Analytical methods for detecting and characterizing microplastics and nanoplastics in the environment

Phillip M. Potter, U.S. EPA, Cincinnati, OH

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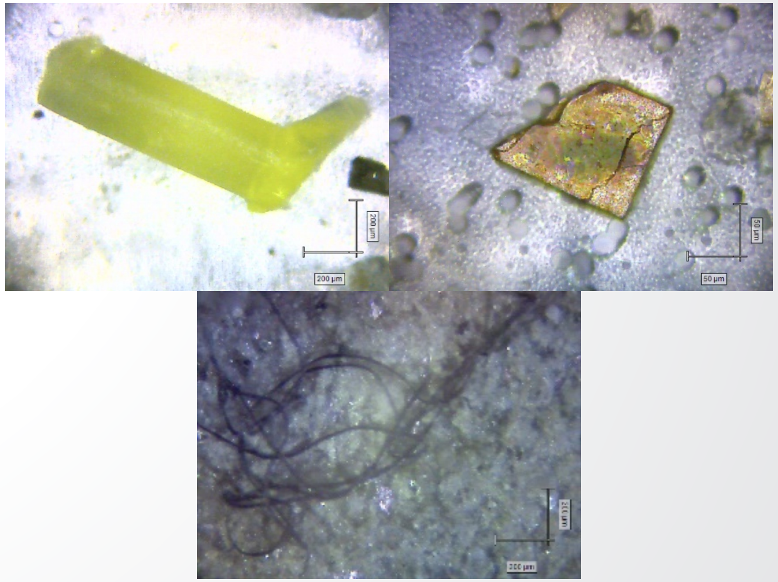
What are microplastics?

- Microplastics (MPs) are small plastic particles (e.g., fibers, fragments, films, and pellets) < 5 mm across
    - *Primary*: Designed to be small. (e.g., PE/PP microbeads in personal care products, glitter, industrial pellets ‘nurdles’)
    - *Secondary*: Breakdown of larger plastic debris, tire wear, nylon/polyester fibers shed from laundry.
- Particles < 100 nm have been classified as ‘nanoplastics’ (NPs). However, most relevant size fraction is still under discussion.

Physical breakdown →

Chemical breakdown →



Where are microplastics?

- Microplastics are ubiquitous
  - Air
  - Soil
  - Water
  - Food & drink

FOOD FOR THOUGHT

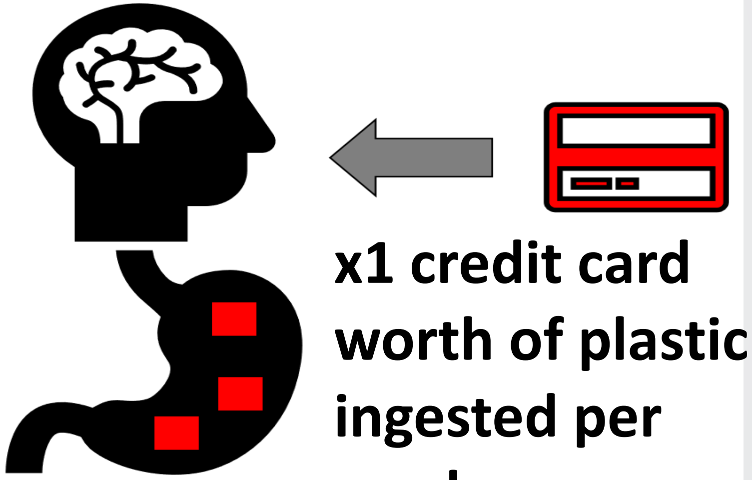
Beer, Drinking Water And Fish: Tiny Plastic Is Everywhere

August 20, 2018 · 11:57 AM ET

ENVIRONMENT | PLANET OR PLASTIC?

Microplastics are raining down from the sky

Scientists discover large amounts of tiny plastic particles falling out of the air in a remote mountain location.



x1 credit card worth of plastic ingested per week

ENVIRONMENT 08/18/2019 10:26 am ET

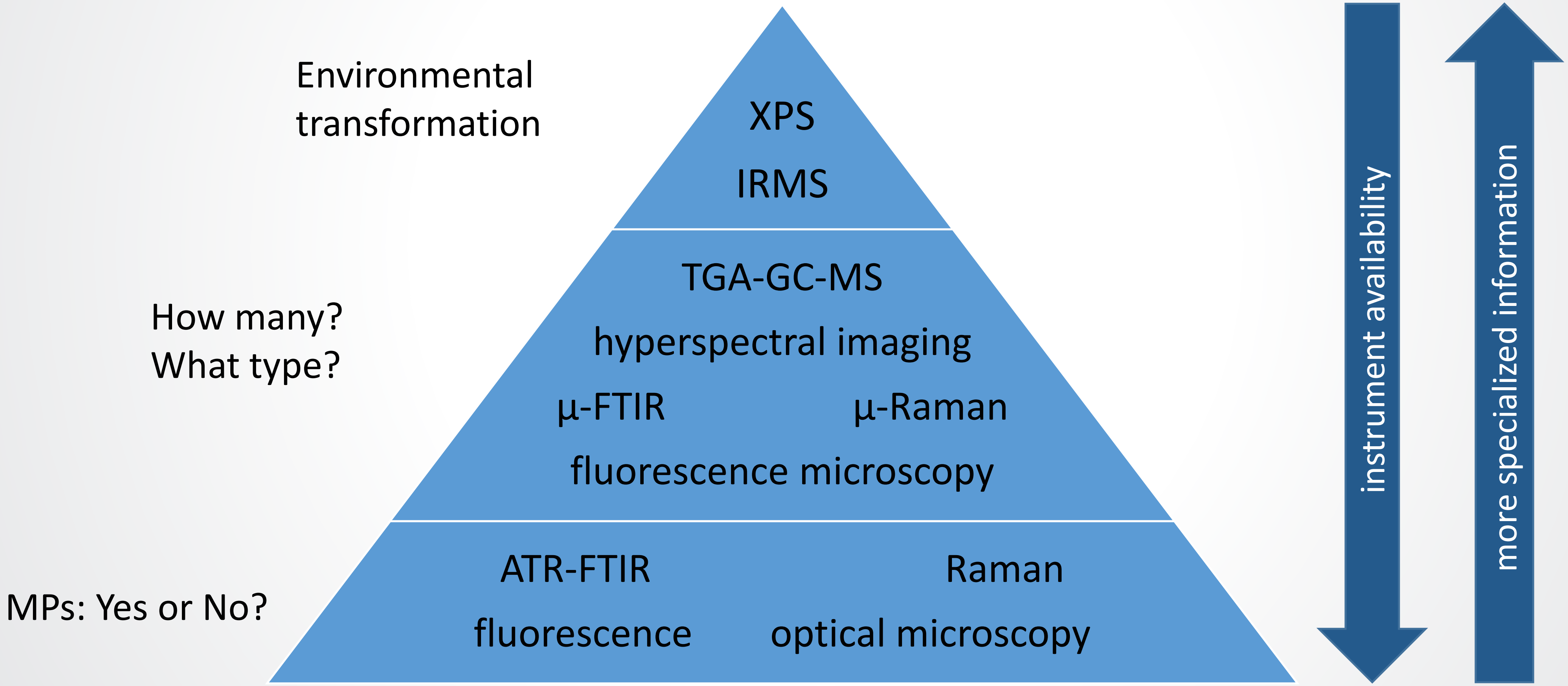
Scientists Astonished After Finding Microplastics In Arctic Snow

FOR IMMEDIATE RELEASE | August 17, 2020

Methods for microplastics, nanoplastics and plastic monomer detection and reporting in human tissues

Sources: huffpost.com, npr.org, nationalgeographic.com, acs.org

MP analytical techniques



Overview

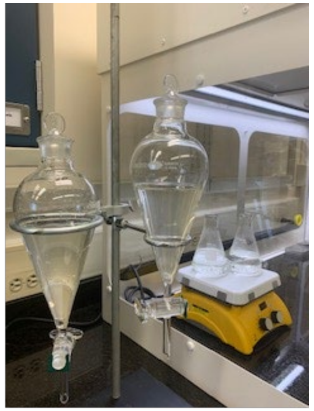
Nano- & Microplastic Formation

- Grind macroplastic material (bags, straws, etc.)
- Nanoplastic formation
- Creates reference standards

Sampling

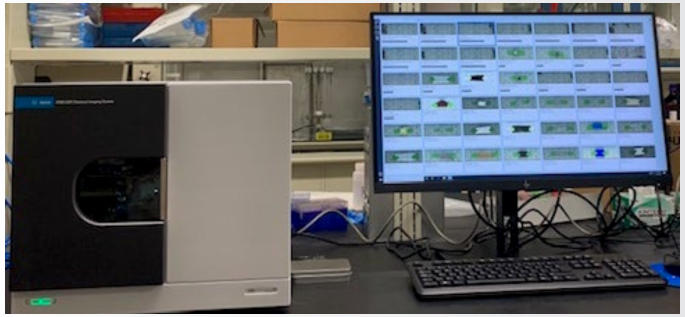
- Stainless-steel containers
- Urban watersheds
- WWTPs
- Agricultural fields
- Water, Soil, & Sludge

Extraction & Separation



- Multiple methods
- Depends on sample
- Extract all plastic material
- Separate from matrix

