Pyrolysis GC-MS Characterization of Microplastics from the Raritan and Passaic Rivers in New Jersey

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NOAA-NMFS-NEFSC

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Rutgers University

Rutgers University - Friday, March 29, 2019


Jersey City
Manhattan
NEW YORK
Queens
Brooklyn
Upper Bay
Frank Charles Memorial Park
Canarsie Pier
Jamaica Bay Wildlife Refuge
Staten Island
Verrazano - Narrows Bridge
Fort Wadsworth
Bergen Beach
Floyd Bennett Field
Lower Bay
Plumb Beach
Miller Field
Hoffman Island
Swinburne Island
Coney Island
Jacob Riis Park
Fort Tilden
Staten Island Unit
Great Kills Park
Breezy Point
Jamaica Bay Unit
Atlantic Ocean
Raritan Bay
Sandy Hook Unit
Fort Hancock Historic District
Sandy Hook Bay
Park Land
Park Water
Gateway Legislative Boundary
NEW JERSEY
Highlands
North
Miles
0 1 2 4


NOAA James J. Howard
Marine Sciences Laboratory


FORT HANCOCK

JAMES J. HOWARD MARINE SCIENCES LABORATORY

50 1961 2011

SANDY HOOK, NJ

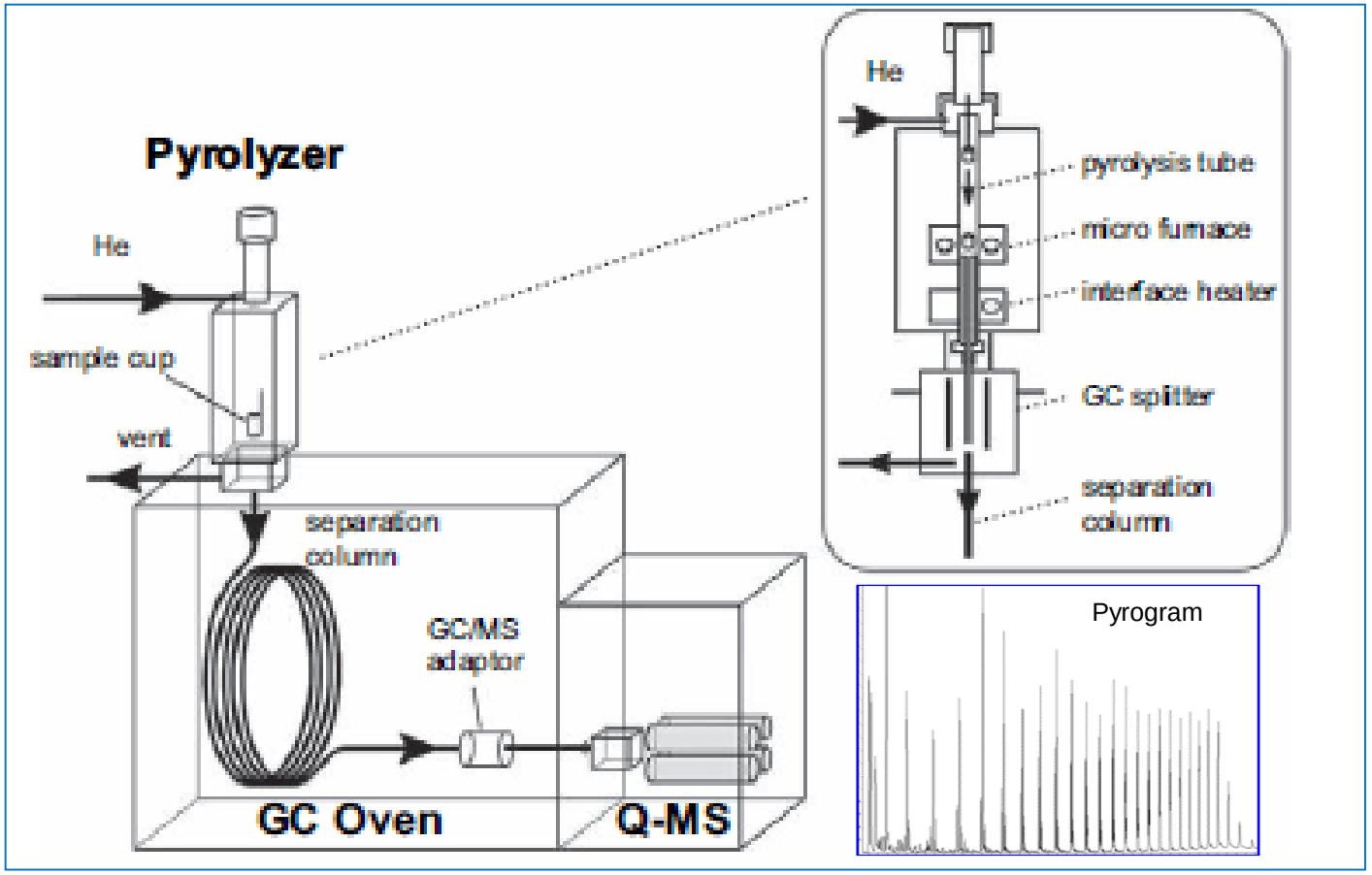
YEARS OF FISHERY RESEARCH

Raman Spectroscopy

Infra-Red Spectroscopy

Mass Spectrometry

PYROLYSIS-GC/MS



Credit: Tsuge, Ohtani and Watanabe

- Microplastic sample is heated at high temperature in the pyrolyzer.
- Thermal degradation results in a unique and reproducible signature of fragment molecules that is characteristic to a given polymer.

