentrations in the surface water samples during recreational activity ranged from 27,798 MPs/m^3 to 222,391 MPs/m^3, depicting an 8 times increase in microplastic concentration at peak activity time at 16:00 hr compared to 8:00 hr (Figure 4.1). The Salt River is accessible in this region for recreational activities from 9:00 hr daily from June-September. The observed variation in microplastic concentrations can be ascribed to the micro-particles released from human activity during tubing, swimming, and rafting in the Salt River. Three samples were collected and analyzed in triplicate at 8:00 hr, 12:00 hr and 16:00 hr during the sampling period (Table C1) and the relative standard deviation was 10%. Microplastics were present in all collected surface water samples on October 13th, 2023, (in the absence of tubers, swimmers and rafters) thereby indicating their ubiquitous presence in the Salt River, Arizona. However, the microplastics concentrations in surface waters of the river in October did not vary over the course of the day as those observed in July (relative standard deviation of concentrations over the day was 11%). Microplastic baseline concentrations during off season in the absence of recreational activities are an order of magnitude lower than those observed on July 1st, 2023 (Figure 4.1). The Salt River water flow data was retrieved from the closest monitoring station upstream, below

Stewart Mountain Dam from the United States Geological Survey (USGS). The average water flow rates in the river did not depict noticeable differences (898 ft^3/s on July 1st and 827 ft^3/s on October 13th). The blank filters identified microplastics through contamination and were found to range between 1 and 5 microplastics/filter with an average of 2 microplastics/filter. Matrix spikes of microplastics (5 μm–5000 μm) to assess for recovery of microplastics showed a recovery percentage of 93%.

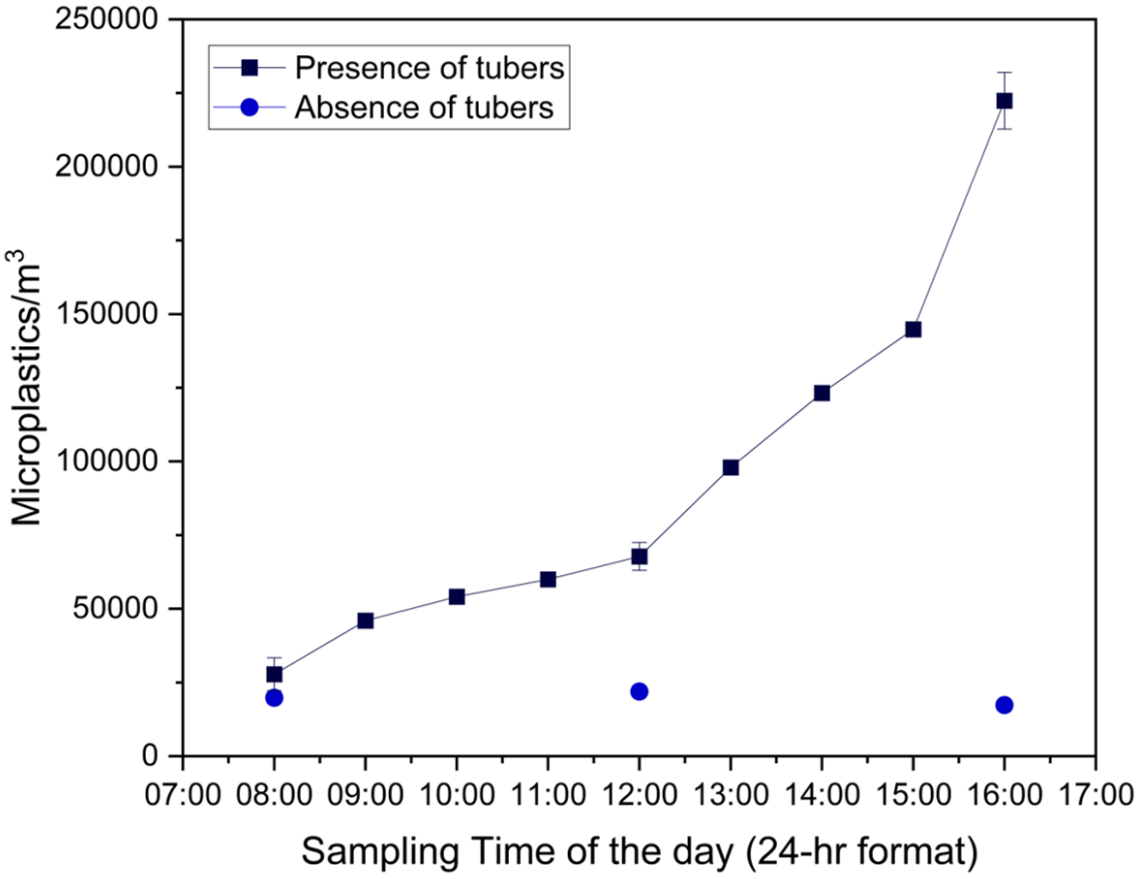

Figure 4.1 Temporal variation of microplastic concentration in the Salt River in the absence (October) and presence (July) of recreational activities. Each error bar represents the standard deviation of the mean obtained from three replicate measurements.

Comparing the observed microplastic concentrations with those reported in literature is not straightforward due to the discrepancies in sampling approaches, sample processing, microplastics identification, operational definitions of microplastics and instrument detection limits. Additionally, studies that report the daily temporal variation of microplastic concentrations in riverine systems used for recreational activities are sparse in literature. However, a few studies report the occurrence of microplastics in lakes and beaches. A study reports the microplastics concentrations ranging from 0.44–9.7 microplastics/m^3 in the recreational surface waters of Lakes Mead and Mohave, reservoirs along the Colorado River, in the arid southwestern U.S. (Baldwin et al., 2020).

Even though the basins are sparsely populated, the authors attribute the concentrations observed to the large number of visitors the locations witness (Baldwin et al., 2020). The lower size limit of interest in the aforementioned study was 355 µm, while that of the current study was 5 µm (Section 4.3.1). Comparing the abundance of microplastics ≤355 µm, the microplastic concentrations observed in the aforementioned study is 4-5 orders of magnitude lower than those observed at peak time (16:00 hr) in the Salt River in the presence of recreational activity. This could be attributed to the vast area covered by the two large reservoirs (759 km^2) (Baldwin et al., 2020) compared to the Salt River, which would result in the dilution of overall microplastic concentrations in water. The St. Croix and Mississippi are other riverine systems that report microplastics in recreational surface waters (Baldwin et al., 2015) with a lower size limit of 333 µm. Microplastics concentrations in surface water samples from the St. Croix and Mississippi Rivers were similar and of the same order of magnitude to those observed in Lakes Mead and Mohave (Colorado river), and could possibly be ascribed to similar lower size limits of interest.

Previously, Venkatesan and colleagues studied the variation of Ti-containing particles and sunscreen additives in the Salt River during recreational activities and report a similar observation; an 80% increase in the particle concentrations at peak activity time (16:00 hr) over initial baseline concentration (Venkatesan et al., 2018). The author attributes the increase of Ti-containing nanoparticles over the course of the day to increased recreational activity occurring upstream of where samples were collected. The concentrations of oxybenzone measured in the same study area previously by Chiu et al., 2010 depicted a similar observation (an increase in the sunscreen additive over the span of one day in the presence of recreational activities) (Chiu et al., 2009). The overall

human impact in the study region of interest is reinstated by a previous study that shows a decrease in the herpetofauna diversity along the Salt River, with the increase in urbanization (Banville & Bateman, 2012).

Fibrous microplastics accounted for the majority of the microplastics in surface water samples in the Salt river (Figure C3). The temporal variation for microplastic shapes depicts a general increase in the fiber percentage in samples over the course of the day, with fibrous microplastics comprising for 96% of all microplastics present in the surface water samples collected at the peak activity time of 16:00 hr. On average, 72% of the microplastics in water samples collected in the absence of recreational activities in October were fibers. The overall large percentages of fibrous microplastics present in samples collected in July are likely an indication of the secondary synthetic micro-particles originated through the shed of micro-fibers from fabrics. The tubes utilized for floating comprise butyl rubber / poly(isobutylene-co-isoprene) or latex (polyisoprene) materials. However, these polymers were not observed in samples during micro-Raman analysis (Section 4.3.3). Therefore, the abundance of fibers could be ascribed to the shedding of micro-particles from fabrics worn by tubers, swimmers and rafters. Fibers can stem from degradation of larger plastics; the abrasion and release of microfibers from synthetic garments (Shamskhany et al., 2021), which was spectroscopically confirmed in the current study (Section 4.3.3). This is consistent with studies which show that greater than 1100 fibers were reported to shed from 1 g of acrylic fabric (Napper and Thompson, 2016). Fragments were observed as the only other morphology present and no spherical pellets and beads were observed in surface water samples in the river.

A previous study reporting soil microplastics in the same arid region of Phoenix, AZ report samples comprising large fractions of fibers (≥87 % in 2005 and ≥ 98 % in 2015) (Chapter 3). Comparably, a study reports that a majority of the airborne microplastics in Tempe, AZ were fibers (≥82%) (Chapter 2). Quite similarly, the present study of microplastics in the riverine system were largely fibrous, with relatively higher fractions. The size distributions of microplastics in surface water samples from the Salt River during recreational activity were analyzed to compare sizes of microplastics over the course of 8 hrs (Figure 4.2). Microplastics were concentrated in the smallest size fraction (5-50) µm that we were able to quantify, in water samples collected early in the day (8:00 hr, 9:00 hr, 10:00 hr, and 12:00 hr). Later in the day the majority of microplastics were present in relatively larger size categories. As the day progressed, the river witnessed increasing number of tubers, swimmers and rafters, that could potentially have resuspended larger micro-particles settled in sediment earlier in the day.

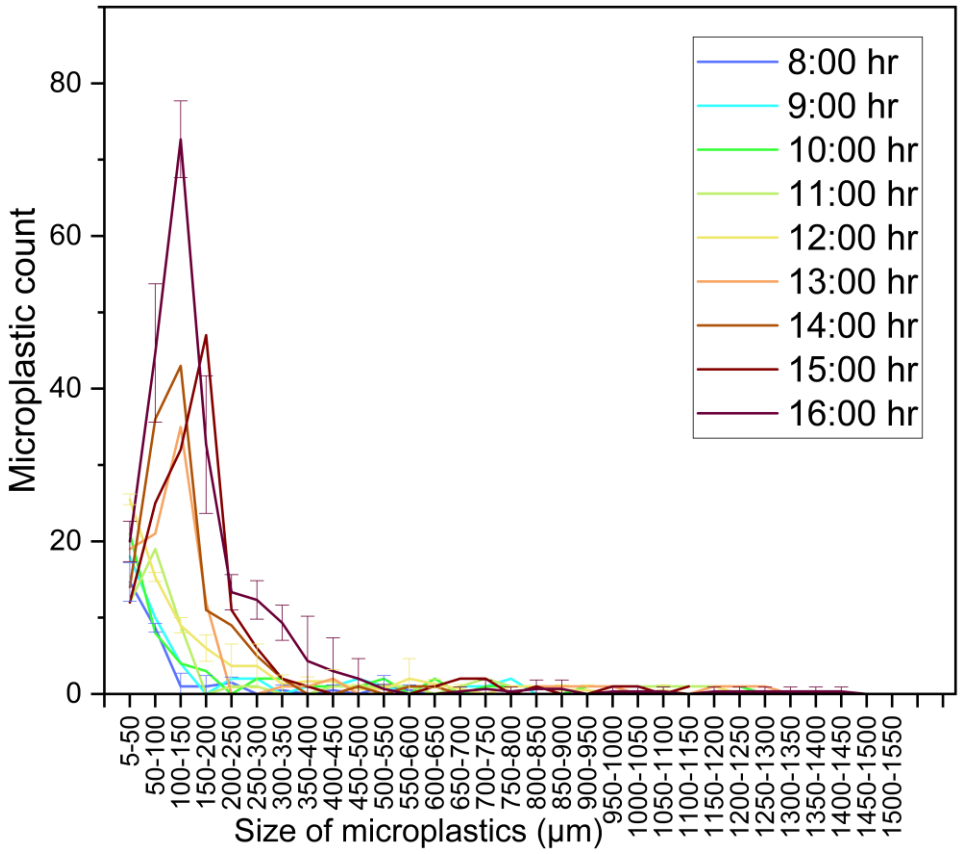

Figure 4.2 Size distributions of microplastics in the Salt River over the course of July 1st, 2023 (Time in 24 hr format) Each error bar represents the standard deviation of the mean obtained from three replicate measurements.

4.3.2 Microplastics in apartment community swimming pools

Microplastics concentrations in surface water samples from apartment community swimming pools (n=7) in Tempe, AZ ranged from 59,160 MPs/m^3 to 254,574 MPs/m^3 in October, 2023 (Figure 4.3). Microplastics were identified in all surface water samples collected and concentrations depicted substantial variability. The relative standard deviation of the measurements was on average 39%. The highest microplastic concentration was found at site SP5 and the lowest microplastic concentration was observed at sampling site SP4 in apartment community pools in Tempe, AZ. Three triplicates were analyzed for microplastics from three apartment community pools during the sampling period. The variability in microplastic concentrations can be attributed to the different filter media employed commonly in swimming pools. Most swimming pools use sand, cartridge or diatomaceous earth (DE) to remove suspended solids as part of the water treatment process implemented to keep water physically attractive, clean and safe (Wood et al., 2019). Microplastic concentrations in swimming pools in the summer (July) were of the same order of magnitude as those observed in October (Figure C4). This reflects the rather low drainage frequency of swimming pools (3-5 years). Microplastics released from secondary degradation of fabrics could accumulate over time, and may possibly explain the relatively high concentrations observed in our study.

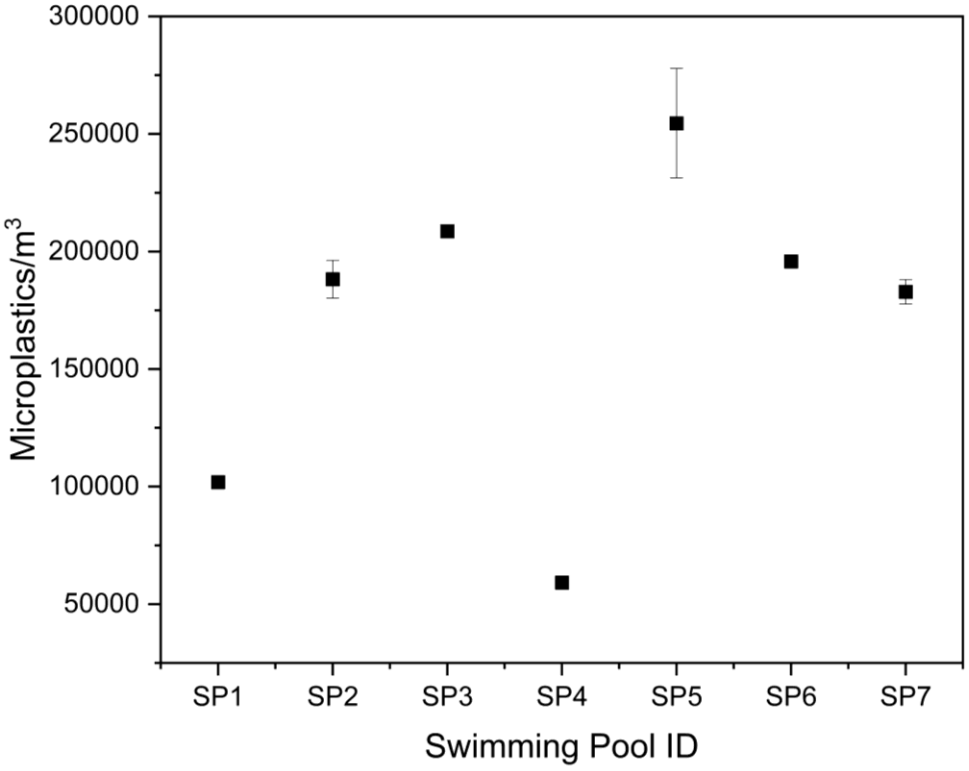

Figure 4.3 Microplastic concentrations in apartment community swimming pools in Tempe, AZ. Each error bar represents the standard deviation of the mean obtained from three replicate measurements. SP1-SP7 are sampling location IDs of swimming pools.