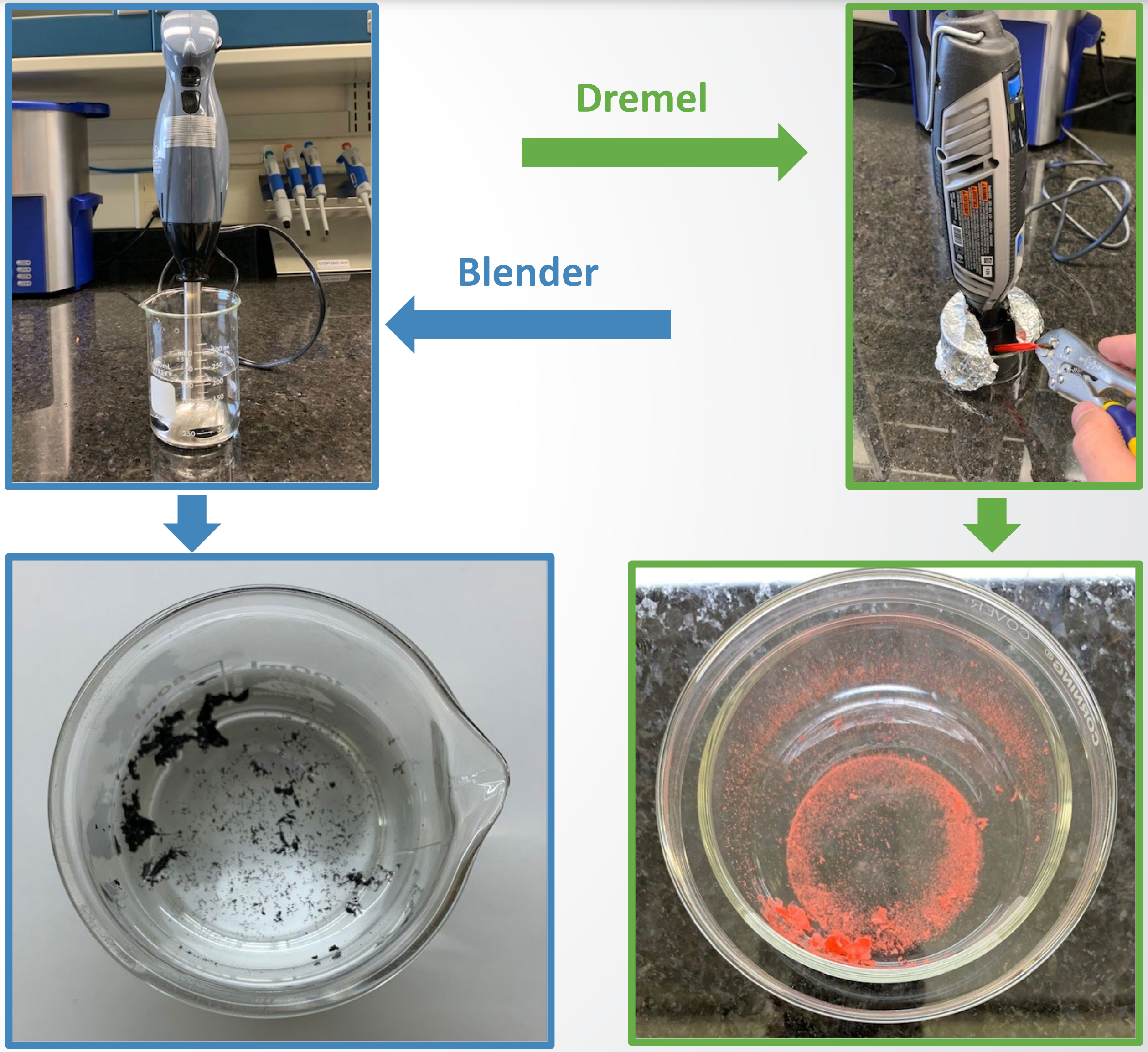
Analysis by LDIR



- Add reference standards to library
- High thru-put
- Simple
- Particle shape, size, and plastic type

Nano- & Microplastic Reference Material

- Currently using an emulsion blender and a Dremel drill with a sandpaper bit
- Use with plastic consumer products (straws, forks, bags, bottles, etc.)
- There are a lack of standards for N&MP analysis so we must make our own



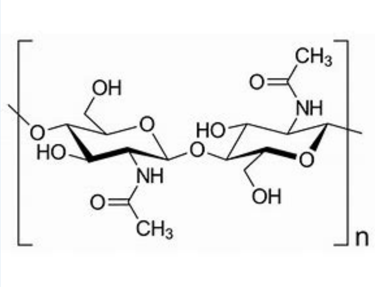
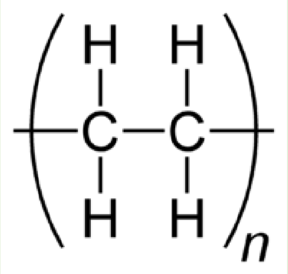
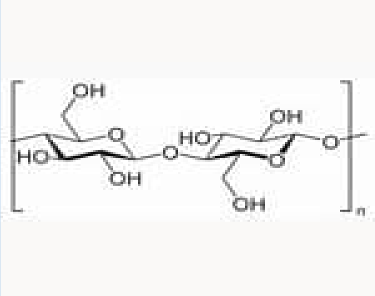
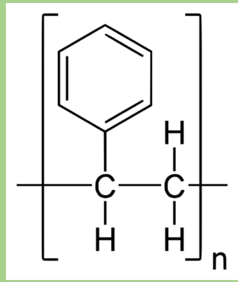
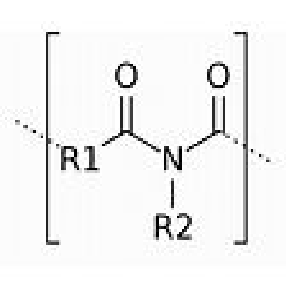
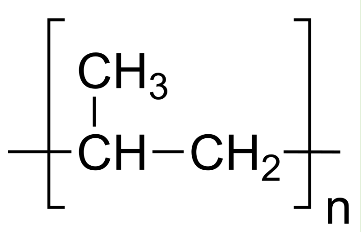
Microplastic Standards

- Use of virgin polymers microbeads
  - Size ranges from 35 – 250 µm
  - Unable to determine effects of additives and shape
- In-house standards
  - Blend or grind consumer plastic products with additives
  - Shape more closely fits with MP shapes in the environment (fragments, fibers, etc.)

Sampling the Urban Watershed

- Minimize plastic use for sample collection
  - Stainless steel containers
- Public access to rivers for sample locations
  - Bike/walk paths, boat launches, parks, etc.
- Sampling will include
  - Surface waters
  - Agricultural Biosolids & Soils
  - WWTP Influent, Effluent, & Sludge

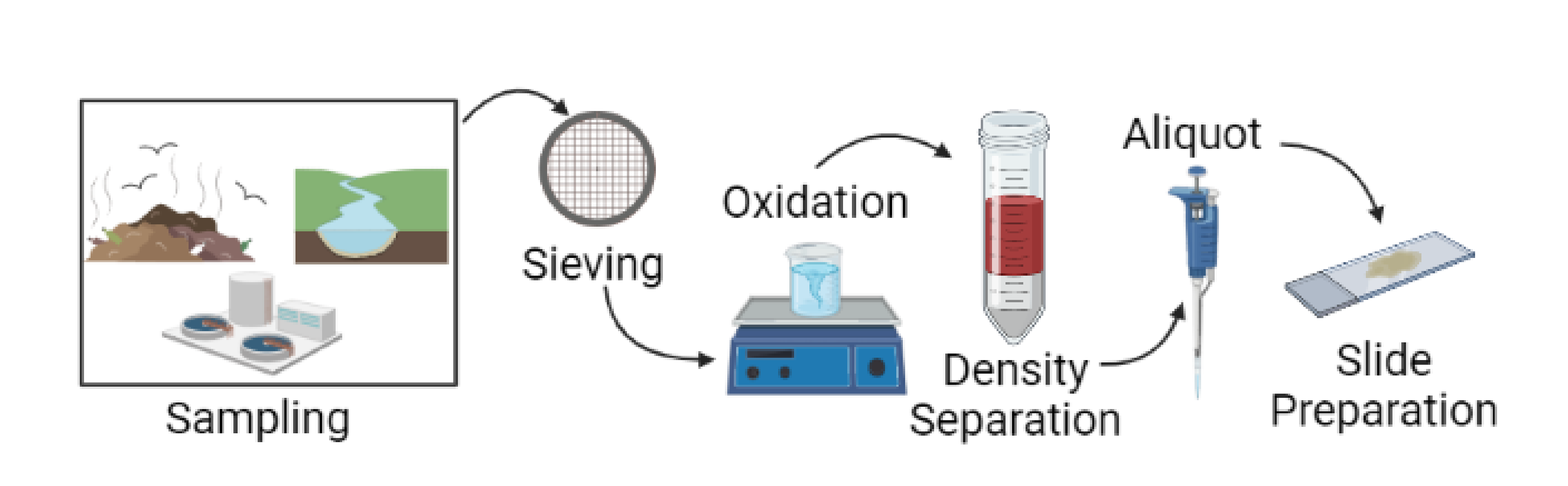
Common Polymers found in Samples

Natural Polymer Identification	Environmental Source	Structure	Anthropogenic Polymer Identification	Source	Structure
Chitin	A component of cell walls in fungi, the exoskeleton of arthropods, and scales of fish		Polyethylene	Packing film, trash & grocery bags, squeeze bottles, toys	
Cellulose/Cellulosic	Component of plant cell walls, bacteria, algae. “Most abundant natural polymer”		Polystyrene	Insulation, protective foam packing material, food packaging	
(Natural) Polyamide	Proteins, collagen, DNA, protein with amide groups		Polypropylene	Packaging, bottles, caps, straws	

Extraction, Separation, & Purification of Plastics from Environmental Media

Method	Description
Sieving	Wet or dry, fractionates solid material by size. Size ranges from 25 µm to 2 mm.
Oxidation	Effectively removes organic matter in sample (H_2O_2 + heat or Fenton reaction).
Density separation	Effectively removes inorganic matter. Create a dense liquid so that plastics float to top and sediments sink to bottom and can be removed. Typical brine density ranges are between 1.2 to 1.8 g/cm^3.