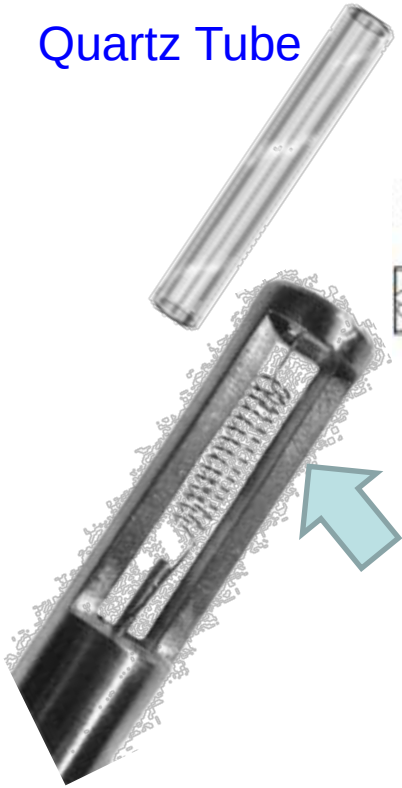
Anatomy of Pyrolysis GC-MS

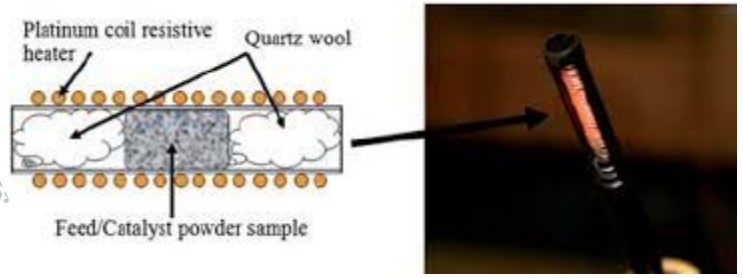
CDS 2000 Pyroprobe

CDS 1500 GC-MS Interface

Agilent 5973 GC-MS

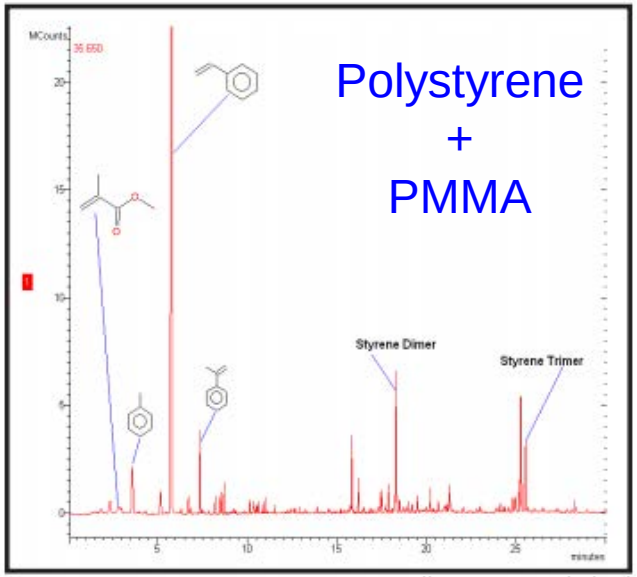
Quartz Tube





Platinum Filament

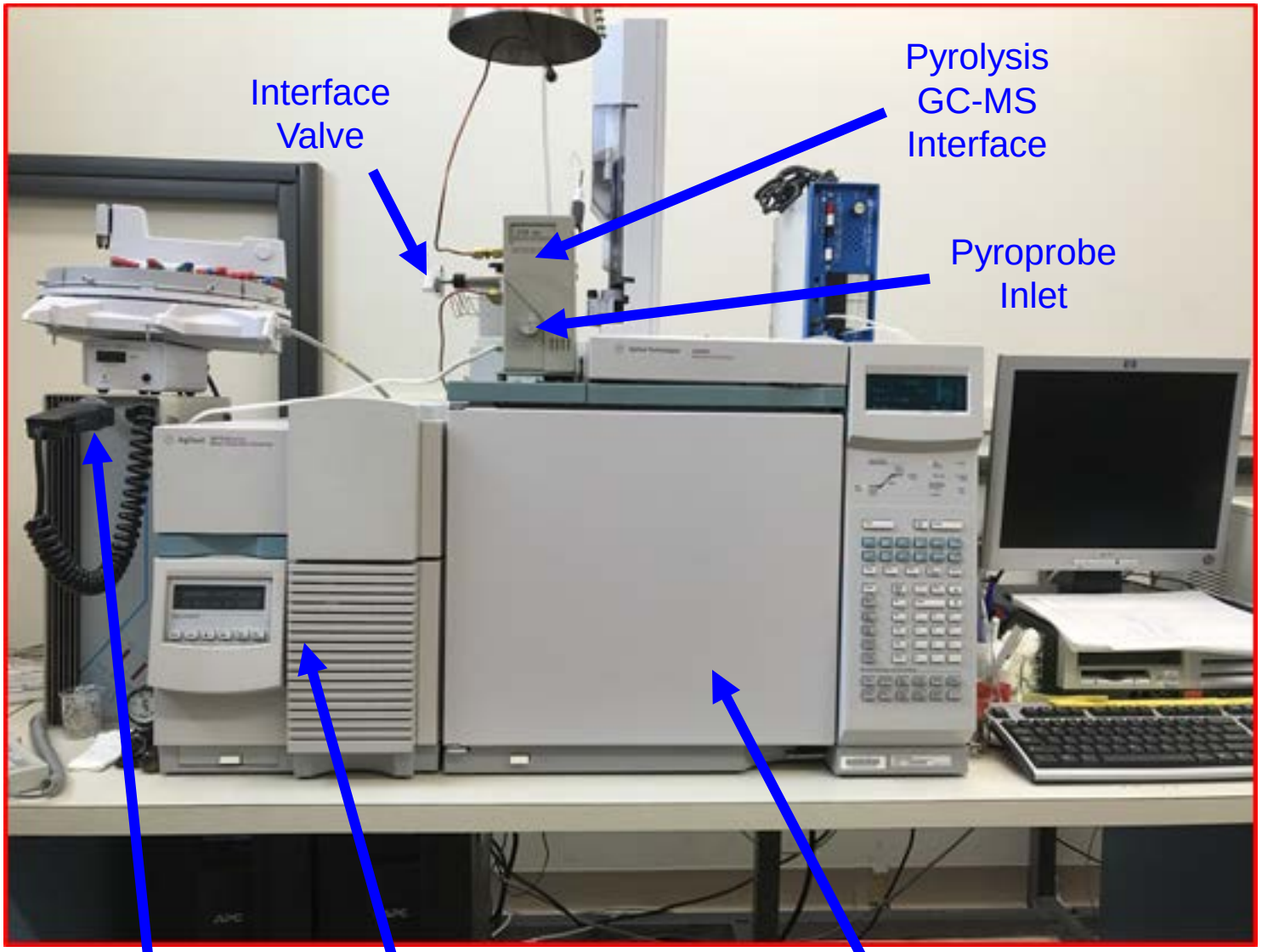
750ºC = 1382ºF

