DETECTION AND QUANTIFYING MICROPLASTIC POLLUTANTS IN BEACH SAND AND RIVER SEDIMENT

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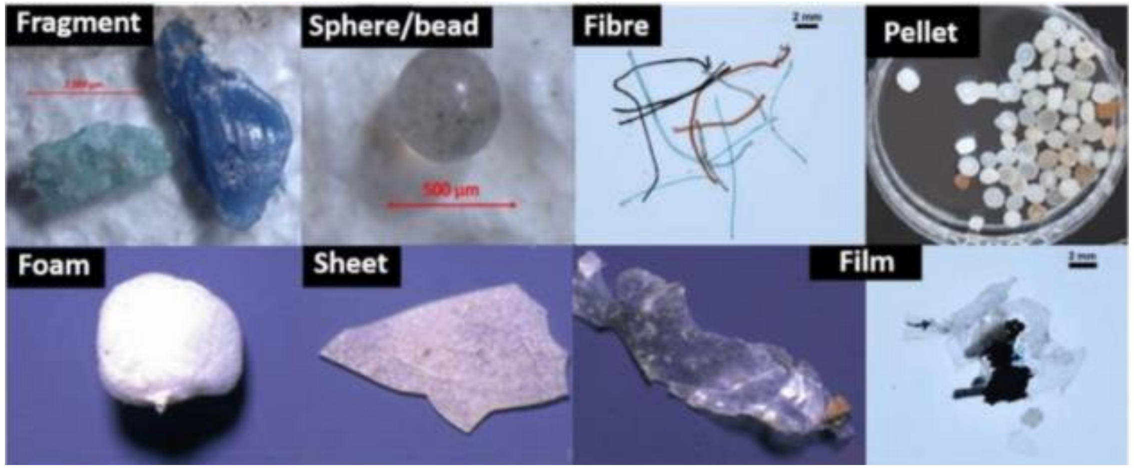
WHAT IS THE MICROPLASTIC PROBLEM?

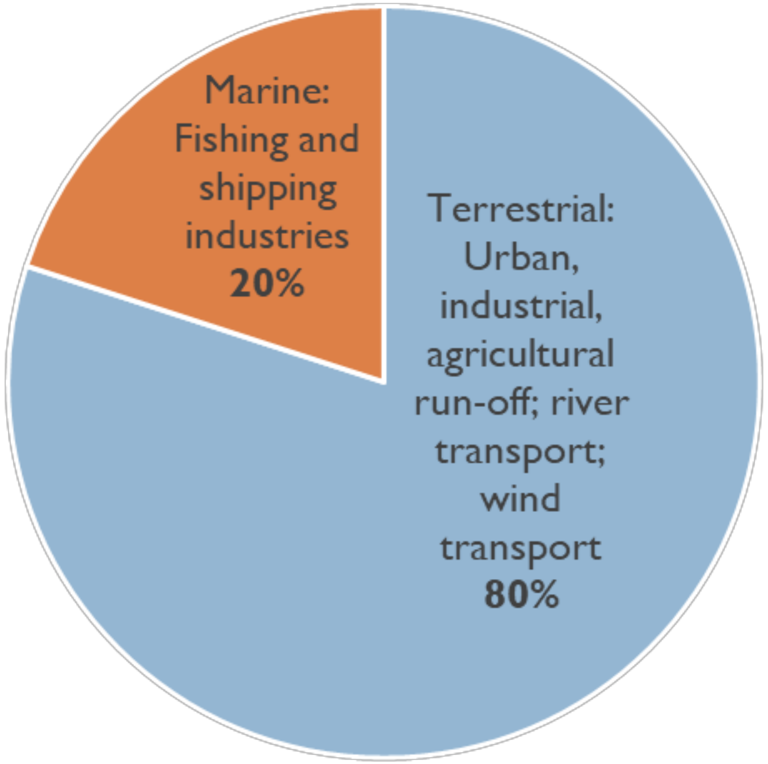
- Microplastics (MPs): Plastic 5mm - 330 µm (NOAA, 2009)
- Classification
  - ***Primary***- designed for commercial use (e.g., microfibers from clothing, microbeads, plastic pellets)
  - ***Secondary***- plastic particles that result from the breakdown of larger plastic items (e.g., fragments from water bottles, fishing nets)



Emerging Microplastics in the Env., Chemosphere, 2022, 297, 134118.

PLASTIC POLLUTION IN OCEANS

- Global plastic production (2020): **>300 million tons** [a]
- **9%** recycled [b]
- Plastic waste discharged to sea: **10 million tons/year** [c]
    - **5.25 trillion pieces** floating on sea
    - **100,000 pieces** per meter of shoreline



