NORTHEAST CONFERENCE
THE SCIENCE OF PFAS:
Public Health & The Environment
Tuesday, March 31, 2020 - Wednesday, April 1, 2020
Sheraton Framingham Hotel & Conference Center
Framingham, MA

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PFAS Adsorption and Concentration in Microplastics and Transport to Surface Water

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April 5, 2022

Outline

- Plastics and microplastics
- PFAS generated from plastic manufacturing
- Microplastics as vector for PFAS
- Recommendations on Mitigation and Treatment

Types of Plastics

1. Biodegradability Potential

- **Non-biodegradable**
  - Biobased: bioPE, bioPETE, PEF
  - Oil-based: PE, PETE, PP, PVC, PS, PA, PU
- **Compostable and biodegradable**
  - Biobased: PLA, bioPBS, PHA
  - Oil-based: PBS, PBAT, PCL

2. Common Plastic Products

Number	1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
Plastic Type	polyethylene terephthalate	high-density polyethylene	polyvinyl chloride	low-density polyethylene	polypropylene	polystyrene	other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass
Example	soft drink bottles, mineral water, fruit juice containers and cooking oil	milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps	trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff	crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings	furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars	toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, audio cassettes, CD cases, vending cups	an example of one type is a polycarbonate used for CD production and baby feeding bottles
Density (g/mL)	1.39 ↓	0.95 ↑	1.3-1.34 ↓	0.92-0.94 ↑	0.9 ↑	1.05-1.07 ↓	Varies

4. Decompose under perfect conditions

3. Density →

modified from: polychem-usa.com

PETE, HDPE, PS has annual % recycled>30%
Seawater density ~1.03 g/mL

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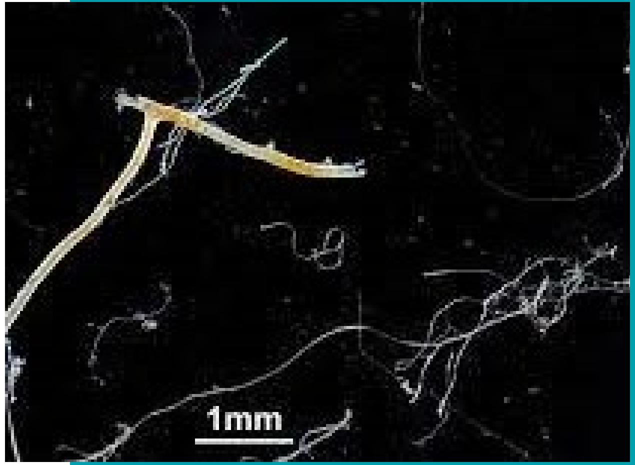
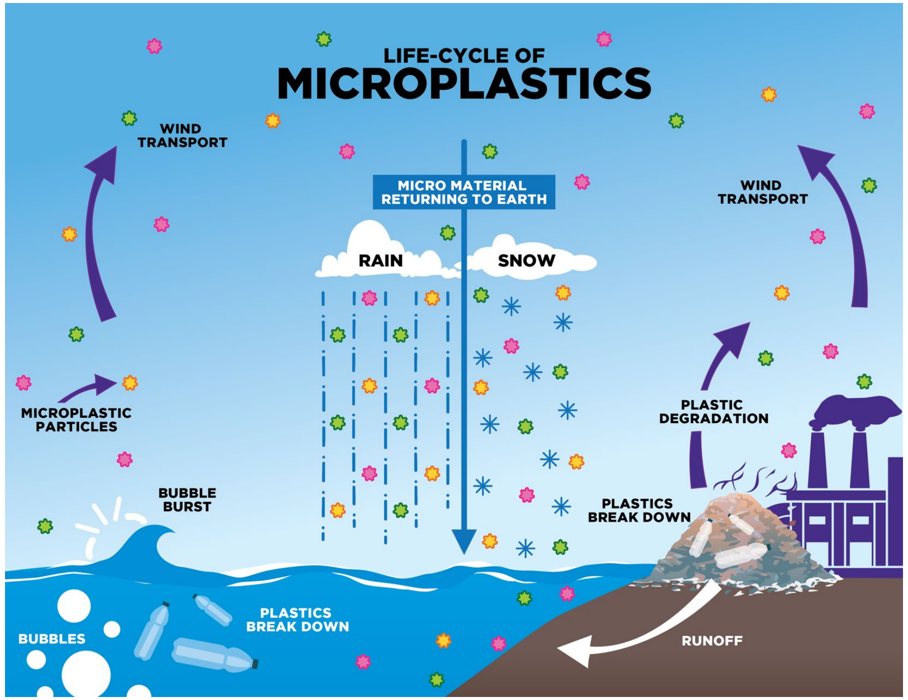
Definitions – Still Developing

- **California Water Board definition**
  - ‘Microplastics in Drinking Water’ are defined as solid polymeric materials to which chemical additives or other substances may have been added, which are particles which have at least two dimensions that are **greater than 1nm and less than 5,000 micrometers (μm)**. Polymers that are derived in nature that have not been chemically modified (other than by hydrolysis) are excluded.
- **EU/ECHA Restriction Proposal**
  - Solid polymer-containing particles, to which additives or other substances may have been added, and where ≥ 1% w/w of particles have (i) **all dimensions 1nm ≤ x ≤ 5mm**, or (ii) for fibres, **a length of 3nm ≤ x ≤ 15mm** and length to diameter ratio of >3.