Comparing the results of the current study with existing research is important to provide context to microplastics concentrations. However, to date, there are no reported studies investigating the presence of microplastics in swimming pools. Overall, the concentrations in the swimming pools are comparable to those in the Salt River during recreational activity in July, and an order of magnitude lower than those in the absence of tubers, swimmers, and rafters in October. Results from a pilot study investigating microplastics in Tempe Town lake depict concentrations two orders of magnitude lower than those in swimming pools in Tempe. The Tempe Town Lake is restricted for

swimmers and the relatively high-water flow in the lake (several hundred to thousand cubic feet per second depending on the season and episodic influences), as opposed to no flow in swimming pools, could possibly explain the lower concentrations in the lake. The microplastic concentrations in the swimming pools in Tempe during July is comparable, and of similar magnitude to that in the Salt River during recreational activity (Figure 4.4). The microplastic concentrations in the Los Angeles river and Colorado Boulder Creek are 1-3 orders of magnitude lower than those in the Salt River during the absence of tubers, swimmers, and rafters (Moore et al., 2011, Woods et al., 2017). This observation could be ascribed to the smaller lower size cut used in the current study (5 µm), compared to that reported in the aforementioned studies (1000 µm). The concentrations in the swimming pool are of similar magnitude to those in in the Tres Rios outflow reported in a previous study (Cisco, 2023). The fibrous microplastics constituted a large majority of microplastics in the surface water samples of swimming pools in Tempe, AZ, sometimes accounting for as large as 87% (SP5). Fragments and spherical transparent beads were observed as the only other morphologies observed in water samples. Overall, the highest counts for microplastics were observed between 5-100 µm in swimming pool surface water samples. Studies on exposure assessment for swimmers in pools report that children (<15 years) swallow more water in swimming pools than adults (on average 31-51 mL based on an 80 minutes swimming activity time) (Schets et al., 2011b). Given the substantial concentrations of microplastics observed in our study (at the highest concentration, 13 microplastics ingested during 80 minutes by a child), swimming pools pose a non-negligible risk of microplastic exposure to humans through ingestion.

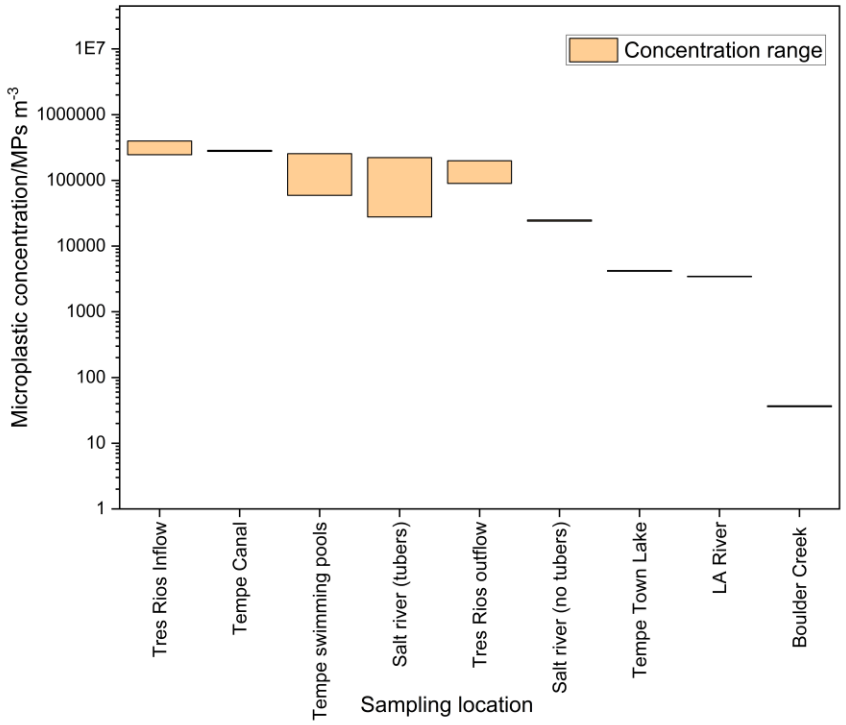

Figure 4.4 Comparison of microplastic concentrations in surface waters

Conductivity measurements made for water samples from swimming pools did not depict a statistically significant correlation with microplastic concentrations (r^2= 0.67, p= 0.094) at $p \leq 0.05$ (Figure C5). This suggests that additional factors such as chlorination of swimming pools could govern the ion concentrations in water, thereby eliminating our ability to investigate if evaporation of water could concentrate ions and microplastics in water in a similar manner.

4.3.3 Chemical Characterization of microplastics

Micro-Raman spectroscopy was used to identify the chemical composition of polymers in the microplastic present in the Salt River and swimming pools. Raman characterization for microplastics surface water samples revealed an array of polymers including PE, PVC, Polyamide (PA), Polyester (PES), and PP depicting a variety of polymers, while some microplastics remain chemically unidentified (Fig. 4.5 and Fig. C6). Overall, a majority of the microplastics identified were Polyamide and Polyester. Swimwear is a significant source of microfibers to the environment and consists of interwoven nylon and polyester fibers (Rathinamoorthy et al., 2023). However, the fraction of unidentified microplastics in the aquatic environments (Salt River) were lower than that found in atmospheric and soil environments in Phoenix, AZ (Chapter 2 and Chapter 3). Chandrakanthan et., al conducted lab experiments and postulated that weathering of microplastics over time could potentially alter surface properties thereby rendering them unidentifiable using μ-Raman spectroscopy. The relatively lower fractions of unidentified microplastics from this study area could possibly be an indication of the recent introduction of the synthetic micro-particles from their sources to the aquatic environment (less time for environmental weathering).

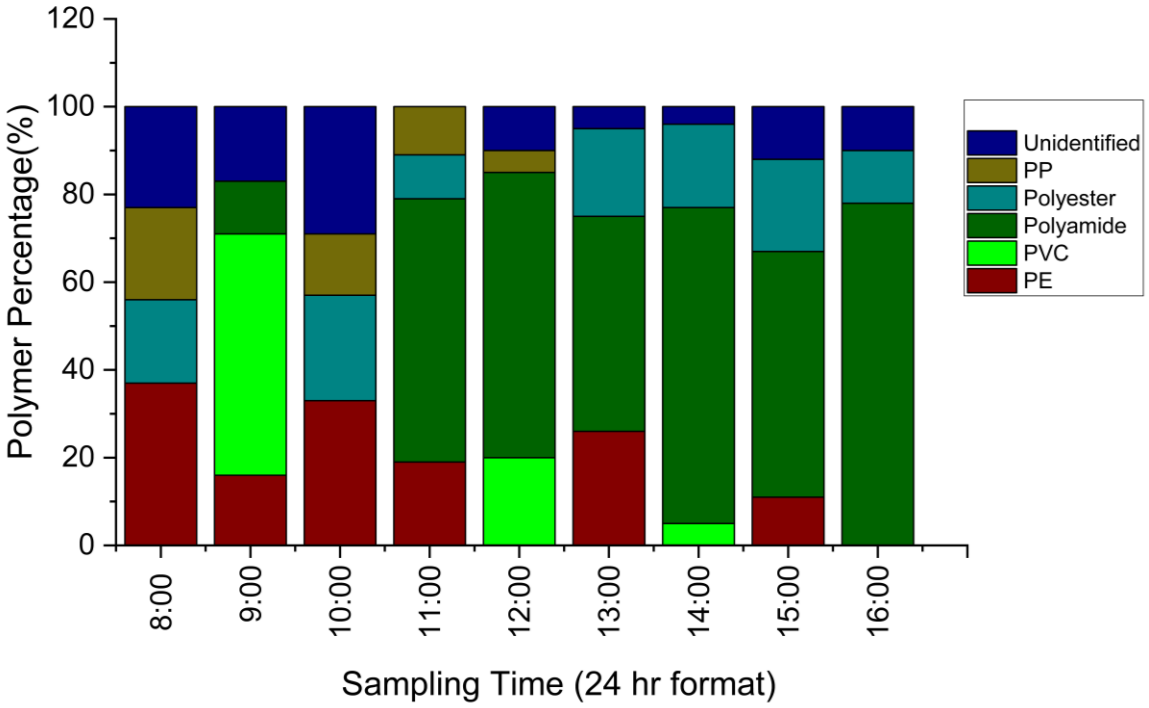

Figure 4.5 Raman Characterization of microplastics of heavily used recreational surface water samples in the Salt River.

Polyamide was present in 67 % of the samples from the Salt River during recreational activities and was the most abundantly identified polymer on average in all water samples (Figure 4.6). Out of all microplastics present, Polyamide constituted 78% of the sample at the peak activity time of 16:00 hr. Additionally, Polyester was prominently present in the identified fraction of microplastics in samples. This is reflective of the possibly high release of microplastic fibers from synthetic textiles (Shamskhany et al., 2021). Polyester is widely used in fabrics for apparel, and is the most produced synthetic fiber on global scale (~50% of the global fiber market) (Rebelein et al., 2021). Polyamide fibers rank second in the list of the most produced synthetic fibers (Carr, 2017). A similar array of polymers was identified in swimming pools in Tempe, AZ (Figure C6).

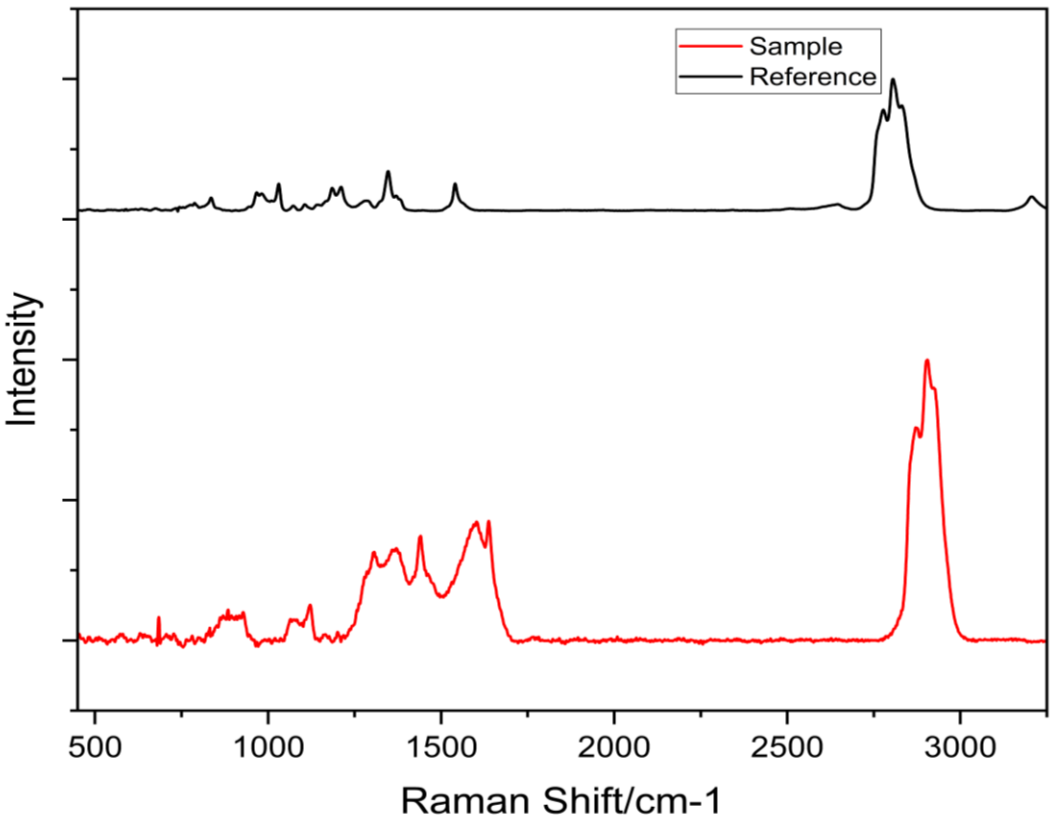

Figure 4.6 An example spectrum of a microplastic sample identified as Polyamide compared to that of a reference spectrum.

4.4 Conclusions

Microplastics were ubiquitous in the heavily used recreational surface waters of the Salt River and apartment community swimming pools in Tempe, AZ. Microplastic concentrations in surface water samples in the Salt river depicted an increase by 8 times at peak recreational activity time compared to baseline concentrations where no tubing, swimming and rafting occurred. Microplastic concentrations depicted substantial variability between apartment swimming pools in Tempe, AZ, at times as high as 254,574 MPs/m^3. Fibrous microplastics accounted for the majority of microplastics in surface waters, with a majority present in relatively smaller size categories (5-200 µm). Raman characterization for microplastics in water samples revealed an array of polymers including PE, PS, PVC, PA, PES and PP, with a certain fraction of the microplastics remaining chemically unidentified. Weathering of microplastics over time could potentially change them thereby rendering them unidentifiable using µ-Raman spectroscopy. However, the fraction of unidentified microplastics was relatively smaller in the river during recreational activity compared to those in swimming pools, air and soil samples in the same arid region, indicating the recent introduction of the micro-particles to the riverine system. Polyamide and Polyester were present and were the most abundantly identified polymers on average in all water samples, indicative of the release of microplastic fibers from synthetic fabrics.

4.5 Acknowledgements

We thank Gabrielle Cano, Christine Hubert, Jason Miech, Jesse Molar and Amelia Stout for their assistance with field sampling in this project.

CHAPTER 5

A METHOD TO DISTINGUISH SOOT AND TIRE WEAR BASED ON PROGRAMMED THERMAL ANALYSES

5.1 Introduction

Tire wear microplastics refer to the particles that form through mechanical abrasion caused by the friction between tires and road surfaces (Panko et al., 2018). With regional differences, the contribution of tire wear particles to microplastic emissions in the environment can reach up to approximately 60% (Eisentraut et al., 2018). However, tire wear microplastics represent an understudied component of microplastic research, particularly in the atmosphere (Kreider et al., 2010, Andrady 2017).

The relatively few studies reporting tire wear microplastics as a component atmospheric particular matter could be ascribed to the limitations posed by conventional separation methodologies and characterization techniques practiced in microplastic analyses. Tire wear particles are often encrusted with mineral matter and bitumen, which increases its overall density, and therefore conventional separation techniques based on density may not account for the heterogeneity (Järlskog et al., 2022). Additional challenges arise when characterizing tire wear using spectroscopic methods such as micro-Raman spectroscopy. Tire wear particles consist of copolymers with additives including Carbon Black, which is a reinforcing filler commonly used in tire manufacturing (Panko et al., 2018). Carbon Black enhances the mechanical properties of the rubber polymers in tires, improving durability and strength (Zafarmehrabian et al., 2012). However, Carbon Black can cause strong fluorescence under the laser light, thereby hindering proper chemical identification using spectroscopic methods including micro-Raman spectroscopy. Therefore, thermo-

analytical methods present an alternative approach to analyzing and identifying tire wear microplastics.

Greater than 97% of Carbon Blacks constitutes Elemental Carbon (EC) arranged as graphite layers to form primary particles (Watson & Valberg, 2001). Soot is a similar refractory material, which is a carbonaceous substance produced during the incomplete combustion of hydrocarbons, is composed primarily of Elemental Carbon (EC), and is often coated or embedded with other materials such as organic matter and sulfates to form internally mixed particles (Haynes & Wagner, 1981; Buseck et al., 2012). The heterogenous reactivities of combustion products such as soot with other gaseous pollutants in the atmosphere, for example NO_2, can have significant implications in the atmosphere (Longfellow et al., 1999).

Refractory carbon or soot is commonly analyzed in the atmosphere based on Thermal Optical Transmittance (TOT) and Thermal Optical Reflectance (TOR) (Fraser et al., 2002; Hang et al., 2010; Pohl et al.,2014; Mancilla et al.,2015; Oyama et al., 2016). Programmed Thermal Analysis (PTA) allows for the differentiation of EC from Organic Carbon (OC) based on the thermal optical transmittance in the Organic Carbon-Elemental Carbon (OC-EC) analyzer. Aerosol samples containing particulate matter on pre-fired quartz fiber filters are placed in the OC-EC analyzer and the sample is subjected to controlled heating cycles under specific and adjustable temperature conditions (Birch & Cary, 1996, Doudrick et al., 2012, Brito et al., 2013). The method makes use of the thermal refractivity of EC which does not volatilize at temperatures of approximately 700 ˚C in an inert atmosphere Previous studies employed PTA with modified temperature

programs to distinguish between different carbonaceous compounds (Doudrick et al., 2012, Nosaka et al., 2018).