Sources of Plastic Pollution

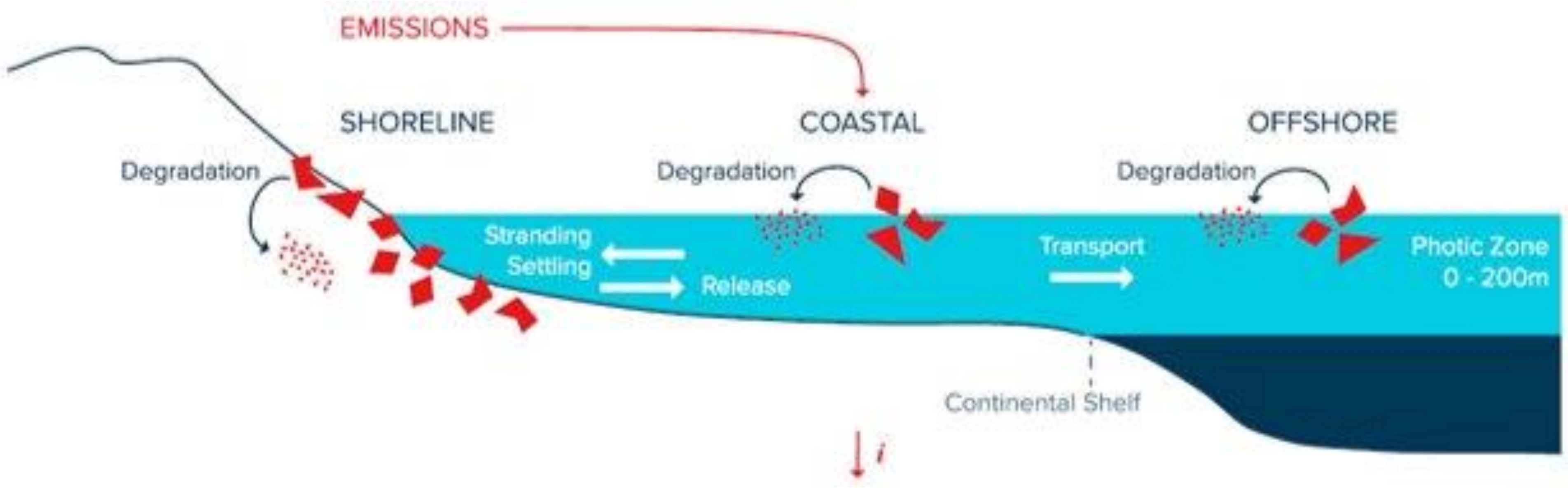
a. Law et al., "Reducing Env. Plastic Pollution by Designing Polymer Materials for EOL", Nature Materials, 2022.
b. "The known unknowns of plastic pollution", Economist, 2018.
c. Eriksen et al., "Plastic Pollution in the World's Oceans", PLoS One, 2014.

Lebreton et al., Scientific Reports, 2019, 9, 12922.
Kane et al., Science, 2020, 368, 1140-1145.

TRANSPORT OF PLASTICS: FROM LAND TO OCEAN

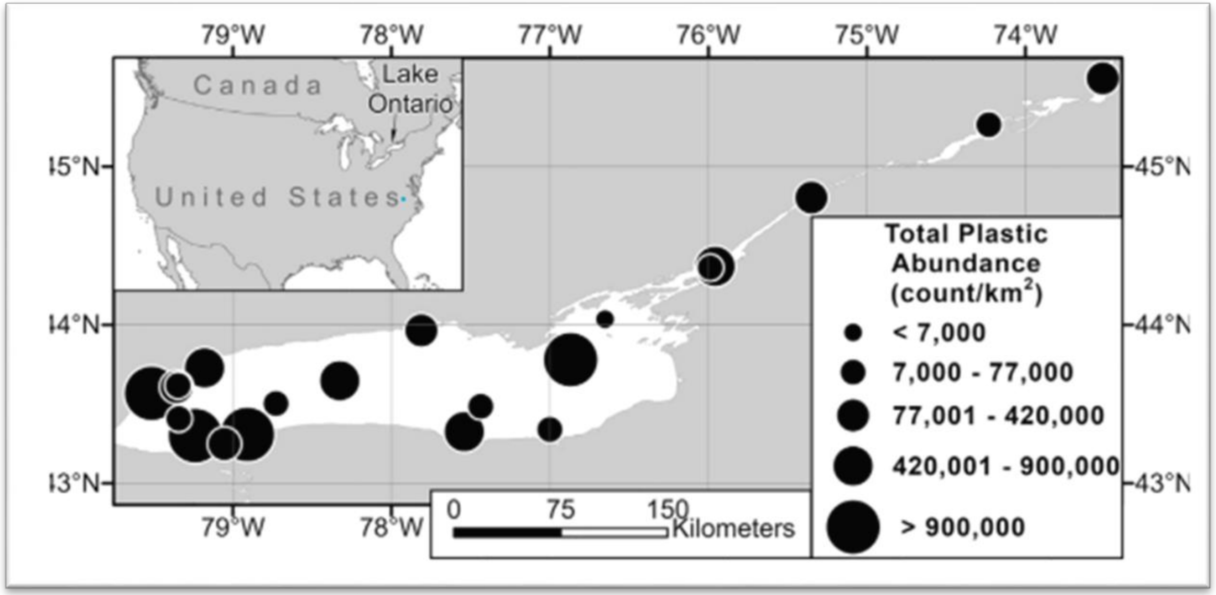
Transport Pathways:

1. Inland to shoreline: run-off, river and wind transport
2. Shoreline to coastal: wave and alongshore currents
3. Coastal to offshore: gravity and deep thermohaline (deep ocean) currents



MICROPLASTICS IN FRESHWATER SYSTEMS

- **Major Sources**
  - Sewage discharge
  - Urban runoff
  - Industry discharge
  - Wind-blown litter
- >90% sinks to bottom [a]
  - Great Lakes sediment samples found high conc. of plastics



b

[a] Corcoran et al., Hiddent Plastics of Lake Ontario Canada, Env. Poll., 2015.