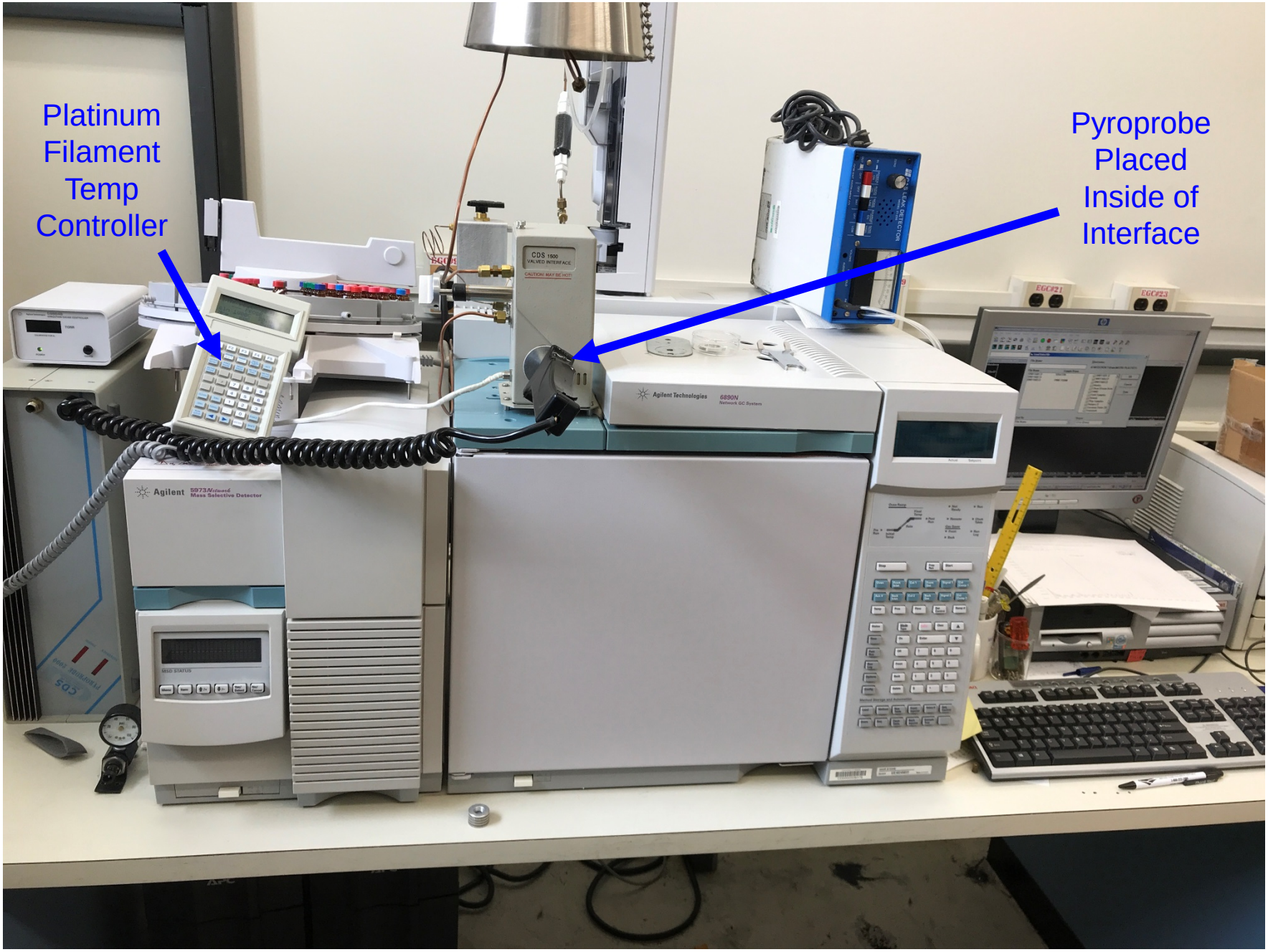


Credit: CDS Analytical

Pyrogram

Pyrolysis GC-MS System at the NOAA Sandy Hook Laboratory




Platinum Filament Temp Controller
Pyroprobe Placed Inside of Interface
CDS 1500 VALVED INTERFACE
Agilent Technologies 6890N Network GC System
Agilent 5973N Mass Selective Detector
LEAK DETECTOR