Here we aim to develop a thermo-analytical method to distinguish between soot and tire wear in aerosol samples based on TOT using the OC-EC Analyzer. Tire wear samples (n=8) were cryo-milled and subsequently thermally analyzed. Commercial grade Carbon Black used in tires and recovered Carbon Black from waste tires were leveraged in the study. Soot samples from different sources (trucks, lamp and diesel exhaust) were used to compare and contrast with tire wear samples. Repeatability measurements for tire wear and soot samples were made to ensure the consistency of data, thereby ensuring the reliability of the measurements made on the OC-EC Analyzer. The effect of the size of the tire wear particle on the position where the high temperature thermal residue of carbon (EC) appears in the thermogram was tested using PM_{10} samples of tire wear. Aerosol samples collected from roads and urban areas typically contain a mixture of soot and tire wear particles. The method was applied on aerosol samples collected at a parking structure in Tempe, AZ and inside two tunnels located in the São Paulo Metropolitan Area, Brazil.

5.2 Materials and methods

5.2.1 Tire wear sample preparation

Tire wear samples (n=8) (CRM of America LLC, Mesa, AZ) were cut into smaller pieces of approximately 3 mm or smaller in diameter using clean, contamination free pliers (Table 5.1). The cut tire wear samples were subsequently cryo-milled using a 6775 Cryogenic Grinder (Spex Sample Prep, NJ, USA) to produce micro-sized particles. The samples were transferred to small polycarbonate center cylinder vials with steel end plugs. The cryogenic grinding time was counted by cycles, where one cycle included 10 minutes of pre-cool time, 2 minutes of grinding at a rate of 10 counts per second (cps) and 2 minutes of rest.

The cryo-milled tire wear samples were subsequently transferred to pre-fired (650˚C, overnight) quartz fiber filters (Whatman QM-A, Sigma Aldrich, MO, USA). Particle sizes of the cryo-milled tire wear were confirmed by examining under a digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software. Soot samples from the tail pipes of trucks (n=4) and soot particles formed during the incomplete combustion of candle wax (Table 1) were similarly transferred to pre-fired quartz fiber filters (QFF) for subsequent thermal analyses (Section 5.2.5)

Table 5.1 Summary of samples analyzed

Summary of samples analyzed	
Tire wear samples (CRM of America LLC, Mesa, AZ)	**Soot samples**
Yokohama Pass	Tailpipe soot (Truck1)
Goodyear Pass	Tailpipe soot (Truck2)
Toyo truck	Tailpipe soot (Truck3)
Bridgestone truck	Tailpipe soot (Truck4)
Crumb Rubber	Lamp soot
Hankook	Diesel soot
Michellin Pass	
Nitto Pass	

5.2.2 Repeatability measurements

Tire wear and soot samples were tested for consistency by taking measurements for repeatability of the same sample on multiple days. A soot sample from the tail pipe of a truck and a cryo-milled tire wear sample (Yokohama) were used for repeatability tests. Subsequent thermal analyses were performed as described in Section 5.2.5.

5.2.3 Tests on impact of tire-wear particle size

A tire wear sample collected as debris from a highway road in Phoenix, AZ was cryo-milled using a 6775 Cryogenic Grinder (Spex SamplePrep, NJ, USA) with larger polycarbonate center cylinder vials and longer grinding times with increased number of cycles and cooling time to produce smaller tire wear particles. The Cryo-milled tire wear sample was resuspended using a laboratory setup (Upadhyay et al., 2015) (Figure D1) to obtain PM_{10} size fractionated aerosols for subsequent PTA. The tire wear samples were placed in a clean Erlenmeyer flask and HEPA-filtered air was passed over the sample to resuspend relatively smaller particles. The resuspended particles were passed through a size-selective cyclone (URG Corporation, NC, USA) and collected on a downstream pre-

fired quartz fiber filter. The operating flow rate was 15.9 L min^{-1} for the PM_{10} sampling. The particle sizes of the collected PM_{10} filter sample were confirmed by examining under a digital microscope (Leica DM6B-Z, Germany) equipped with the Leica DFC7000 T camera and the Leica Application Suite X (LAS X) software. The sample was subsequently analyzed using the OC-EC Analyzer (Section 5.2.5).

A Carbon Black tire grade sample (N300) (Milagro Rubber Company, Inc., TX, USA) with a particle size range of 30-35 nm was transferred to a pre-fired quartz fiber filter and tested using the OC-EC Analyzer. Similarly recovered Carbon Black samples (n=2) from waste tires (Contec, Warsaw, Poland) with particle diameters, $d<12$ μm and $d<26$ μm, were tested using the OC-EC Analyzer. The samples were analyzed using the OC-EC Analyzer as described in Section (5.2.5)

5.2.4 Applying the method on urban aerosol samples

The approach in developing a method to distinguish soot and tire wear was applied on urban aerosol samples collected as part of previous reported studies investigating the effect of the concentration of extraction solution on Fe solubility measurements in atmospheric particulate matter, and characterizing the particulate matter inside two road tunnels in the São Paulo Metropolitan Area (Brito et al., 2013; Upadhyay et al., 2011).

Ambient aerosol $PM_{2.5}$ samples were collected from the Tyler Street parking garage at the Tempe campus of Arizona State University (ASU), Tempe, AZ (Upadhyay et al., 2011). The sampling site is a semi-closed parking structure that accommodates approximately 300 parking spaces with a traffic flow that is steady during the class times at the University (Majestic et al., 2009; Upadhyay et al., 2011). $PM_{2.5}$ samples were collected using a high-volume air sampler (Tisch Environmental Inc., OH, USA) equipped with a $PM_{2.5}$ impactor stage (TE 231, Tisch-Environmental Inc., OH, USA) by drawing air through pre-fired (650 °C, overnight) quartz fiber filters (Whatman QM-A, Sigma Aldrich, MO, USA) at a rate of 1.13 m^3 min^{-1} (Upadhyay et al., 2011).

Particulate matter samples were collected in two tunnels (Jânio Quadros (JQ) tunnel and the tunnel no. 3 of the Beltway Rodoanel Mário Covas (RA)) in the São Paulo Metropolitan Area, Brazil in 2011 (Brito et al., 2013; Oyama et al., 2016). The JQ tunnel is located southwest in the São Paulo city and a majority of the fleet passing through the tunnel are Light Duty Vehicles (LDVs), ethanol-powered vehicles, and motor cycles powered by gasohol. The RA tunnel is part of a highway that runs around the city with an approximate radius of 23 km away from the center, and is characterized mainly by Heavy

Duty Vehicles (HDVs) (Brito et al., 2013). Particulate matter was collected on quartz membrane filters (Pall Life Sciences, NY, USA) using a MiniVol sampler (Airmetrics, OR, USA) at a rate of 5 liters min^{-1} (Brito et al., 2013).

The quartz filter punches containing the urban aerosol samples were analyzed using the OC-EC Analyzer (Sunset Laboratory, Inc., Forest Grove, OR, USA) using the same temperature program as in Section 5.2.5.

5.2.5 Programmed Thermal Analyses

PTA was performed using an OC-EC Analyzer (Sunset Laboratory, Inc., Forest Grove, OR, USA). The heating process involving the different temperature ramps allows the volatilization and oxidization of carbonaceous compounds in the sample, and OC and EC are differentiated based on their distinct thermal characteristics (Birch and Cary, 1996). The sample was placed on a (1.5×1) cm punch of the QFF and placed in the quartz oven. The oven is purged with He and a stepped temperature ramp increases the temperature in the quartz oven that leads to the thermal desorption of organic compounds. The evolved carbon goes through an oxidizing oven and is quantitatively converted CO_2. The carbon dioxide is swept out of the oven by He and mixed with hydrogen. The gaseous mixture is passed over a Ni catalyst to produce methane. The CH_4 produced is then measured using a Flame Ionization Detector (FID). The oven is then cooled to a temperature of 550˚C after the initial temperature ramp and a second temperature ramp in the oxidizing He/O_2 carrier gas mixture is used to oxidize any EC present in the filter. EC is then determined similarly as the OC (Figure D2). A red diode laser corrects the evolved EC measured by distinguishing the portion of EC that is naturally occurring in the sample and that formed by the charring of the OC in the initial temperature ramp.

The samples on filters were analyzed with variable time steps lasting between 80 and 110 s during the evolution of OC at temperature plateaus of 310˚C, 475 ˚C, 615 ˚C, and 870˚C. The temperature profile during the evolution of EC included 45 s time step plateaus at 550˚C, 625 ˚C, 700˚C, 775˚C, and 850˚C, with a final hold at 870 ˚C for 110 s.

5.3 Results and Discussion

5.3.1 Distinction of soot and tire wear based on PTA

A clear distinction was observed between tire wear and soot tested in the region of the thermogram where the more combustion-resistant EC component is released during the PTA (Figure 5.1). On the basis of our results, soot and tire wear can be clearly separated and distinguished based on the temperatures at which the EC fraction evolves in the thermogram. Tire wear samples were relatively thermally stable compared to soot under He/O_2 conditions, and did not begin oxidation until ~ 630°C. The range of temperatures where the oxidation of tire wear occurred was broader (~630 °C to ~ 850 °C) compared to that of soot. Soot appeared thermally 'weak' relative to tire wear, and oxidation started occurring at ~550°C to ~630 °C under He/O_2 conditions (Figure 5.2). The particle sizes of the cryo-milled tire wear examined ranged from (6-250) µm (Figure D3). Depending on the source, soot can have smaller particle sizes and higher surface areas, which can increase its ability to interact with other molecules (oxygen). Owing to the larger number of carbon atoms exposed to oxygen molecules, thermal stability of soot can decrease.

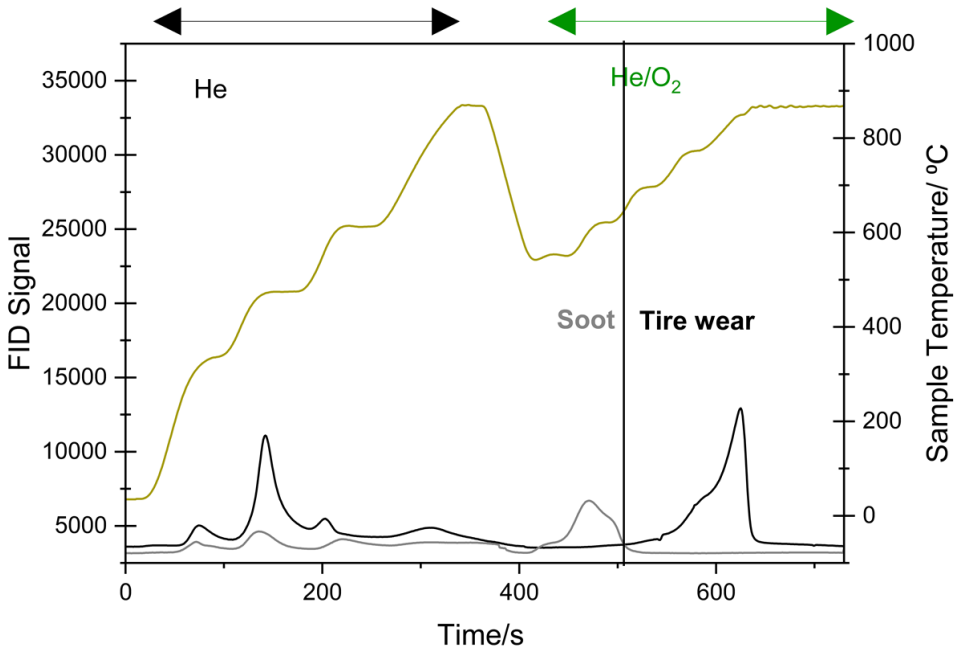

Figure 5.1 Thermograms of tire wear and soot samples from PTA.

Repeatability measurements were made to ensure confidence and consistency in the reported data. Soot and tire wear samples depicted good repeatability when tested under the OC-EC Analyzer (Figure D4).

5.3.2 Effect of the size of tire wear particles on their thermal stability under oxidizing carrier gas conditions

The temperatures at which the EC evolves in PTA is determined by the thermal stability of the sample. Smaller-sized particles can combust at lower temperatures owing to their higher surface area/volume ratio which allows them to efficiently transfer heat across their entire surface area. This facilitates the transport of oxygen molecules to the surface of particle which promotes faster combustion under oxidizing conditions. Therefore, the EC associated with the smaller particles is likely to be oxidized earlier in the thermal analyses. A tire wear sample subjected to longer cryo-milling grinding times with increased number of cycles produced particles ranging in size from (6-87) µm. PM_{10} filter samples from resuspension observed under the digital microscope depicted particles with diameters less than 10 µm (Figure D5). Contrary to the expected results based on aforementioned size effect on thermal stability of the sample, PM_{10} of tire wear depicted a clear separation from soot based on the temperatures at which the EC fraction evolves in the thermogram (Figure 5.2). It is important to note that the compositions of soot and tire wear differ largely. Additionally, soot is more oxygenated compared to tire wear. Compounds can adsorb to the surface of soot, including metal and sulfur impurities (Popovicheva et al., 2004). In contrast, tire wear predominantly consists of rubber copolymers, additives, including non-black fillers used to enhance tire performance and stability (Rauert et al., 2022).

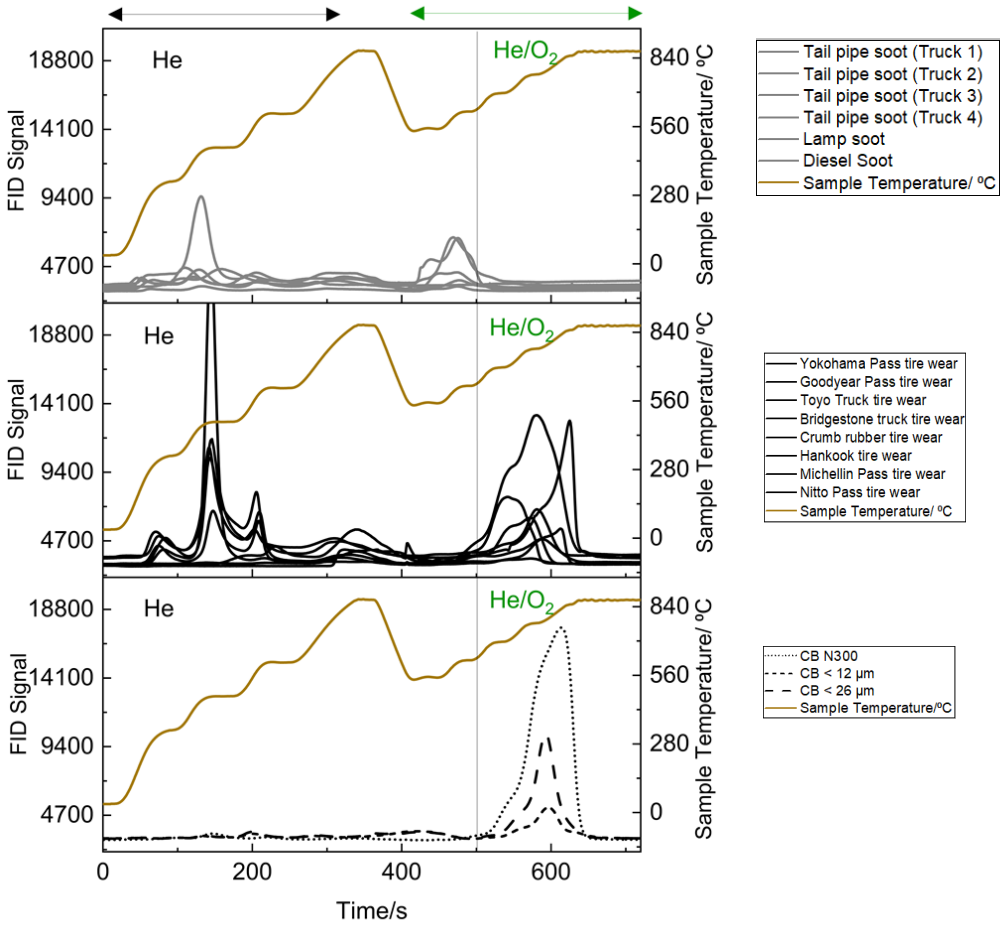

Figure 5.2 Soot, tire wear and Carbon Black samples under PTA

Carbon Black N300 tire grade (30-35 nm) depicted a clear distinction from soot under oxidizing carrier gas conditions in PTA (Figure 5.2). A similar observation was made for the recovered Carbon Blacks from waste tires (d<12 µm and d<26 µm) samples in the OC-EC Analyzer (Figure 5.2).