[b] Mason et al., High levels of pelagic plastic pollution within the surface waters of Lakes Erie and Ontario, Journal of Great Lakes Research 46, 2020

DEGRADATION AND FRAGMENTATION IN THE ENVIRONMENT

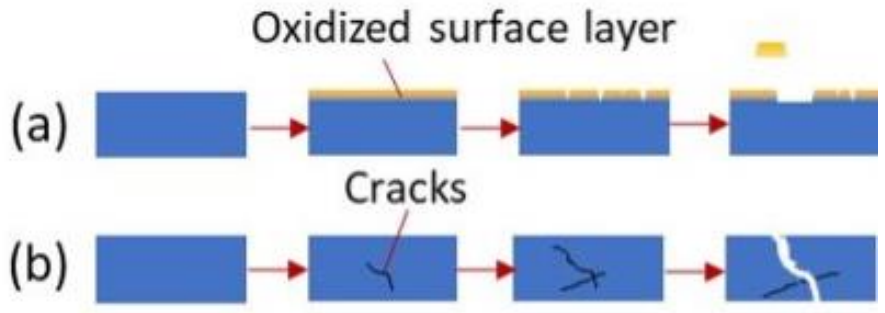
Two modes of degradation and fragmentation of plastics in the environment:

(a) Surface Erosion

- Initiated by UV exposure/surface oxidation
- Confines to a thin surface layer, develops cracks
- Surface chips off, exposing new surface

(b) Bulk Fragmentation

- Polymer embrittlement due to weathering
- Development of internal fractures



As size decreases…
- Risk of ingestion increases
- Risk of bioaccumulation in humans increases
- Specific surface area increases= larger carrying capacity for other contaminants

OBJECTIVES

- Develop methods to **identify** and **quantify** different types of microplastic debris in local beach sand and river sediment
- **Analyze** the **size and depth dependent distribution** of microplastics in environmental media

METHODS

Inspection

- Beach survey
- River and coastal water surveillance

Field Sampling

- Collecting beach sand and river sediment

Sample Processing

- Sieving
- Disinfection
- Density separation
- Wet peroxide oxidation
- Solvent Extraction

Sample Analysis

- Visual Inspection (confocal microscopy, FTIR, Raman)
- **Thermal analysis via PY-GCMS** (used in this study)

FIELD SAMPLING- BEACH SAND

- Two transects, each100 m long
  - Transects divided into 20 sections, each 5 m
  - Samples collected in stainless steel buckets from 4 sections randomly

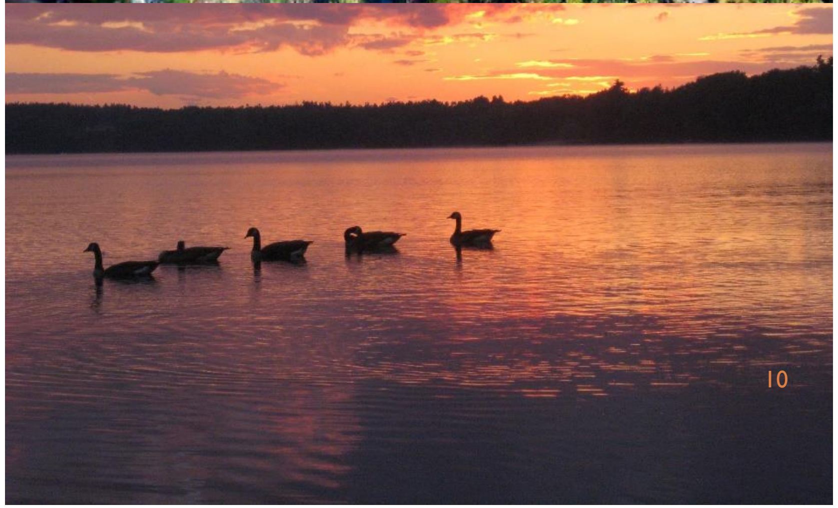
Beach	Time	Description
Salisbury	June 18, 2021	Surface (0-5 cm) Subsurface (5-10cm)
Hampton	June 18, 2021	Surface (0-5 cm) Subsurface (5-10cm)

