United States Environmental Protection Agency

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Preliminary assessment of IRMS and FTIR for characterization of microplastics

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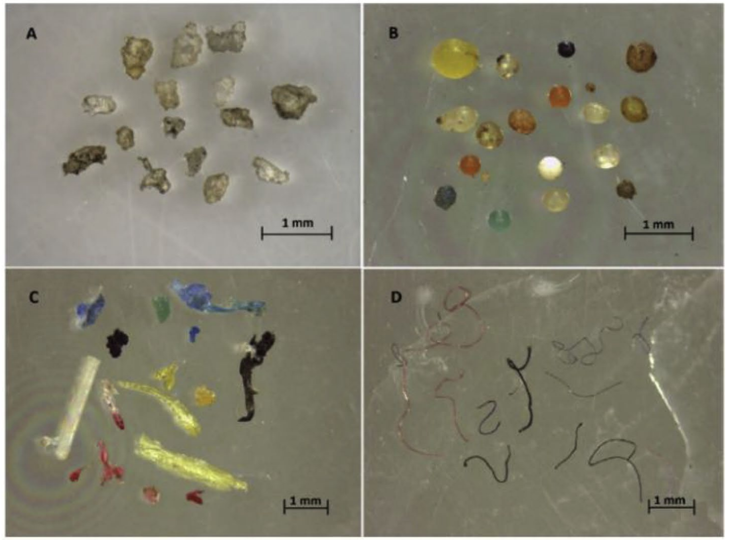
What are microplastics?

- Microplastics (MPs) are small plastic particles: fibers, fragments, films, and pellets.
- < 5 mm across (largest crosswise dimension).
- Two categories:
  - *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.

A



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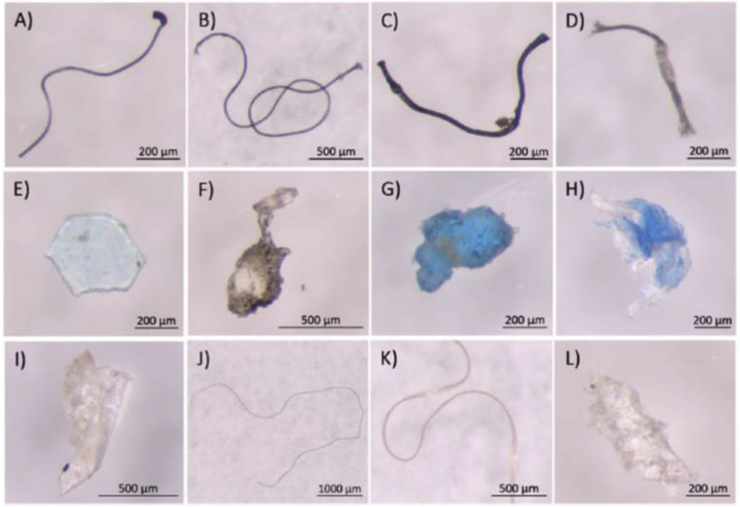
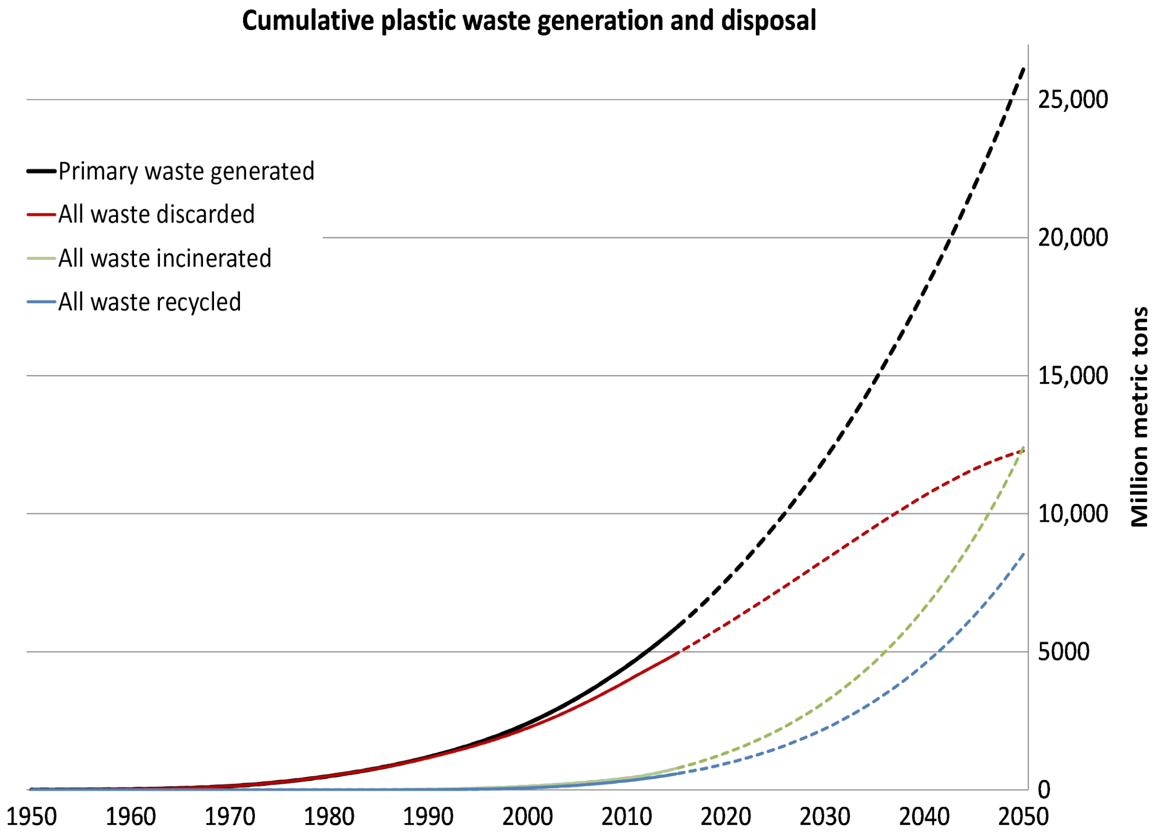


Source: Sun et al (2019)