Going Above & Beyond
Just Peak Comparisons

Creation of Pyrolysis
GC-MS Database

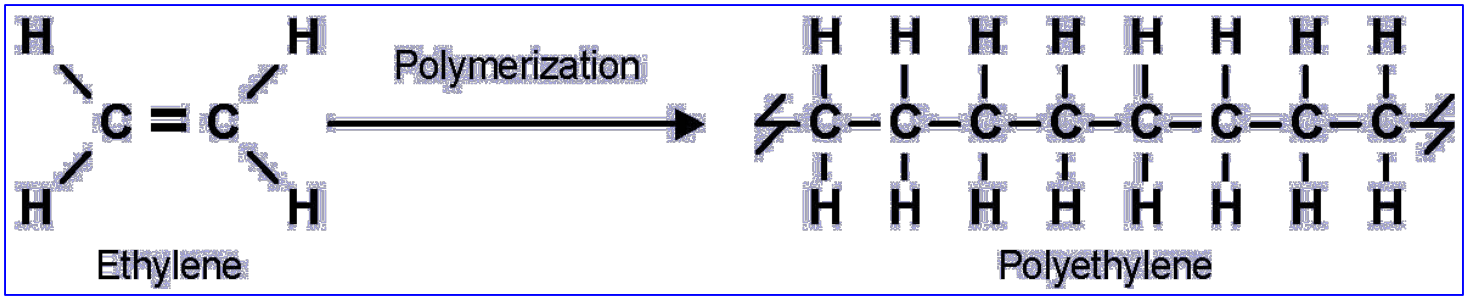
Involves

Systematic and Sequential

Identification of Marker Peaks

That can be later used for