5.3.3 Application of the tested method on urban aerosol samples

Current concerns about health, and the environment compel us to study the differences between these carbonaceous materials; soot and tire wear. This concern is understandable, as certain types of soot, specifically chimney soot, was the causative agent in the first occupation induced cancer reported in 1775 (Medalia et al., 1983). Ambient $PM_{2.5}$ samples collected from the Tyler Street Parking structure depicted the presence of a mixture of soot and tire wear where EC evolved from ~ 550 ˚C to ~800 ˚C in the thermograms (Figure 5.3). Ambient aerosol samples collected in the vicinity of roads and urban areas can often contain a mixture of soot and tire wear particles. Tire wear generated as vehicles drive on roads can mix with the airborne soot generated from vehicle exhaust. The thermograms display relatively high proportions of soot and tire wear in the $PM_{2.5}$ samples collected from the parking structure. This is not surprising as the parking space witnesses a substantial vehicular inflow and outflow during the time of University classes.

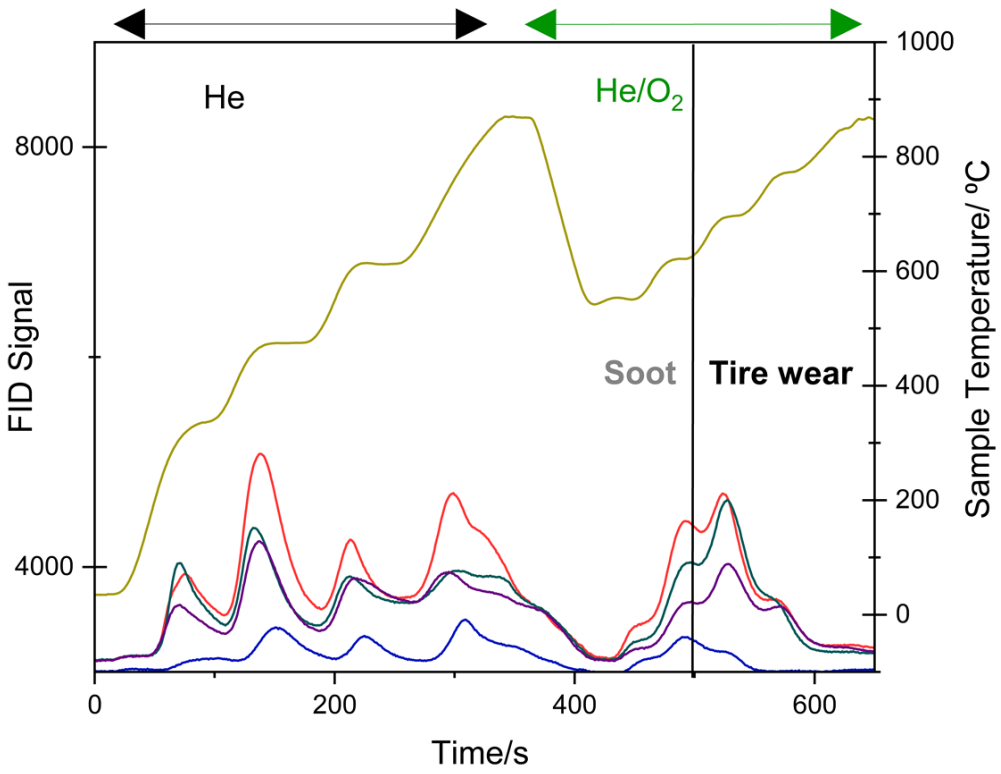

Figure 5.3 Thermograms of $PM_{2.5}$ samples from the Tyler Street Parking Structure, Tempe, AZ from PTA

A similar observation was made but with relatively higher EC contents for the aerosol samples collected from two tunnels in the São Paulo Metropolitan Area, Brazil (Figure 5.4, Figure D6, Figure D7). A higher proportion of tire wear was observed compared to soot in the aerosol samples collected from both the tunnels. Substantially lower soot and tire wear signatures were observed in ambient aerosol samples from the JQ tunnel, which witnesses mainly Light Duty Vehicles (LDVs), compared to those in the RA tunnel (Heavy Duty Vehicles predominant).

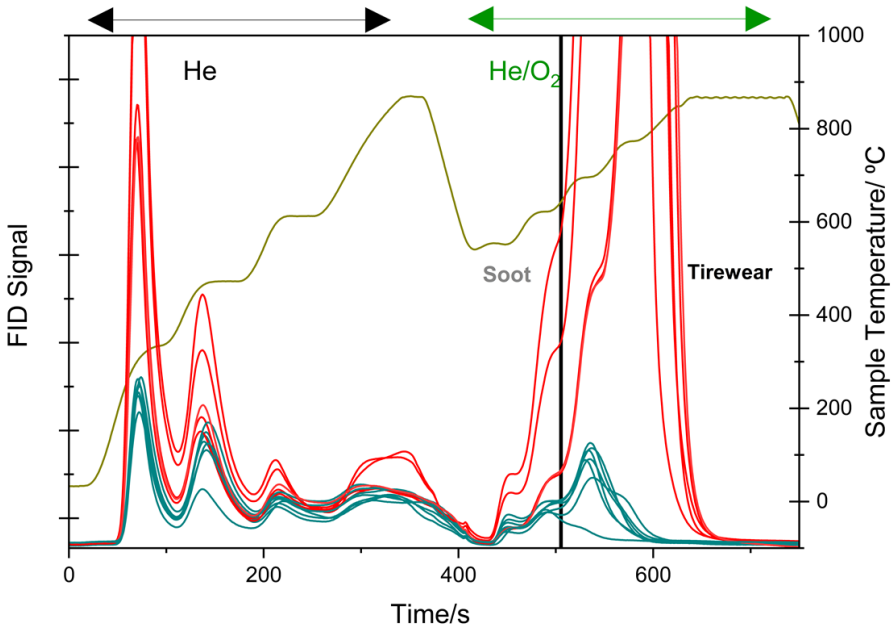

Figure 5.4 Thermograms of aerosol samples collected from JQ and RA tunnels in São Paulo Metropolitan Area in 2011, Brazil from PTA.

5.4 Conclusions

An approach in separating soot and tire wear based on where elemental carbon evolves in thermograms from Programmed Thermal Analysis looks promising. This method would allow re-analyses of aerosol samples collected in the past to identify tire wear in atmospheric particulate matter. Tire wear samples and soot samples from different sources depicted a clear distinction for time and temperature parameters of EC evolution in thermograms. Carbon Black Tire Grade samples showed a similar behavior to tire wear, separated from soot. The method was applied to urban aerosol samples from Tempe, AZ and Sao Paolo Metropolitan area, Brazil, and results show the presence of a mixture of tire wear and soot.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

Microplastics are emerging pollutants and continue to receive attention owing to their potential health impacts on organisms including humans via different exposure routes such as the food chain, drinking water and air. However, their distribution and impacts on the environment remain largely unexplored. This thesis presents a synthesis of results from exploratory studies on the presence of microplastics in aquatic, atmospheric and terrestrial environments in the desert southwest. The impact of representative weathering processes in the environment on our ability to characterize microplastics was investigated. The last part of this work seeks to develop a thermo-analytical method to identify tire wear that overcomes limitations posed by traditional techniques practiced in microplastics literature.

Chapter 2 details findings on airborne concentrations of microplastics in Tempe, AZ and studies their physical and chemical alterations through representative weathering processes in the environment. Microplastics were found in all suspended particulate matter samples collected over the period of one year (2020-2021), indicating their ubiquitous nature in the air in Tempe, AZ. Microplastic concentrations ranged from 0.02-1.1 microplastics/m^3 with a majority being fibers predominant in the smaller size categories (5 μm–100 μm). There was no clear variation of microplastic concentrations with meteorological parameters (average wind speed and maximum wind speed). The sampling location of interest witnesses dust storms frequently during the North American

monsoon season, and therefore microplastic concentrations are largely affected by such episodic influences. Chemical characterization of microplastics through micro-Raman spectroscopy revealed that polyvinyl chloride was the most abundantly identified polymer on average in all samples. Large fractions of microplastics in suspended particulate matter samples were chemically unidentified. Therefore, representative weathering processes (physical abrasion, chemical oxidation and UV exposure) were simulated to understand how microplastics alter in the environment, and the resulting impact on Raman spectra and our ability to identify the plastics. Weathered microplastics could also have altered surface polarities, thereby enhancing their interaction with polar compounds in the environment. Experiments simulating physical abrasion show that weathered polyethylene microplastics are significantly altered after 14 weeks of simulation, compared to their pristine state, as physical abrasion can alter the nature of the surface and micro-scratches on the surface could increase the surface average roughness, therefore increasing the background noise in spectra, and thereby hindering their proper identification. Surface average roughness measurements were conducted using an optical profilometer and results show a substantial increase in the average roughness. A distinct change in spectra were not observed for the remaining polymers (PVC, PET, PS and PP), showing that the nature of the plastic is a factor that determines the extent it undergoes weathering in the environment. Chemical oxidative experiments did not depict a drastic change over time, however CH_2 peaks of polyethylene appear to be less intense as the experiment time progressed. Future studies could investigate the resulting changes in Raman spectra by simulating a combination of weathering processes

simultaneously. This could also provide an insight into which combinations of weathering processes result in more significant changes.

Chapter 3 presents results for the investigations on the spatiotemporal distribution of soil microplastics in Phoenix, AZ and the surrounding areas of the Sonoran Desert. The microplastic abundance in soil samples from 2015 ranged from 122 to 1399 microplastics/kg with a heterogeneous spatial distribution indicating no clear spatial trends, with a few relatively remote areas with higher microplastic concentrations. Findings show substantial deposition fluxes, sometimes as high as 389 microplastics/m^2/day, occurring in the same area of interest that could possibly explain unclear spatial trends. Additionally, re-entrainment and resuspension of material, especially during local dust storms could affect observed soil microplastic abundances. The temporal variability of soil microplastics indicate a systematic increase in the abundance of microplastics from 2005 to 2015 at all the studied sampling sites. The highest count for microplastics, on average, was observed in the size range of 5 μm −50 μm in soil samples from 2015. In contrast to this observation from 2015, microplastics were predominantly found between 50μm - 100 μm on average in soil samples from 2005. This finding could be explained by the secondary degradation of microplastics, particularly by physical abrasion resulting in smaller microplastics over time. Fibrous microplastics accounted for the large majority (≥87 % in 2005 and ≥ 98 % in 2015) of the microplastics in soil. Fragments were observed as the only other morphology present. Chemical characterization for microplastics in soil samples depicted an array of polymers

including PE, PS, PVC, PA, PES, PP depicting a variety of polymers. Consistent with the findings in Chapter 2, a majority of microplastics remain chemically unidentified. Polyethylene was present in 75 % of the sampling sites indicative of its large global production. Future studies could leverage soil samples collected through ESCA by CAP-LTER to investigate the spatial and temporal variation of microplastics in 2024. Furthermore, an in-depth quantitative study on how atmospheric deposition fluxes contribute to soil microplastic abundances in the arid region would provide an understanding into the transport of microplastics between different environments. Moreover, existing scientific research indicates the lack of standardized methods for microplastic sampling, quantification and characterization. Standardized protocols would allow the comparison of results in future research.

Chapter 4 details findings on the temporal variation of microplastics in the Salt river during recreational activities in summer in Mesa, AZ. Results show an 8 times increase in microplastic concentrations in surface waters from initial 8:00 hr to peak activity time at 16:00 hr, with fibers predominantly present in samples. Surface water samples collected concurrently from swimming pools in Tempe, AZ depict concentrations as high as 254,574 MPs/m^3. Microplastics sizes depicted a wider range with larger fibers (5-200 µm) compared to those found in terrestrial and atmospheric environments in Tempe, AZ. Polyamide and Polyester fibers were dominant in samples, indicating the release of fibers from synthetic fabrics during recreational activities. Future studies could investigate other possible co-contaminants in the surface waters of the Salt river, such as sunscreen

(oxybenzone), to further show the impact of recreational activities on environmental pollutants in aquatic environments.

Chapter 5 discusses an approach to distinguish between soot and tire wear microplastics using Programmed Thermal Analyses (PTA). Tire wear and soot samples from different sources depicted a clear distinction for time and temperature parameters of EC evolution in thermograms. Carbon Black materials with specifications typically used in tire manufacturing depicted a similar behavior to tire wear, separated from soot. The thermal method was applied to urban aerosol samples collected from Tyler street in Tempe, AZ and two tunnels in Sao Paolo, Brazil (2011), and results indicate the presence of a mixture of tire wear and soot. Future work could investigate and apply this method to identify tire wear in soil and aquatic matrices. Moreover, the method could be employed in the future to quantify tire wear microplastics in aerosols. Furthermore, the developed method could help assess if tire wear is mistakenly identified as soot in ambient air. Constituting to as large as approximately 60% of total microplastic emissions, tire wear poses a non-negligible risk on environmental health. However, despite their non-negligible emissions, tire wear is an underreported component of microplastics in the current context of literature due to the current methodological limitations in their characterization by spectroscopic techniques. Therefore, the developed thermo-analytical technique promises to be an exciting tool for microplastics research in identifying tire wear in diverse environments.

This work shows the ubiquitous and pervasive nature of microplastics in the diverse environments of an arid region in the Desert Southwest. The findings deepen our understanding about the ever-increasing microplastics in the environment, and therefore highlights the need for further research on their impact on ecological and human health. On the broader scale, responsible use of plastics and collective action for a more sustainable future are of paramount importance.

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APPENDIX A

CHAPTER 2 SUPPORTING INFORMATION

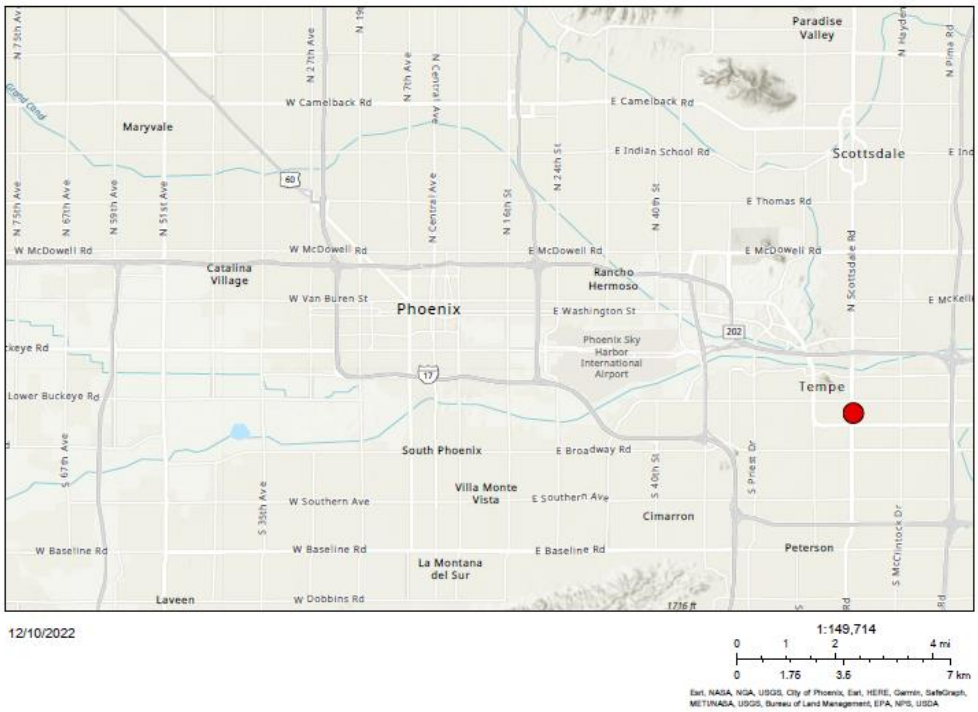

Figure A1. Location of sampling

Table A1. Spreadsheet of microplastics concentrations

Date of sampling	Microplastics concentration /MPs m^{-3} (Replicate 1)	Microplastics concentration /MPs m^{-3} (Replicate 2)	Microplastics concentration /MPs m^{-3} (Replicate 3)	No. of microplastics counted on average	Average Concentration of microplastics/MPs m^{-3}	Standard deviation of microplastics concentration
Day 1	0.4627	0.6044	0.5829	40	0.55	0.076
Day 7	0.4413	0.5249	0.5338	36	0.5	0.051
Day 13	1.2212	0.8574	1.2215	79	1.1	0.210
Day 19	1.0314	0.6344	0.8242	61	0.83	0.199
Day 25	0.7570	0.7750	0.5680	51	0.7	0.115
Day 31	0.1389	0.1946	0.2665	15	0.2	0.064
Day 37	0.0480	0.0391	0.0629	5	0.05	0.012
Day 43	0.1142	0.1065	0.1125	7	0.1	0.025
Day 49	0.4159	0.4066	0.3775	29	0.4	0.020
Day 55	0.5948	0.4372	0.4980	36	0.51	0.079
Day 61	0.0731	0.0983	0.0386	5	0.07	0.030
Day 67	0.4490	0.1821	0.3889	25	0.34	0.140
Day 73	0.0708	0.0309	0.0483	4	0.05	0.020
Day 79	0.6651	0.6862	0.6887	49	0.68	0.013
Day 85	0.5396	0.2588	0.7016	36	0.5	0.224
Day 91	0.2553	0.3802	0.4746	27	0.37	0.110
Day 97	0.0589	0.0809	0.0701	5	0.07	0.011
Day 103	0.6597	0.8139	0.6264	50	0.7	0.100
Day 109	0.4562	0.4774	0.4764	34	0.47	0.012