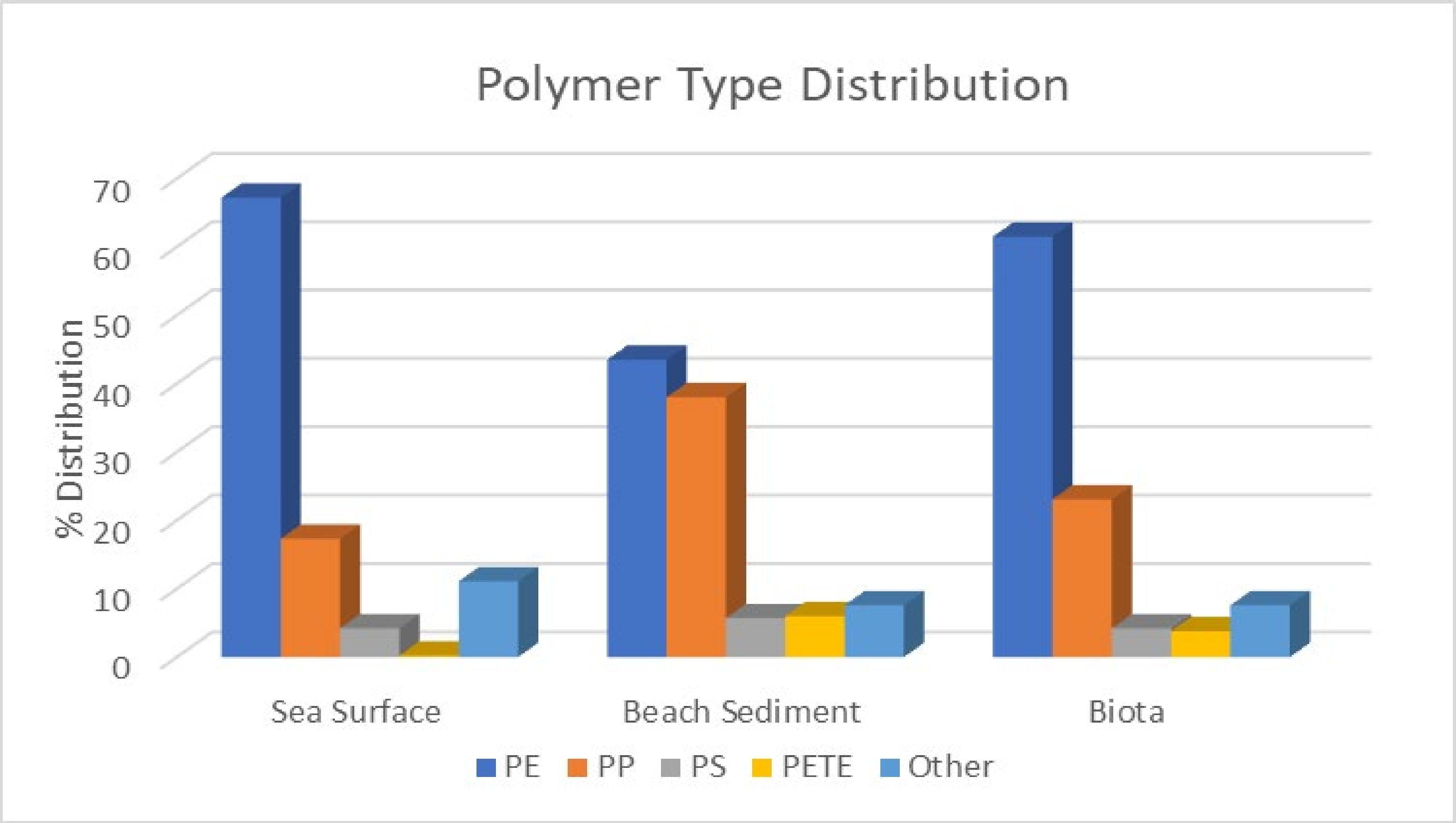
Why to study MPs?

- Plastic pollution is persistent, pervasive, and growing.
- MPs are *everywhere*: Arctic, Antarctic, deep sea, ice cores, remote islands. Can disrupt marine ecosystems globally.
- Freshwaters are recognized sources, especially in urban areas, but not well studied (98% of studies were performed on marine environments).
- WWTPs can release large numbers of MPs (and nanoplastics [NPs]) due to high discharge volumes. Even with high (e.g., up to 99%) removal rates.
- Environmental and health impacts need further study.



Source: Cumulative plastic waste generation and disposal, Geyer (2017)

What makes up MPs?



Source: Digka et al (2018)

Environmental Impact?

- What impacts do MPs (and NPs) have on different species (aquatic, terrestrial)?
- Do they bioaccumulate and amplify up the food chain?
- Does particle uptake of chemicals/pathogens enhance toxicity?
- Do MPs act as vectors for transport and ingestion of associated toxins by many species?
- Lack of standardized monitoring methods has slowed progress in understanding impacts of MPs in the environment.

- Plastic from stomach of a seabird.

Source: Franeker (2019)

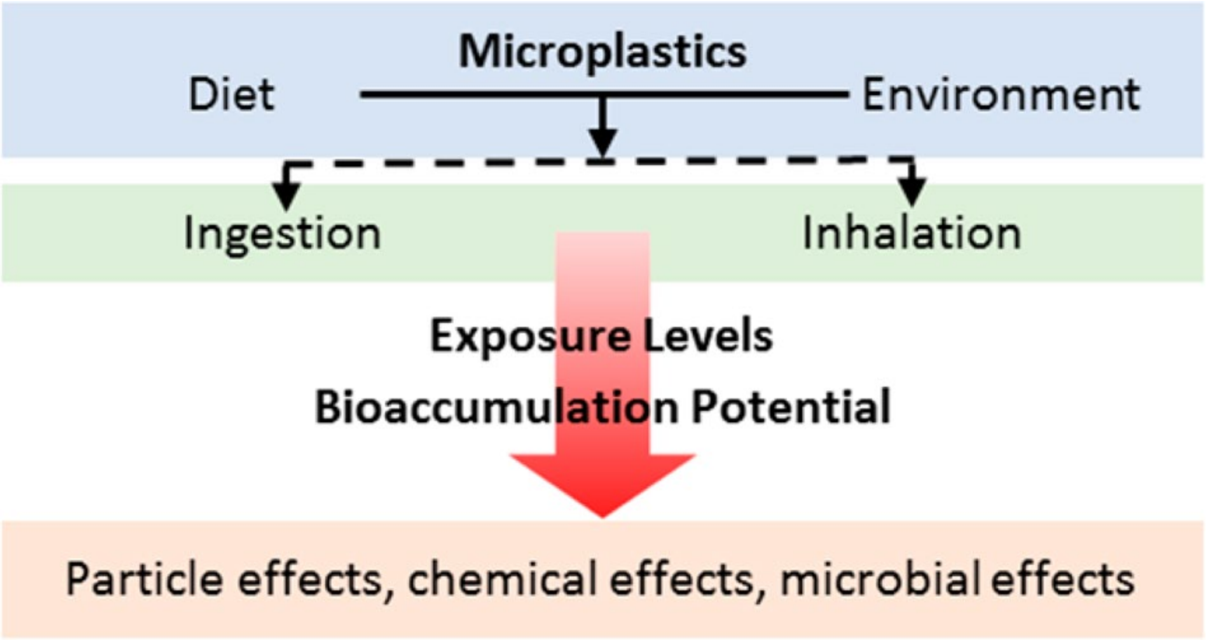
Human health impact?

