Microplastics in Water and Air in the Urban Environment: Using Visual Identification and Pyrolysis/Gas Chromatography-Mass Spectrometry

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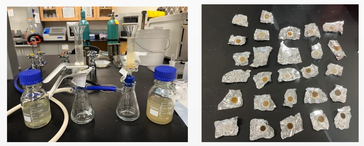
Background

- MP pollution is an escalating concern due to the exponential use of plastics and continuous releases into the environment
- MPs are derived from the breakdown of plastic products and by-products of production, forming various shapes, colors, sizes and with different polymer mixtures
- MPs are **difficult to remove** from the environment due to their durability and small size (< 5 mm)
- MPs are **easily transported, absorbed, and diffused into the environment**, especially in air and water mediums

Sample Collection and Processing

Figures (left): Set-up of the active air sampler in Arlington, TX indoor and outdoor

Figures (right): Microfiltration set-up of water samples and filter results collected in Arlington, TX



- Water: Homogenized samples (200 mL) were micro-filtrated (size cut off: 0.7 µm) under vacuum by using in-house microfiltration units
- Air: GF/B and GF/F filter papers (pore size: 1 µm and 0.7 µm, respectively)
- Biological digestion on water samples using 30-60 mL of 30% H_2O_2 and 10 mL of DI water followed by overnight oven drying

Pyrolysis-Gas Chromatography-Mass Spectrometry (Pyr/GC-MS)

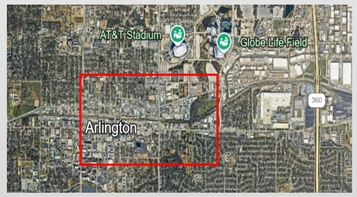
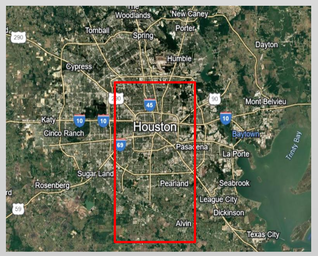
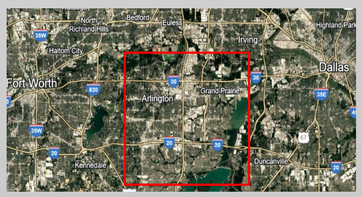
Targeted Polymers and Oligomers for Each Polymer:
Polystyrene (PS) = styrene, styrene dimer, styrene trimer- 5-Hexene-1,3,5-triyltribenzene, alpha-methylstyrene
Polypropylene (PP) = 2-methylpentane, 2,4-dimethyl-1-heptane, 2,4-dimethyl-1-heptene trimer
Polyvinyl Chloride (PVC) = benzene, naphthalene
Polyethylene Terephthalate (PET) = benzoic acid, vinyl benzoate
Polymethyl methacrylate (PMMA) = methyl methacrylate, 2-propenoic acid-methyl ester
Polycarbonate (PC) = phenol, p-isopropylphenol, bisphenol A

(*These polymers and identifiers were reported semi-quantitatively due to high signal disturbances derived from background or impurities of analytical standards)

Accelerated Solvent Extraction (ASE): DCM as solvent with Ottawa Sea sand as dispersant, Preheat = 0 min, Heat = 9 min, Static = 5 min, 80% Flush, Purge = 75 sec, 2 cycles, 1500 psi, 180°C
Pyrolysis: Single Shot, Interface = 120°C, Transfer Line and Valve Oven = 300°C, Final Temperature: 600°C for 1 minute, Clean = 1000°C for 20 seconds, Dry = 100°C for 10 seconds, Rest = 120°C
GC-MS: Ion Source = 230°C, Interface = 280°C
LOQ-water: 0.14 ~ 7.35 ng (*c.f.* PVC-Naphthalene: 170 ng)
LOQ-air: 0.01 ~ 20.3 ng

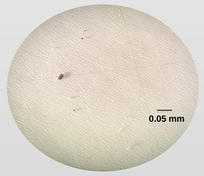
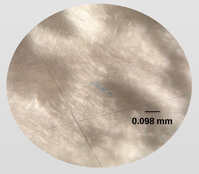
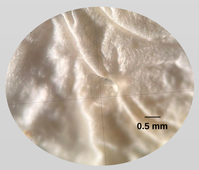
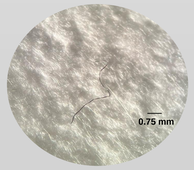
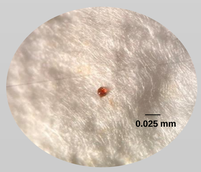
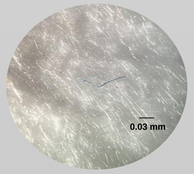
Sampling Scheme

Air: In- and out-door space in DFW, heavy traffic route in Houston area
- Sampling condition: a) active sampler at 3 LPM for 15-20 hours // b) mobile air quality monitoring system at 2 LPM for 2-6 hours
Water: Surface water, stormwater, wet deposition
- Sampling condition: spot grab sampling (250-500 mL)

Matrix/ Region	Sampling Locations (images taken from Google Earth)
Indoor and Outdoor Air Arlington, TX	
Roadside Air Houston, TX	
Water Arlington, TX Grand Prairie, TX	