Day 115	0.0200	0.0346	0.0954	4	0.05	0.040
Day 121	0.0507	0.0761	0.0532	5	0.06	0.014
Day 127	0.0182	0.0850	0.0168	4	0.04	0.039
Day 133	0.1336	0.0346	0.0717	6	0.08	0.050
Day 139	0.5739	0.4649	0.4612	36	0.5	0.064
Day 145	0.5690	0.6909	0.5401	44	0.6	0.080
Day 151	0.3960	0.3927	0.4114	29	0.4	0.010
Day 157	0.0314	0.0475	0.0711	4	0.05	0.020
Day 163	0.0124	0.1271	0.1005	6	0.08	0.060
Day 169	0.0802	0.0046	0.0352	4	0.04	0.038
Day 175	0.1184	0.0186	0.0430	5	0.06	0.052
Day 181	0.0573	0.2132	0.0295	8	0.1	0.099
Day 187	0.0317	0.0186	0.1597	5	0.07	0.078
Day 193	0.0358	0.0296	0.0546	3	0.04	0.013
Day 199	0.1606	0.1387	0.1507	11	0.15	0.011
Day 205	0.1074	0.0152	0.0274	4	0.05	0.050
Day 211	0.0261	0.0909	0.0150	3	0.044	0.041
Day 217	0.0802	0.0402	0.0596	5	0.06	0.020
Day 223	0.0650	0.0431	0.0419	4	0.05	0.013
Day 229	0.0652	0.1233	0.0815	7	0.09	0.030
Day 235	0.0084	0.0442	0.0074	4	0.02	0.021
Day 241	0.0061	0.0364	0.1074	4	0.05	0.052
Day 247	0.0451	0.0263	0.0486	4	0.04	0.012
Day 253	0.2046	0.2214	0.1740	15	0.2	0.024

Day 259	0.1260	0.1263	0.1677	11	0.14	0.024
Day 265	0.0812	0.0879	0.1009	7	0.09	0.010
Day 271	0.0777	0.1121	0.2302	11	0.14	0.080
Day 277	0.0431	0.0247	0.0522	4	0.04	0.014
Day 283	0.0497	0.0732	0.0572	5	0.06	0.012
Day 289	0.0686	0.0808	0.0906	6	0.08	0.011
Day 295	0.1052	0.1210	0.0738	8	0.1	0.024
Day 301	0.0323	0.0417	0.0760	4	0.05	0.023
Day 307	0.0092	0.1067	0.2441	9	0.12	0.118
Day 313	0.0620	0.0482	0.0699	5	0.06	0.011
Day 319	0.0223	0.1624	0.0253	6	0.07	0.080
Day 325	0.0714	0.0962	0.0724	6	0.08	0.014
Day 331	0.0462	0.3207	0.0830	11	0.15	0.149
Day 337	0.0969	0.0209	0.0322	4	0.05	0.041
Day 343	0.0829	0.2995	0.0375	11	0.14	0.140
Day 349	0.0713	0.1870	0.1017	9	0.12	0.060
Day 355	0.0900	0.1100	0.0999	8	0.1	0.010
Day 361	0.0863	0.1002	0.4135	15	0.2	0.185
Day 367	0.3643	0.4151	0.4205	29	0.4	0.031
Day 373	0.4639	0.4428	0.4434	33	0.45	0.012

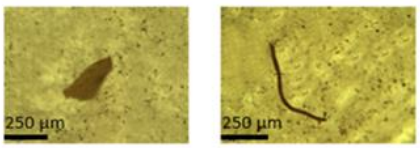

Figure A2. Fragment and Fiber in samples

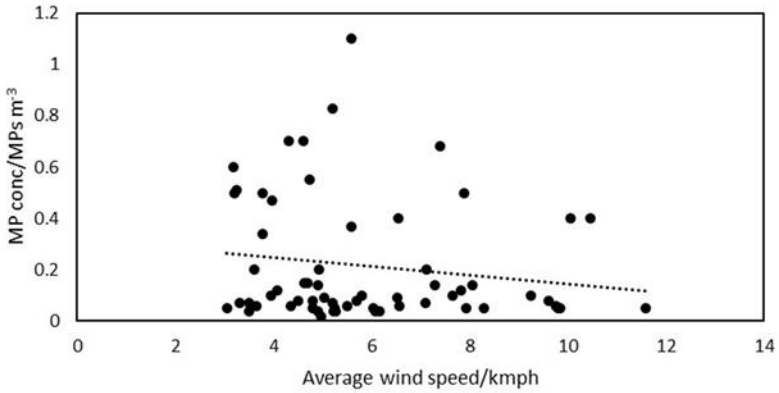

Figure A3. Correlation of average wind speed and microplastics suspended in air.

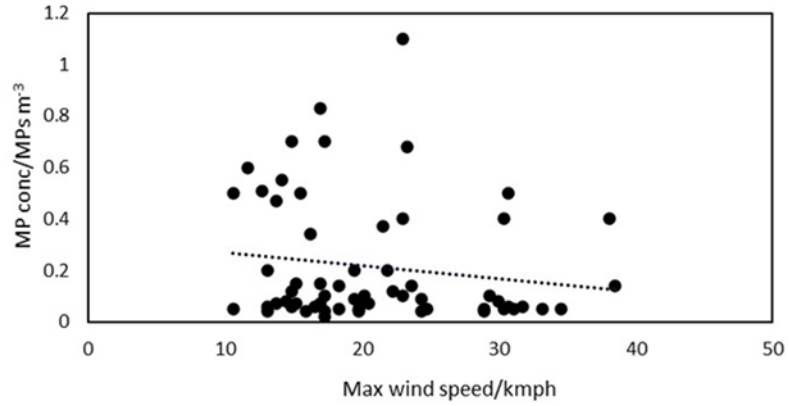

Figure A4. Correlation of maximum wind speed and microplastics suspended in air.

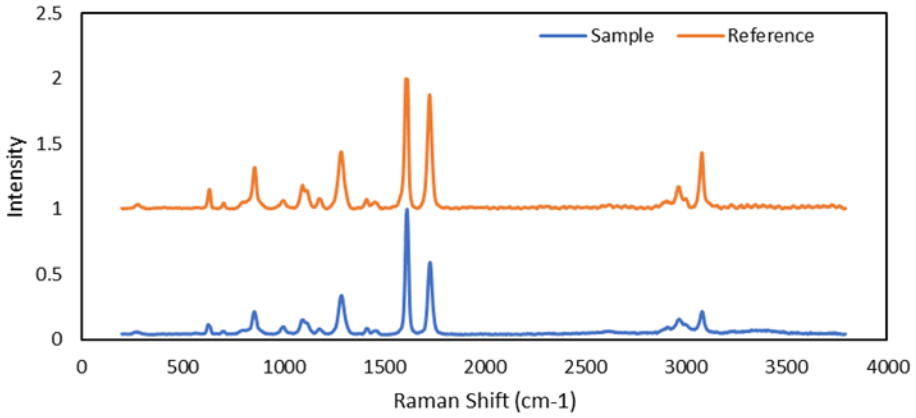

Figure A5. Micro-Raman spectrum of a sample verified as Polyester

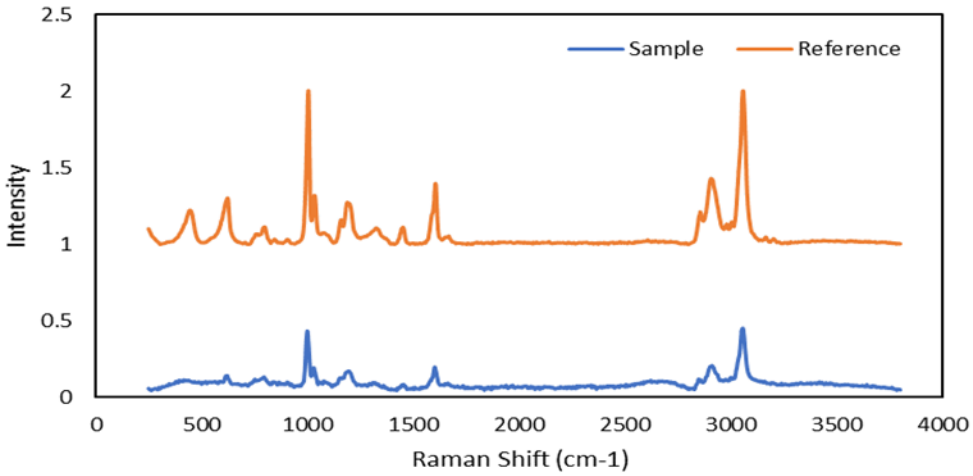

Figure A6. Micro-Raman spectrum of a sample verified as Polystyrene

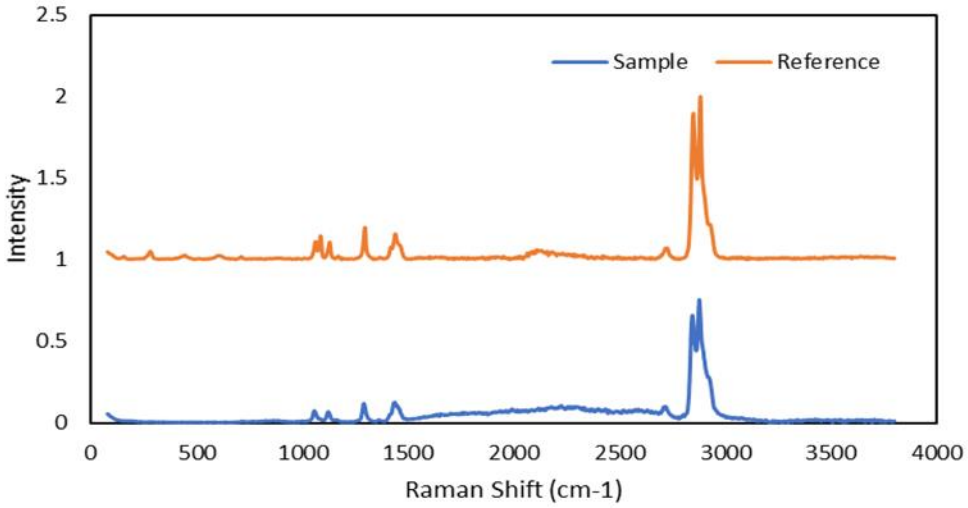

Figure A7. Micro-Raman spectrum of a sample verified as Polyethylene

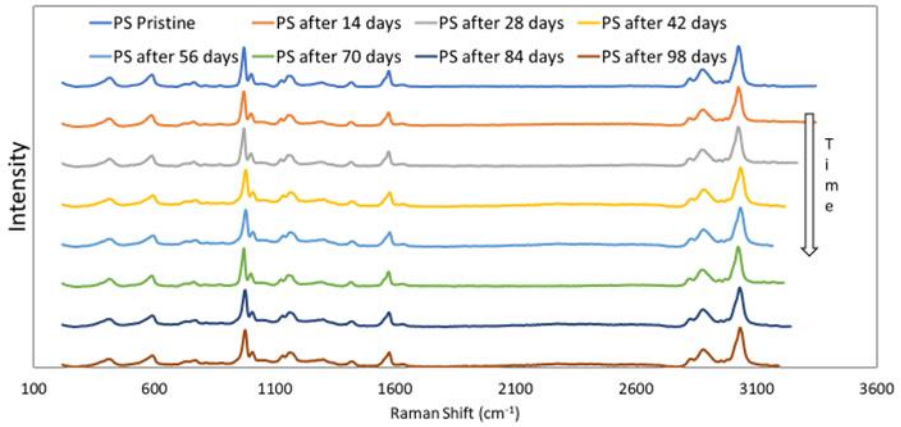

Figure A8. Raman spectra of PS weathered microplastic through physical abrasion

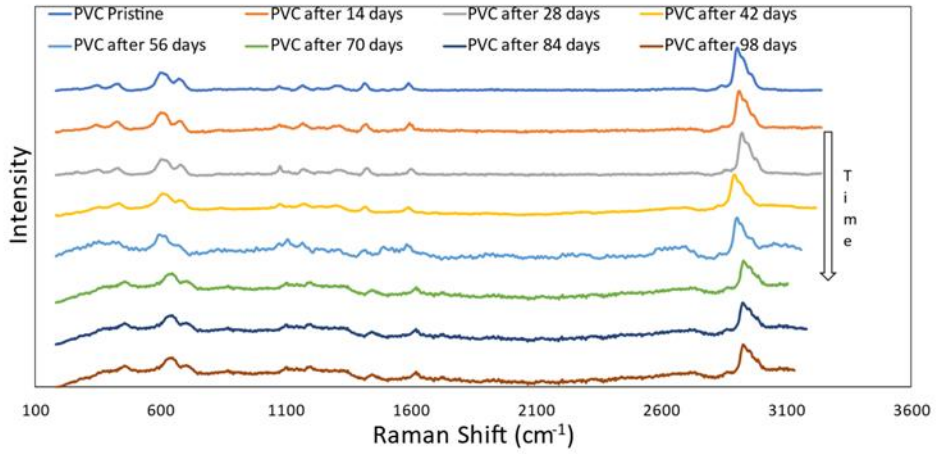

Figure A9. Raman spectra of PVC weathered microplastic through physical abrasion

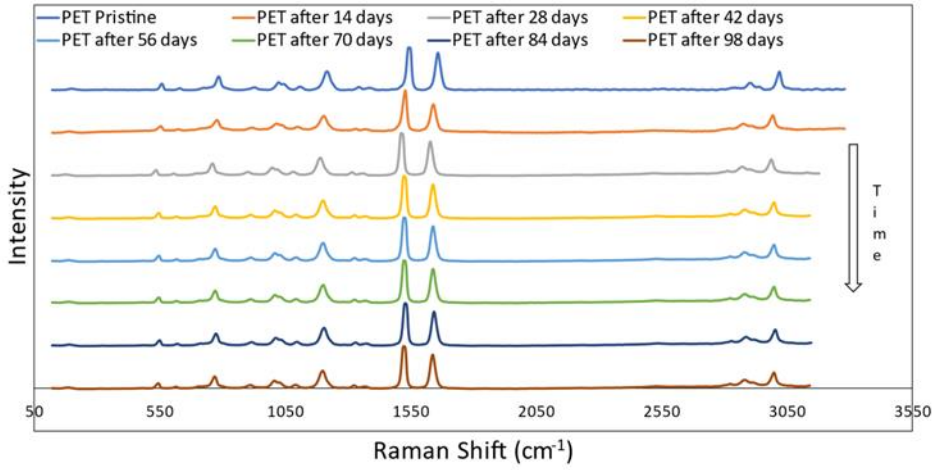

Figure A10. Raman spectra of PET weathered microplastic through physical abrasion