Extraction, Separation, & Purification of Plastics from Environmental Media: Workflow



- A combination of any separation, extraction & purification techniques may be used
- No separation, extraction & purification techniques may be used
- Depends on the properties of the sample (amount of inorganic material and organic material present)

Particle Analysis by Laser Directed Infrared (LDIR)

- Agilent LDIR Chemical Imaging System
  - Used in pharmaceutical industry
  - Appling to microplastic research
- Obtains IR spectra of all particles and identifies the polymer type
  - Uses an IR reference library
- Obtains particle size and shape parameters
  - 10 µm is the detection limit

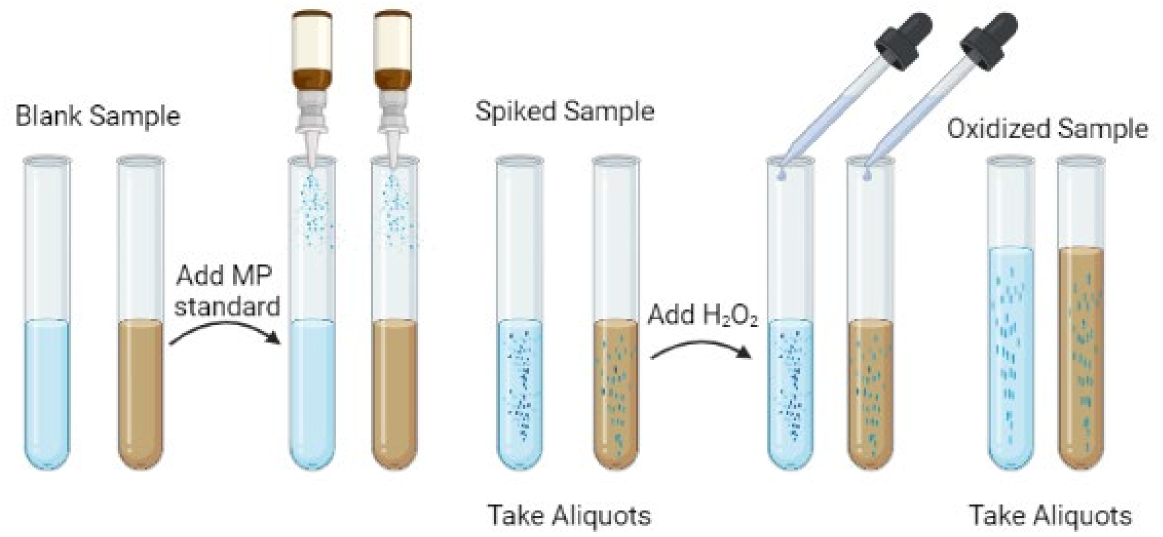
LDIR Interface of Actual River Water Sample with PS Spike

Method Development:

1. Oxidation as a Sample Preparation Step
2. LDIR Method Optimization for Particle Detection and Analysis Time

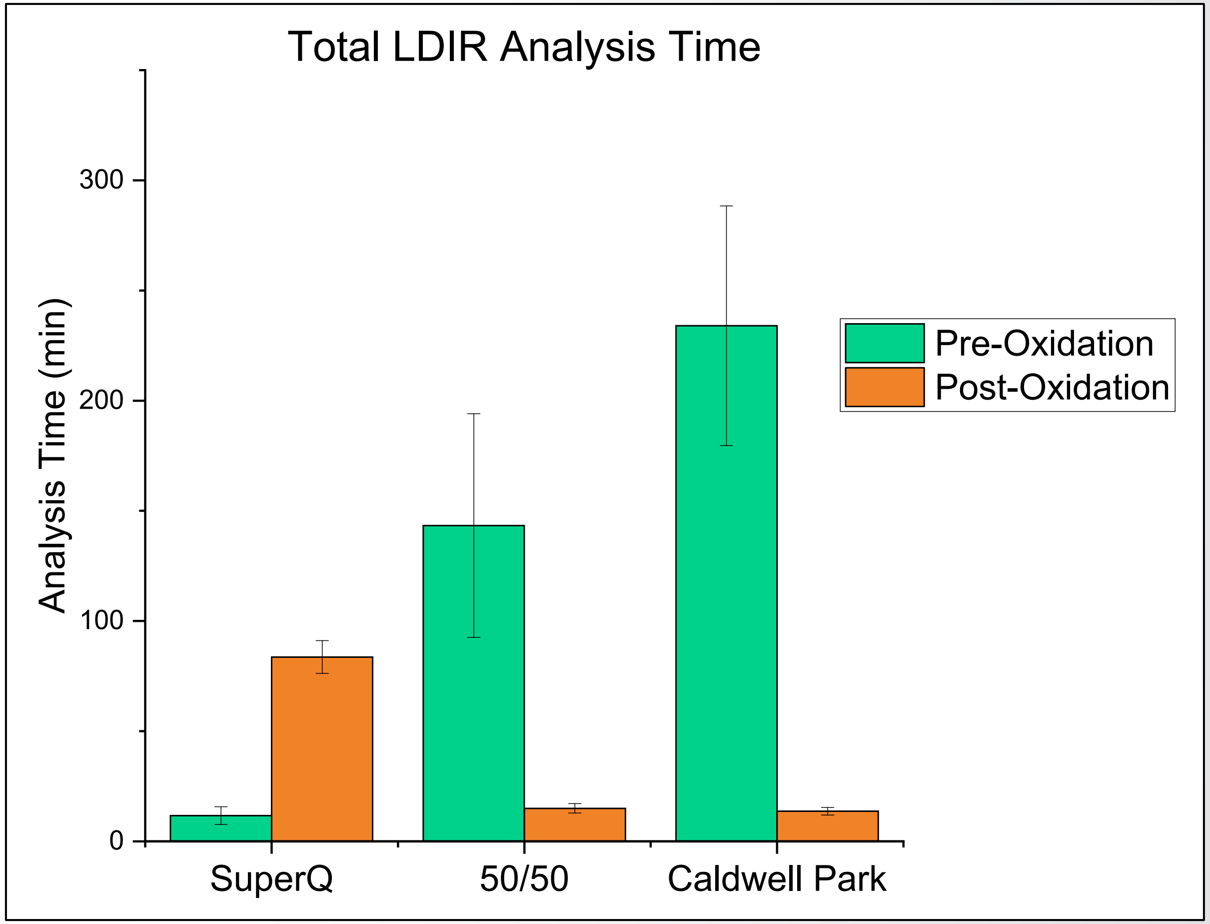
Oxidation Effects on Polystyrene Standard

- Super Q and Caldwell Park water samples
- Spiked with Polystyrene standard
- Oxidized with H_2O_2 + heat
- Determine if oxidation will remove organic matter without damaging MPs
- Determine effect of oxidation on analysis time, particle count, quality, and size



Oxidation Effects on LDIR Analysis Time

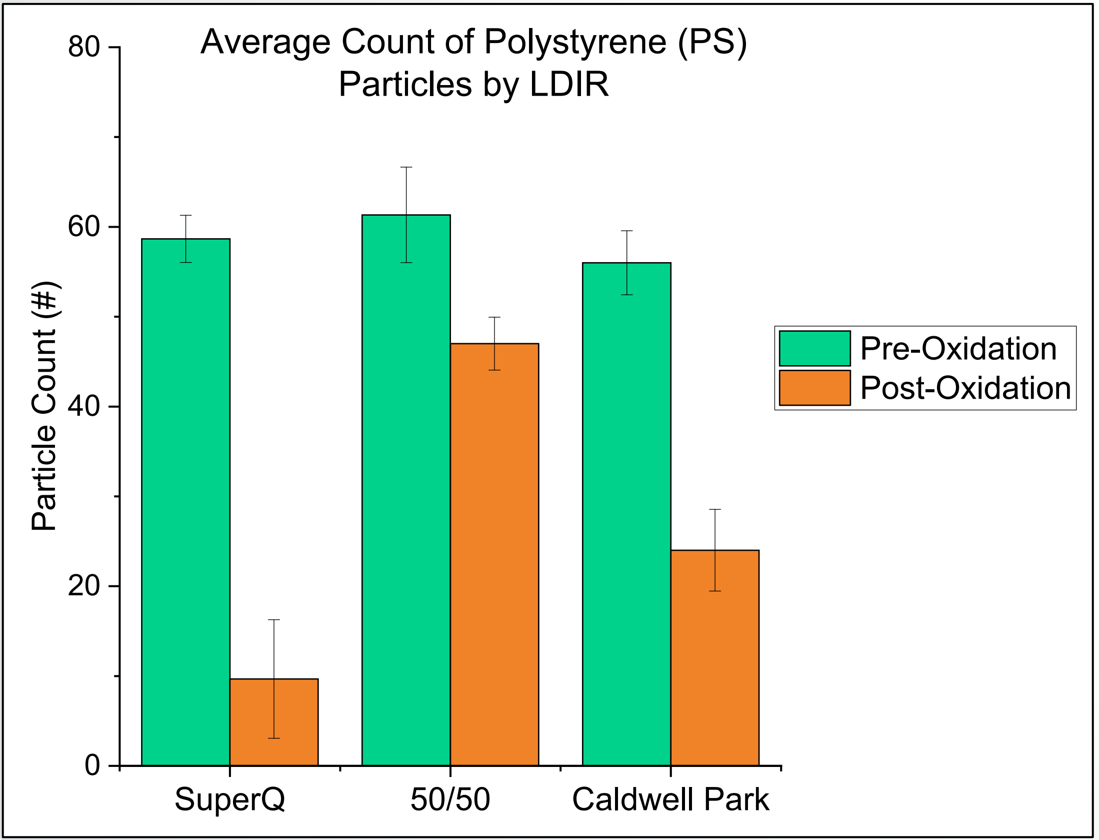
- The total time spent on the LDIR analysis dropped after oxidation
  - Due to a change in total particle count

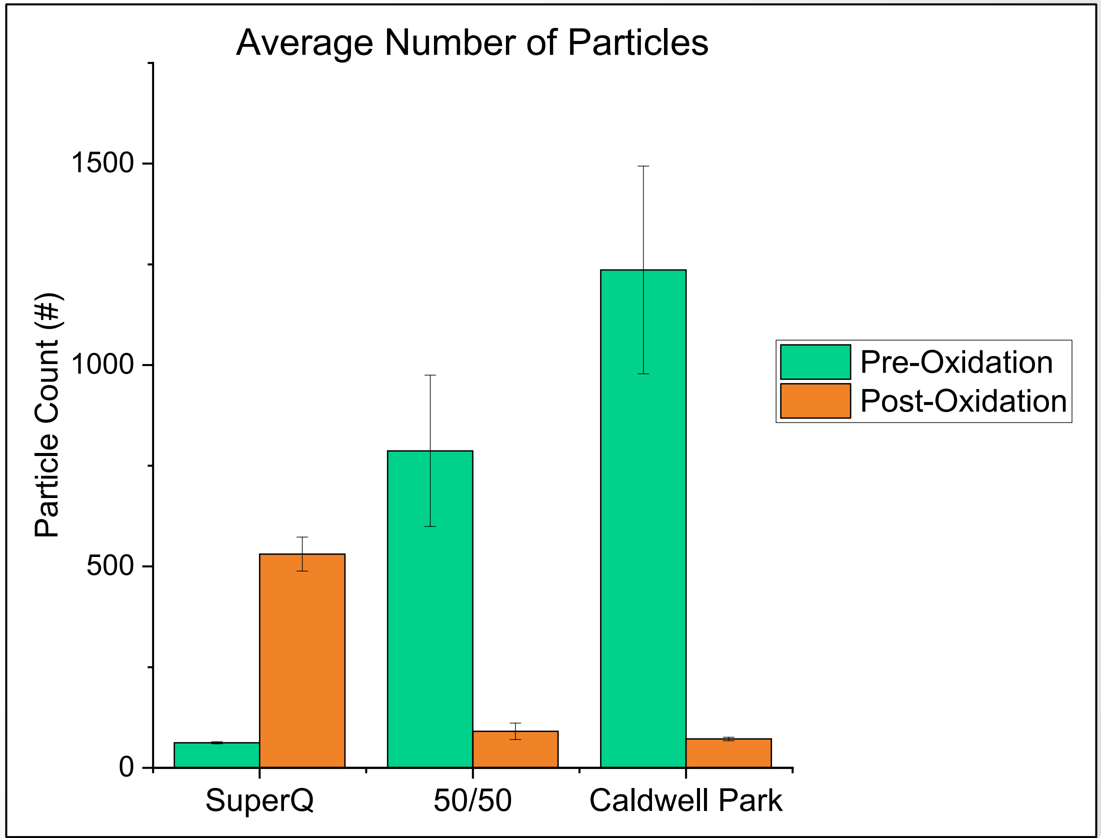


Oxidation Effects on Particle Count

- Decrease in PS particles from evaporation
- Mitigate loss with tight sealed caps or oxidation method that doesn't require heat (Fenton reaction)