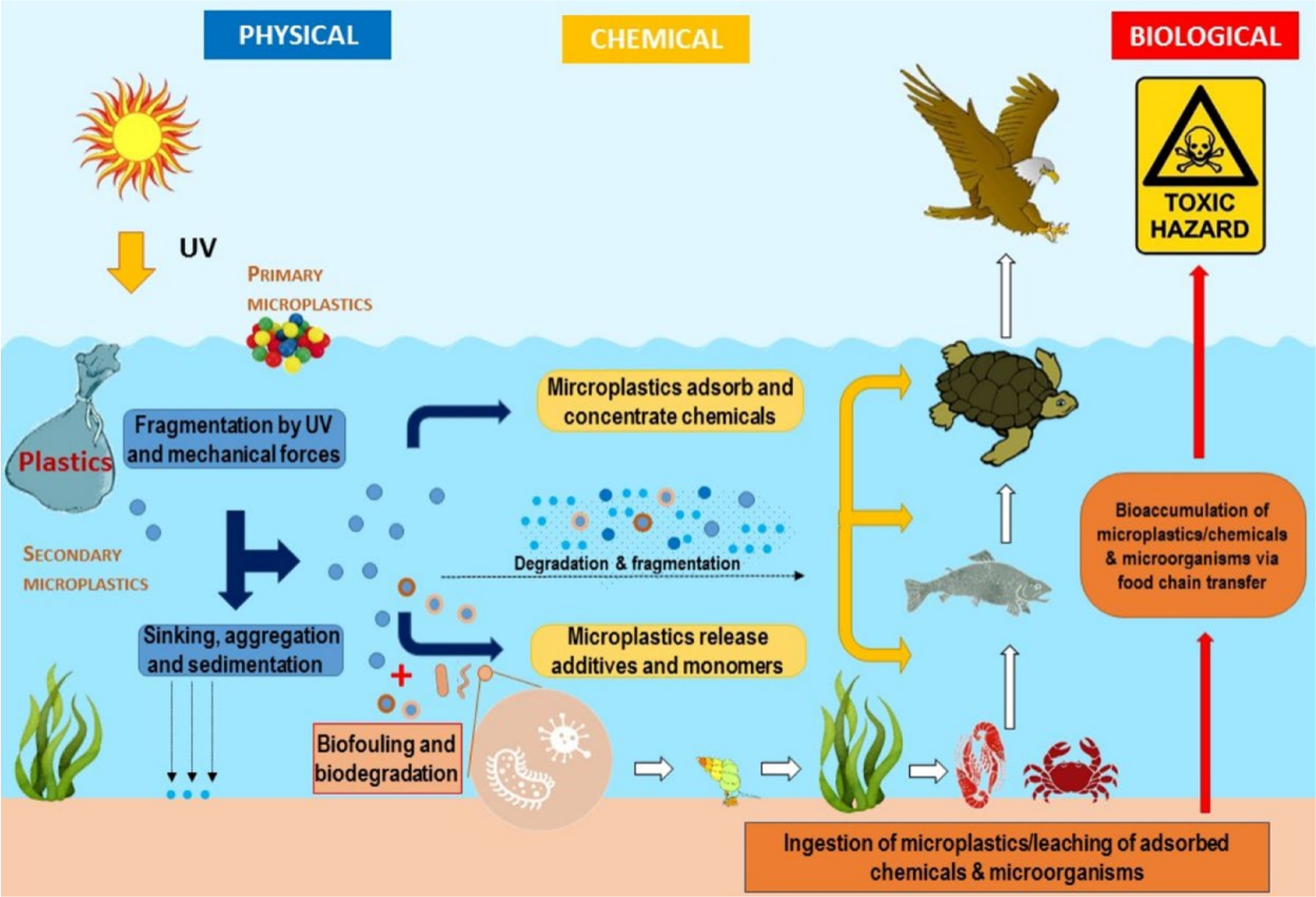


MP Life Cycle in the Environment



https://ysjournal.com/airborne-microplastics-a-global-issue-with-implications-for-human-health/