Stainless steel tools used for surface and subsurface sampling

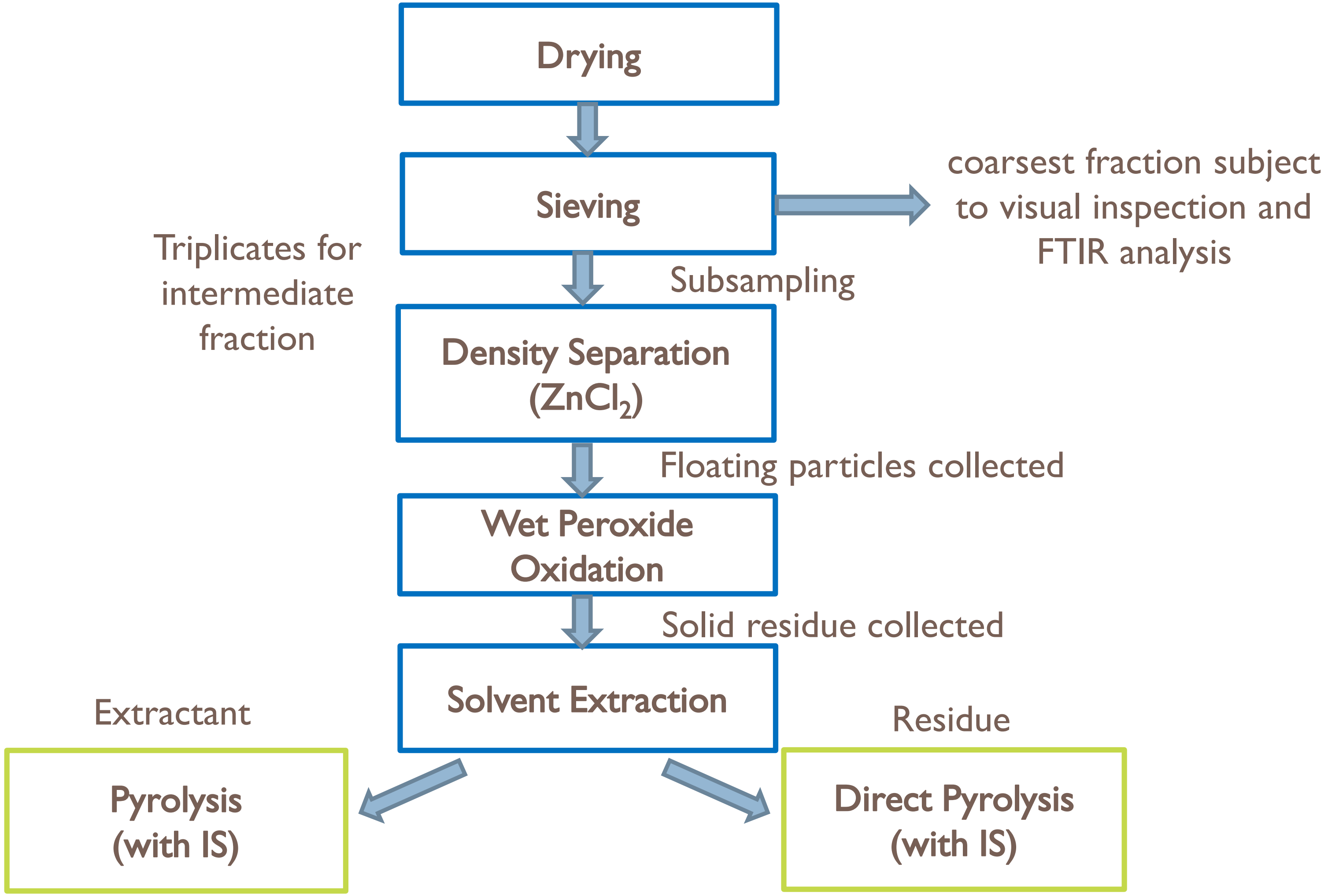
FIELD SAMPLING- RIVERBED SEDIMENT

- Forge Pond - Westford, MA
  - 203 acres
  - Max depth 37 ft; Avg depth 15 ft

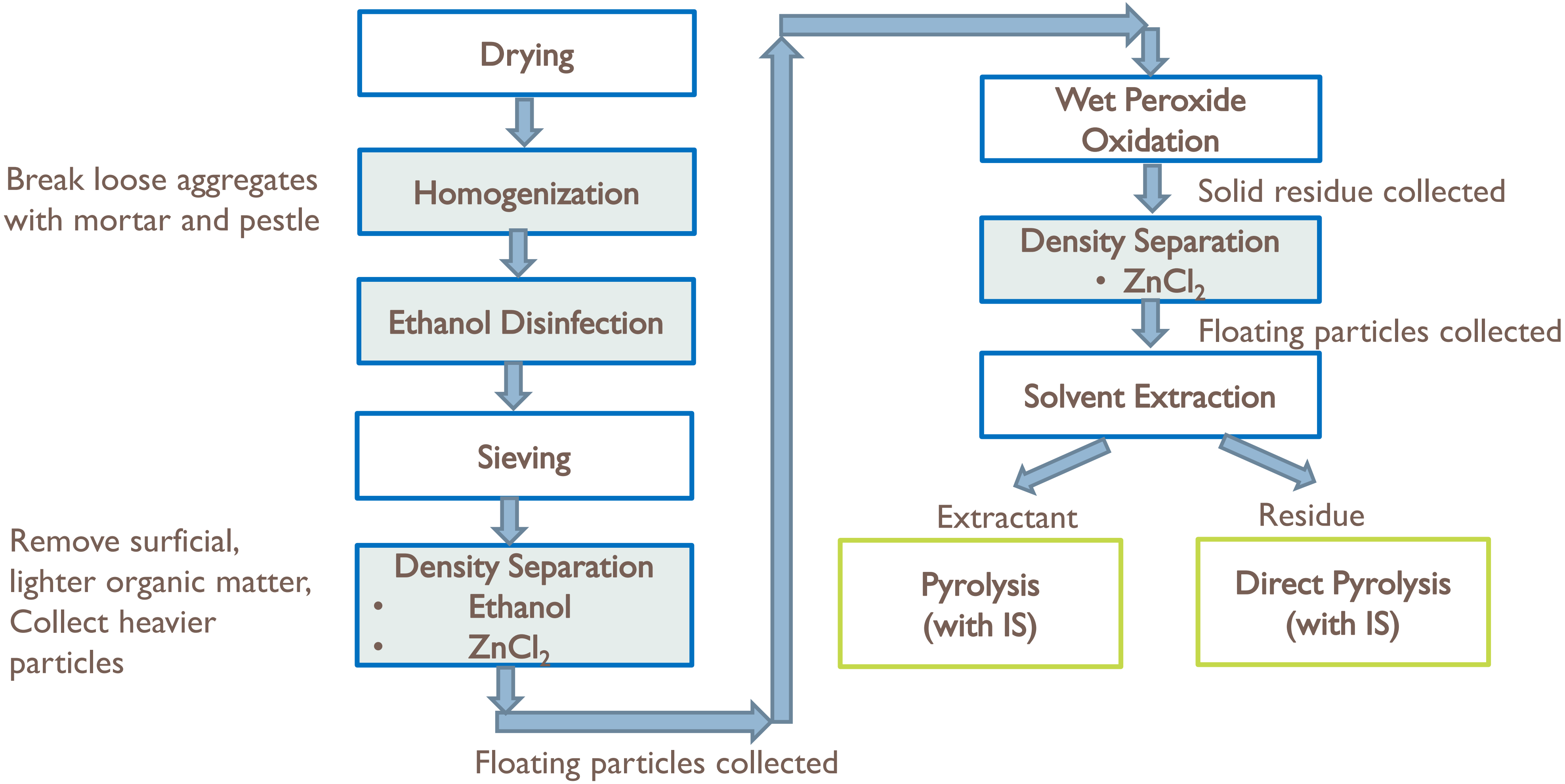
Sample ID	Time	Description
SAP 7A	8/25/2021	Above Forge pond dam at forge pond park upstream of boat launch, Dammed Indian head river, slow to no movement, pond. 0-3"
SAP 7R	8/25/2021	Above Forge pond dam at forge pond park downstream of boat launch, Dammed Indian head river, slow to no movement, pond. 0-3"
SAP 9R	8/25/2021	Below Forge pond Dam upstream of boat launch. Flowing with strong current. Sample taken from side with slower flow. Riverbed. 0-3"