MPs found in:

- Air
- Tap and bottled water
- Beer
- Seafood
- Honey
- Salt

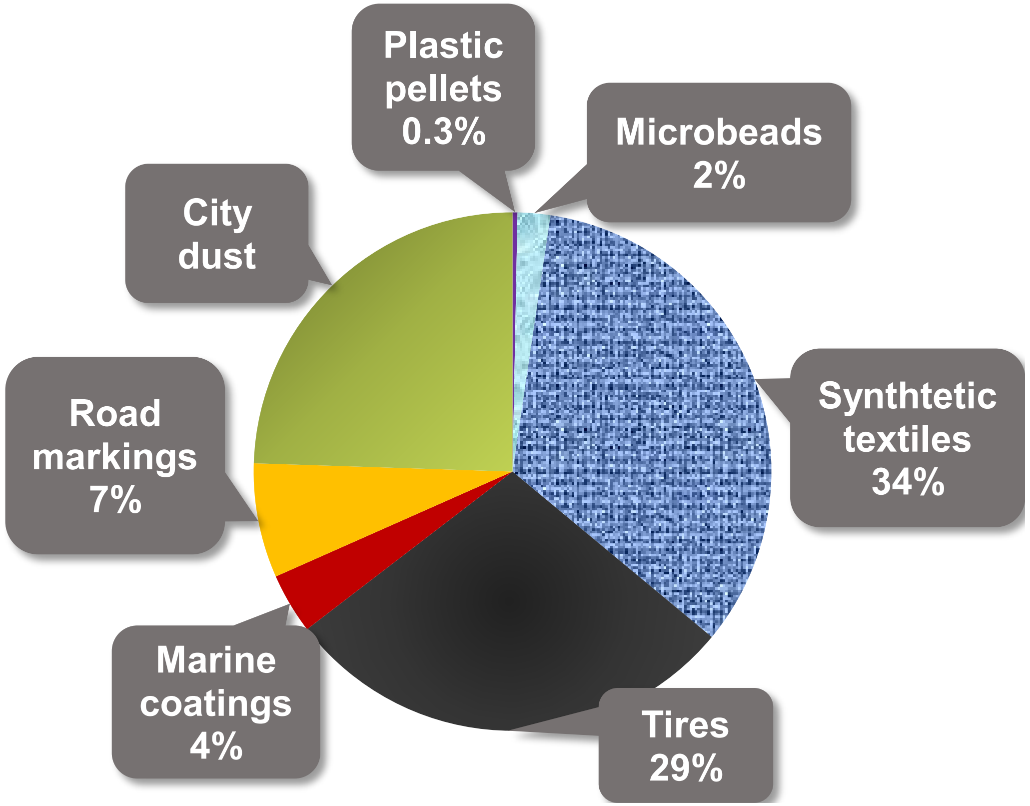
Health impacts unknown but could result in:

- Bioaccumulation
- Chemical exposure
- Immune response
- Respiratory effects



Source: Wright and Kelly (2017)

MP sources: direct release to oceans



Source: International Union for Conservation of Nature and Natural Resources (IUCN) .

Microfibers from synthetic textiles may pose a much greater problem than originally thought (IUCN, 2017):

- Of the total plastics (2.7- 4.8 Mtons) released to oceans annually, 5% - 31% could originate *directly* as MPs from homes and industrial products (3.2 Mtons/year). About 48% ends up in oceans.
- Nearly two-thirds of total MPs released attributed to washing synthetic textiles (35%) and tire wear (29%). Microbeads represented just 2%.
- MP releases to oceans by Europe and Central Asia alone equivalent to adding 54 plastic bags per person year.

Project Objectives

Overall objective: identify and characterize the types and sources of MPs in an urban watershed.

Specific aims:

- To analyze bulk polymers (e.g., standards, pellets, packaging, field samples to generate $\delta^{13}C$ isotope signature and spectral libraries).
- To characterize polymers using FTIR, micro-Raman, and IRMS.

Methods: IRMS, FTIR, Raman

- Polymers characterized by stable carbon ***isotope ratio mass spectrometry*** (IRMS) and Fourier transform infrared (FTIR) spectroscopy. Raman spectra also collected.
- IRMS has been applied to studies on origins of organic matter in the environment. Shows promise for tracking fate, transport, and transformations of MPs[4].
- Advantages of IRMS:
  - High sensitivity.
  - Small sample amount.
  - Fast, automated, low-cost.
  - No limitations with black/dark samples (unlike spectroscopy).
- Disadvantages relative to spectroscopic techniques:
  - IRMS is not a confirmatory technique and is destructive.