- Oxidative scoring increased SuperQ particle count
- Otherwise, a large decrease in total particle count

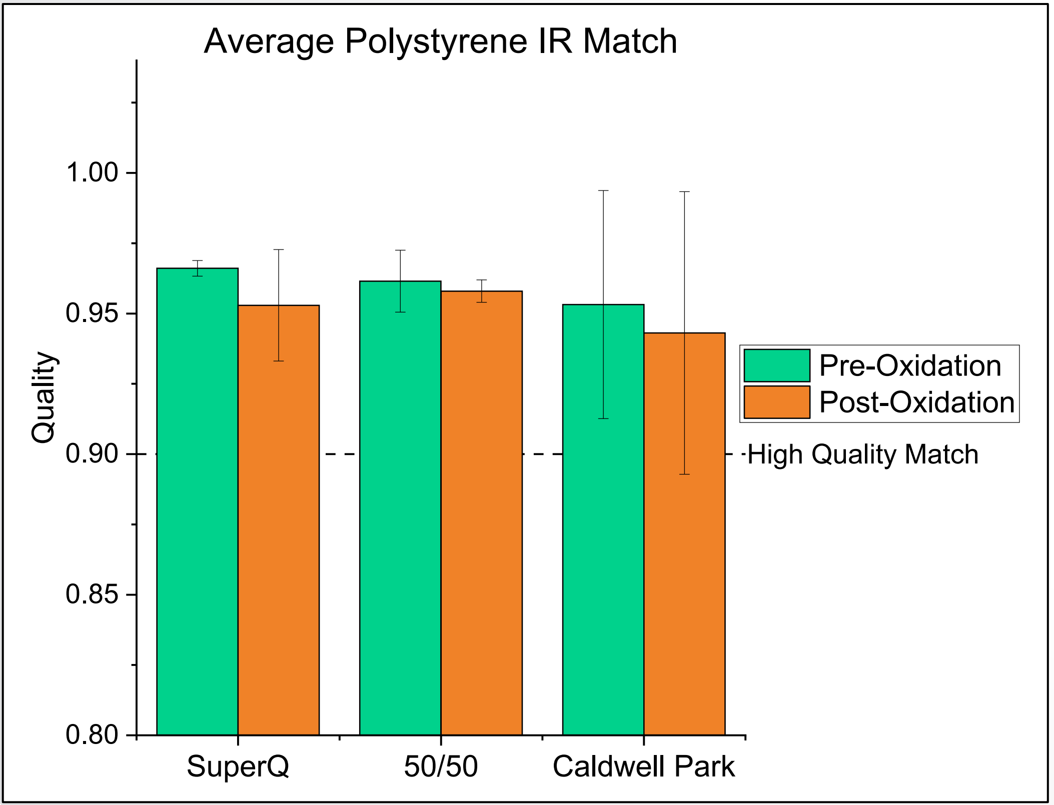


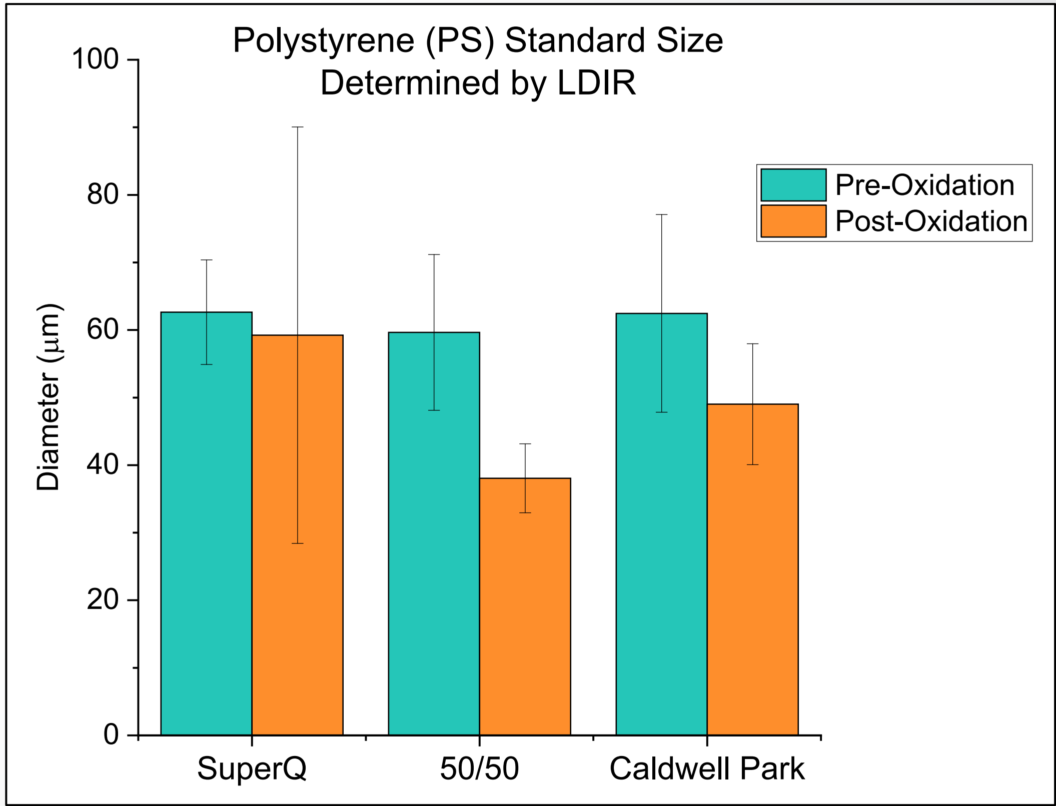


Oxidation Effects on PS Particle Quality & Size

- Trend of lower quality IR match post-oxidation
- All have high quality matches (> 0.9)
- Evidence that oxidation doesn't chemically effect PS standard

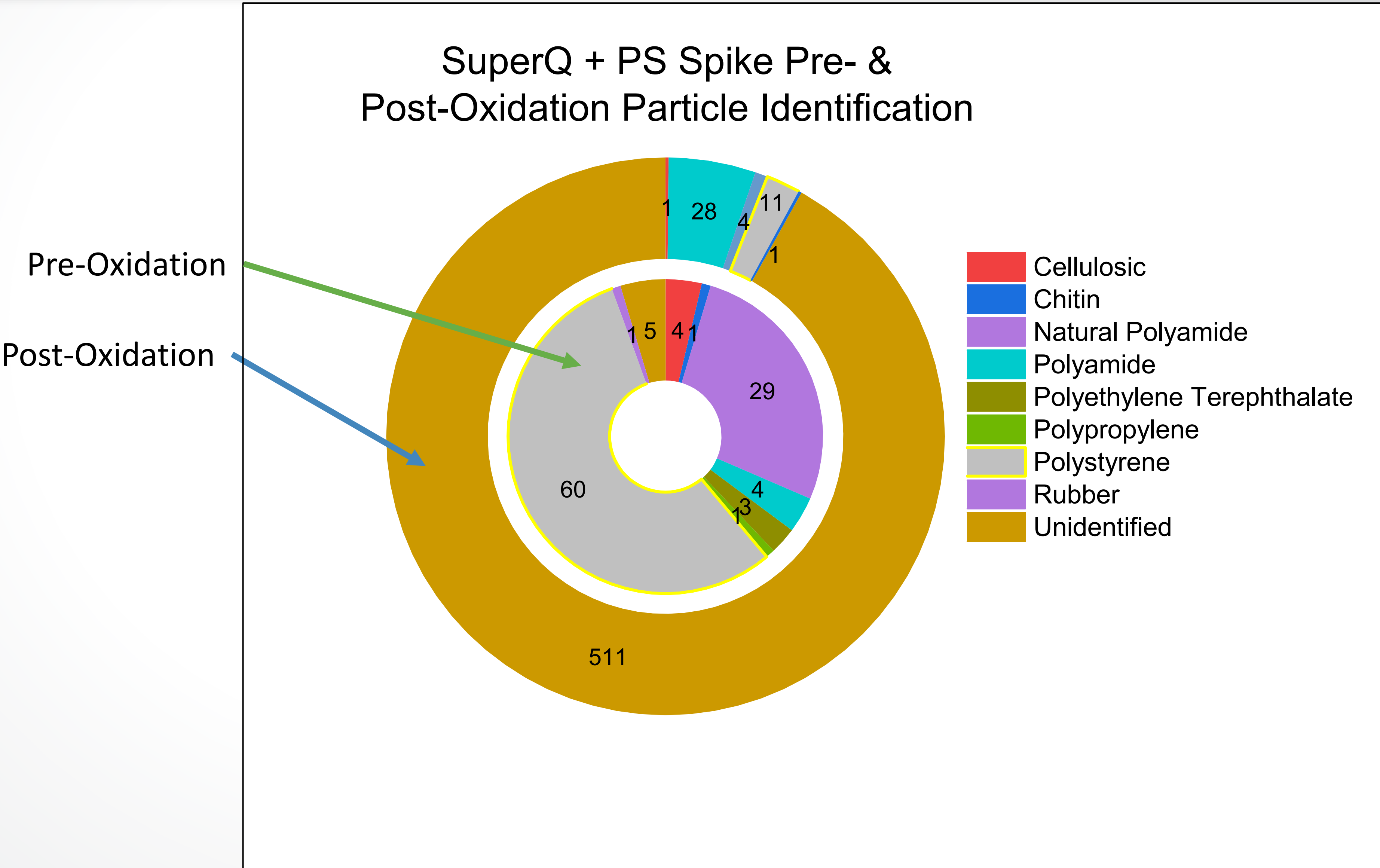
- PS standard beads are 45 µm
- Clumped together yields 100-150 µm
- Reason for larger average diameter and error bars