SAMPLE PRETREATMENT PROCESSING METHOD: BEACH SAND



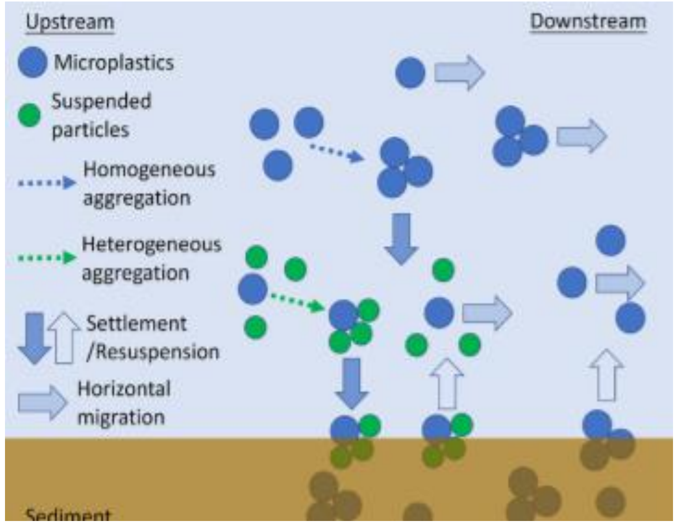
SAMPLE PRETREATMENT PROCESSING METHOD: RIVER SEDIMENT



NATURAL ORGANIC MATTER IN RIVER SEDIMENT

- High content of biomass and natural organic matter (NOM) in river sediment in general
- Microplastics aggregate and trapped within clumps of sediment and fluffy biota
- Microplastics and NOM settle out during density separation, causing potential loss of sample
- NOM consumes oxidant during wet peroxide oxidation (WPO)
- NOM creates interference in thermal analysis

Important to clean a sample and remove NOM before wet peroxide oxidation.



DRYING AND SIEVING

- Beach sand sun-dried for 24-48 hrs.; River sediment oven-dried @ 100 °C for 24 hrs.
- Dried samples sieved to obtain 3 size ranges:
  - Fine fraction(<100 μm)
  - Intermediate fraction (100 μm -1.2 mm)
  - Macro debris fraction (>1.2 mm)

Sieving machine, continuous sieving for 5 mins

Hampton beach sand (<100μm)

DENSITY SEPARATION

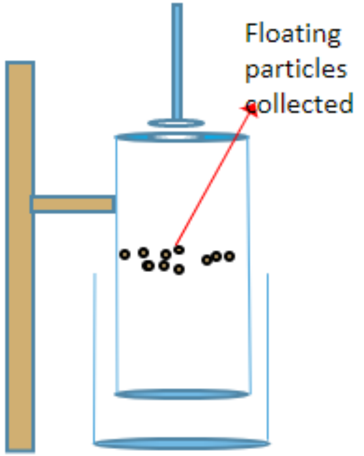
Beach Sand

- Separation Media: Zinc Chloride (ρ=1.6 g/mL)
- In-house designed device
- Settling Time:
  - Fine fraction: 3 hrs
  - Intermediate fraction: 1.5 hrs

Type of Plastic	Density of common plastics (g/mL)
Polyethylene (PE)	0.91-0.97
Polypropylene (PP)	0.94
Polyethylene Terephthalate (PET)	1.3-1.4
Polystyrene (PS)	1.05
Nylon 6,6 (PA66)	1.13
Polyvinyl Chloride (PVC)	1.4

River Sediment

- Ethanol density separation (ρ=0.79), heavier particles collected)
- $ZnCl_2$ density separation w/ in-house DS column, lighter particles collected
- 2nd $ZnCl_2$ density separation after WPO to remove remaining NOM



Schematic In-house Designed Density Separation Device

WET PEROXIDE OXIDATION (WPO)

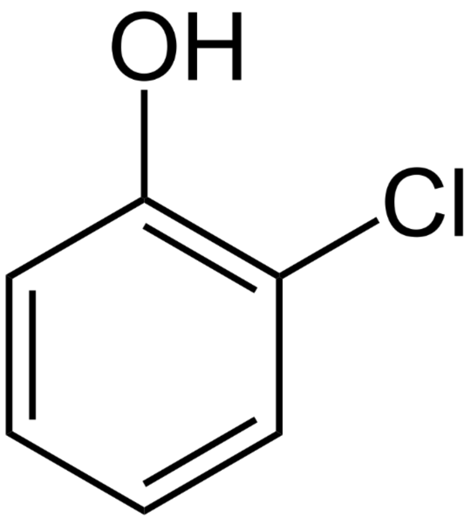
- Digest organic material; minimize background interference when quantifying microplastics
- Using Fenton's Reagent: Ferrous Sulfate + Hydrogen Peroxide

  (0.05 M $FeSO_4 \cdot 7H_2O$ + 3-6 drops of conc. H_2SO_4 + 30 % H_2O_2)
- Conditions: 75 °C for 30 mins
- Digestion Time:
  - Fine fraction: 48 hrs
  - Intermediate fraction: 24 hrs
- Residue after digestion collected via filtration and oven-dried at 100 °C for 24 hrs

SOLVENT EXTRACTION

- Solid extracted with 2-chlorphenol
  - Soluble: PET, PS, Nylon, and others
  - Not soluble: PP and PE
- Extraction time:
  - Fine fraction: 24 hrs
  - Intermediate fraction: 48 hrs