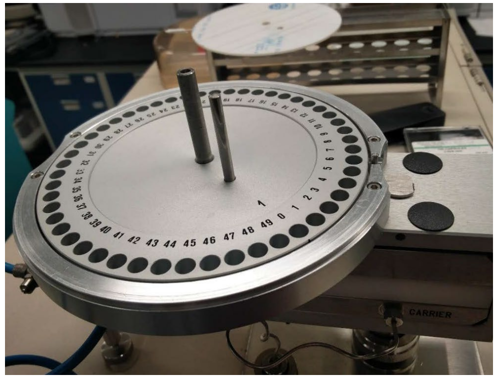
[4]*Berto et al. 2017*

IRMS

- Stable carbon isotopic ratios ($^{13}C/^{12}C$) expressed, by convention, relative to the ratio of a standard, as $\delta^{13}C$ values (‰):

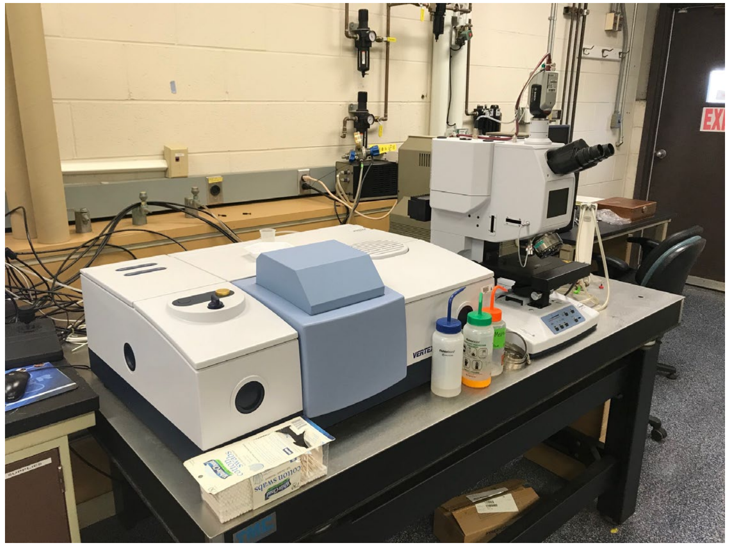
$$\delta^{13}C\ (‰) = \left[\frac{^{13}C/12C_{sample}}{^{13}C/12C_{VPDB}} - 1\right] \times 1000$$

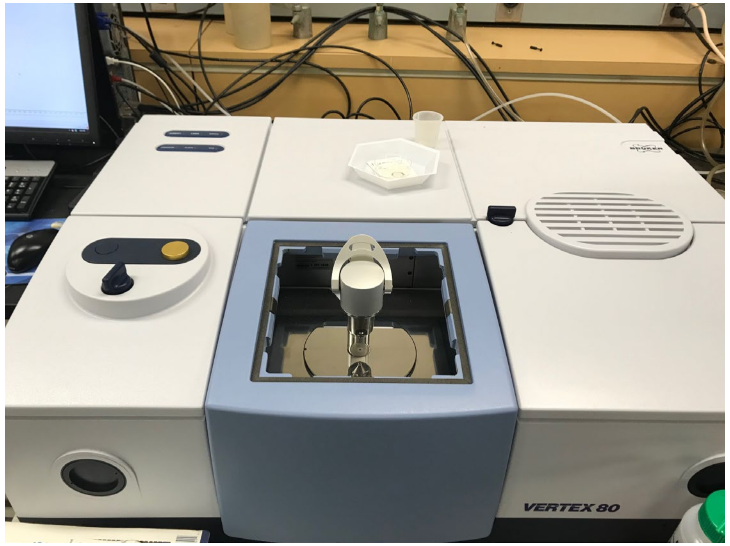
- Small amount (from 100 to 250 µg) of sample weighed and analyzed.
- CE Instruments NC 2500 Elemental Analyzer fitted with Thermo Conflo III device. Stable Isotope Mass-Spectrometer – Thermo Finnigan, DeltaPlus with Conflo III device.



FTIR

- Desktop FTIR: Bruker Vertex 80
- Advantages:
  – Relatively quick process that produces qualitative and quantitative data.
  – Nondestructive procedure.
  – No Sample preparation.
- Disadvantages:
  – Sensitive to water.





Raman

- Model: Renishaw InVia Raman microscope.
- Advantages:
  - Relatively quick process that produces qualitative and quantitative data.
  - Nondestructive procedure.
  - No sample preparation.
  - No interference with water.
- Disadvantages:
  - Impurities within sample (e.g., colorants) can hide spectrum of polymer of interest.

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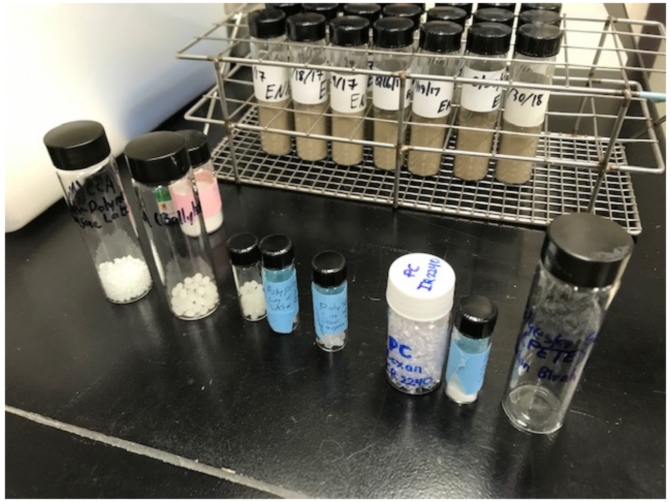
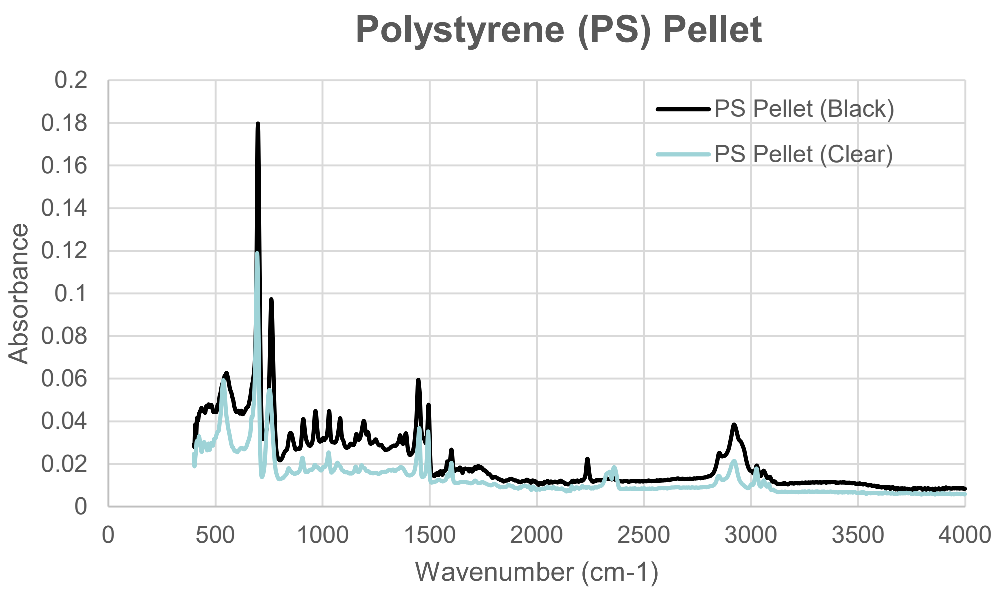
Studied Polymers