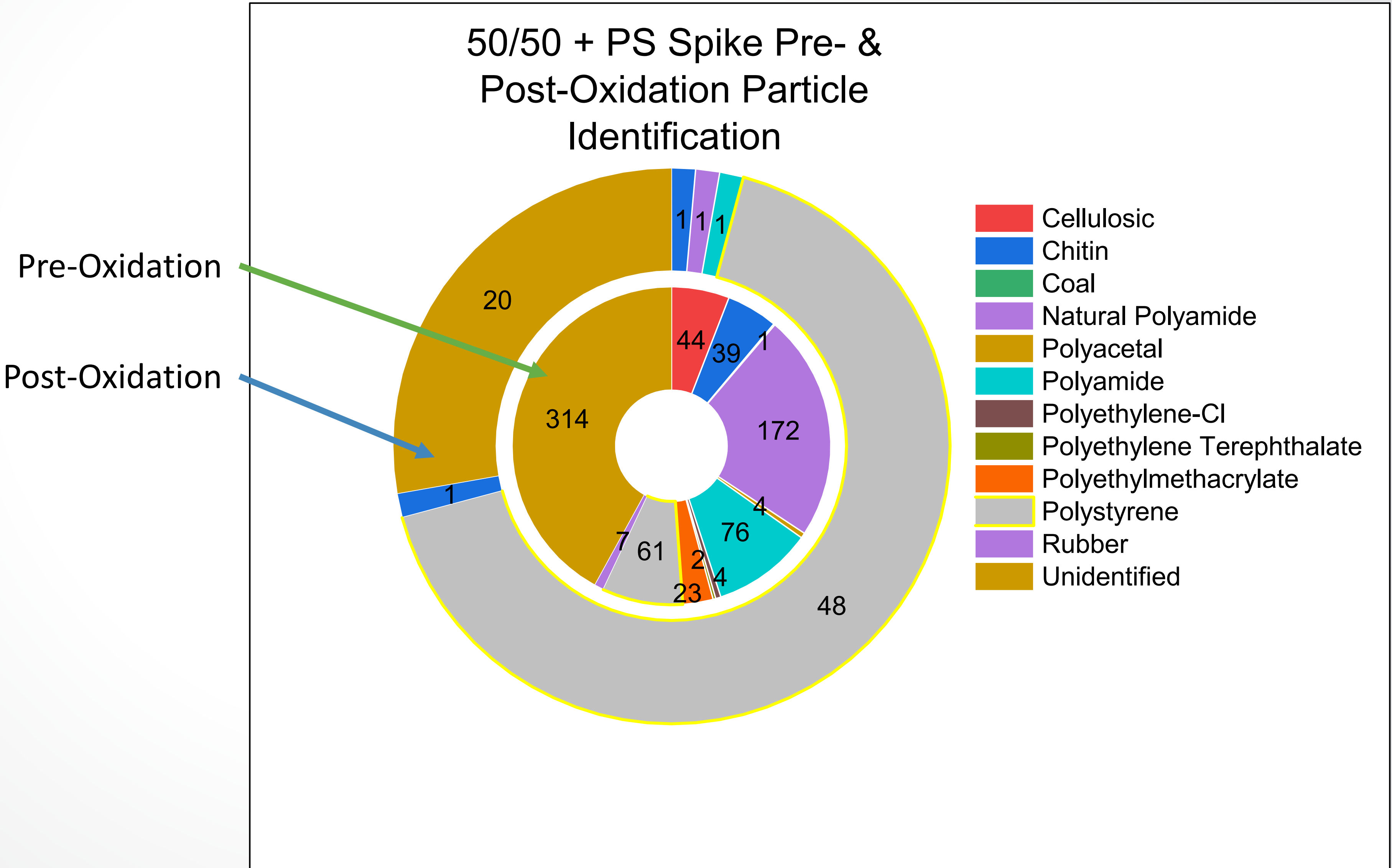
Oxidation Effects on Particle Identification in Lab Water

- Increase in Unidentified due to oxidative scoring
- Decrease in other contaminants
- Decrease in PS
    - Most likely from evaporation



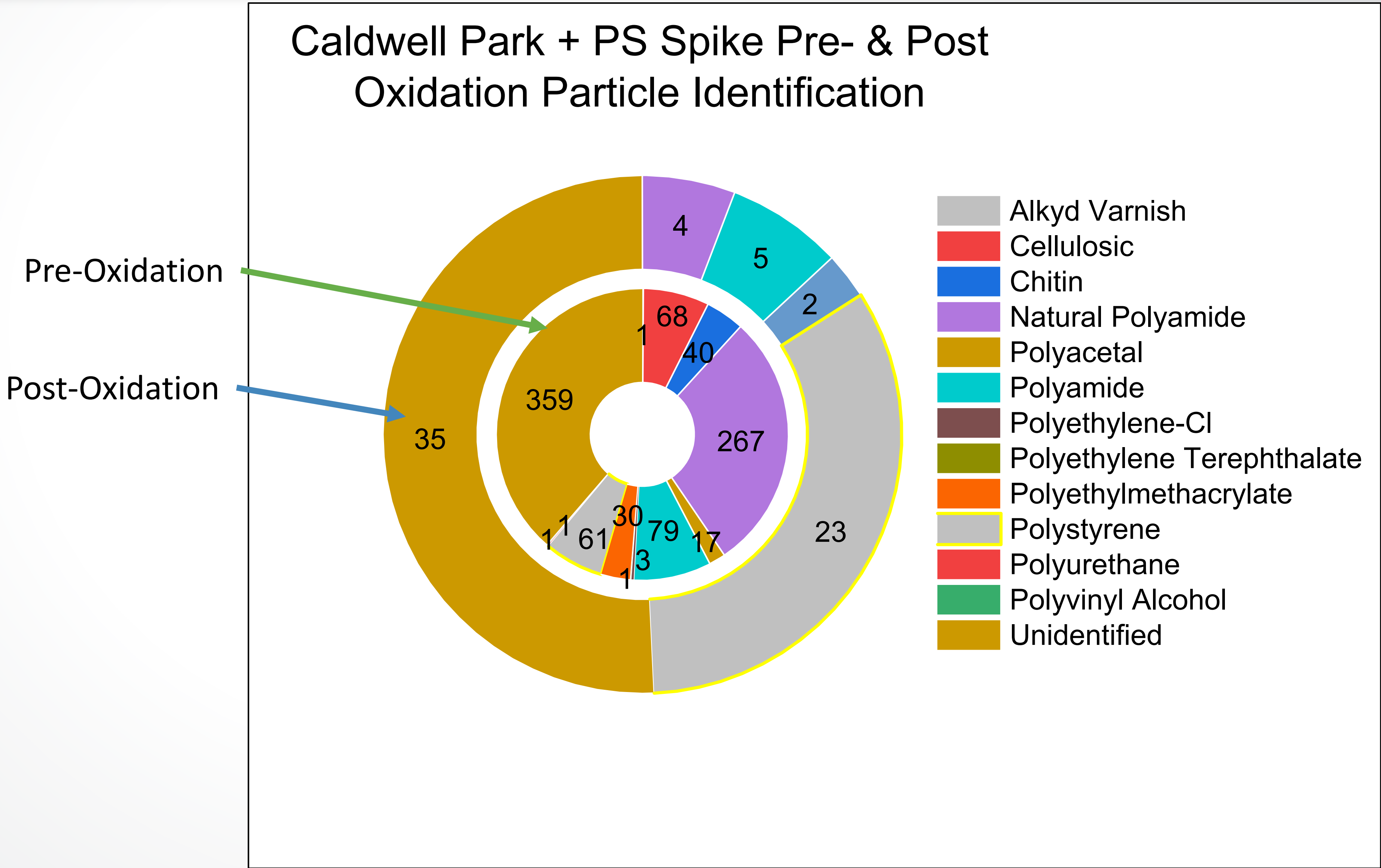
Oxidation Effects of Particle Identification of 50/50 Lab Water and Caldwell Park

- PS became most abundant after oxidation
- Removed natural polymers
- Decreased unidentified particle count