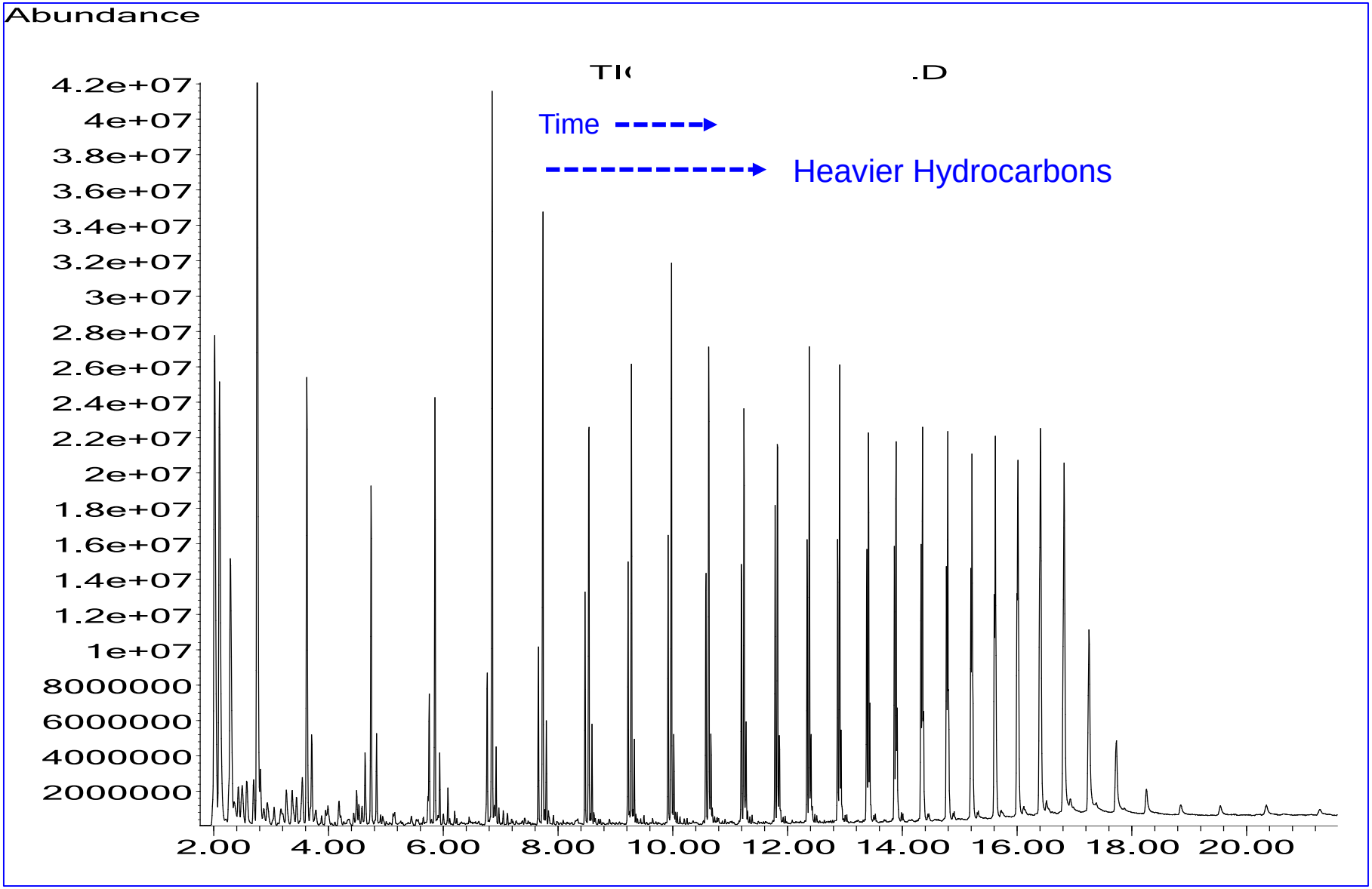
Polymer Characterization



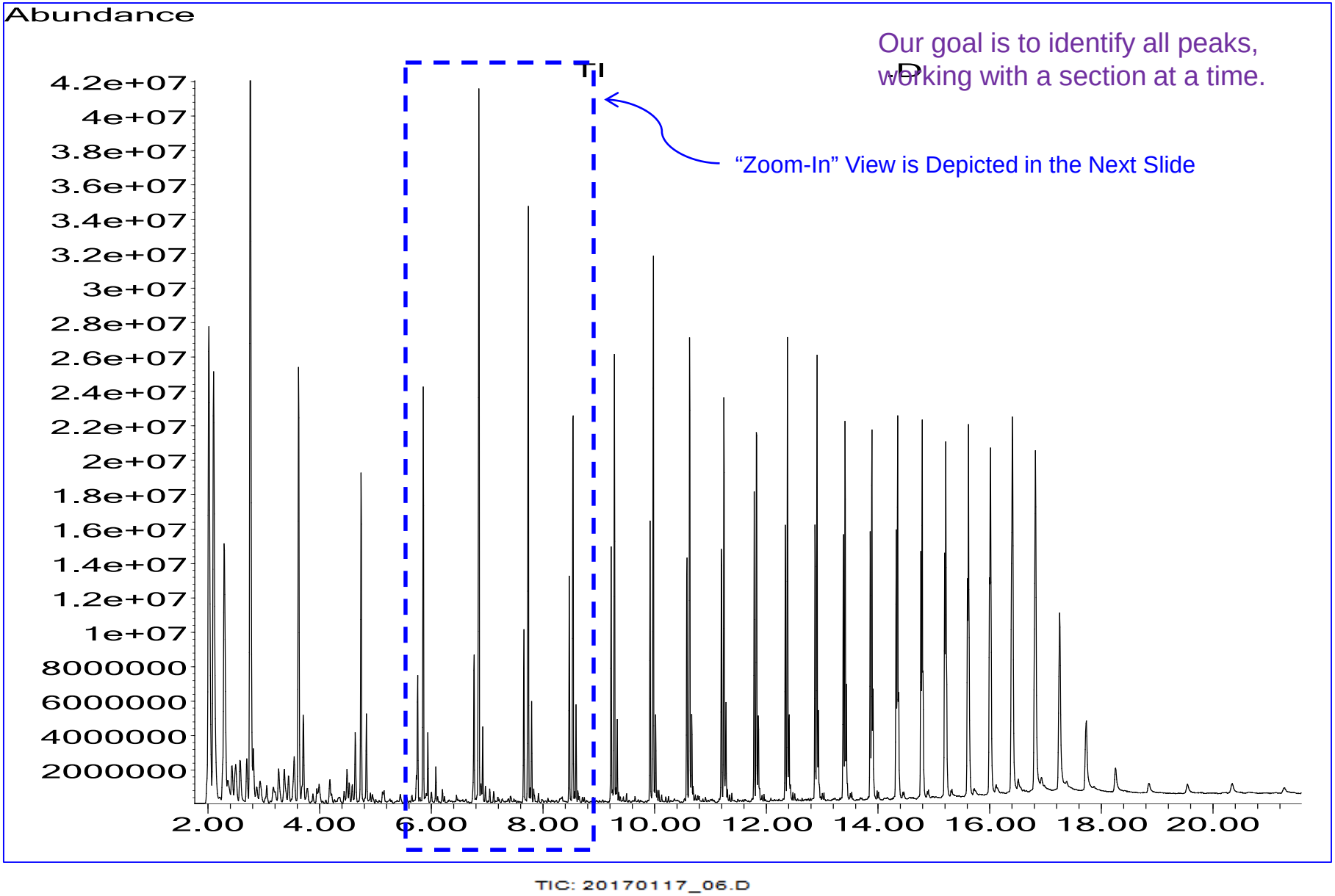
Pyrolysis

C-C bonds at different sites along the polymer chain break due to intense heat to yield a variety of short-chain molecules