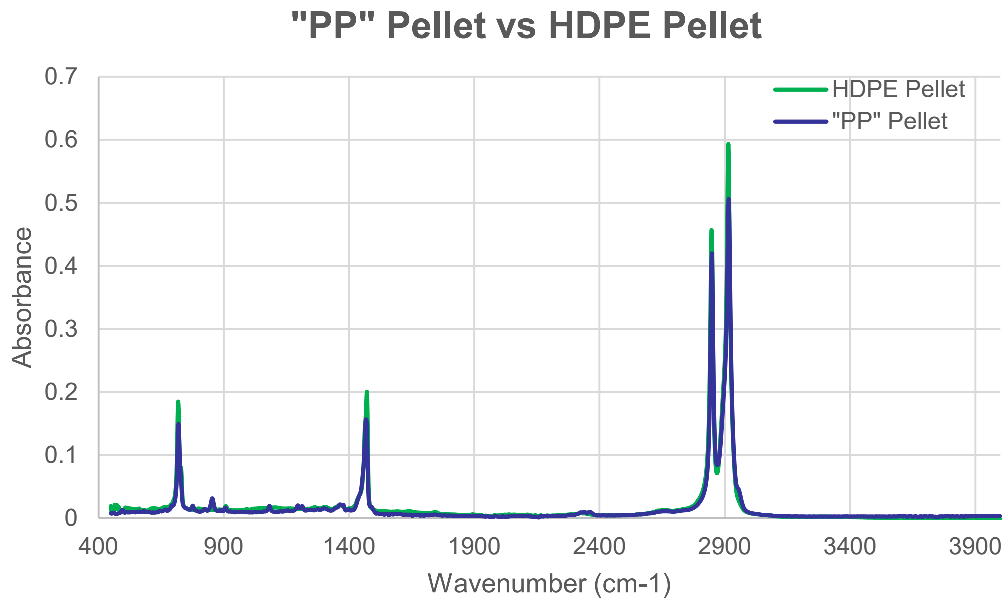
Polymer Type	Sample Name	Sample Type
Polyethylene Terephthalate	Polyester Scarf	Clothing
	Ice Mountain Bottle	Food Container
	Blue Food Packaging	Food Container
	Clear Bottle	Food Container
	Clear Green Bottle	Food Container
	Clear Food Packaging (Recycled)	Food Container
High-Density Polyethylene	HDPE Pellet (UC)	Plastic Resin
	HDPE White Bottle	Food Container
Polyvinyl Chloride	PVC Powder (AWBERC)	Plastic Powder
Low-Density Polyethylene	Target Plastic Bag	Shopping Bag
	UDF Plastic Bag	Shopping Bag
	Walmart Plastic Bag	Shopping Bag
	Kroger Plastic Bag	Shopping Bag
	CRG Plastic Bag	Shopping Bag
	"PP" Pellet (Ballyhoo)	Plastic Resin
	Ziplock Bag	Consumer Product

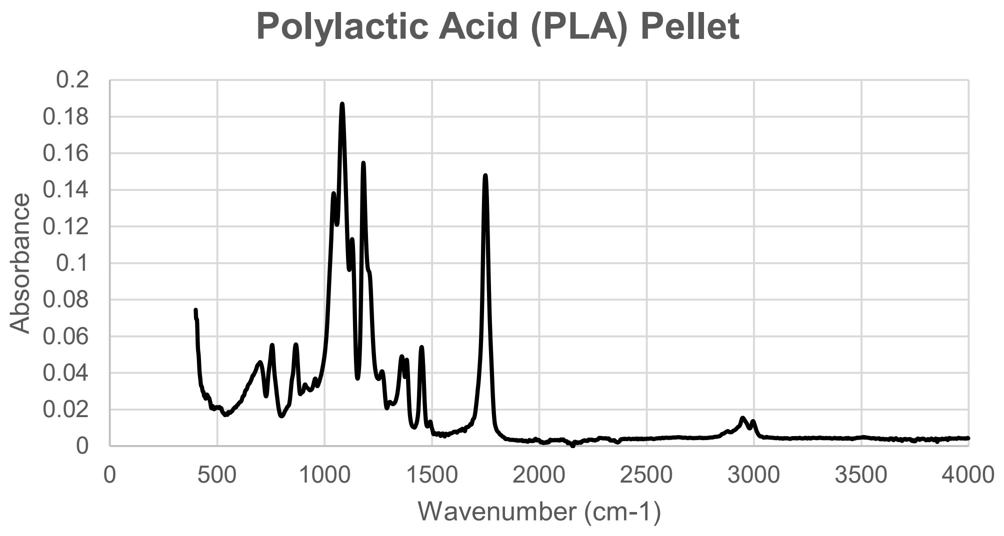
Polymer Type	Sample Name	Sample Type
Polypropylene	PP Pellet (AWBERC)	Plastic Resin
	Black Food packaging	Food Container
	Opaque Food packaging	Food Container
	Sistema Cup	Food Container
	Yogurt Container	Food Container
	Yogurt Lid Container	Food Container
	Soup Container	Food Container
Polystyrene	PS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