Oxidation Effects of Particle Identification of Caldwell Park

- Decreased Unidentified particle count
- Removed natural polymers



LDIR Method Development

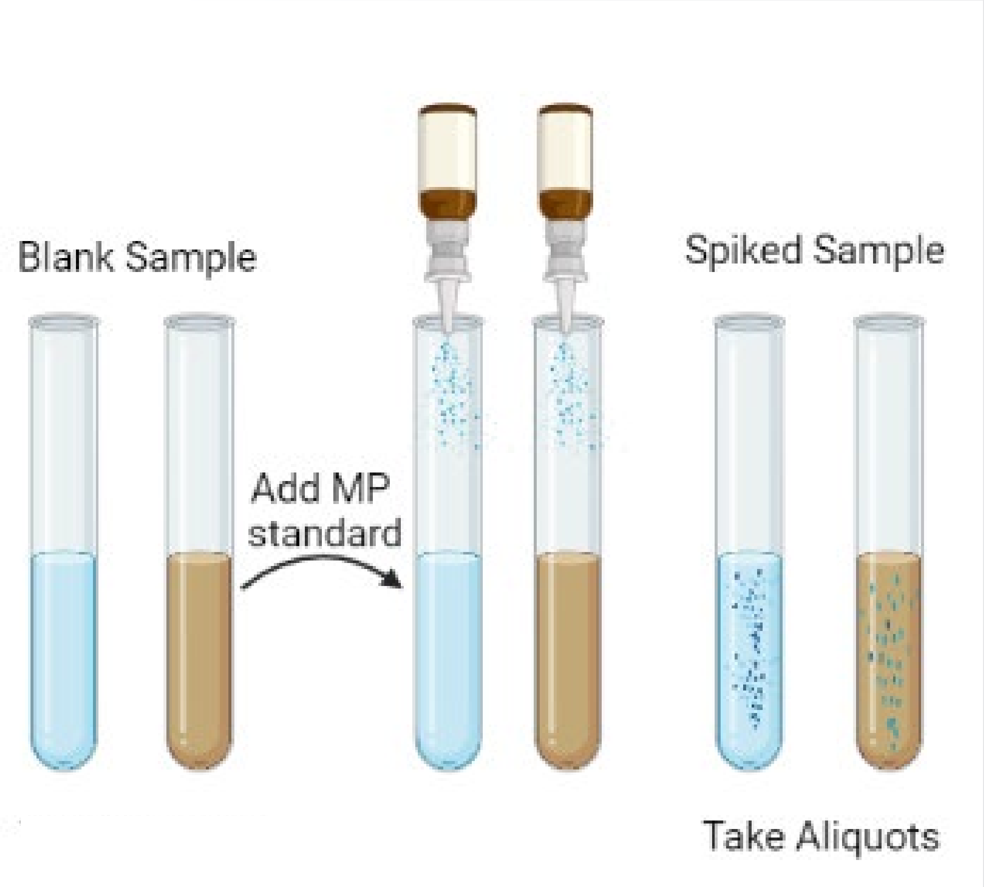
- Three settings control the analysis time
  - **Scan speed-** time to acquire an image
  - **Sweep speed-** time to acquire a spectrum
  - **Particle Sensitivity-** sensitivity of particle detection
- Particle size also relates to analysis speed
  - Particles < 50 µm typically need laser refocusing for each particle, increasing analysis time

GOALS

- Determine best extraction & separation methodologies for environmental samples
- Optimize LDIR detection method to maximize particle identification and quality while minimizing analysis time
- Determine particle size, shape, and polymer type by LDIR

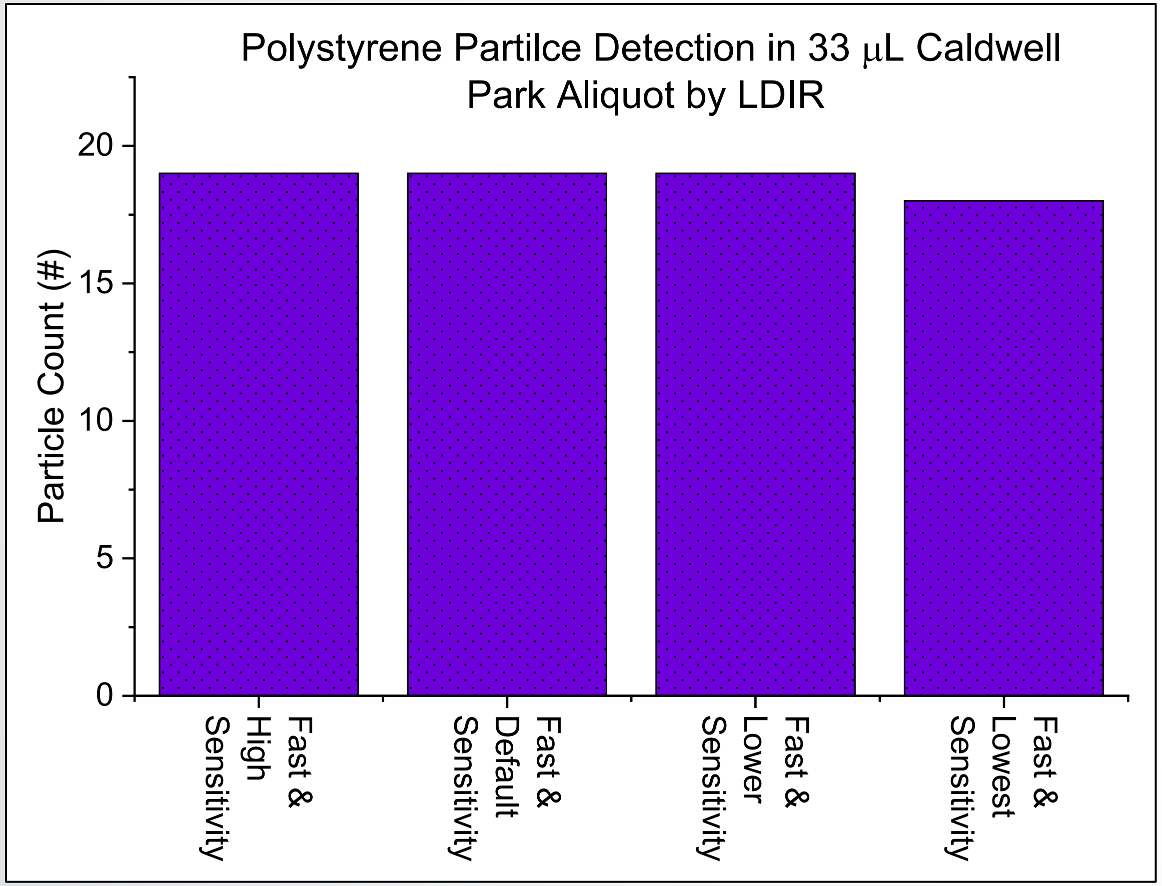
LDIR Method Development

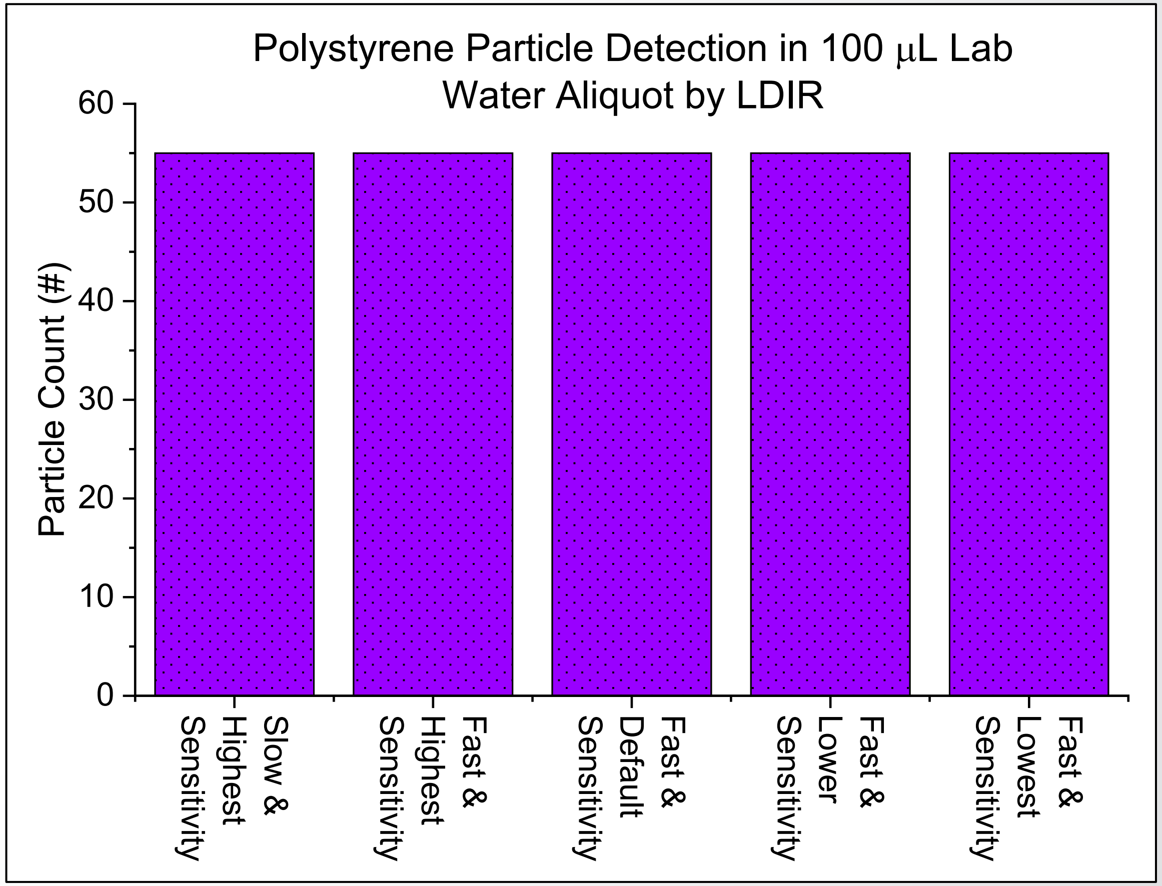
- Super Q and Caldwell Park water samples
- Spiked with Polystyrene standard
- Determine if changing LDIR parameters changes particle analysis and time
- Monitoring particle count, quality, size, and analysis time