Secondary MP Transport Processes in the Aquatic Environment



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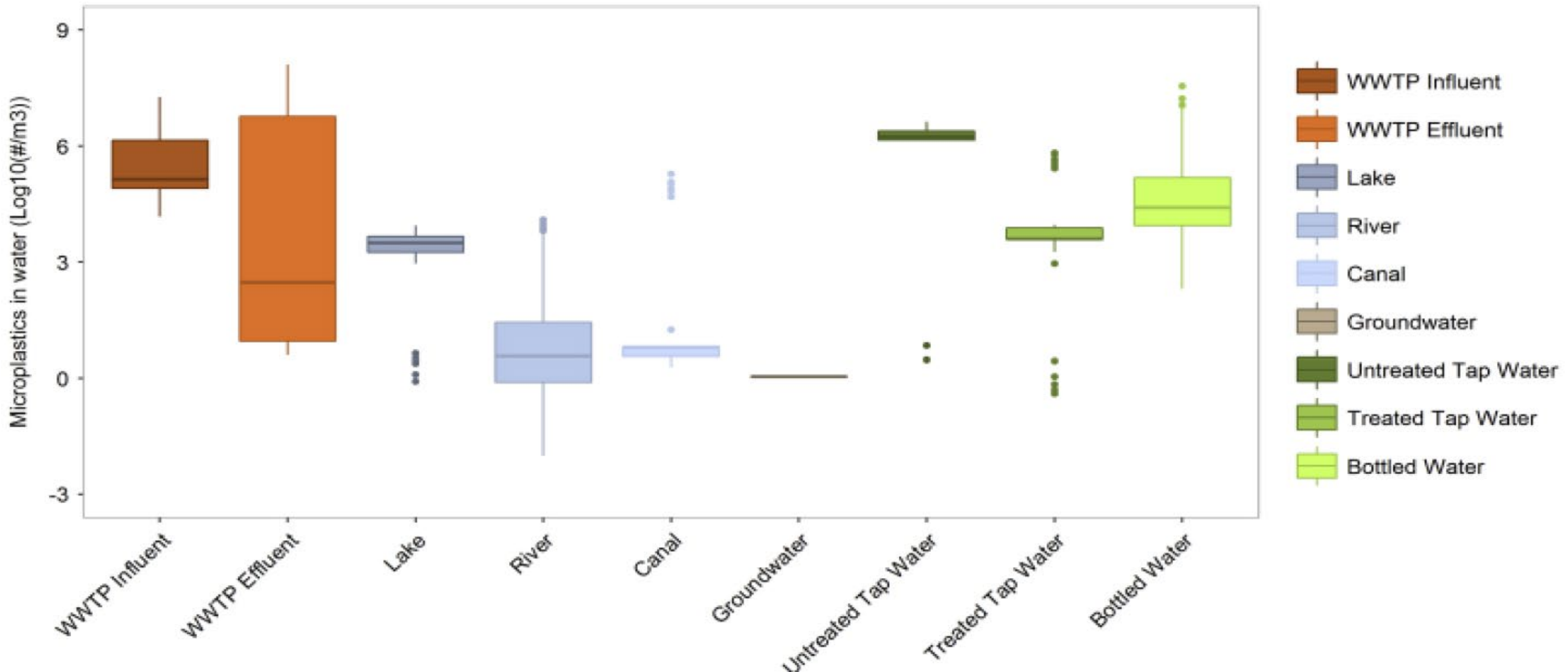
MPs Detections in Environmental Samples

- MPs are frequently present in freshwater, wastewater and drinking water
- Fragments, fibers, film and pellets were the most frequently reported shapes
- Commercial and industrial areas emitted more MPs in stormwater than residential and highway areas
- Globally detected polymers: PE ≈ PP > PS > PVC > PET
- A higher tendency for PVC and PET to settle because of their higher densities
- PVC had the largest particle size and mass.



(Koelmans et al 2019)

(Liu et al, 2019)

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PFAS from Plastics vs. PFAS on MPs

"Given the prevalence of PFAS and microplastics in natural waters, coupled with the extremely long persistence time of both classes of pollutants, these two groups of emerging contaminants may act synergistically in food webs to cause adverse effects in fish and wildlife, as well as humans." – Scott et al, 2021

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PFAS from Plastics

- U.S. Plastics Pact includes PFAS on the "Problematic and Unnecessary Materials List" as a first step to accelerating process toward a circular economy for plastic packaging
  - Problematic and Unnecessary Materials: items that are not currently reusable, recyclable, or compostable in the US and are not projected to be kept in a closed loop in practice and at scale by 2025
- PFAS can be unintentionally present in plastics, as residuals and impurities of PFAAs, mainly derived from processing aids used in the manufacturing process
- The polyethylene **fluorination process** forms a barrier on the plastic's surface and it strengthens the packaging. This process leads to creation of PFAS leached into the products
  - **EPA identified eight PFAS from HDPE containers for mosquito control pesticide (USEPA, 2021)**