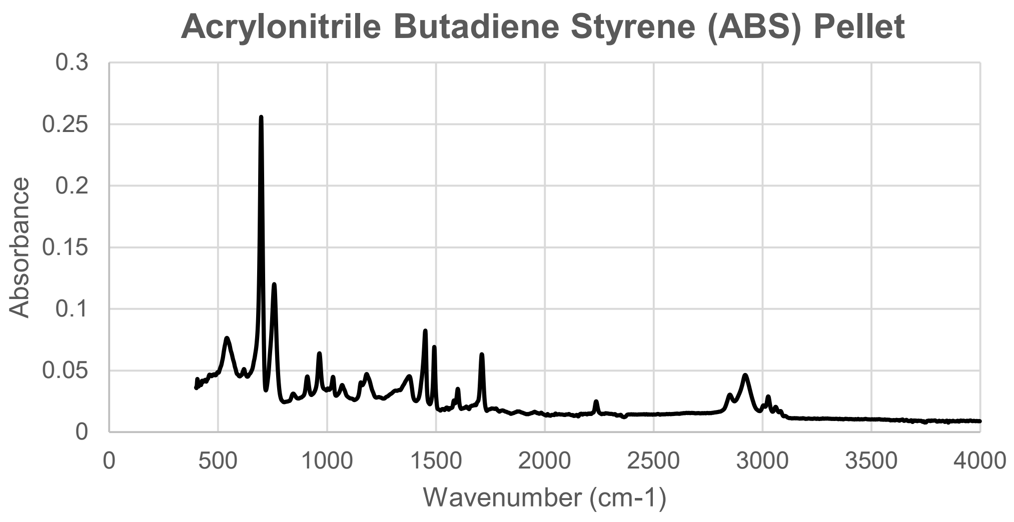


FTIR Data

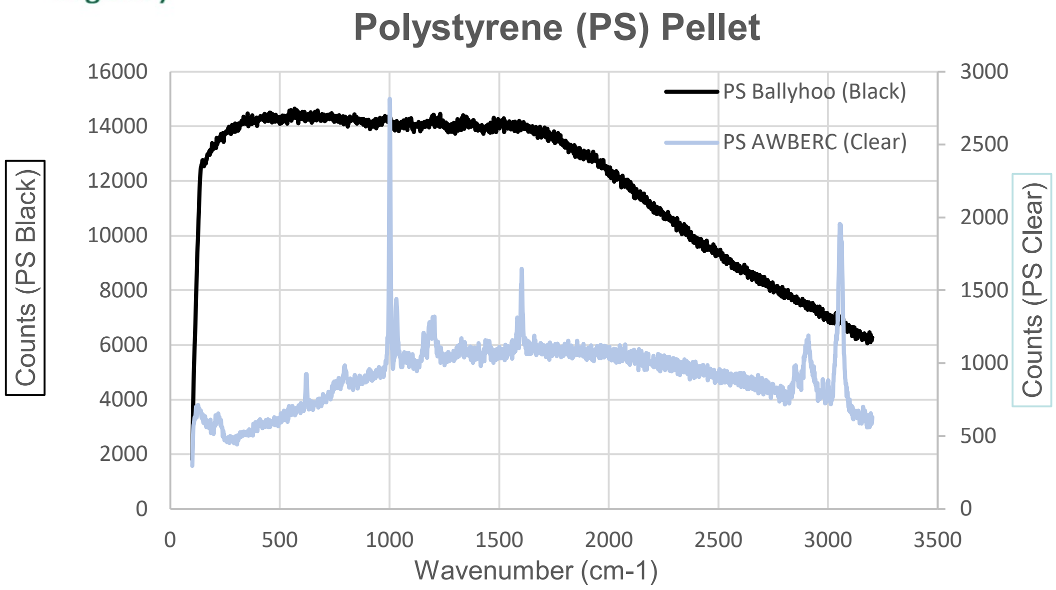

Polystyrene (PS) Pellet
PS Pellet (Black)
PS Pellet (Clear)
Absorbance
Wavenumber (cm-1)
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
500
1000
1500
2000
2500
3000
3500
4000


"PP" Pellet vs HDPE Pellet
HDPE Pellet
"PP" Pellet
Absorbance
Wavenumber (cm-1)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
900
1400
1900
2400
2900
3400
3900

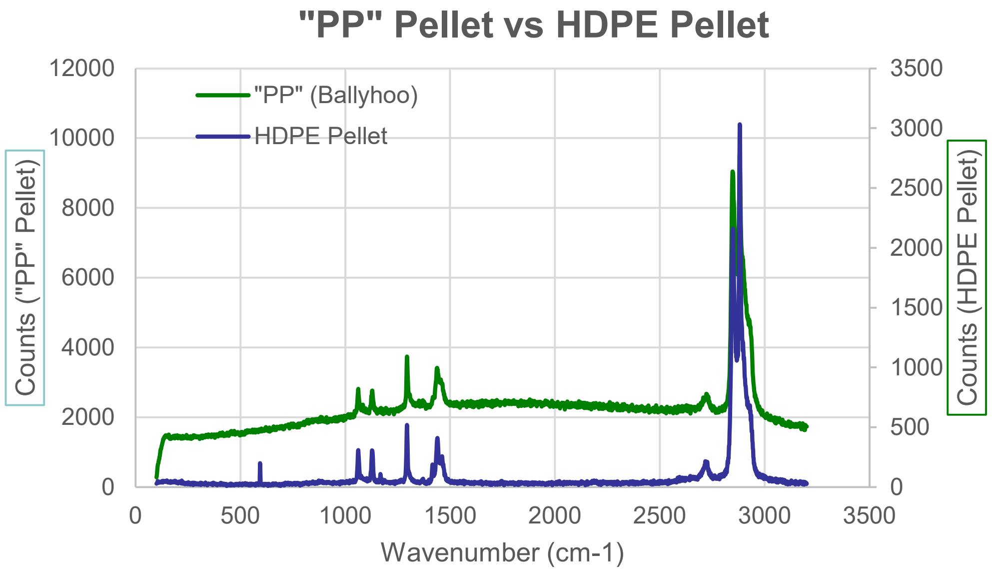

Polylactic Acid (PLA) Pellet
Absorbance
Wavenumber (cm-1)
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
500
1000
1500
2000
2500
3000
3500
4000


Acrylonitrile Butadiene Styrene (ABS) Pellet
Absorbance
Wavenumber (cm-1)
0.3
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
2000
2500
3000
3500
4000