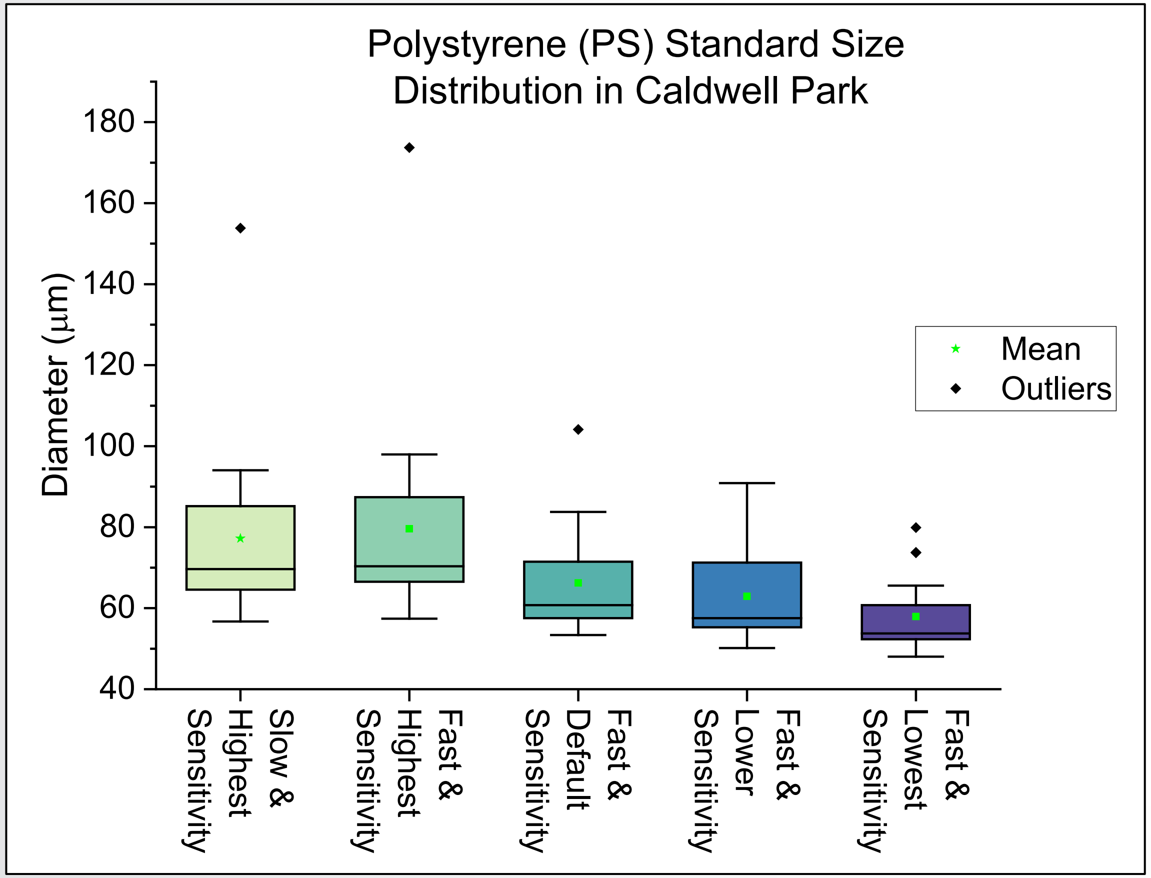
Polystyrene Standard Count by LDIR

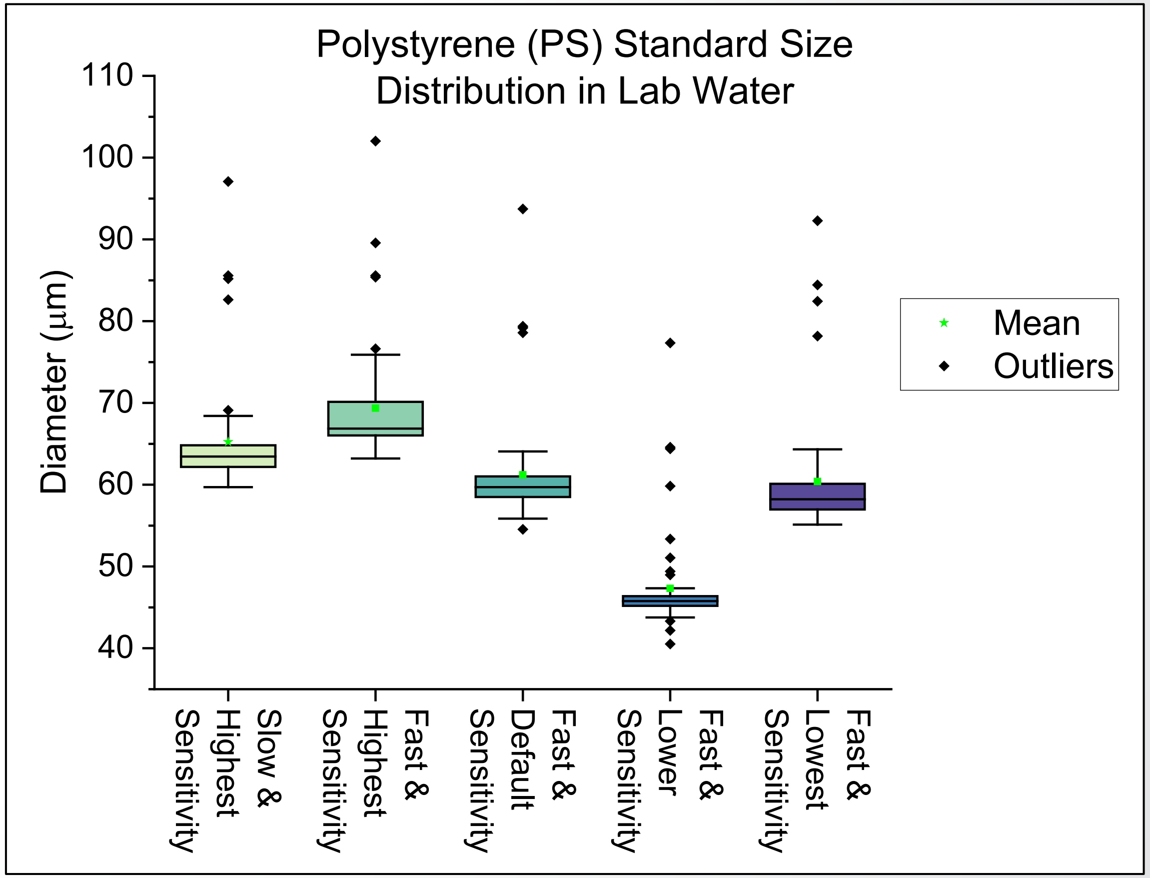
- Loss of PS count with fast scan & sweep speed and lowest sensitivity in Caldwell Park