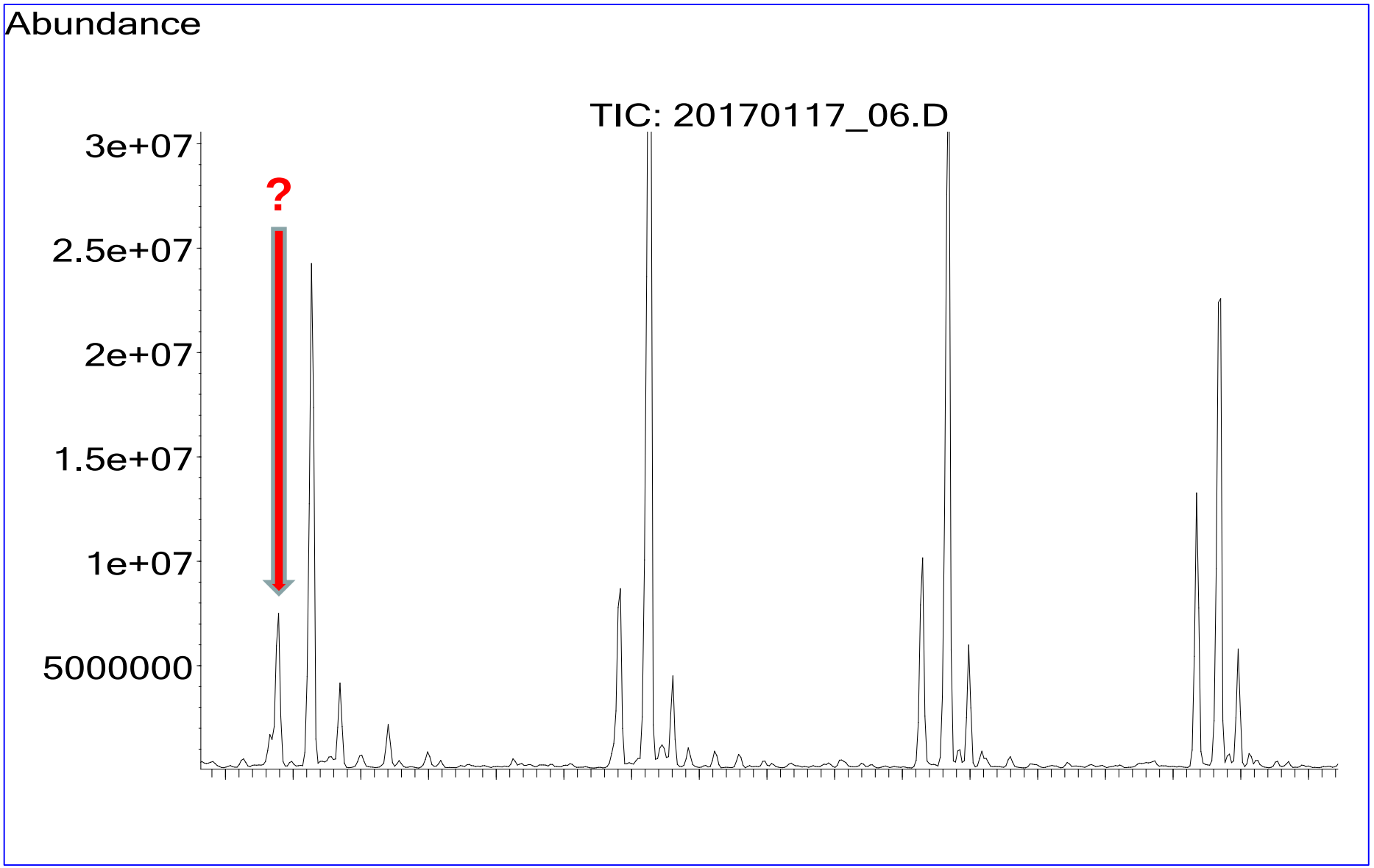
Total Ion Chromatogram (Pyrogram) of High-Density Polyethylene (HDPE)