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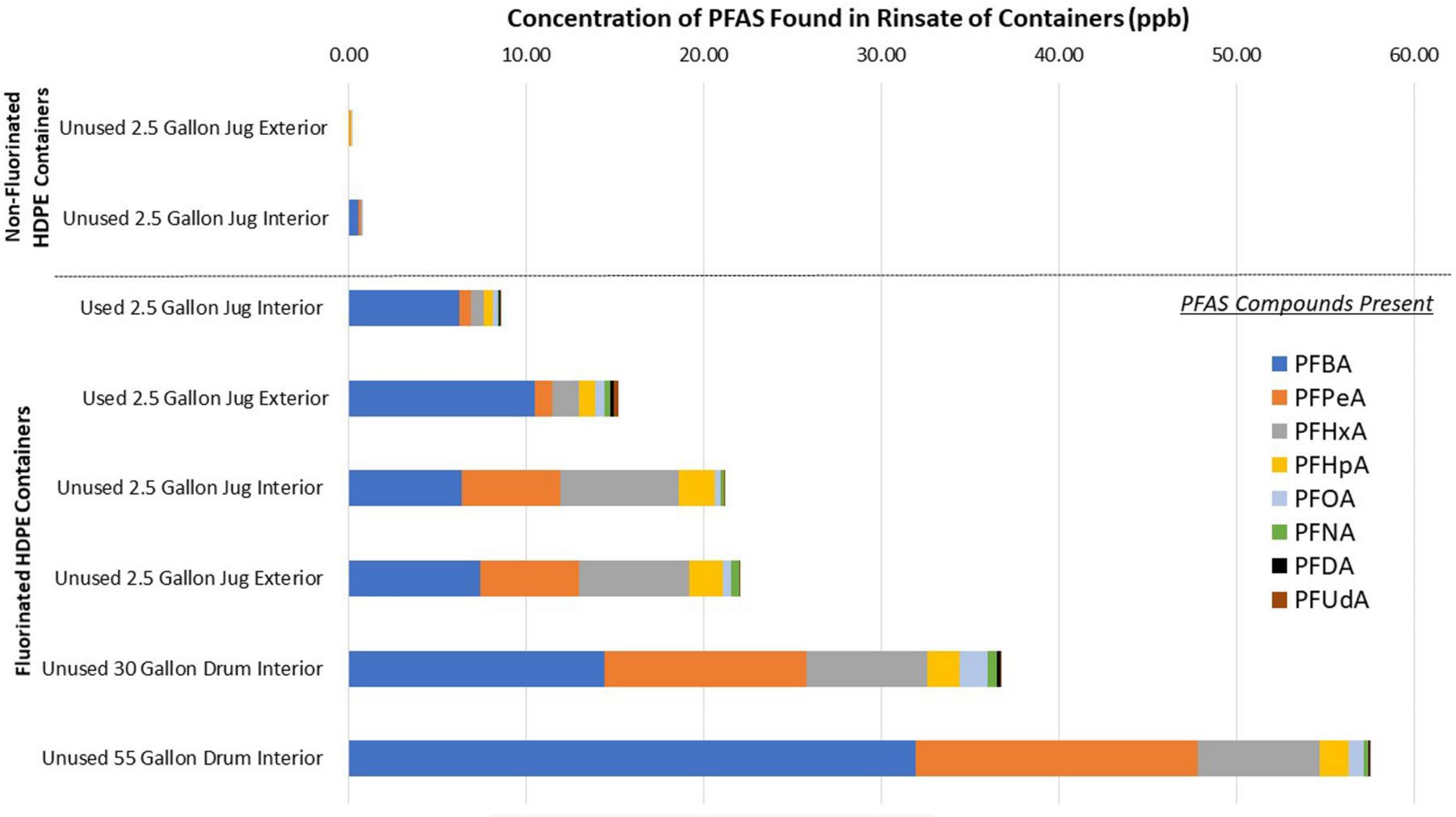
PFCAs detected in Methanol Rinsate of HDPE Containers



EPA's Analytical Chemistry Branch PFAS Testing Rinses from Selected Fluorinated and Non-Fluorinated HDPE Containers

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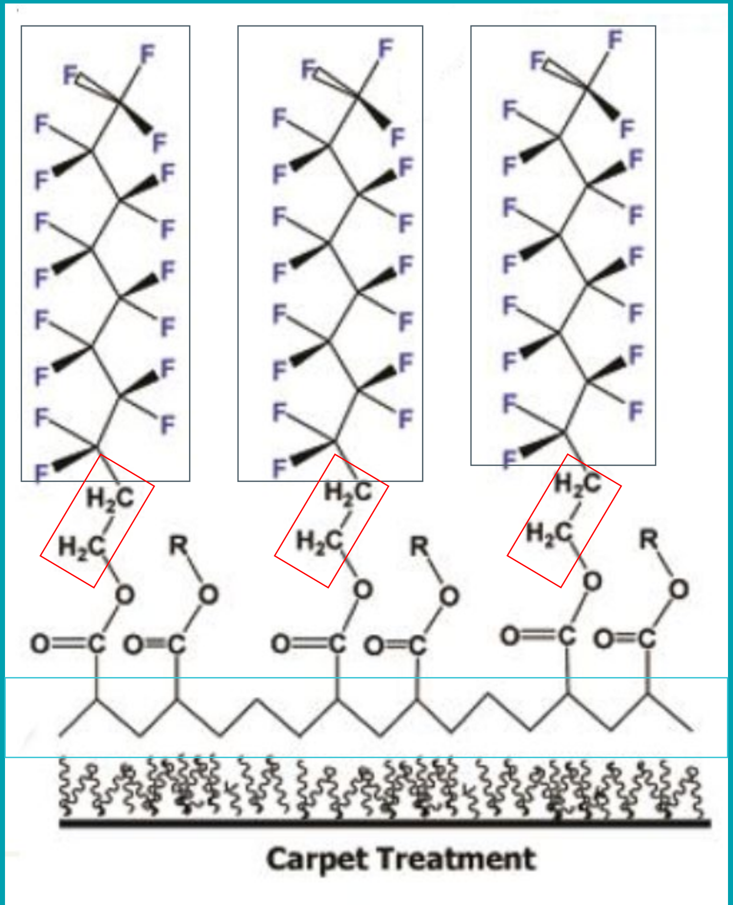
Side-Chain Fluorotelomer-Based Polymers (FTPs)

