Tracking microplastics to their source: analytical techniques for characterizing weathered polymers

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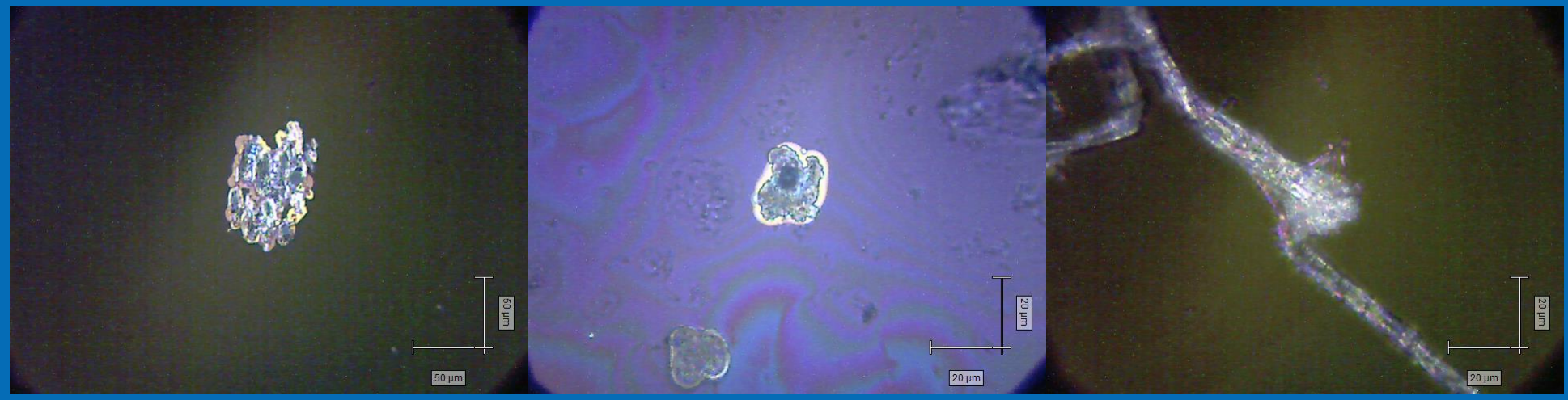

Office of Research and Development
National Risk Management Research Laboratory, Land & Materials Management Division

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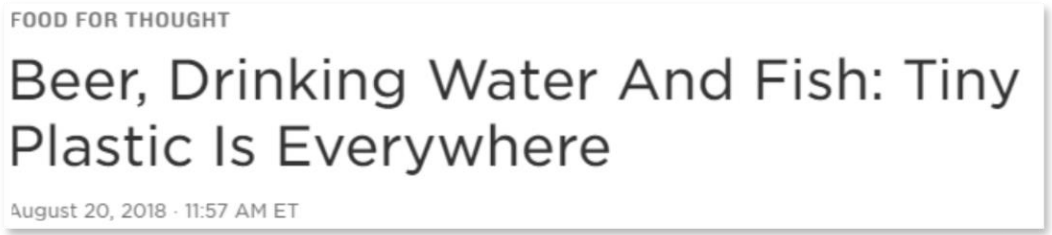
What are microplastics?

- Plastic particles of various shapes (fragments, fibers, films) that are < 5 mm (largest crosswise dimension)
- Can be manufactured (primary) or result from breakdown of larger products (secondary)
- Currently, includes subcategory as nanoplastics

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.


ENVIRONMENT 08/18/2019 10:26 am ET

Scientists Astonished After Finding Microplastics In Arctic Snow

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

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Ecotoxicity and human health impacts

- Bioaccumulation affecting plants and small animals
- Respiratory effects
- Vectors for persistent organic pollutants (POPs) and plastic-associated chemicals (PACs)

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Current analytical methods

- Separation from sample matrix
  - sieving, density separation, digestion of organic material
- Identification/characterization
  - Most common: µ-FTIR, µ-Raman
  - Less common: TGA-GC/MS, hyperspectral imaging

Most of these techniques can only be used on microplastics > 10 microns, need new methods for nanoplastics