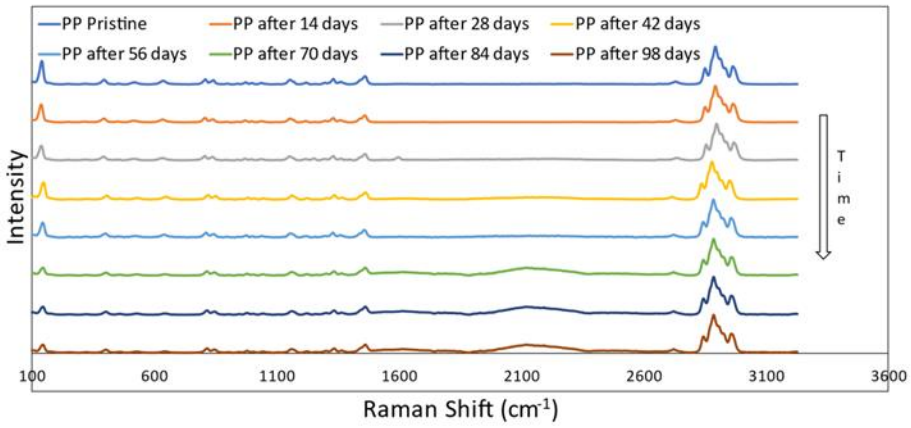

Figure A11. Raman spectra of PP weathered microplastic through physical abrasion

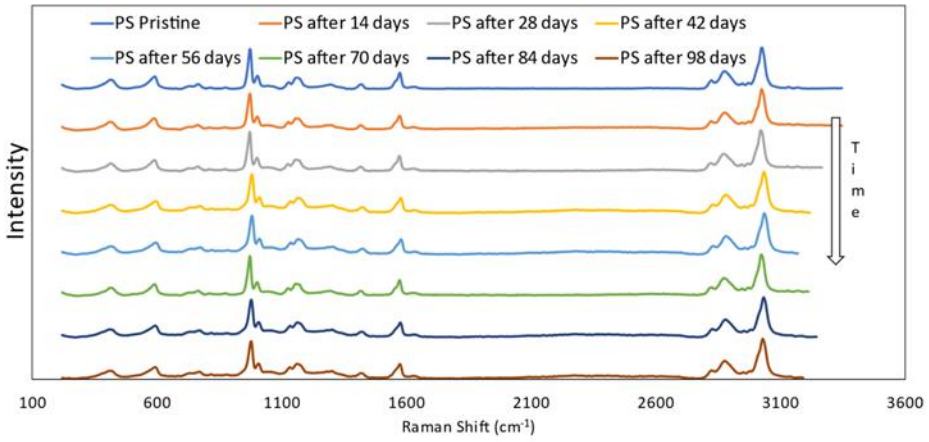

Figure A12. Raman spectra of PS weathered microplastic through chemical oxidation

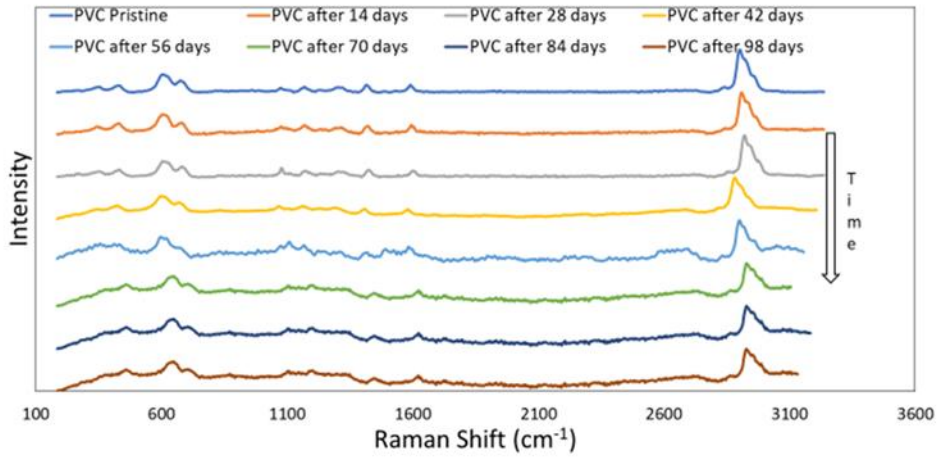

Figure A13. Raman spectra of PVC weathered microplastic through chemical oxidation

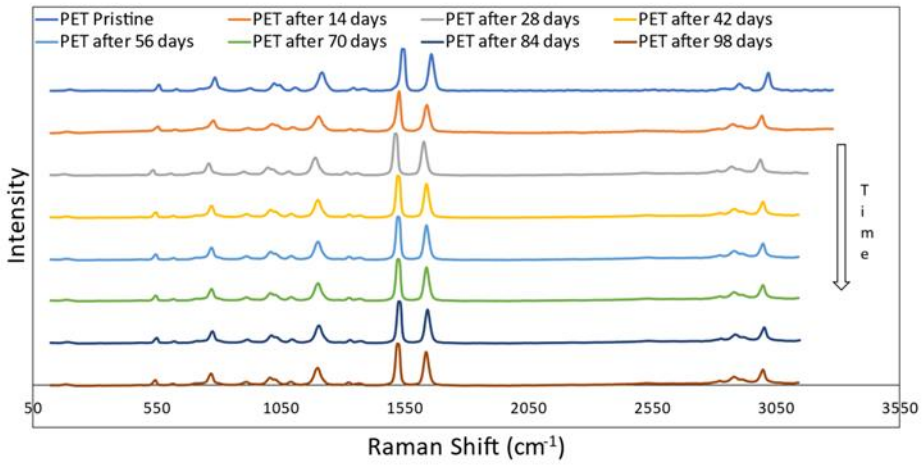

Figure A14. Raman spectra of PET weathered microplastic through chemical oxidation

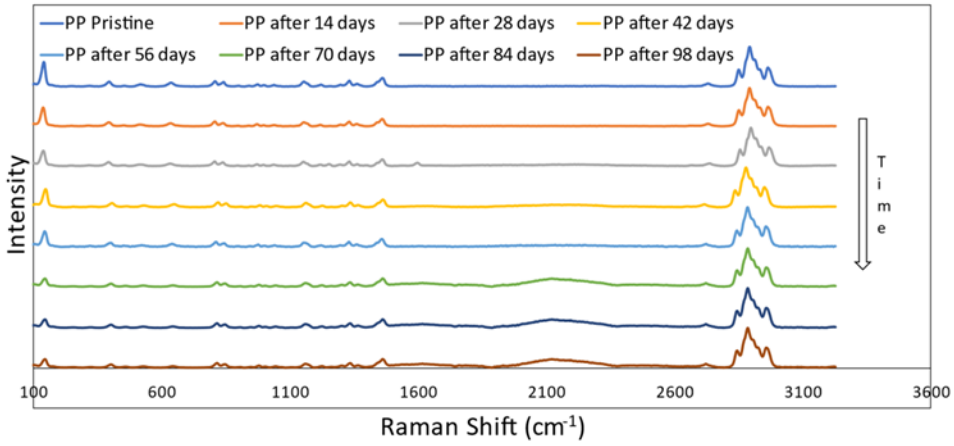

Figure A15. Raman spectra of PP weathered microplastic through chemical oxidation

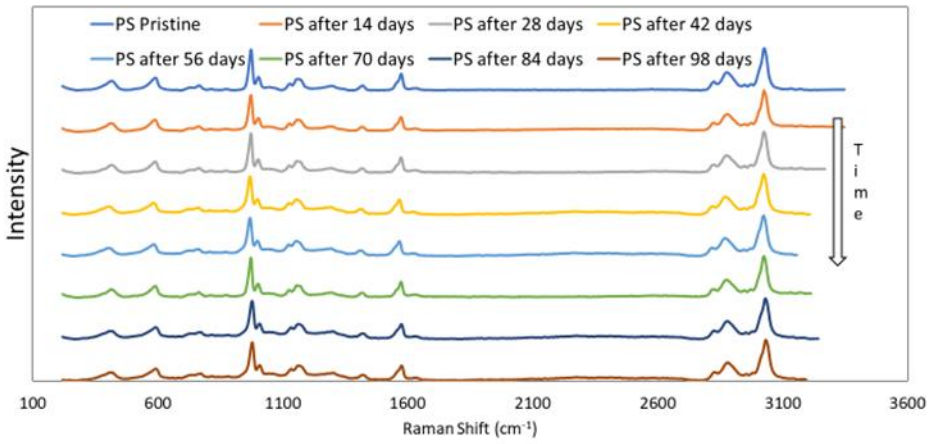

Figure A16. Raman spectra of PS weathered microplastic through UV exposure

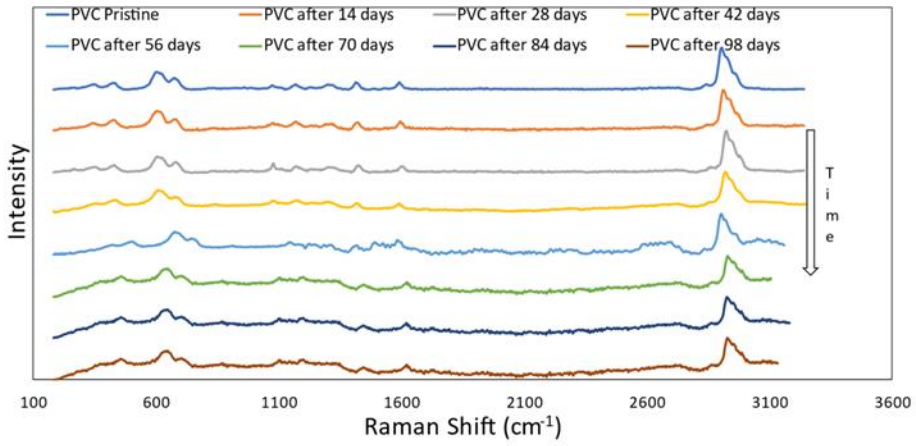

Figure A17. Raman spectra of PVC weathered microplastic through UV exposure

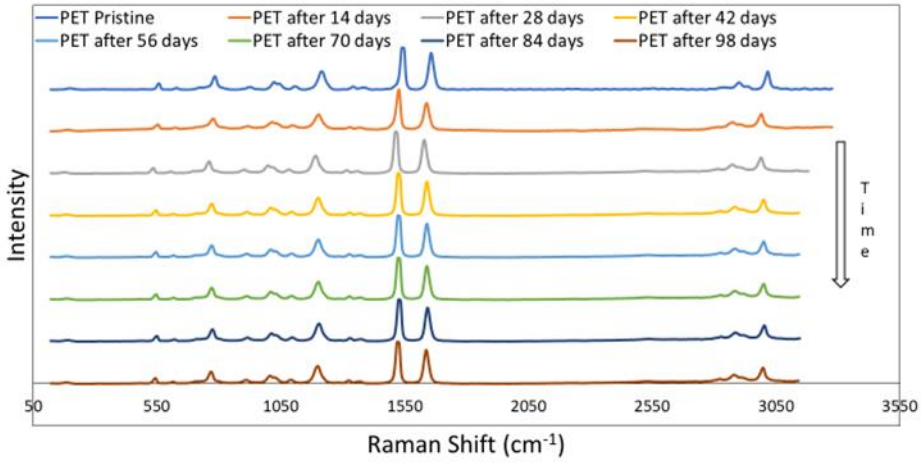

Figure A18. Raman spectra of PET weathered microplastic through UV exposure

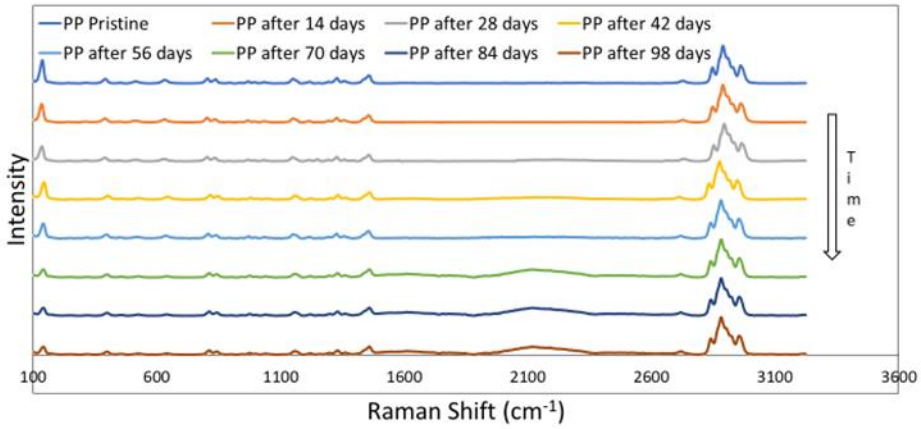

Figure A19. Raman spectra of PP weathered microplastic through UV Exposure

APPENDIX B

CHAPTER 3 SUPPORTING INFORMATION

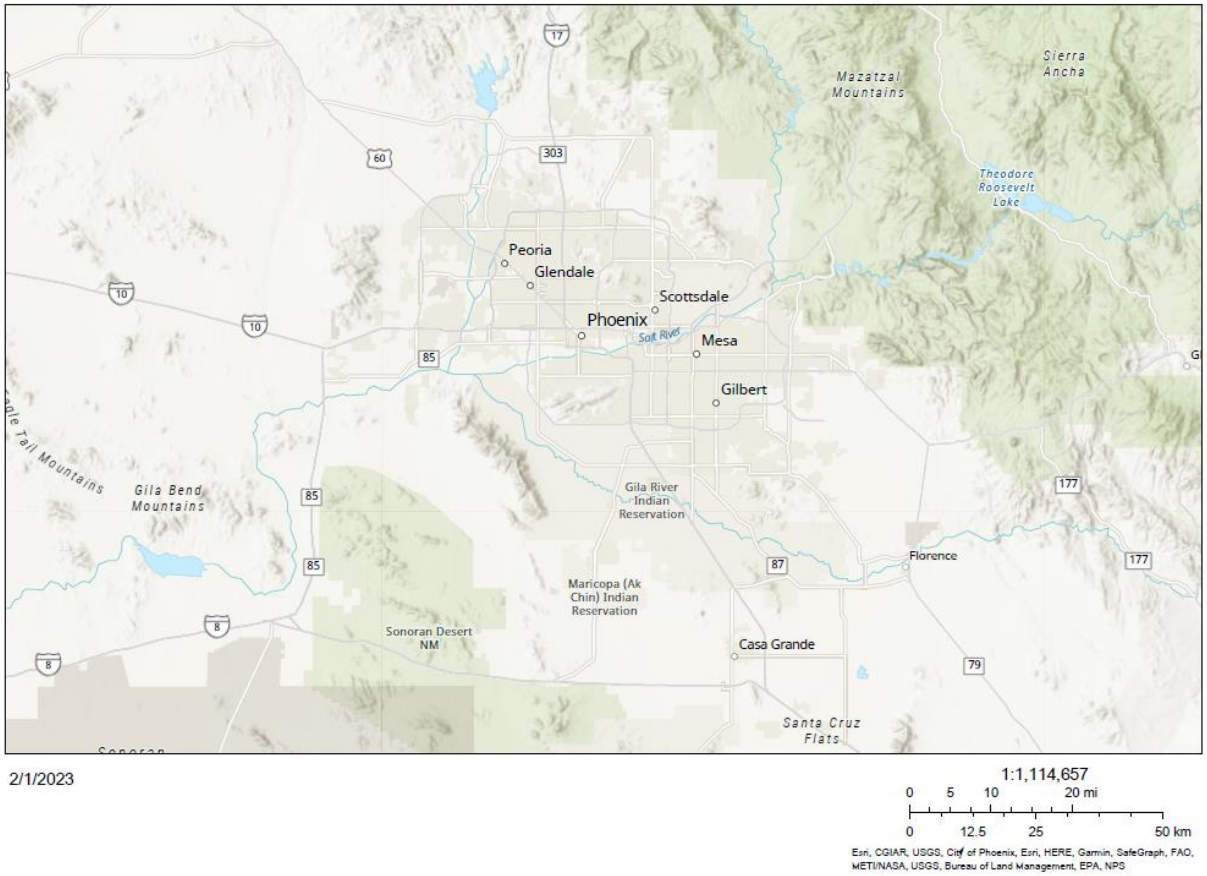

Figure B1. Sampling areas included in the CAP LTER ESCA 200-point Survey

Figure B2. Deposition Samplers deployed on the rooftop of the Interdisciplinary Science & Technology Building #4 (ISTB4), ASU, Tempe