- FTPs have been applied as durable water repellents on:
  - Furnished textiles
  - Fabrics
  - Carpets
  - Garments. (Li et al 2017)
- FTPs are used as oil and grease repellents in:
  - Paper industry
  - Packaging industry
  - Other miscellaneous applications. (Li et al 2017)
- Potential **precursors** of FTOHs, FTCAs and PFCAs

Acronyms
FTOHs: fluorotelomer alcohols
FTCAs: Fluorotelomer carboxylates
PFCAs: perfluoroalkyl carboxylates, e.g., PFOA

Lang, 2018



(Lang 2018)

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MPs Concentrate and Transport Pollutants

Chemical additives (plasticizers)

Urban beaches

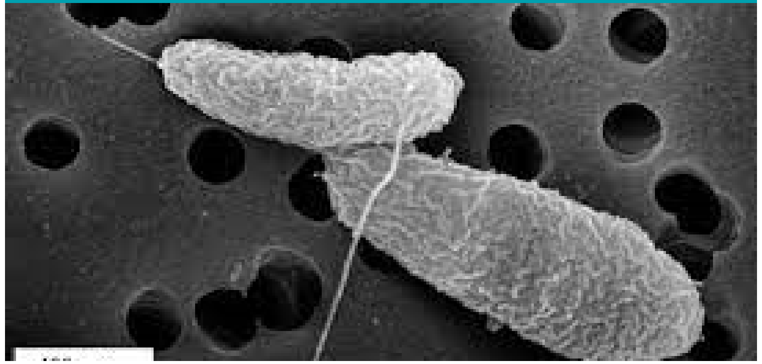
- Bisphenol A, up to 700 ng/g
- Phthalates, up to 3940 ng/g
- Polybrominated diphenyl ethers, up to 9900 ng/g

POPs

Analyzed 85 POPs on 3 types of MPs deployed in Lake Muskegon, MI for 3 months

- PAHs: up to 280x background levels
- PCBs: 380x background levels
- PFAS: up to 259x background levels
- Biological materials may enhance the adsorption of PFAS in the environment.

Pathogens

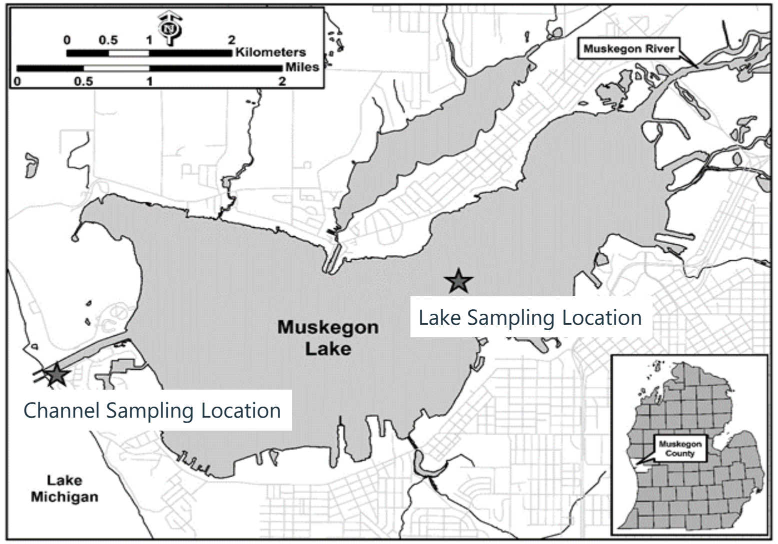


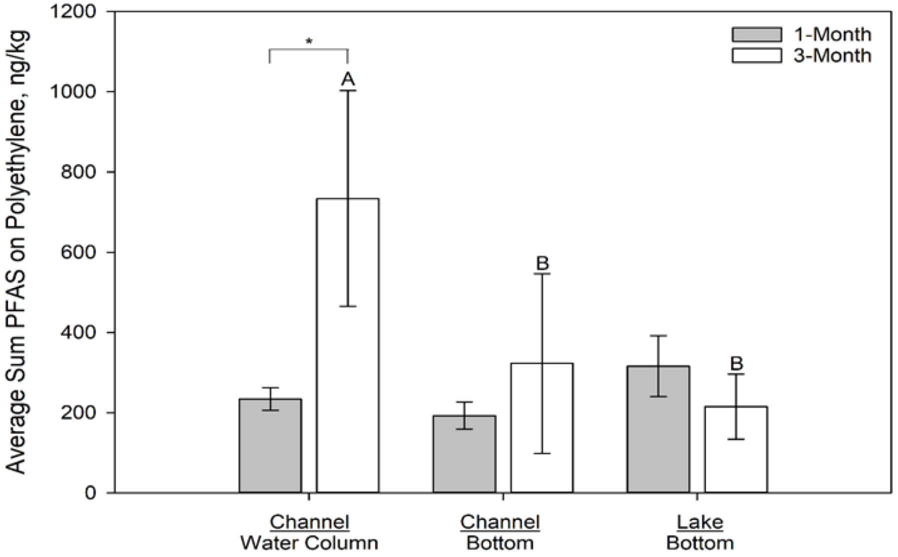
- Bacteria accidentally attach to the surface and secrete glue-like extracellular substances
- NJIT researchers found certain bacteria elevated antibiotic resistance by up to 30 times while living on microplastic biofilms in activated sludge