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Nanoplastics

- Increased transport
- Increased risk of biological uptake
- Increased difficulty of removal

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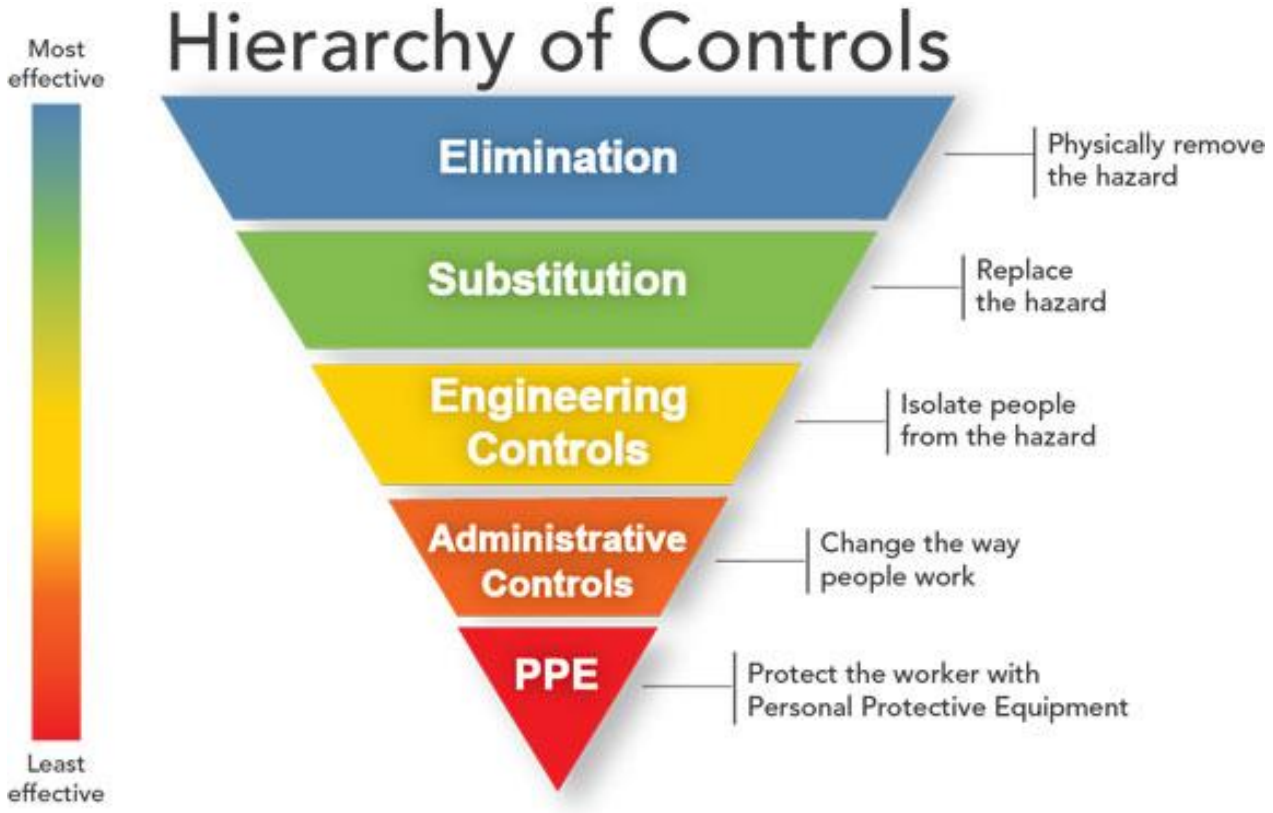
Nanoplastics

- Definition?
  - Most commonly 1-100 nm but this leaves large fraction (100 nm - 10 um) that are not classified as nanoplastics and also outside capabilities of microplastic analysis techniques
- Separation?
  - Most separation/purification techniques utilizing density separation and oxidation have not been tested on nanoplastics, may require adjustments such as longer settling time or less harsh oxidation methods
- Detection?
  - Will require concentration or aggregation prior to spectroscopic analysis, followed by deconvolution of spectra to determine polymer type distribution