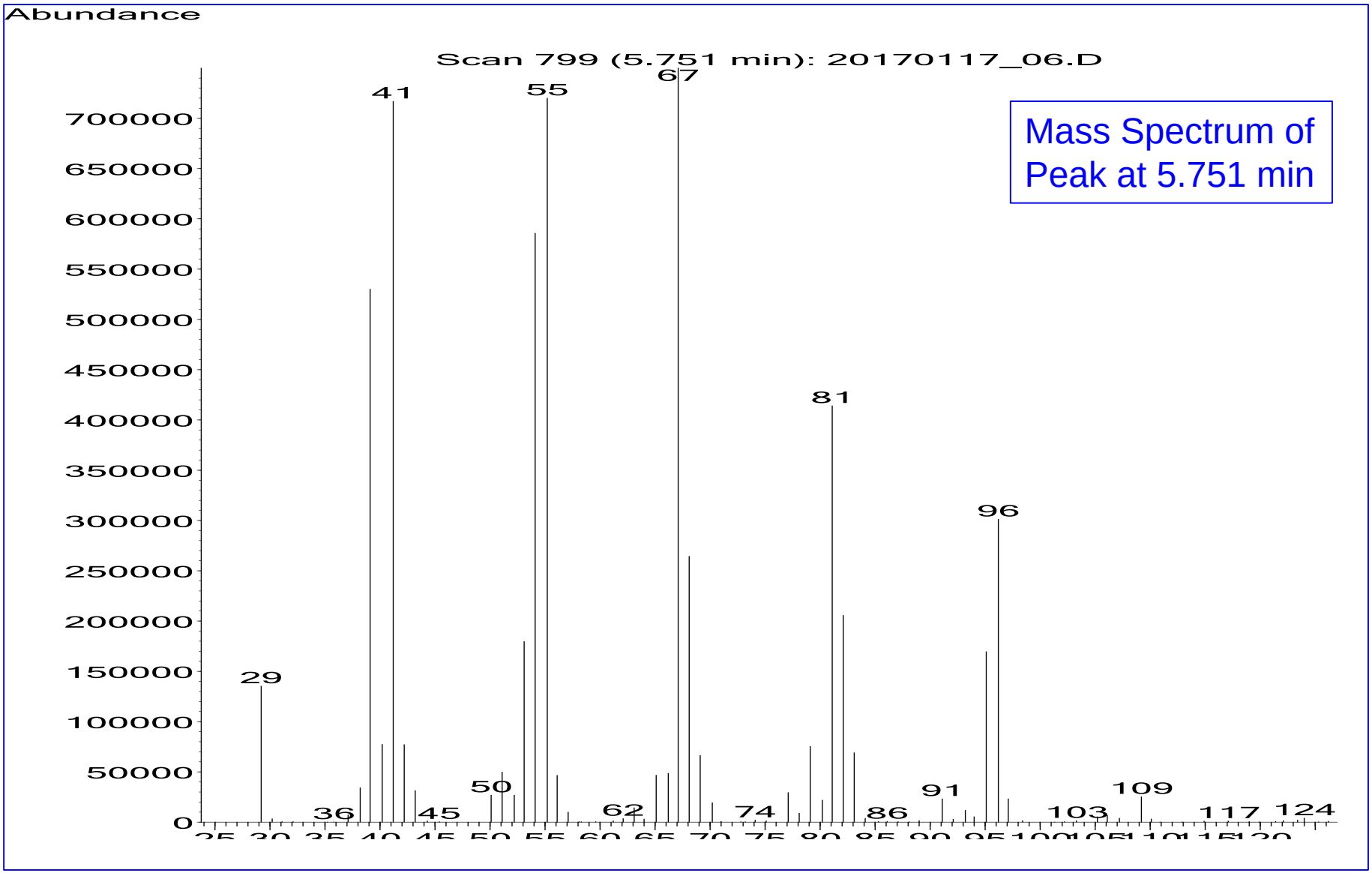
Pyrogram of High-Density Polyethylene (HDPE)



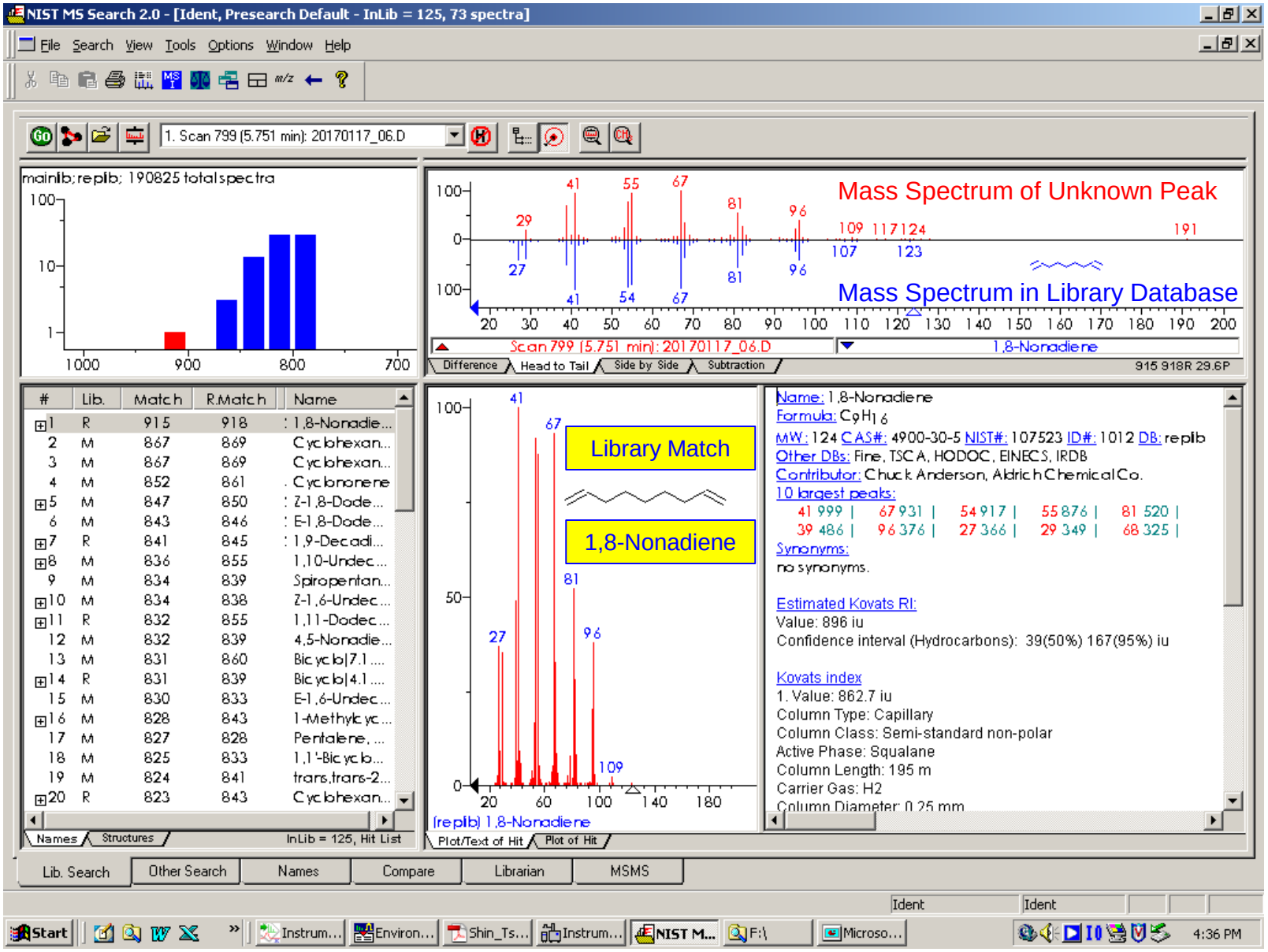
High-Density Polyethylene (HDPE): “Zoom-In” Part of the Pyrogram