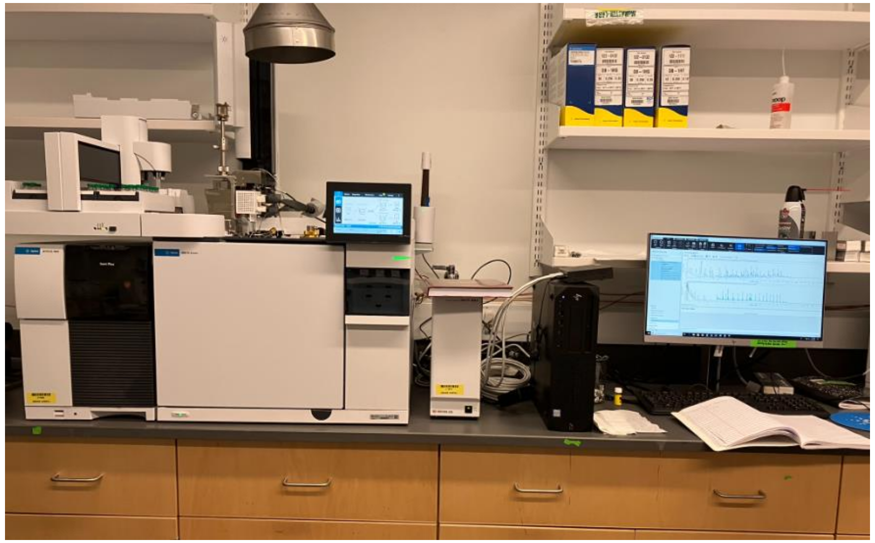
Type of Plastic	Type of Solvent		
	Acetone	Dichloro-methane	2-Chlorphenol
PE	×	×	×
PP	×	×	×
PET	×	×	√
PS	×	√	√
PA66	×	×	√
PVC	×	×	√