Plastic waste – hazard control



- Elimination – stop using plastic
  - Not feasible in short term
- Substitution – use different polymers
  - Need to identify primary polymer targets for substitution

1. Geographical source – where are most MPs originating?

2. Polymer source – which polymer types are contributing the most MPs?

Source: https://www.cdc.gov/niosh/topics/hierarchy/default.html

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Project objective

- Utilize isotope-ratio mass spectrometry (IRMS) to identify differences in carbon isotope ratio of polymers due to geographical manufacturing origin and environmental exposures

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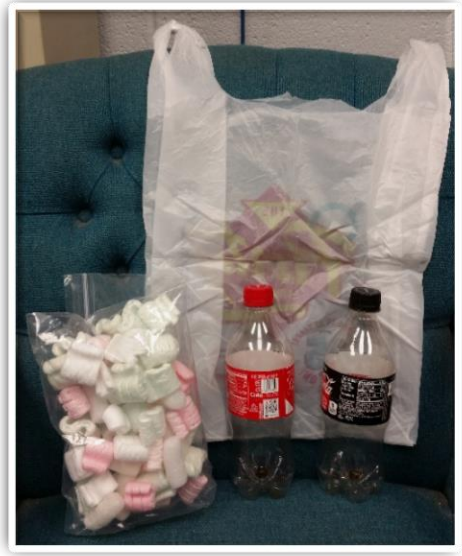
Sample collection

Polymer Type	Sample Name	Sample Type
Polyethylene Terephthalate	Polyester Scarf	Clothing
	Water Bottle	Food Container
	Blue Food Packaging	Food Container
	Clear Bottle	Food Container
	Clear Green Bottle	Food Container
	Clear Food Packaging (Recycled)	Food Container
High-Density Polyethylene	HDPE Pellet	Plastic Resin
	HDPE White Bottle	Food Container
Polyvinyl Chloride	PVC Powder	Plastic Powder
Low-Density Polyethylene	Store #1 Plastic Bag	Shopping Bag
	Store #2 Plastic Bag	Shopping Bag
	Store #3 Plastic Bag	Shopping Bag
	Store #4 Plastic Bag	Shopping Bag
	Store #5 Plastic Bag	Shopping Bag
	LDPE Pellet	Plastic Resin
	Disposable food baggie	Consumer Product

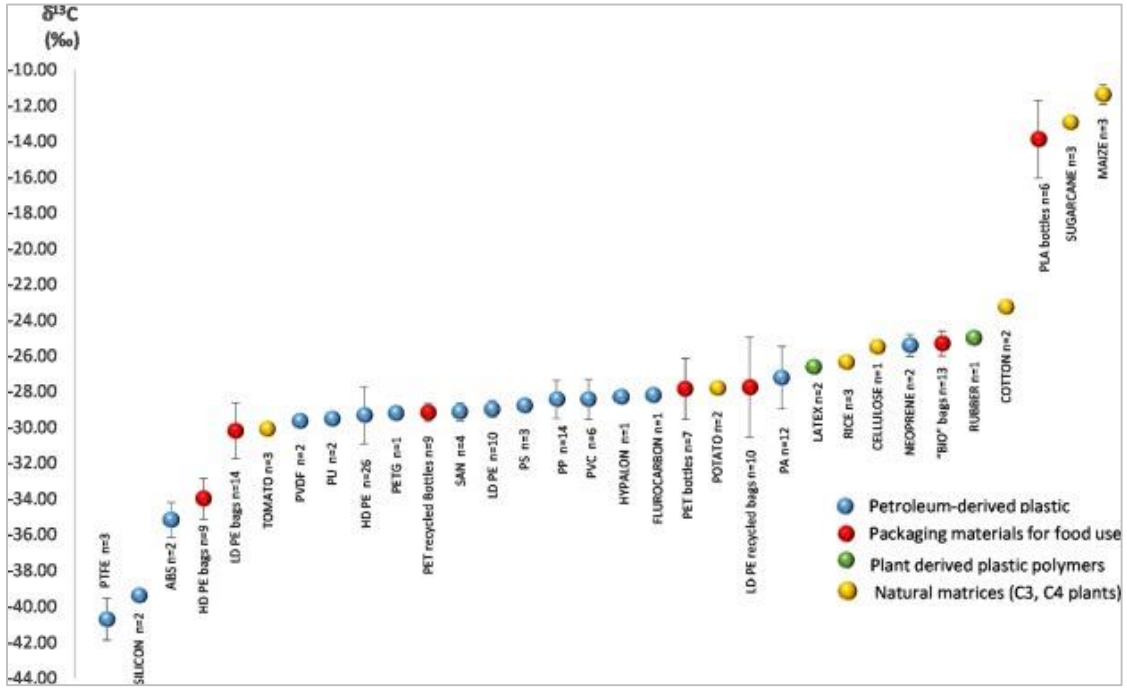
Polymer Type	Sample Name	Sample Type
Polypropylene	PP Pellet	Plastic Resin
	Black Food packaging	Food Container
	Opaque Food packaging	Food Container
	Reusable plastic cup	Food Container
	Yogurt Container	Food Container
	Yogurt Container Lid	Food Container
	Soup Container	Food Container
Polystyrene	PS Pellets	Plastic Resin
	PS Pellets	Plastic Resin
	Clear food packaging	Food Container
	Calibration Film	Plastic Standard
	Expanded polystyrene foam	Polymer Foam
Additional Polymer types	Polylactic Acid (PLA) Pellets	Plastic Resin
	Acrylonitrile Butadiene Styrene (ABS) pellets	Plastic Resin
	Polyurethane foam	Polymer Foam
	Nylon 6	Plastic Resin
	Dryer Lint (containing various polymer fibers)	Fiber