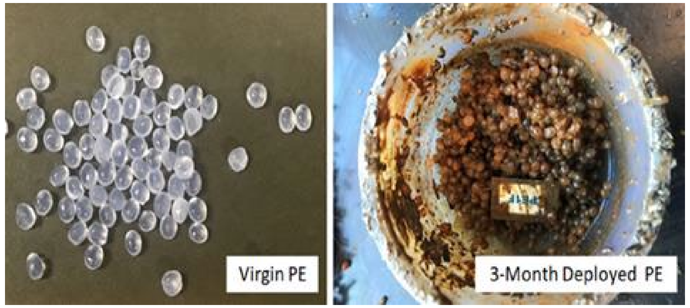
Muskegon Lake, MI Case Study

3 types of MPs tested : polyethylene (LDPE), polypropylene and polyester

- Greater adsorption in field samples than those treated in the laboratory
- Short exposure time and large particle sizes of MPs (2-4mm) of this study representing conservative estimate for MP adsorption of PFAS
- Identified factors for PFAS sorption on MPs: surface areas of MPs, inorganic and organic matters and biofilms
- Adsorption on material type: PE>PP>PET







(Scott et al 2021)

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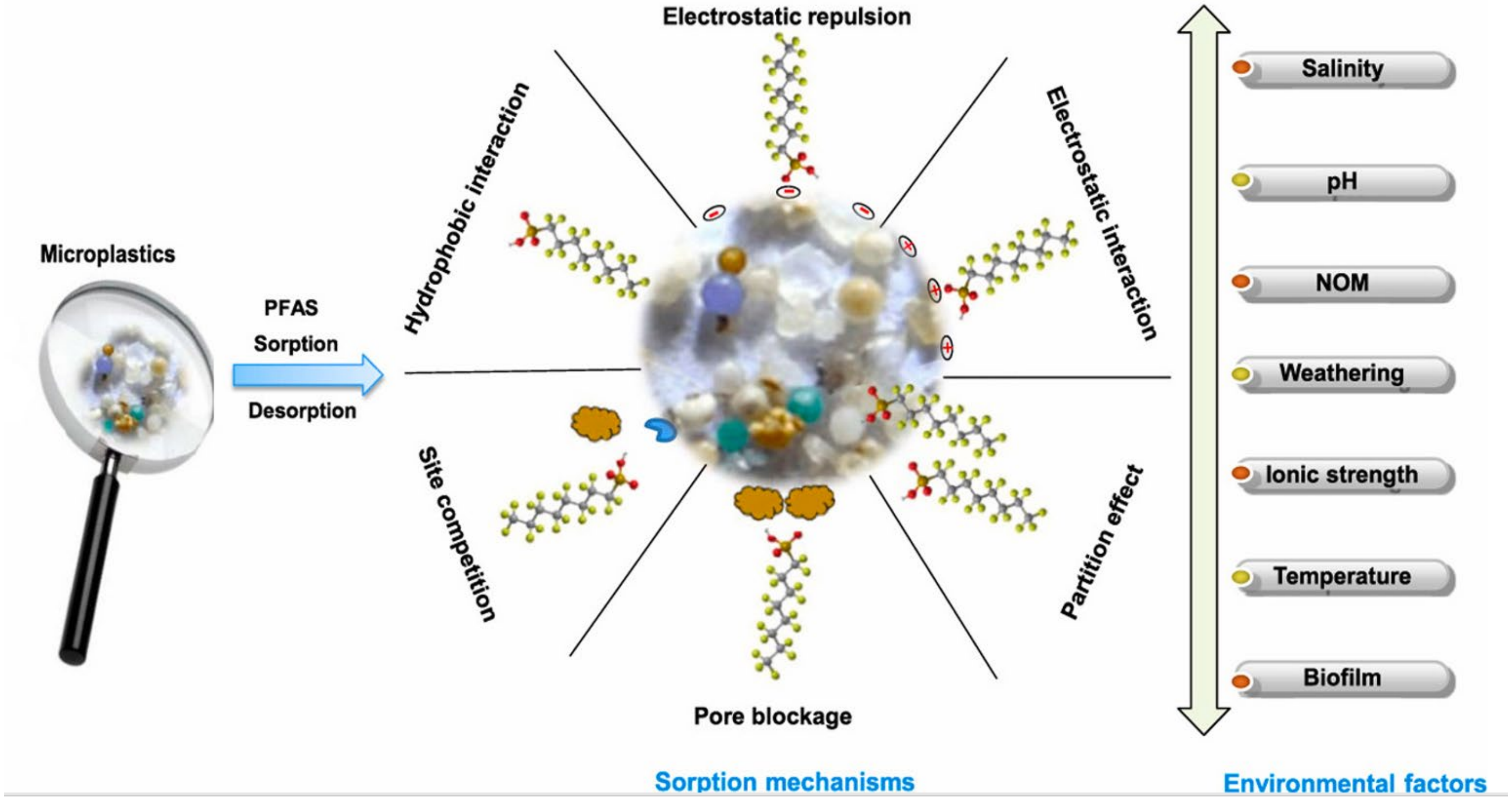
Review of PFAS and MPs Interactions