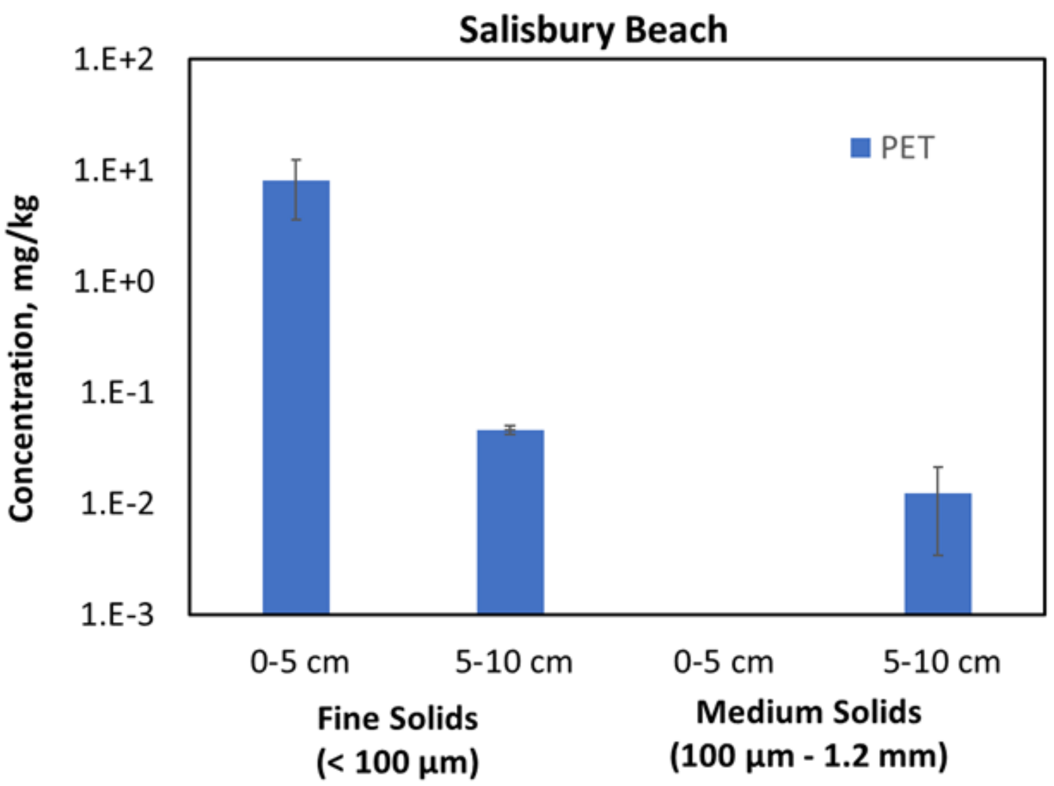
2-chlorophenol

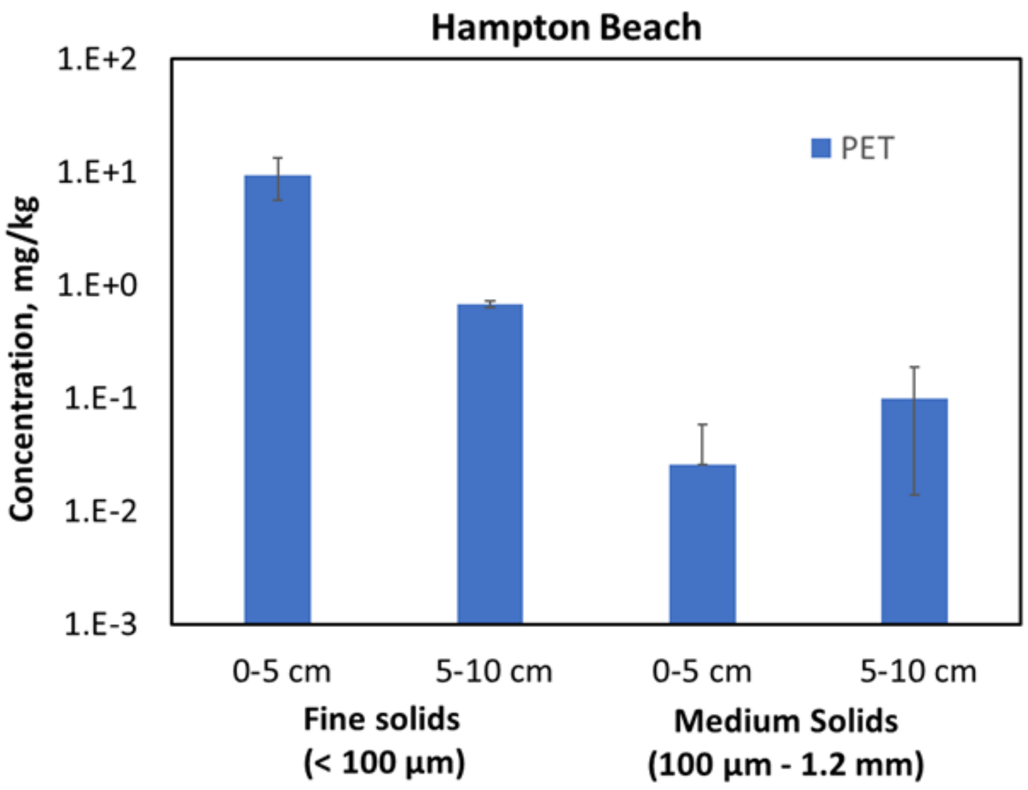
PY-GC-MS

- Pyrolysis-Gas Chromatography-Mass Spectrometry: use thermal degradation to identify nonvolatile compounds including polymeric materials
- Sample pyrolyzed to produce smaller molecules which are separated by GC and detected by MS
- Advantages
  - Detect small mass of analytes quantitatively (microliters)
  - Eliminate need for inconclusive optical methods
  - Identify plastic type



RESULTS – SOLVENT EXTRACT OF BEACH SAND





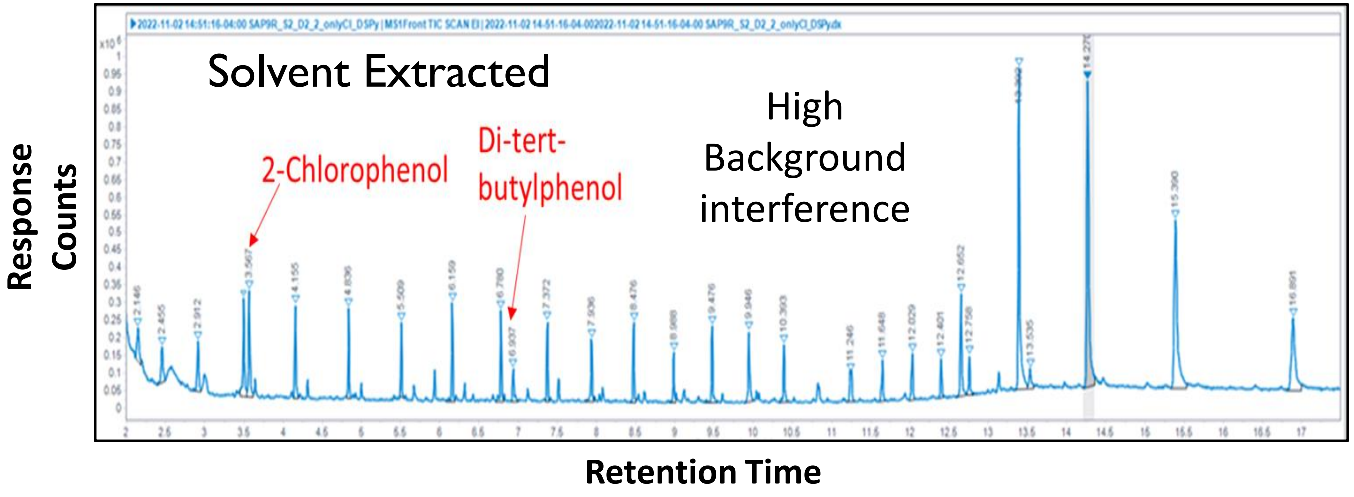
Highest average concentration of PET found in surface layer in the fine fraction