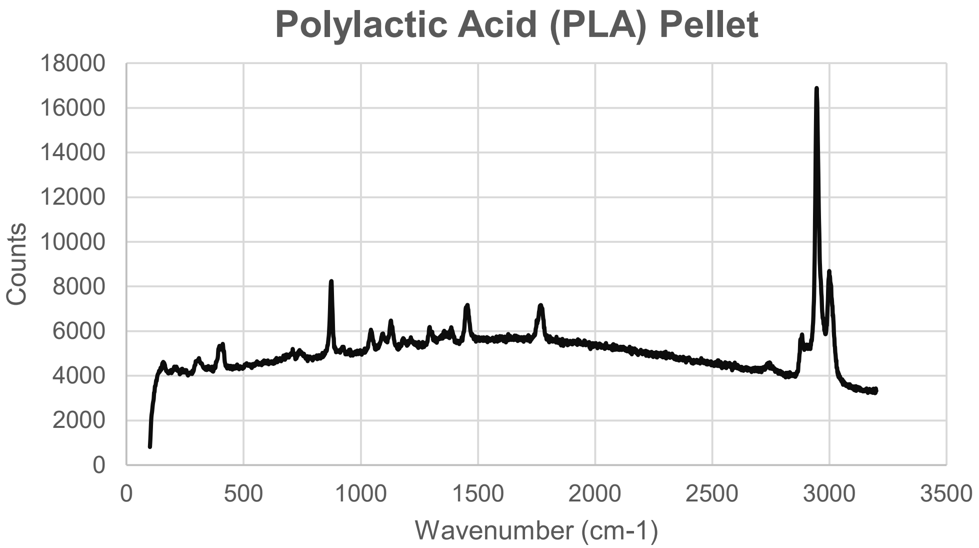
Raman Data



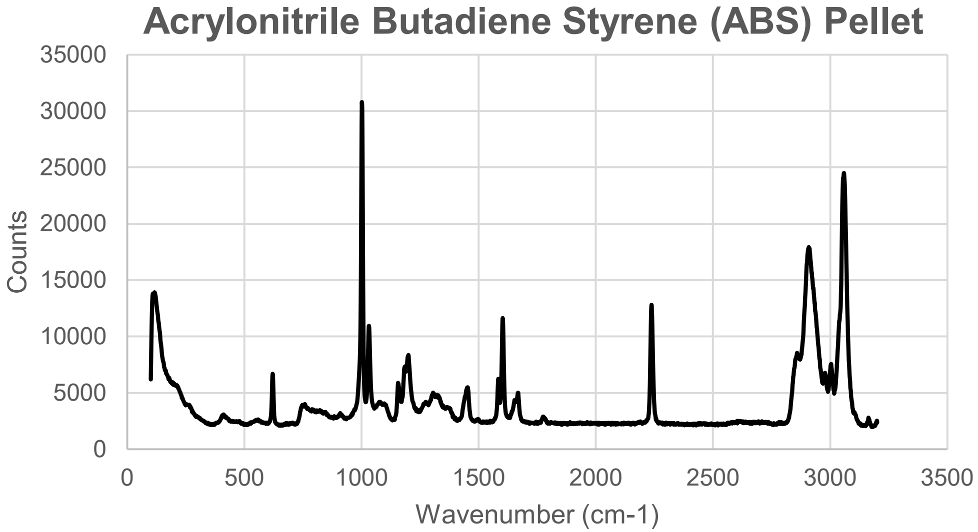
Polystyrene (PS) Pellet
PS Ballyhoo (Black)
PS AWBERC (Clear)
Counts (PS Black)
Counts (PS Clear)
Wavenumber (cm-1)



"PP" Pellet vs HDPE Pellet
"PP" (Ballyhoo)
HDPE Pellet
Counts ("PP" Pellet)
Counts (HDPE Pellet)
Wavenumber (cm-1)