Barhoumi et al 2021

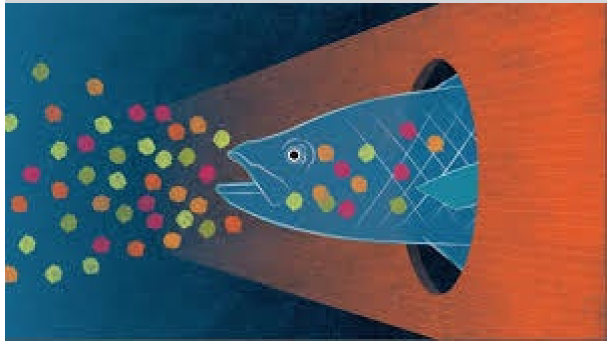
MP Risk Control and Reduction

Downstream- Exposure Point Protection

Monitoring regulatory framework at local, national and international levels

Assessing potential exposure points

- Drinking water
- Food
- Coastal areas/surface water



Upstream- Point Source Mitigation

Facility source control

Pollution prevention

Mitigate MP discharges from the facility

- Storm water
- Wastewater
- Air emission

Regulatory Framework

- Microbead-Free Waters Act (2015)
- Trash-Free Waters under Clean Water Act, Superfund, RCRA
- Save Our Seas Act 2.0 (2020)
- State-level focus areas
  - Single Use plastics
  - Pre-production plastics
  - Other plastic products, waste handling, drinking water

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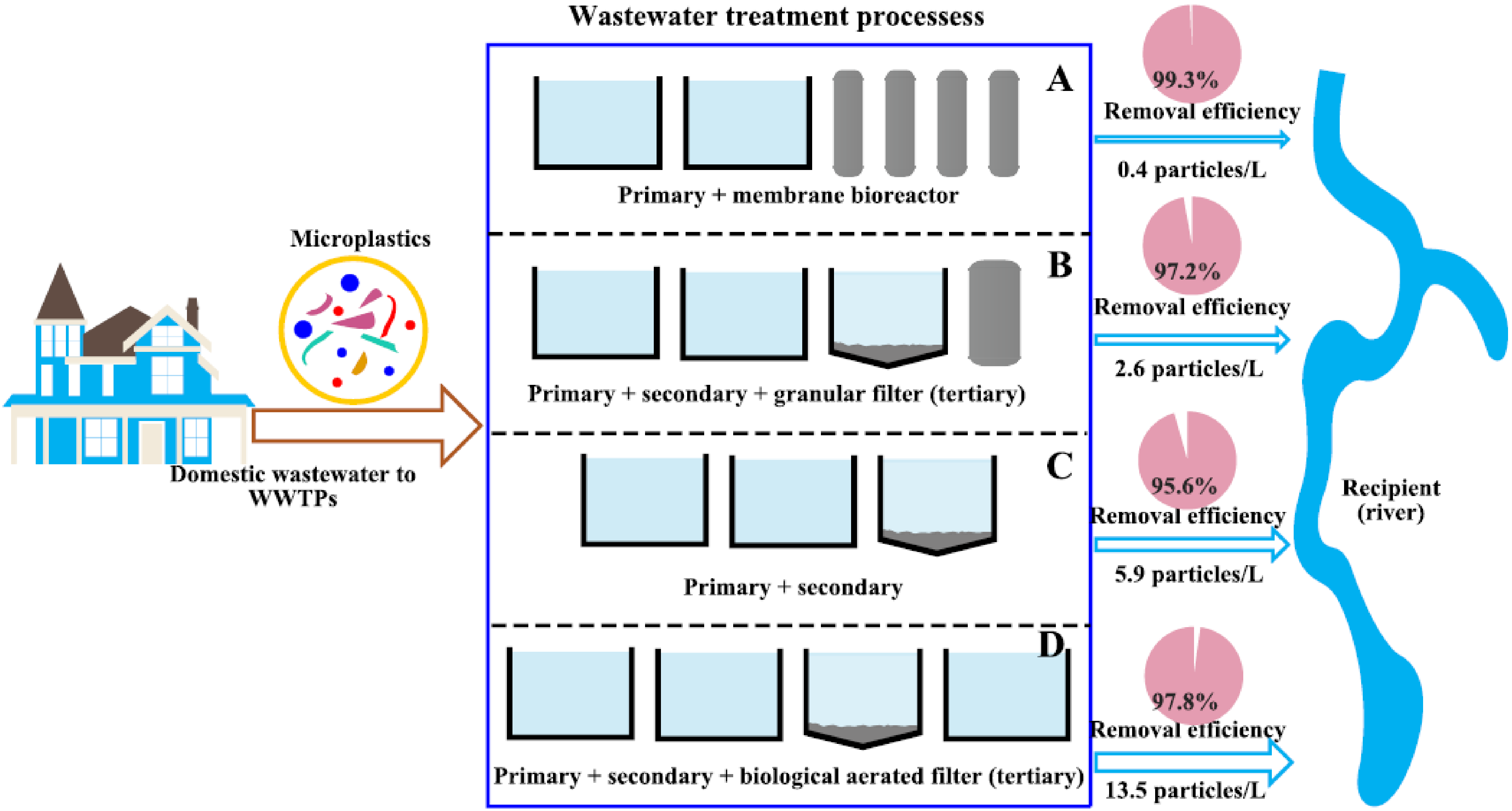
Most Evaluated - WWTP