- Salisbury: 8.05 mg/kg;
- Hampton: 9.44 mg/kg

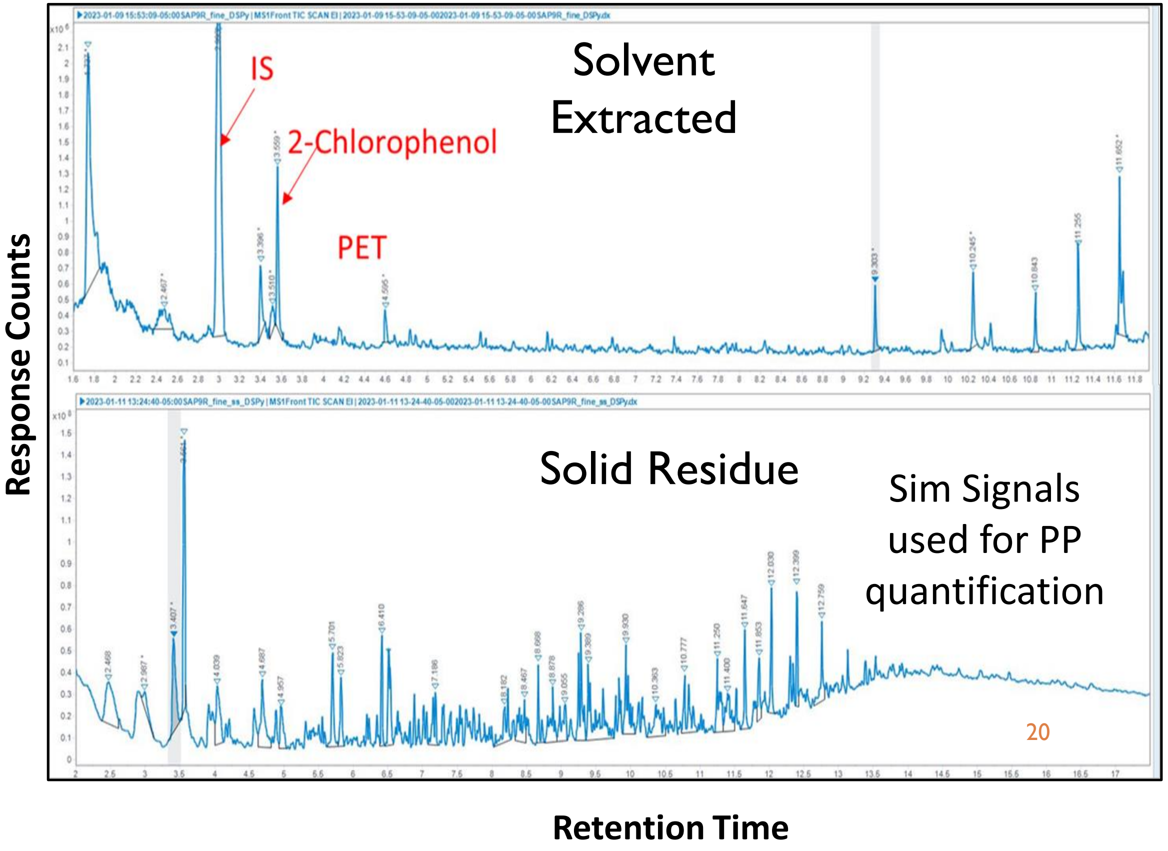
OPTIMIZATION OF PRETREATMENT FOR RIVER SEDIMENT

SAP9R Medium Fraction

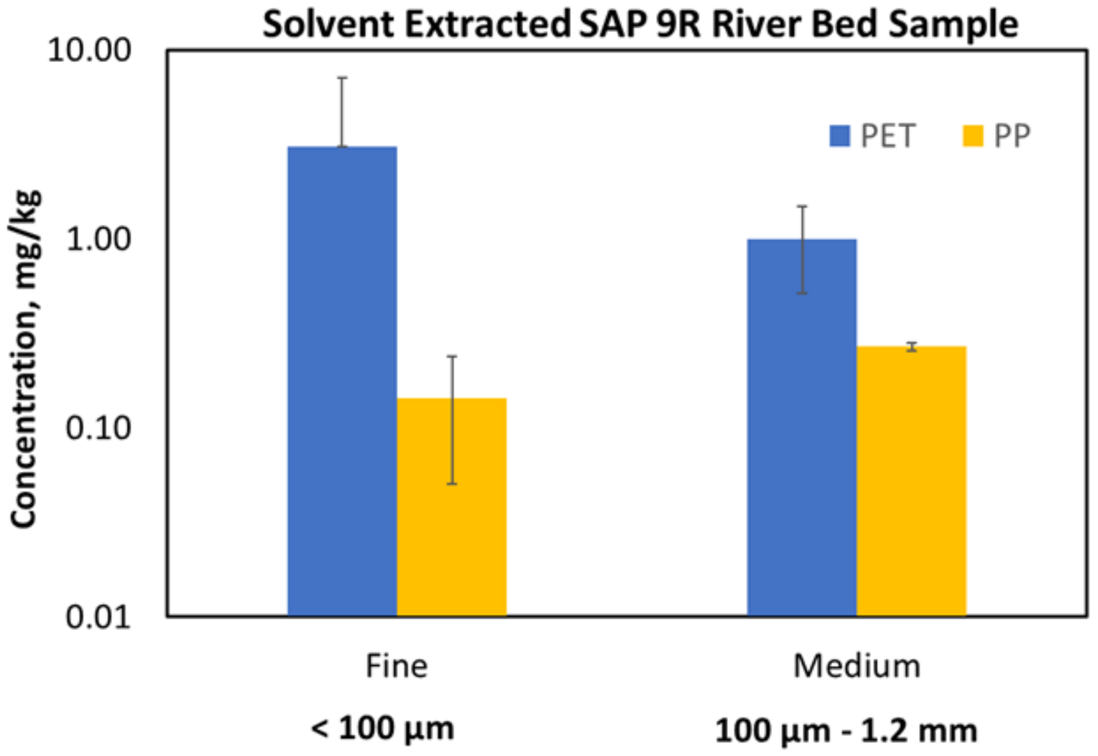
Results obtained with Non-optimized Pretreatment Flow



Results obtained with Optimized Pretreatment Flow



RESULTS- RIVERBED SEDIMENT



Grain Fraction	Avg PET Concentration (mg/kg)	Avg PP Concentration (mg/kg)
Fine (<100 µm)	3.056	0.144
Medium (100 µm-1.2 mm)	1.001	0.269

CONCLUSIONS

- Beach sand
  - Only PET identified in beach samples
  - Microplastics more abundant at the surface level in the finest fraction (<100 µm)
- River sediment
  - Extra steps for homogenization and organic removal is necessary to isolate plastics from NOM
  - PET and PP were identified in one sample (other samples pending analysis)
  - PET more abundant in the finest fraction; PP more abundant in medium grains
- Future work:
  - Effects of fragmentation on different plastics; how it effects settling behavior; rate of degradation
  - Compare beach sand and river sediment microplastic data from different months; data trends from population fluxes
  - Continue work on improving the quality of the calibration curve

ACKNOWLEDGMENTS

- Dr. Yan and Mythreyi Sivaraman (Department of Civil and Environmental Engineering, University of Massachusetts, Lowell)- collecting beach sand samples, providing all GCMS data
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- NEWEA