Figure B3. Location of Phoenix, AZ, USA

Table B1. Spreadsheet of soil microplastics concentrations

2015						
Sampling Location ID	Replicate 1 (MPs/kg)	Replicate 2 (MPs/kg)	Replicate 3 (MPs/kg)	Average MPs/kg of soil	Standard deviation of the mean	No. of MPs counted on average
Site 1	784	821	747	784	37	47
Site 2	1171	1019	1136	1109	80	67
Site 3	1026	955	998	993	36	60
Site 4	1013	1039	1005	1019	18	61
Site 5	1061	986	965	1004	50	60
Site 6	1020	964	995	993	28	60
Site 7	321	295	330	315	18	19
Site 8	94	120	153	122	29	7
Site 9	164	151	139	151	13	9
Site 10	262	254	278	265	12	16
Site 11	256	289	307	284	26	17
Site 12	622	592	658	624	33	37
Site 13	1270	1192	1152	1205	60	72
Site 14	1419	1404	1375	1399	22	84
Site 15	971	964	1000	978	19	59
Site 16	212	187	229	209	21	13
Site 17	761	753	691	735	38	44
Site 18	361	376	394	377	16	23
Site 19	916	963	896	925	34	56
Site 20	308	315	338	320	16	19
Site 21	877	802	865	848	40	51
Site 22	526	572	543	547	23	33
Site 23	911	991	1002	968	50	58
Site 24	429	444	421	431	12	26
Site 25	231	259	251	247	15	15
Site 26	224	248	260	244	18	15
Site 27	258	338	286	294	40	18
Site 28	851	831	868	850	18	51
Site 29	347	362	381	363	17	22
Site 30	431	444	481	452	26	27
Site 31	550	515	565	543	26	33
Site 32	806	744	784	778	32	47
Site 33	661	656	614	644	26	39
Site 34	360	375	396	377	18	23
Site 35	238	250	280	256	22	15
Site 36	538	545	585	556	26	33

Site 37	301	314	287	301	13	18
Site 38	456	380	421	419	38	25
Site 39	737	699	685	707	27	42
Site 40	1109	1123	1043	1092	43	66
Site 41	254	267	281	267	14	16
Site 42	364	314	327	335	26	20
Site 43	590	609	626	608	18	36
Site 44	625	606	617	616	10	37
Site 45	500	483	474	485	13	29
Site 46	366	317	332	338	25	20
Site 47	583	560	551	565	16	34
Site 48	287	256	297	280	21	17
2005						
Sampling Location ID	Replicate 1 (MPs/kg)	Replicate 2 (MPs/kg)	Replicate 3 (MPs/kg)	Average MPs/kg of soil	Standard deviation of the mean (MPs/kg)	No. of MPs counted on average
Site 23	397	467	531	465	67	28
Site 38	88	92	115	98	15	6
Site 26	70	58	66	65	6	4
Site 29	65	77	89	77	12	5
Site 36	227	271	246	248	22	15
Site 40	562	603	579	581	21	35
Site 45	189	216	198	201	13	12
Site 47	730	663	717	703	36	42
Site 34	72	78	66	72	6	4
Site 14	1490	1548	1582	1540	47	92
Site 32	579	665	619	621	43	37
Site 11	226	250	260	245	17	15
Site 12	212	174	201	196	20	12
Site 6	383	331	321	345	33	21

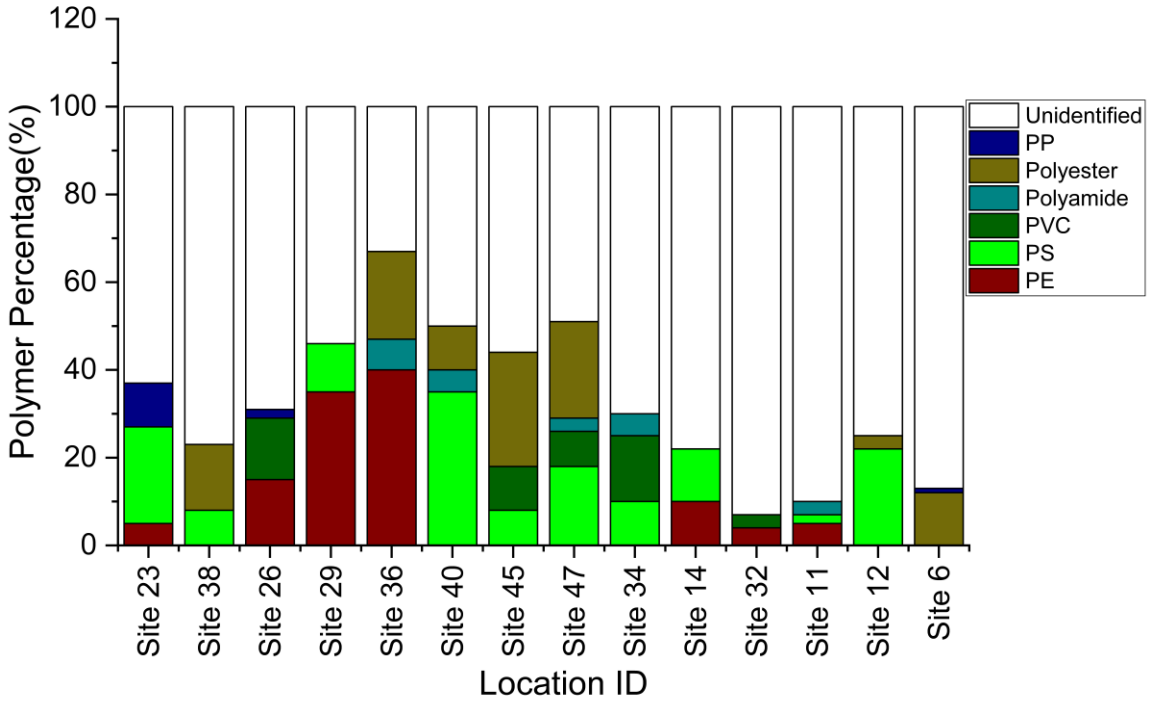

Figure B4. Raman Characterization of microplastics in soil samples from 2005

APPENDIX C

CHAPTER 4 SUPPORTING INFORMATION

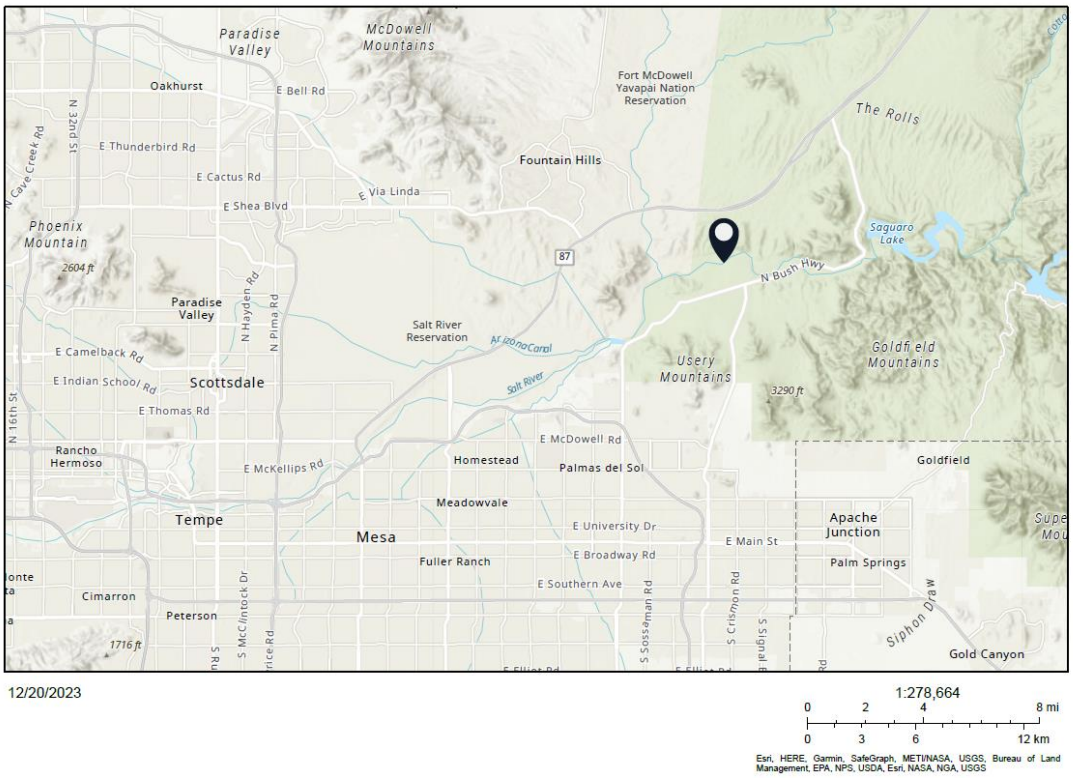

Figure C1. Sampling location of Salt River, AZ.

Figure C2. Sampling locations of Swimming pools in Tempe, AZ.

Table C1. Table of surface water microplastic concentrations in the Salt River, AZ.

Salt River, Arizona						
Sampling Time (24-hr format)	Replicate 1 (MPs/m3)	Replicate 2 (MPs/m3)	Replicate 3 (MPs/m3)	Average MPs/m3	Standard deviation of the mean	No. of MPs counted
8:00	29580	32457	21356	27798	5574	28
9:00	46013					46
10:00	54127					54
11:00	60004					60
12:00	69922	62027	71439	67796	4746	68
13:00	98006					98
14:00	123219					123
15:00	144810					145
16:00	227923	210188	229063	222391	9572	221

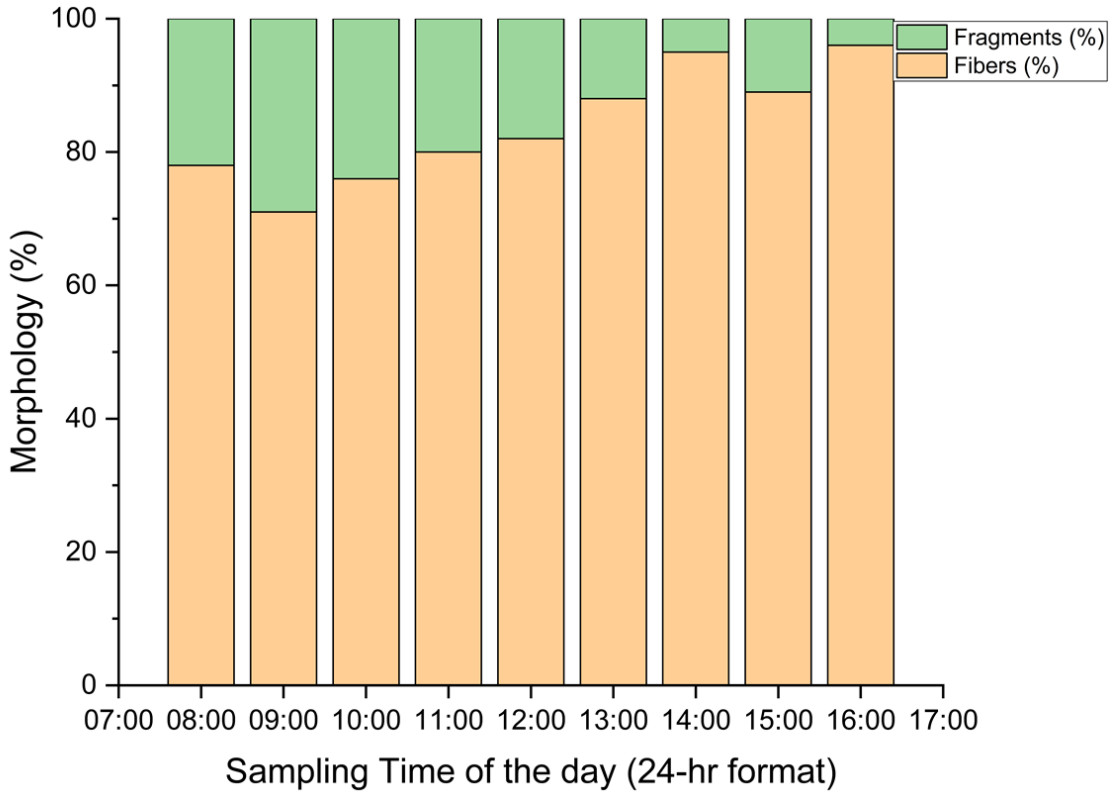

Figure C3. Morphology of microplastics in hourly samples collected at the Salt River, AZ.

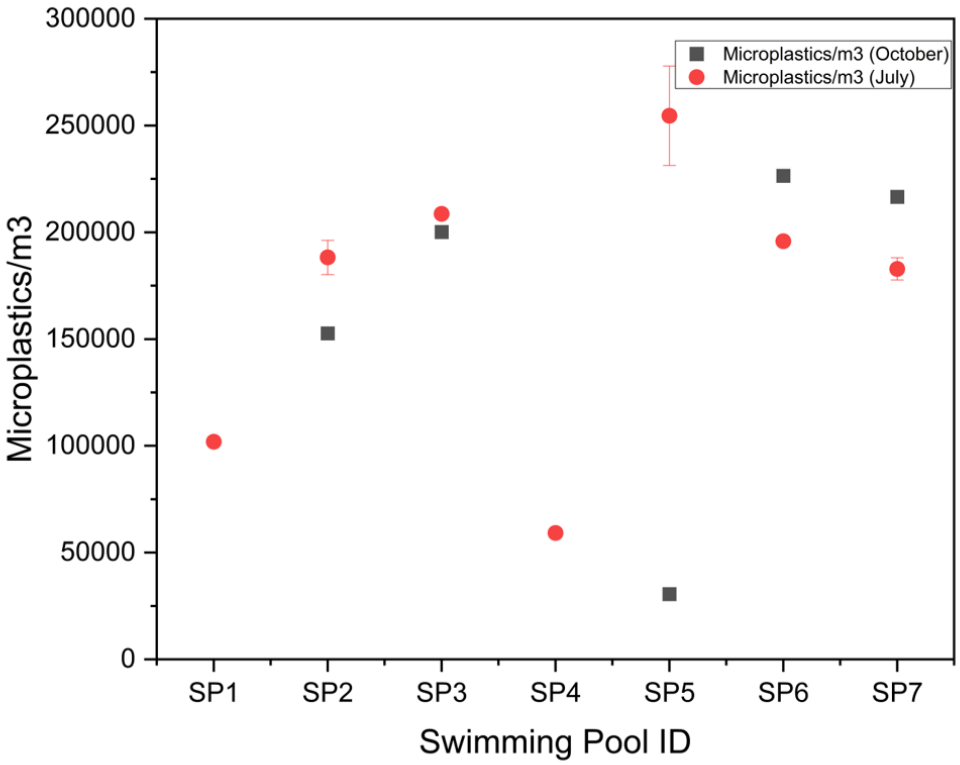

Figure C4. Microplastics concentrations in swimming pools in July and October, 2023.