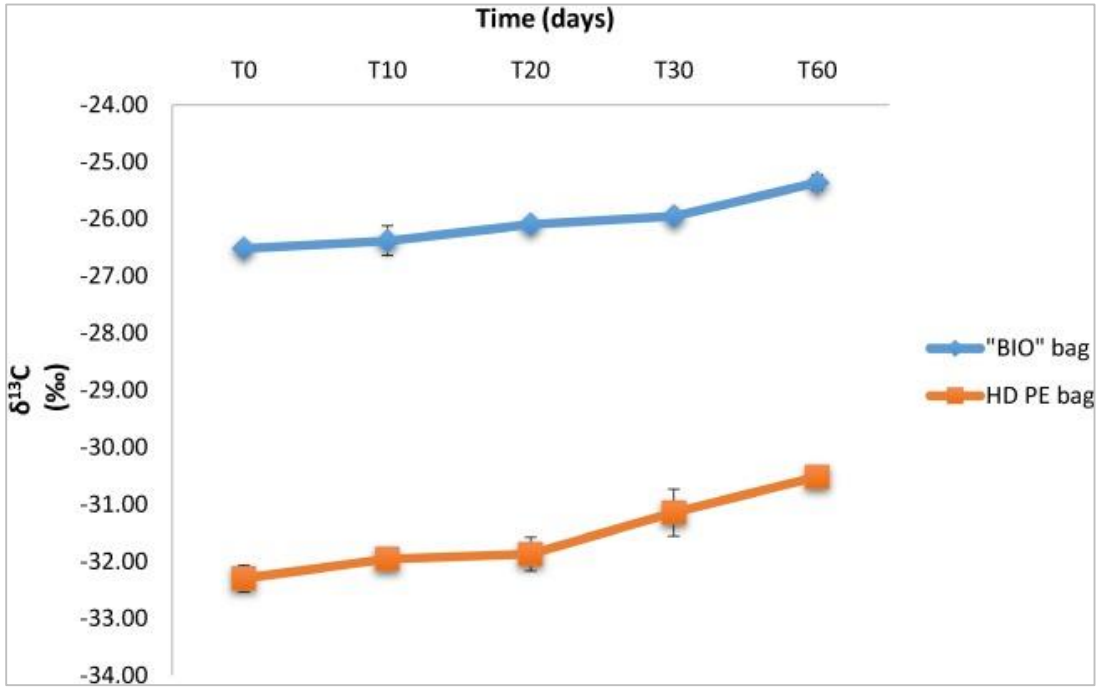


Isotope-ratio mass spectrometry (IRMS)