WWTP efficiently remove 95%+ MPs, however:
- **MPs are still in effluent and discharged**
- **MPs also in sludge and biosolids**



(Shen et al, 2020)

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MP Removal Efficiency

Technology	MP removed	Removal measured	Source	Ref
Filtration	>90μm	Turbidity from 195 to<1	Synthetic wastewater	Li, 2018
MBR	>20-100μm	99.9%, regardless of shapes	WW effluent	Talvitie, 2017
MBR, AS		MBR-99.4% (eff=0.4±0.1 MP/L), AS-98.3% (1±0.4MP/L)	Municipal WW	Lares, 2018
Multiple		>90%, highest for fiber rayon and PET	11 WWTP	Ma 2019
Multiple	18 polymers (PET and PE dominant)	Aerated grit-71.67% Overall filtration and bio- 95.16%	Municipal sewage plants	Yang 2019
Coagulation	PE	Al^{3+} better than Fe^{3+} <0.5mm 61.19% with PAM addition; 18.34% for 2-5mm MP		Ariza-Tarazona 2019
Electrocoagulation	PE	>90%, 99.24% when pH=7.5 and NaCl @0-2 g/L and current density of 11A/m2	WW, lab study	Perren 2018
Biological	PE, PP, polystyrene, PET	Mostly >20% depending on microbial community, half-life: 363 and 431 days for polystyrene and PE, respectively	Lab study	Auta 2017

AS: activated sludge MBR: membrane bioreactor PAM: polyacrylamide

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Summary

- PFAS and MPs are both prevalent and persistent in natural waters, these two groups of emerging contaminants may act synergistically in food webs to cause adverse effects in fish and wildlife, as well as humans
- PFAS in plastics and on the MPs
  - Depending on manufacturing processes (e.g., HDPE and FTPs), PFAS can be associated with plastics
  - MPs can adsorb and concentrate PFAS. The factors on controlling sorption are discussed but data driven findings are limited
- Knowledge gaps exist in assessment, perception and communication of exposure vs. risk for both PFAS and MPs
- Near-shore coastal areas (waters and sediments) appear to be more at risk from particle effects than other areas
- The importance of PFAS migration pathways through interactions with MPs is very limited
- We don’t know how much we don’t know

Thank You

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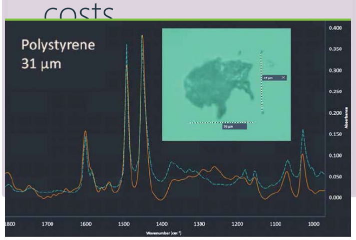
Monitoring and Analysis

Identification

Confirmation

Microscopy	FTIR/Raman	LDIR	Pyrolysis GC-MS
• Microscopy – 50um • SEM – 10 µm • Microscopy with staining – 3 µm? • Is it a plastic? Differentiating still a challenge • Microscopy with staining potential for first pass screening method	• Characterize plastics by type and provenance • FTIR (20 µm) and Raman spectroscopy (1µm) methods available • ASTM/SCCWRP methods in progress • Will likely be more of a research support tool • Extremely time consuming	• Relatively new technique using laser direct infrared chemical imaging (LDIR) • Characterize and counts particles down to 10 µm • Much faster than FTIR/Raman • High instrument costs	• Scalable method to report total plastic by plastic type • Not limited by size • Does not count, but measures mass of plastic by GC-MS • Maybe more amenable to regulation due to ease of use? • Specialized techniques needed to lower reporting limits



SCCWRP: Southern California Coastal Water Research Project
FTIR: Fourier-transform infrared spectroscopy

Information provided by SGS

Sampling – D8332-20 ASTM

- ASTM, California through Water Board and SCCWRP have methods done/in review
- Water/Wastewater – ASTM D8332–20
- Sediments – In progress
- Tissue – NOAA/other agencies
- ITRC in process of writing sampling guidance

Preparation - ASTM D8333-20

- California, other groups evaluating methods
- Need to remove non-plastic interferences from sample
- Uses wet peroxide or enzymatic digestion

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