Visual Identification

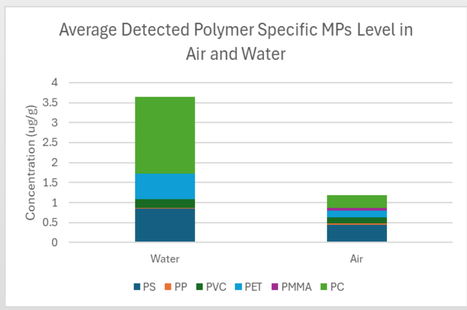
Instrumentation: Binocular microscope equipped with an adjustable halogen light source, 4x, Plane-Polarized Light, Conscopic Lens on
Observation: Post-treated filter papers were observed 4 times per each sample, focusing on each quadrant area per observation attempt to ensure clear recording of MPs on filter

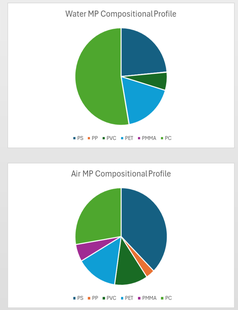
Microbeads and Micropellets	Microfibers
 8/7/23 Traffic Road Air Filter, Houston, TX	 Baseline Monitoring Water Sample, Johnson Creek @ Center St., Arlington, TX
 Baseline Monitoring Water Sample, W. Division @ Rush Creek, Arlington, TX	 11/29/23 Air GF/B Filter, Arlington, TX Indoor space
 Baseline Monitoring Water Sample, Bob-Findley Park River, Arlington, TX	 11/8/23 Air GF/F Filter, Arlington, TX Indoor space

- Bead and pellet (<0.01 mm – 0.07 mm) and fiber (0.06 mm – 3 mm in longer axis) type MPs were majorly observed
- MP size distribution between air and water were not significant
- MPs separated from water experienced more color variations than those from air

Results & Discussion

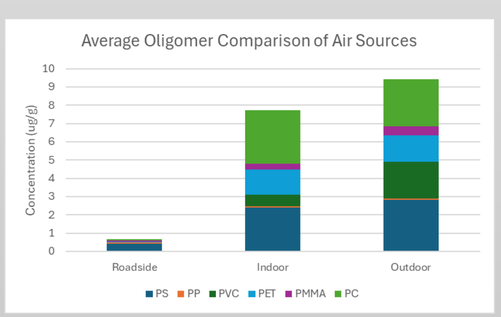
Comparing Water and Air Concentrations and MP Polymer Profiles

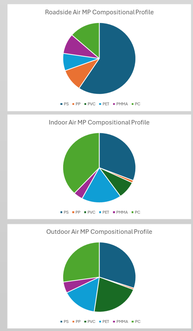




- Water experienced ~3x more MP concentrations (ug/g) than air samples, although air experienced more polymer variability. *Atmospheric transport can override MP suspension and deposition (Fan et. al 2021).*
- PC and PS were main contributors to both matrices.

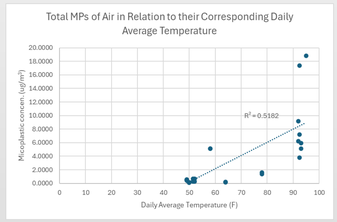
Comparing Air Concentrations and MP Polymer Profiles By Sample Type

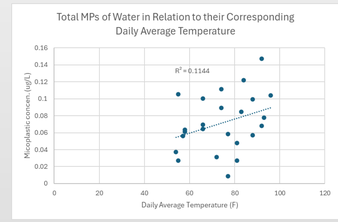




- Between air samples, roadside air had the least MP concentration but entailed great polymer variability. Human, industrial, and traffic activity can create more polymer sources, contributing to this variation.

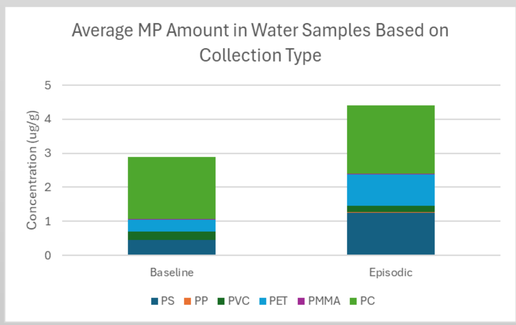
Comparing Total MP Water and Air Concentrations to the Daily Average Temperature (°F)





- MP concentrations in air were more influenced by the daily average temperature than water samples. Water was poorly correlated with temperature, while air was moderately correlated. Other meteorological and socioeconomic factors such as human activity, season, precipitation, wind, etc. likely play a heavier role in influencing these concentrations.

Comparing Water Concentrations and MP Polymer Profiles By Sample Type



- Episodic (wet weather) water samples were ~1.5x higher in MP concentrations than baseline (dry weather) samples. *Results aligned with Fan et al. (2021), where wet vs dry results had a 1-2 magnitude difference. Increased hysteresis effect and surface runoff are the suggested main contributors.*

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Future Plans

- Air and water interfacial fate of MPs will be elucidated by scaling up the paired air-water sample collection
- Technical improvements (e.g., serial sieving to get size distribution profiles of MPs, centrifuge prior to microfiltration for high turbidity water samples) will be adapted in the experimental protocol to increase time efficiency and minimize digestion-induced degradation of MPs
- Raman microscope and FTIR will be used in addition to currently established visual identification method to compare polymer specific information with Pyro-GC/MS
- MP standard creations with ASE will be performed with all polymer types to minimize background contamination