- NC 2500 Elemental Analyzer (CE Instruments Ltd.) interfaced to a DELTAplus IRMS (Thermo)
- Analysis procedure
  - Sample weighed and placed in tin capsule
  - Capsule is dropped from autosampler into furnace and flash combusted at 1000˚C
  - Carbon converted to CO_2
  - CO2 passes through H2O trap and enters gas chromatography column
  - $^{13}C/^{12}C$ elute at different retention times and are quantified
- Complimentary technique to FTIR & Raman
  - does not give definitive identification of polymer
- Limitations specific to microplastics
  - destructive – must complete all other analysis first!
  - requires 100 µg minimum – only possible for larger microplastics (>1 mm)

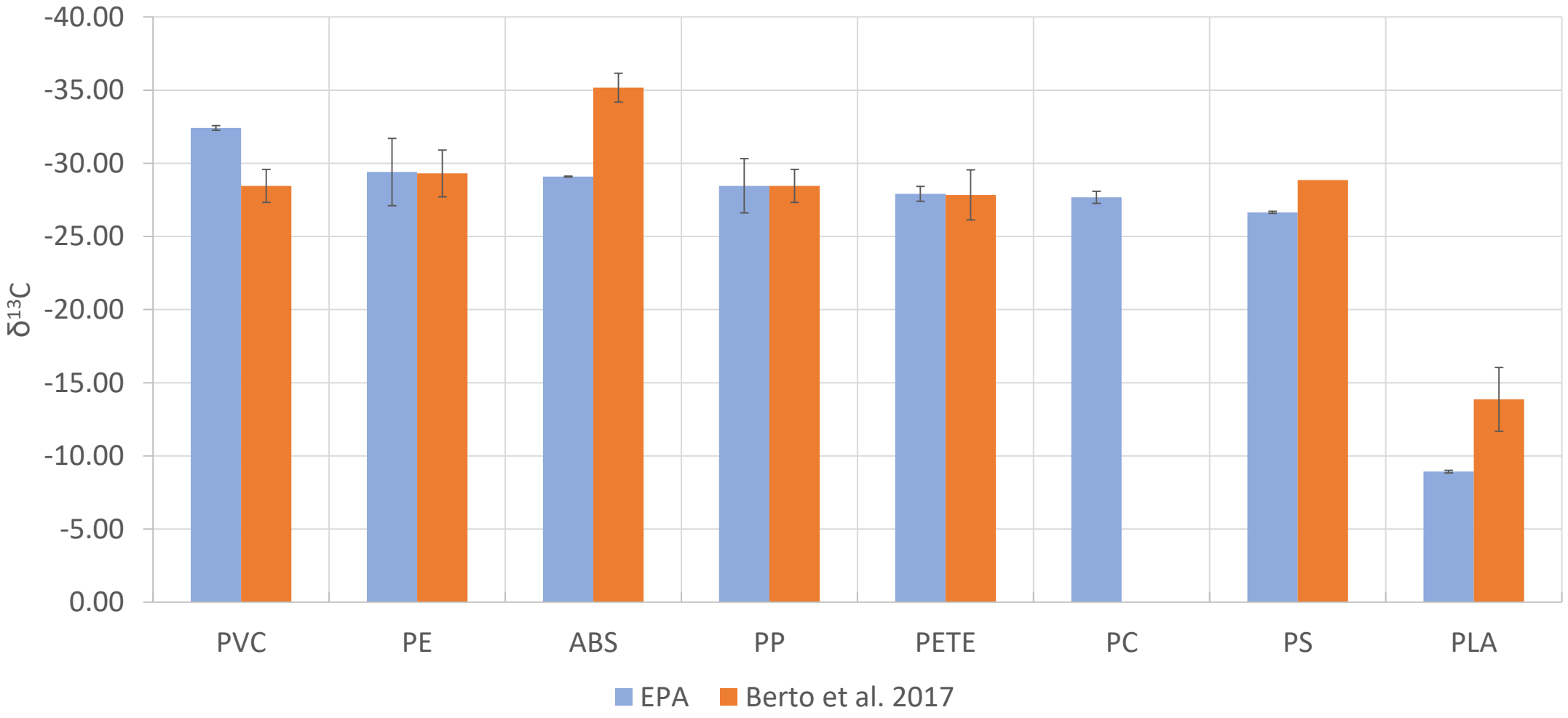
IRMS of various polymers



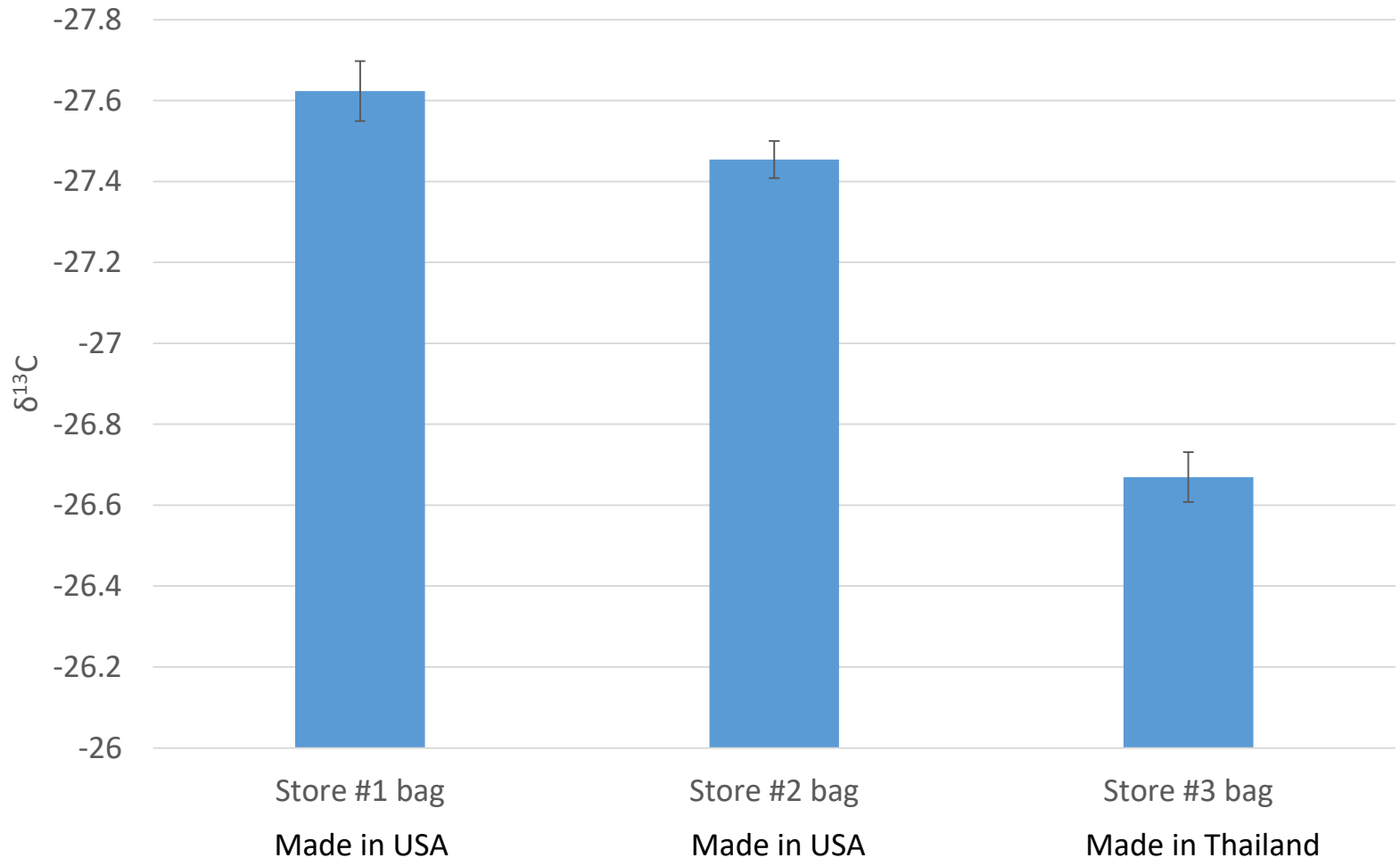


Berto et al. 2017

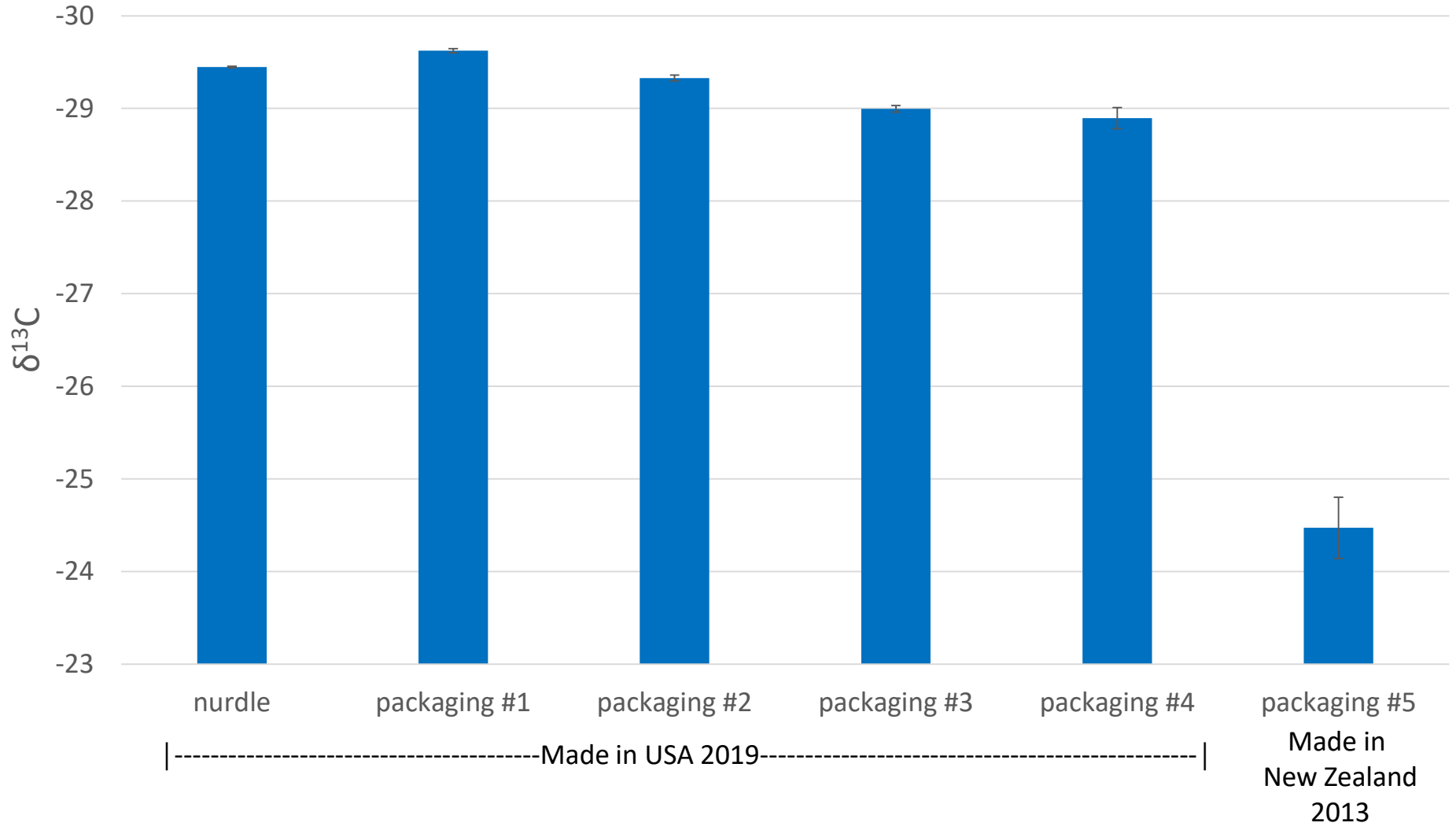
IRMS of various polymers (cont.)