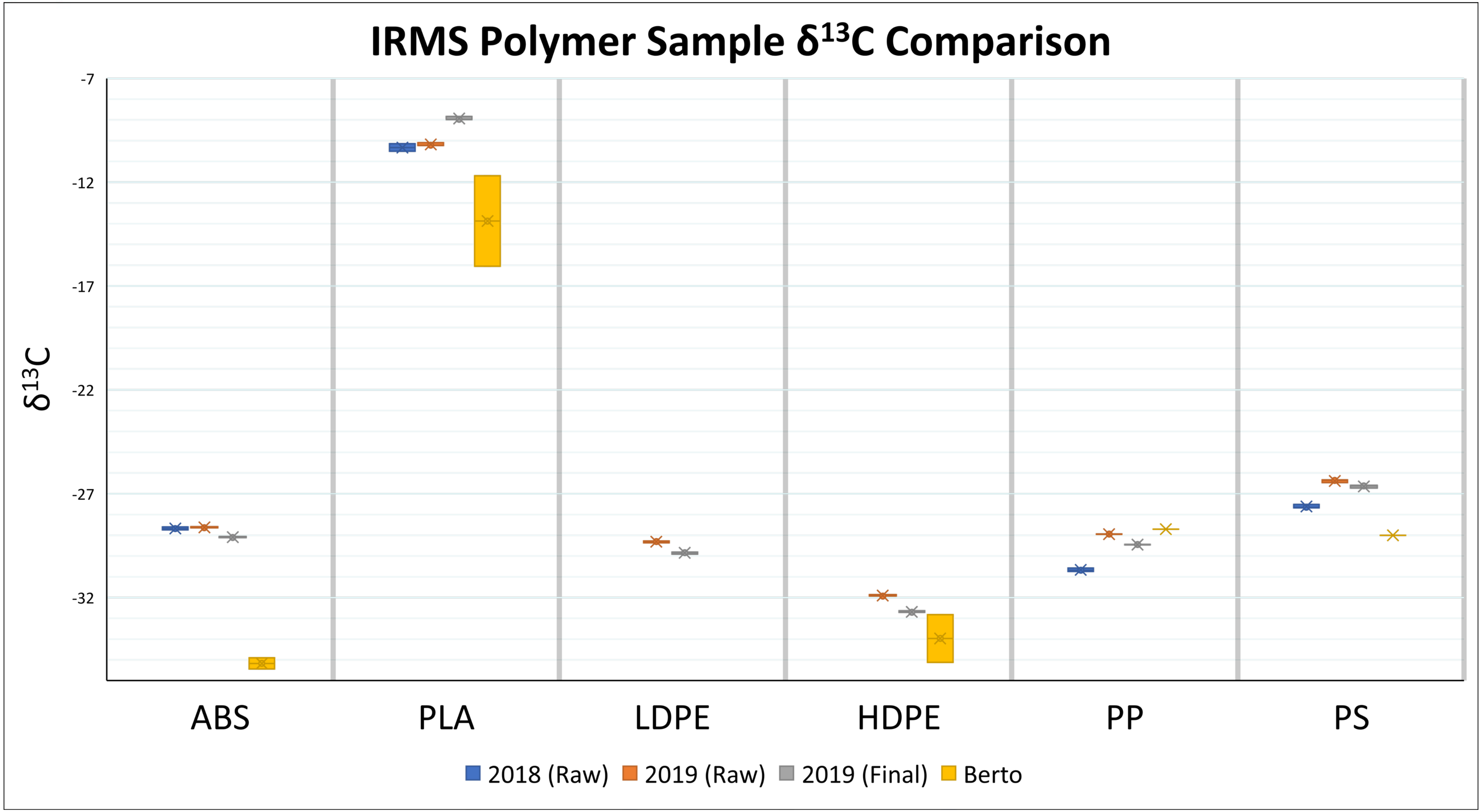


Polylactic Acid (PLA) Pellet
Counts
Wavenumber (cm-1)



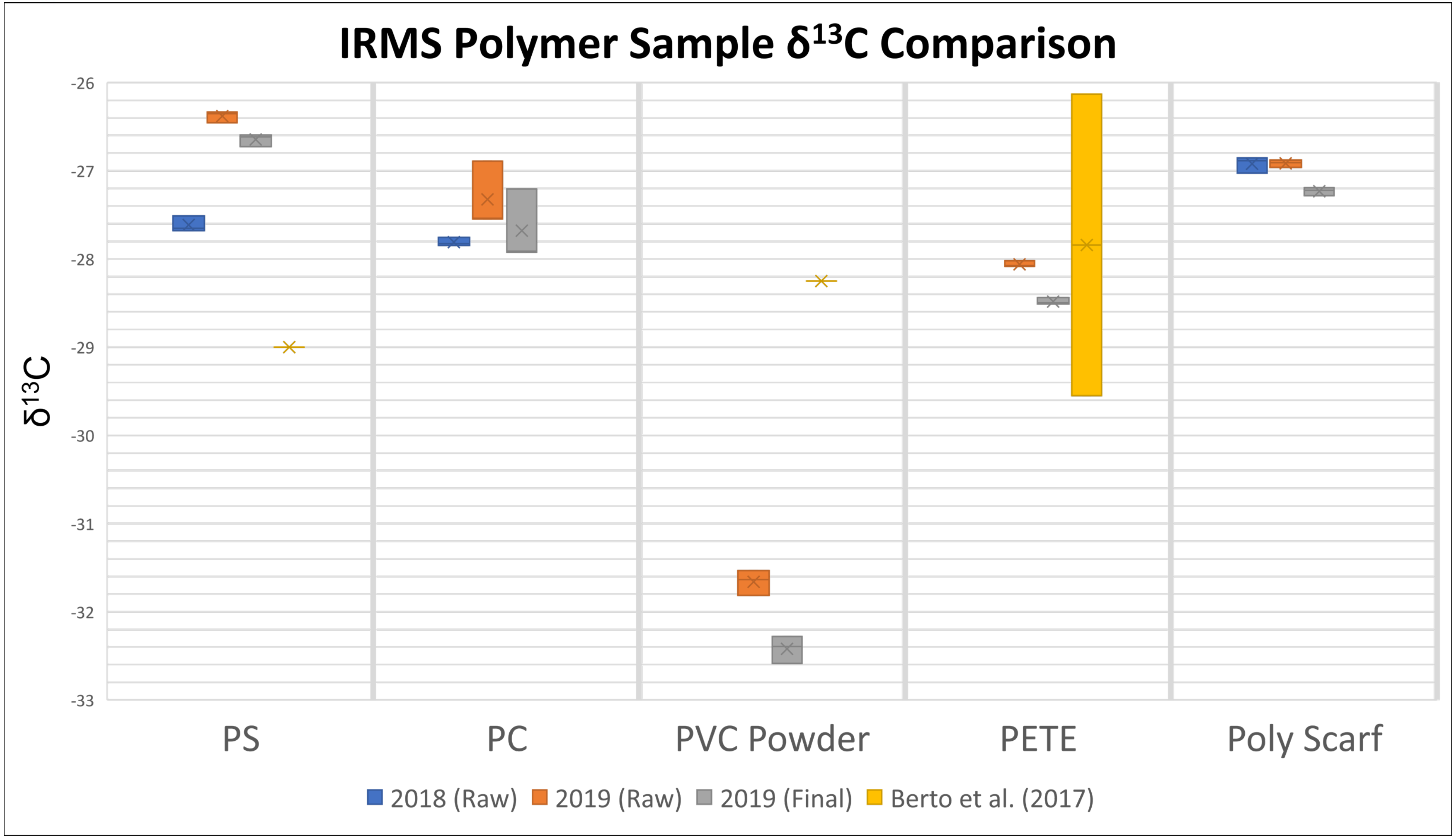
Acrylonitrile Butadiene Styrene (ABS) Pellet
Counts
Wavenumber (cm-1)

IRMS Data



IRMS Polymer Sample δ13C Comparison
δ13C
-7
-12
-17
-22
-27
-32
ABS
PLA
LDPE
HDPE
PP
PS
2018 (Raw)
2019 (Raw)
2019 (Final)
Berto

IRMS Data (Continued)



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Conclusions and future work

- Based on preliminary results, IRMS appears to be a promising tool for MP studies. The $\delta^{13}C$ values for petroleum- and plant-derived polymers reflected their sources, while recycled materials had intermediate values.
- Spectroscopic methods had problems with some materials, especially those with black additives.
- Dyes in polymers do not appear to affect the IRMS analysis, based on $\delta^{13}C$ results for PET samples.

Future work:

- Evaluate utility of IRMS in investigating rates of plastic degradation, based on change in $\delta^{13}C$ values for plastics (e.g. food packaging) subjected to simulated aging/weathering conditions.
- Analyze field samples for evidence of biotic/abiotic degradation of plastics in the environment.

Questions?

Disclaimer: The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.
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