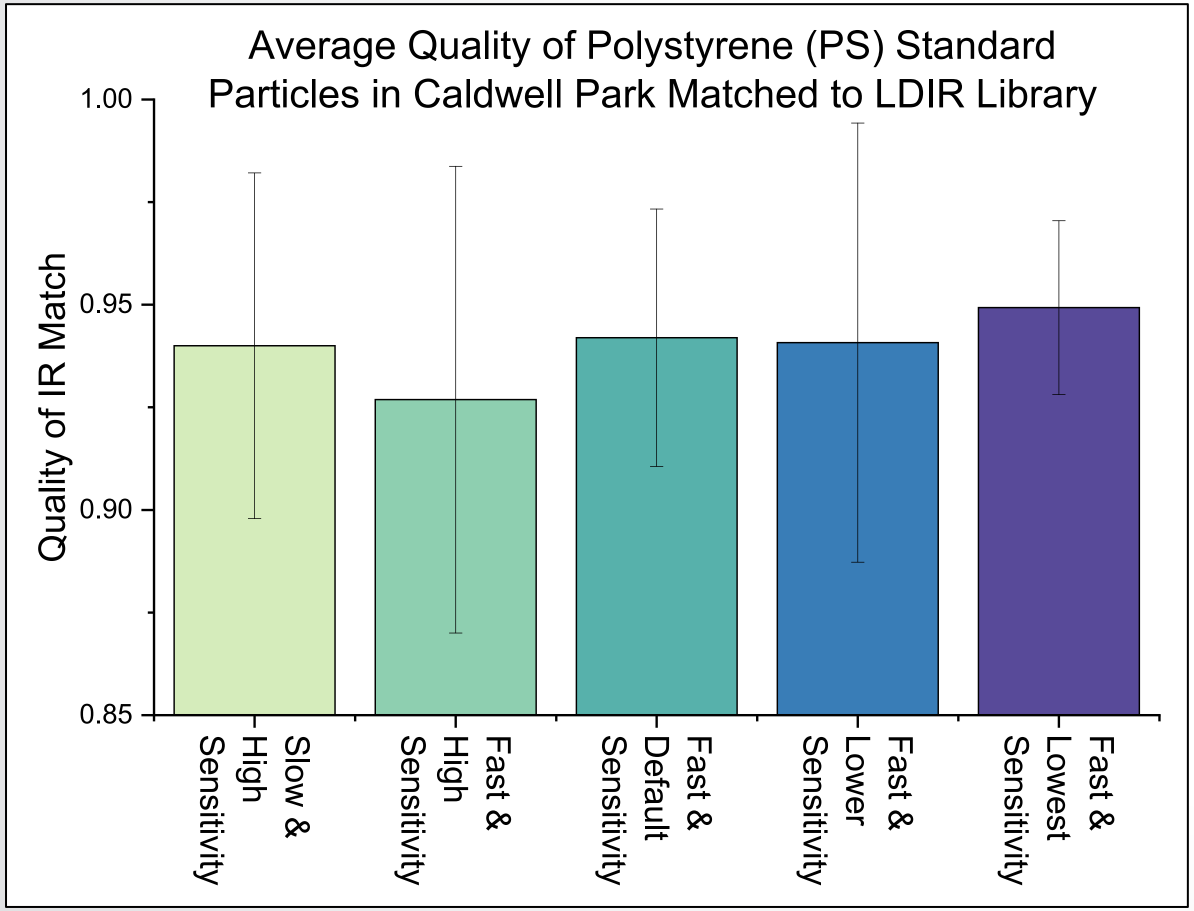


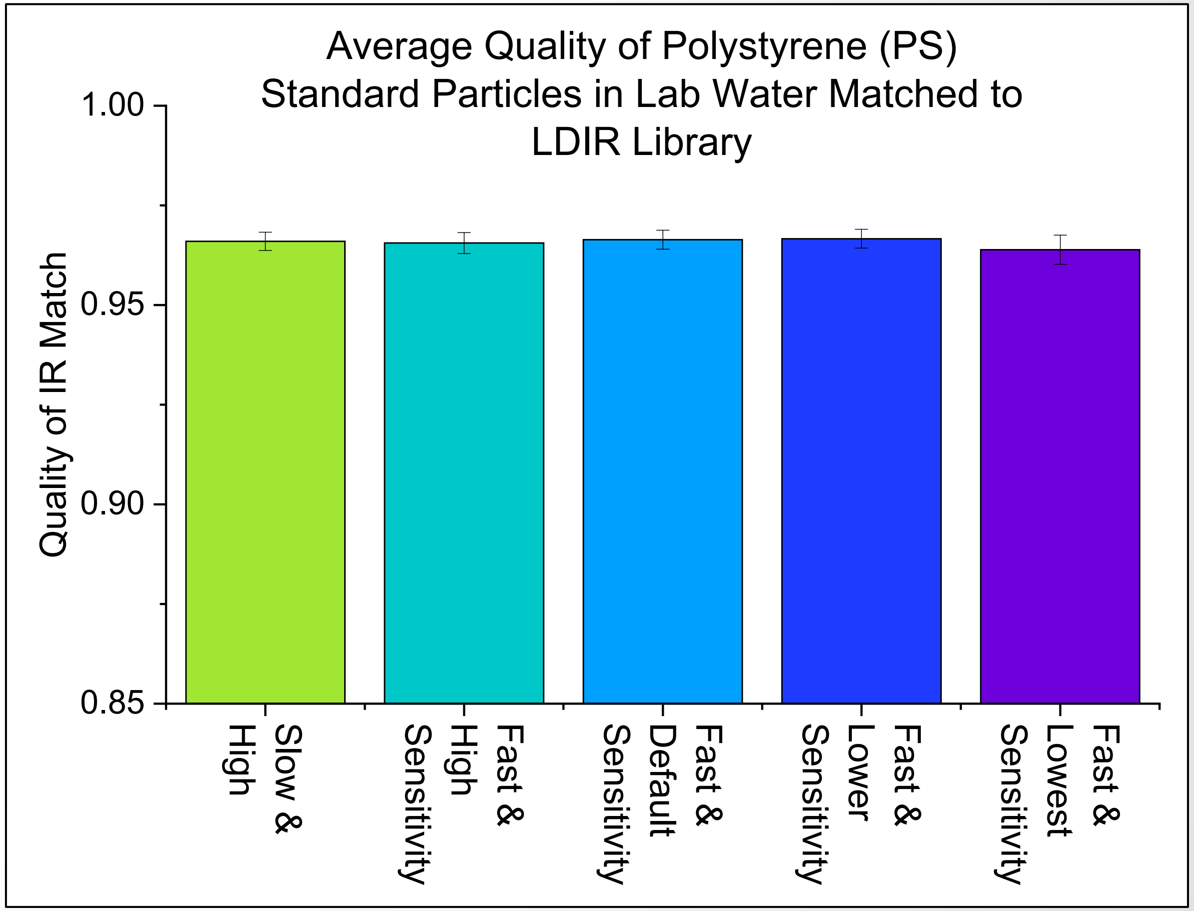
Polystyrene Standard Sizes



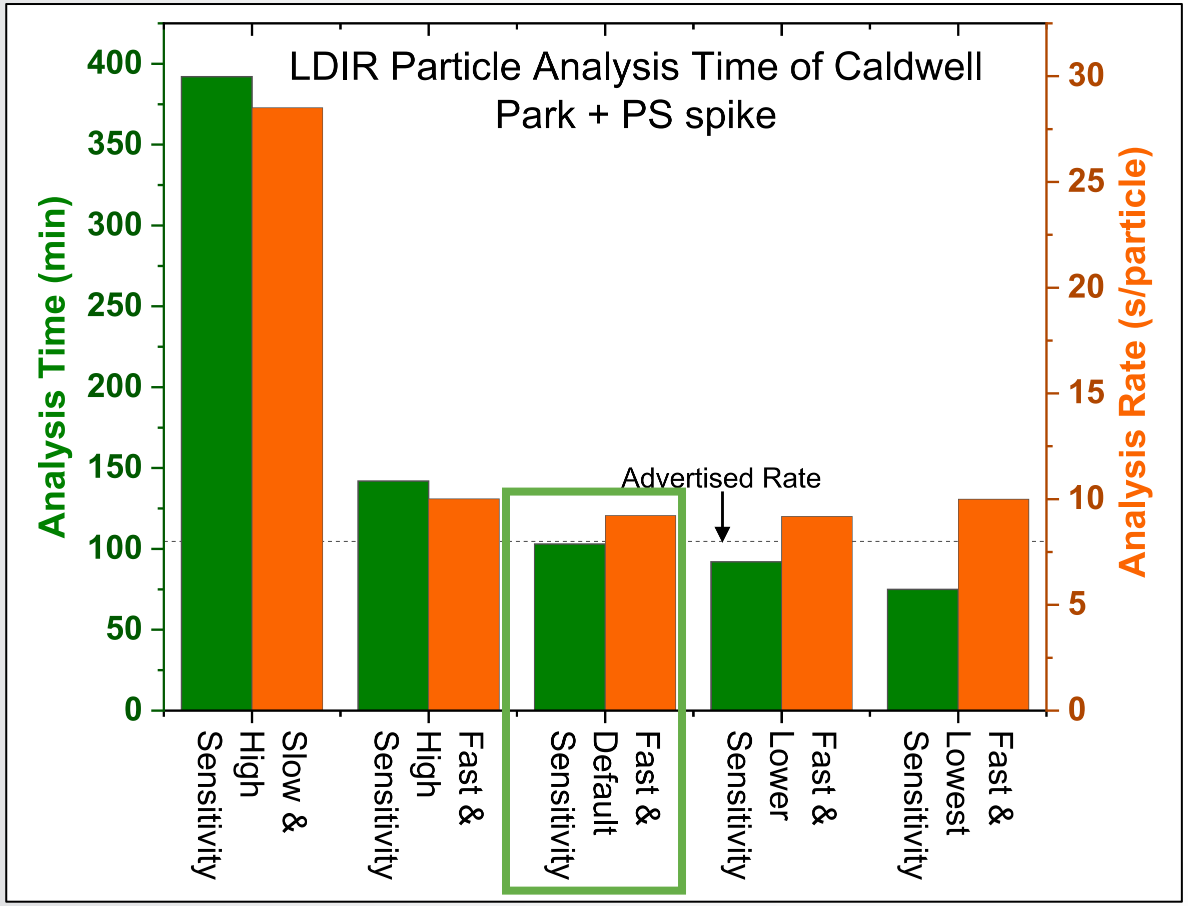


Polystyrene Particle Quality

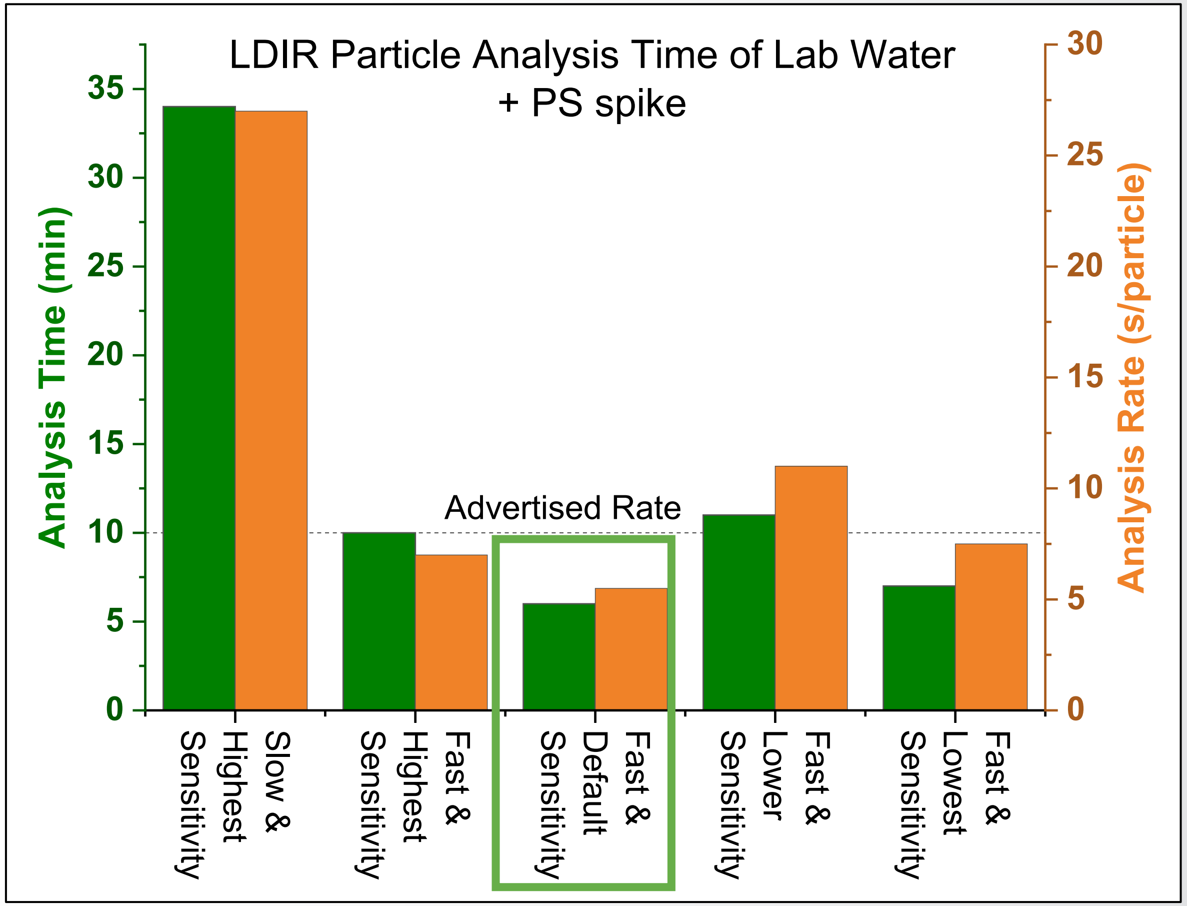




LDIR Analysis Time

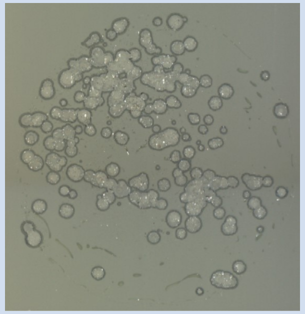


Ideal conditions



Ideal conditions

Challenges We Are Working On

Challenge	Description	Options to Overcome Them	Picture
Oxidative Scoring of Kevley Slide	Reactive oxygen species (ROS) degrade the reflective coating of the slide which the LDIR misidentifies as particles. Doesn’t necessary cover real particles, just adds to particle count	1. Use Fenton Reaction instead of H_2O_2 + heat to react all ROS before taking aliquot 2. Filter using a gold coated (IR reflective) filter to reduce contact time with ROS	
Salt Deposit on Kevley Slide after Density Separation	Brine solution forms large salt deposit after the aliquot dries. It covers all particles, not allowing for LDIR analysis.	1. Filter using a gold coated (IR reflective) filter to remove brine from MPs before drying 2. Use a different liquid than a brine solution	
Misidentification or Unidentified Identification of Particles	Large amounts of particles have a IR match quality < 0.70, which is classified as unidentified.	1. Increase IR reference library with virgin polymers, environmentally degraded polymers, natural polymers, and organic matter commonly found in samples	

Acknowledgements

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