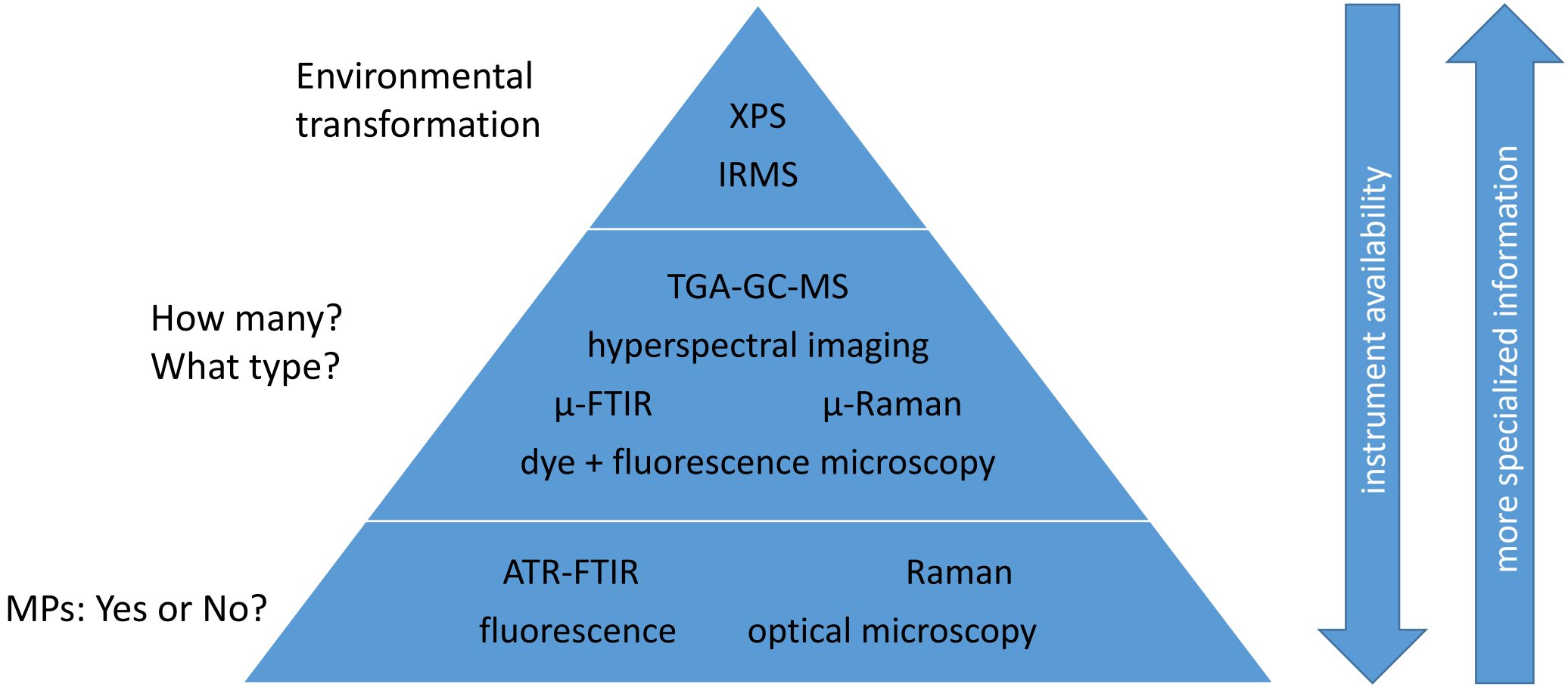
IRMS values – geographical origin



IRMS values – geographical origin/age



Hierarchy of MP analytical techniques



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Conclusions & Future Work

- IRMS shows potential as a tool for determining geographical origin of plastic waste
  - More work needed to differentiate aged/weathered samples
  - More samples needed from around the globe (send us plastic!)
- Nanoplastics possibly pose a greater risk than MPs due to increased number, mobility, and reactivity; there is a critical need for:
  - Standardization of nanoplastic definition
  - New methods for extraction of nanoplastics from environmental media
  - Investigating nanoplastic properties (formation, adsorption, aggregation)

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