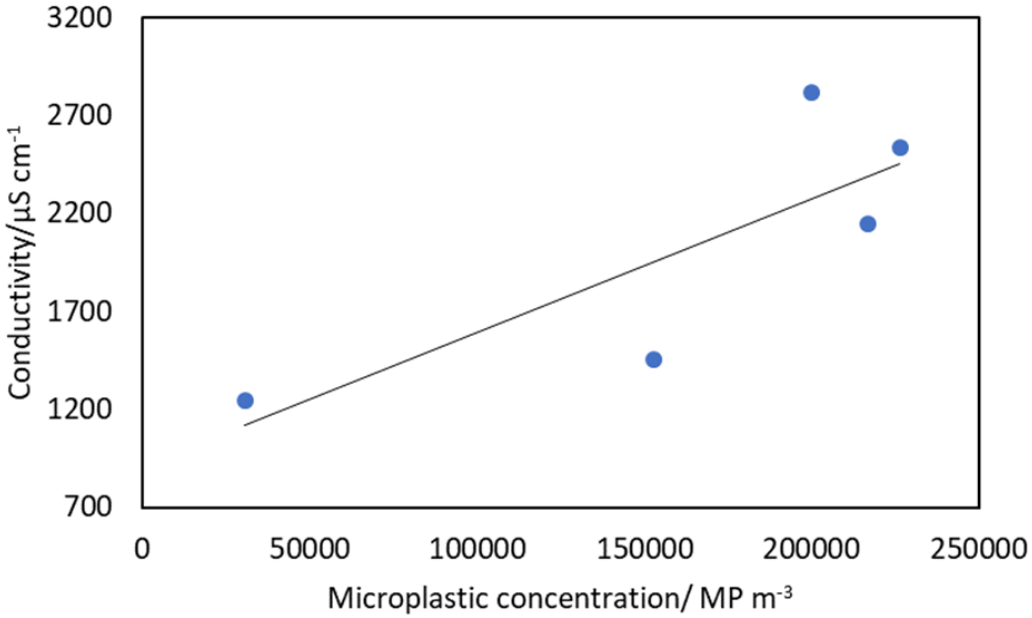

Figure C5. Conductivity measurements and microplastic concentrations in swimming pools in Tempe, AZ

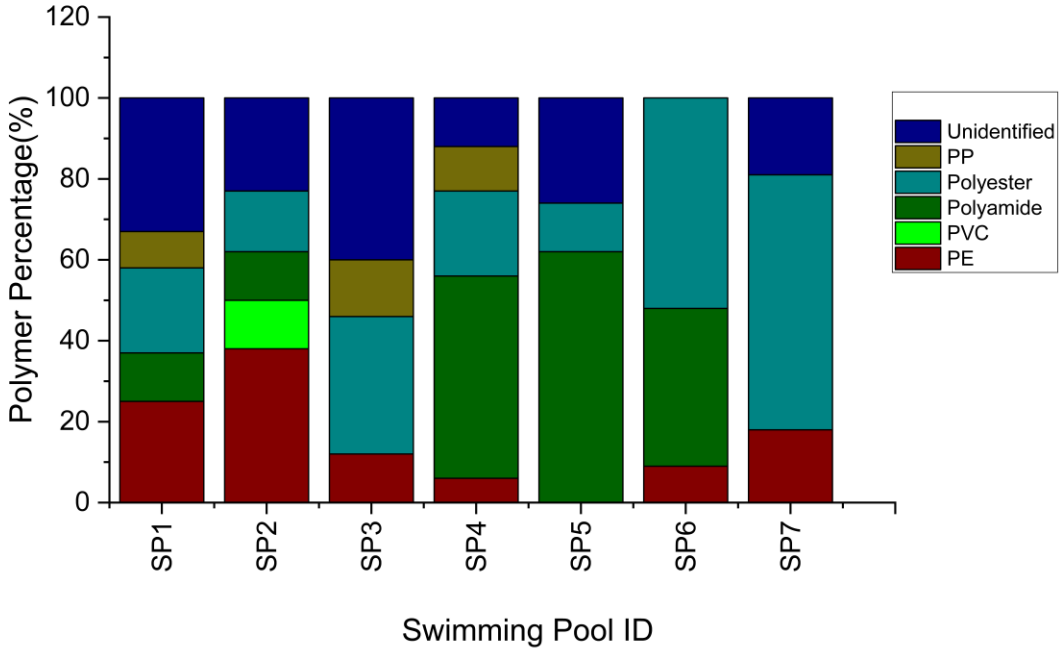

Figure C6. Raman Characterization of microplastics in swimming pools in Tempe, AZ.

APPENDIX D

CHAPTER 5 SUPPORTING INFORMATION

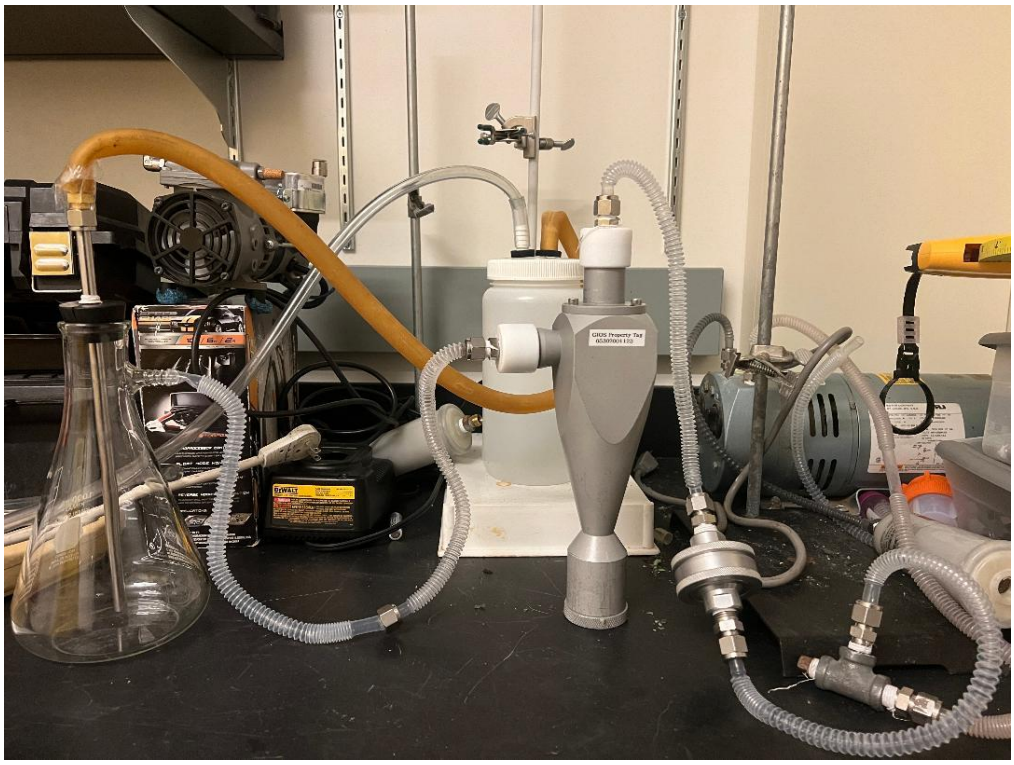

Figure D1. Resuspension setup in the laboratory to obtain PM_{10} tire wear samples.

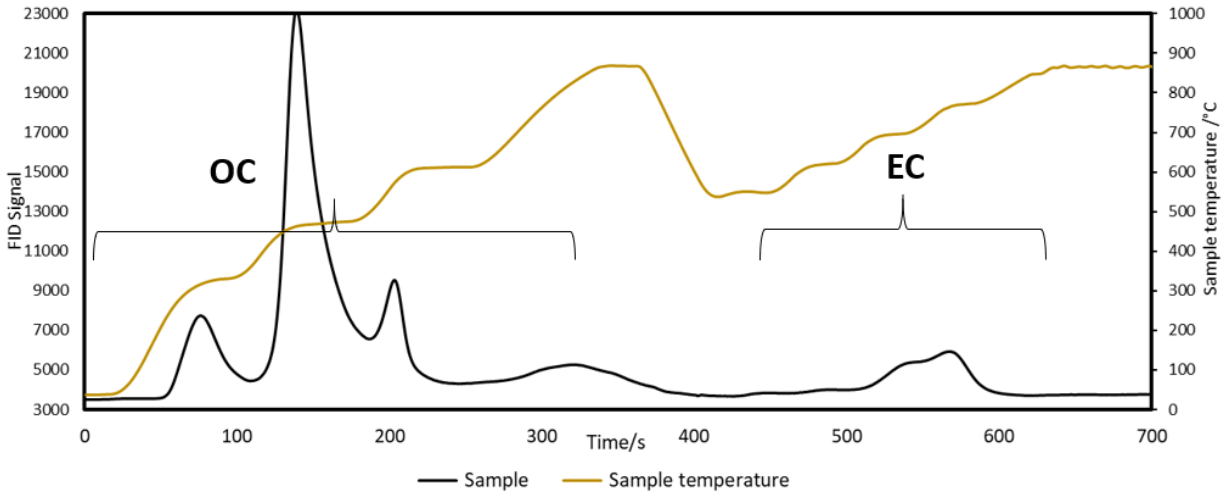

Figure D2. OC and EC distinction in an example thermogram from PTA.

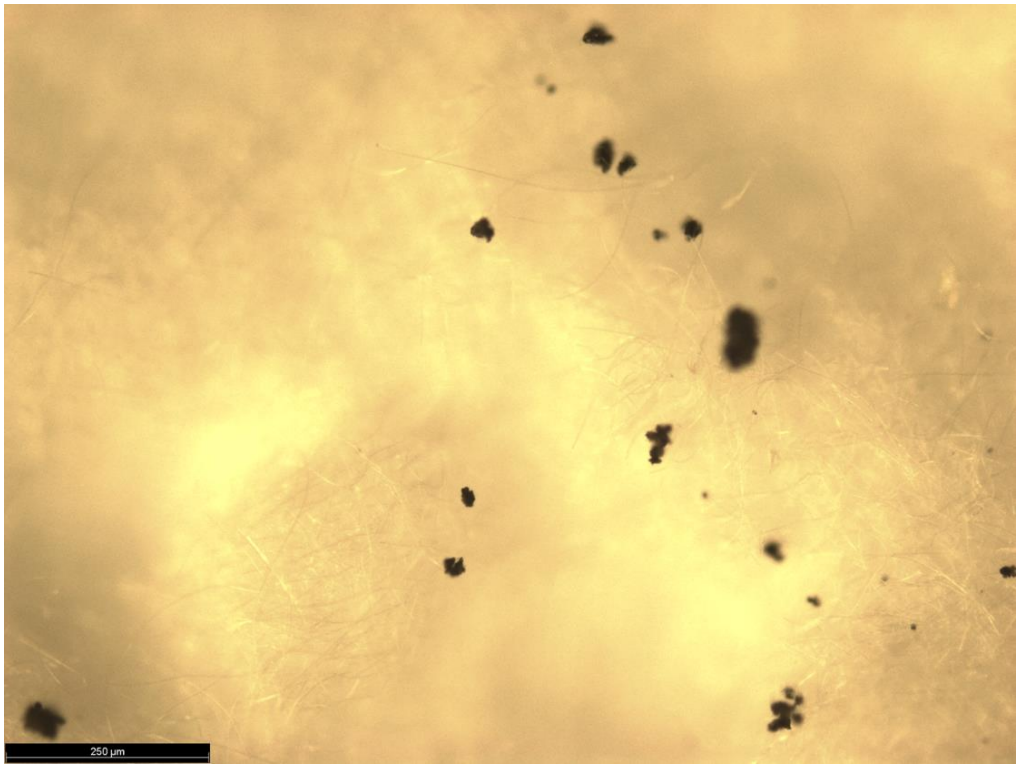

Figure D3. Particles of the cryo-milled tire wear.

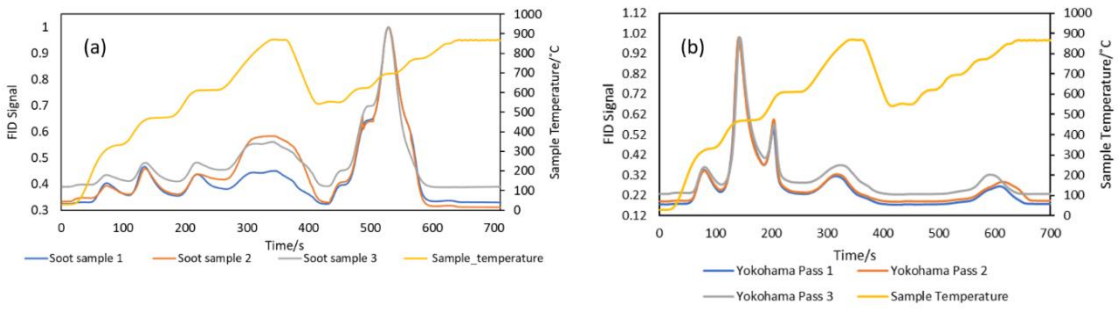

Figure D4 (a) Thermograms to test for repeatability of tailpipe soot samples from PTA. (b) Thermograms to test for repeatability of tire wear samples from PTA.

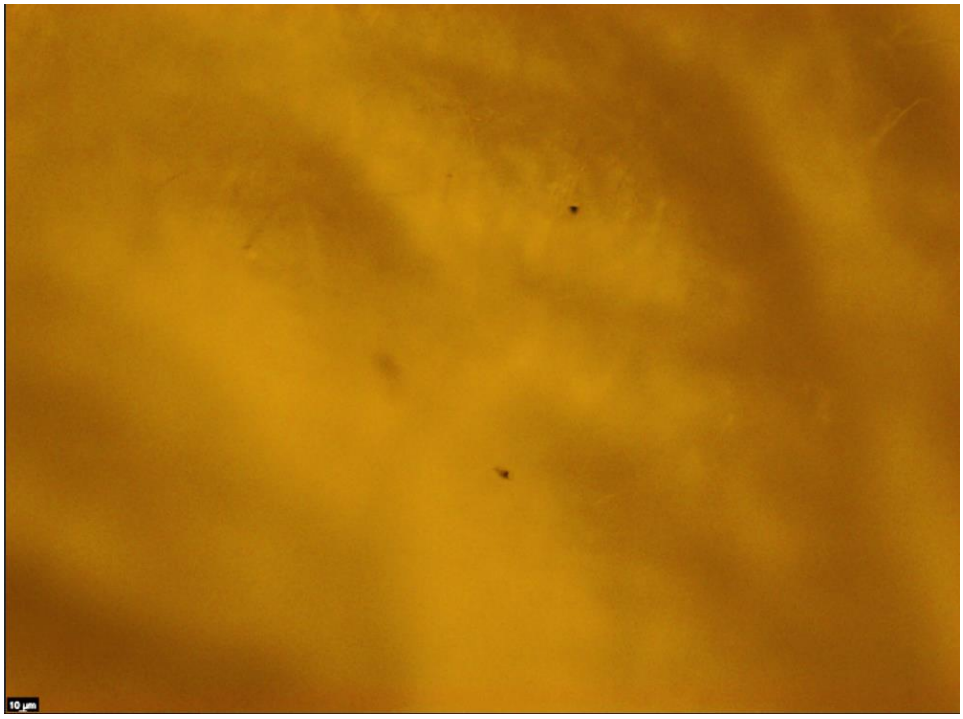

Figure D5. Particles on the PM_{10} tire wear samples from the resuspension setup.

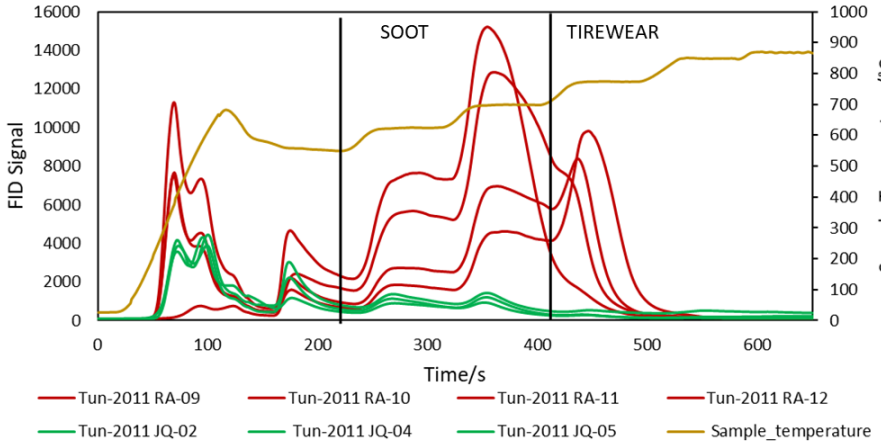

Figure D6. RA and JQ Tunnel 2011 samples under PTA (modified temperature program)

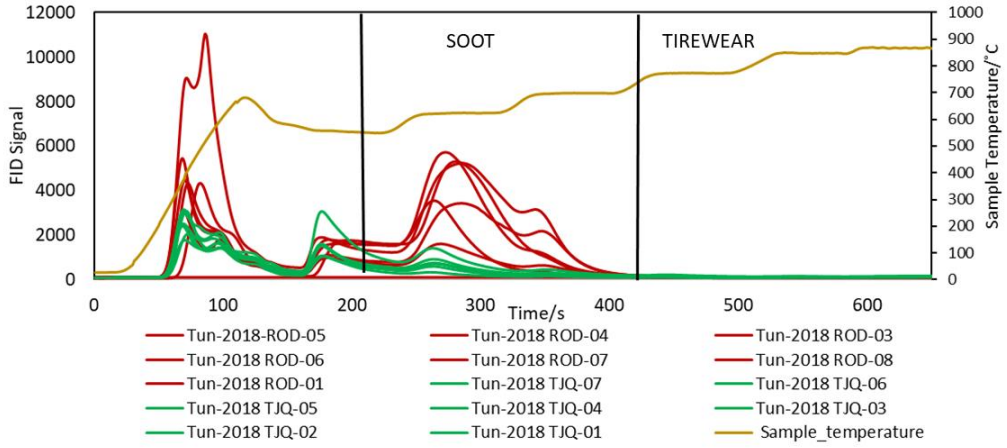

Figure D7. RA and JQ Tunnel 2018 samples under PTA (modified temperature program)

APPENDIX E

CONSENT STATEMENT OF CO-AUTHORS FOR ARTICLE INCLUSION

The co-authors of the papers appearing in this dissertation have given their written consent for the papers' reproduction in this dissertation.