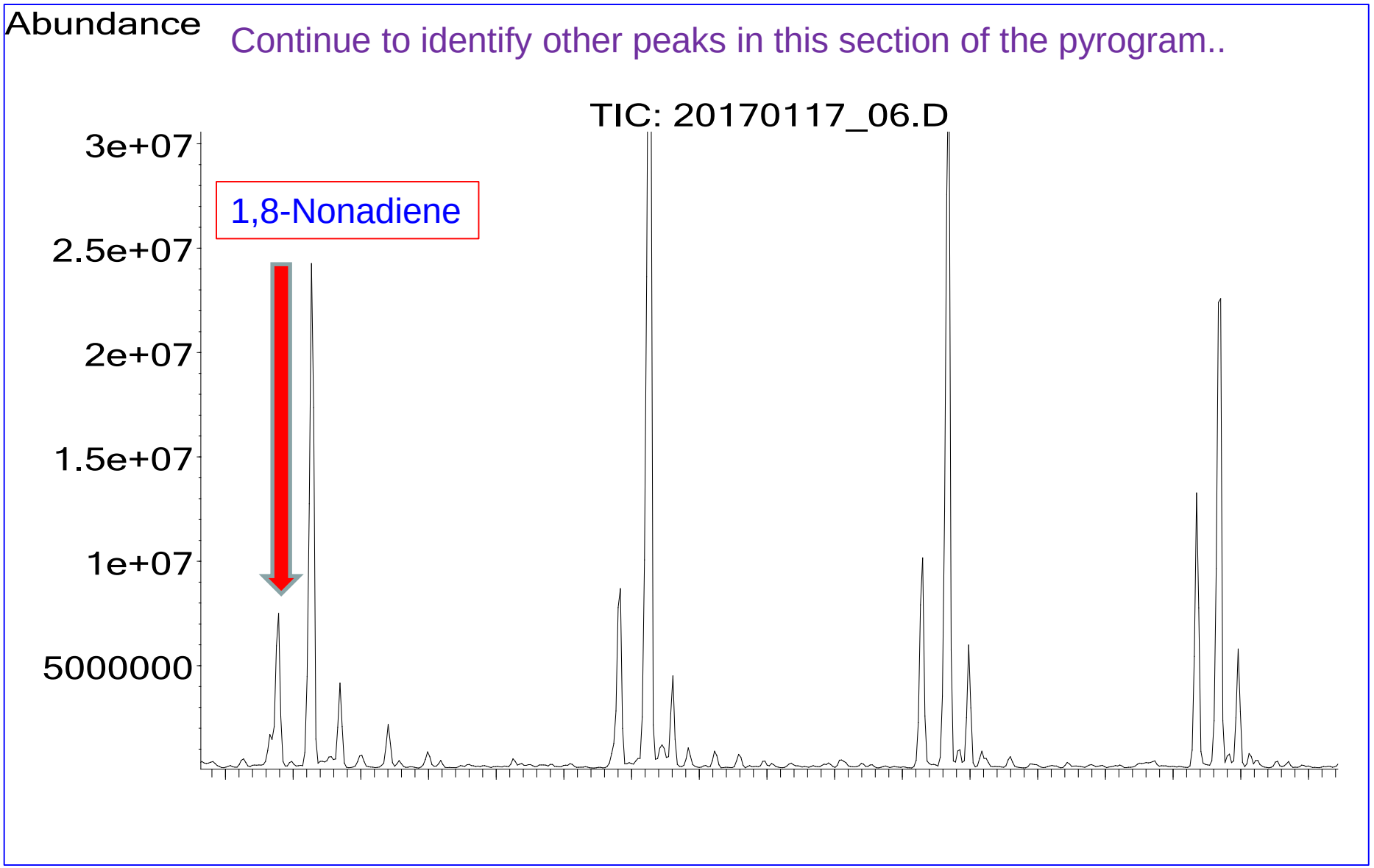
High-Density Polyethylene (HDPE)



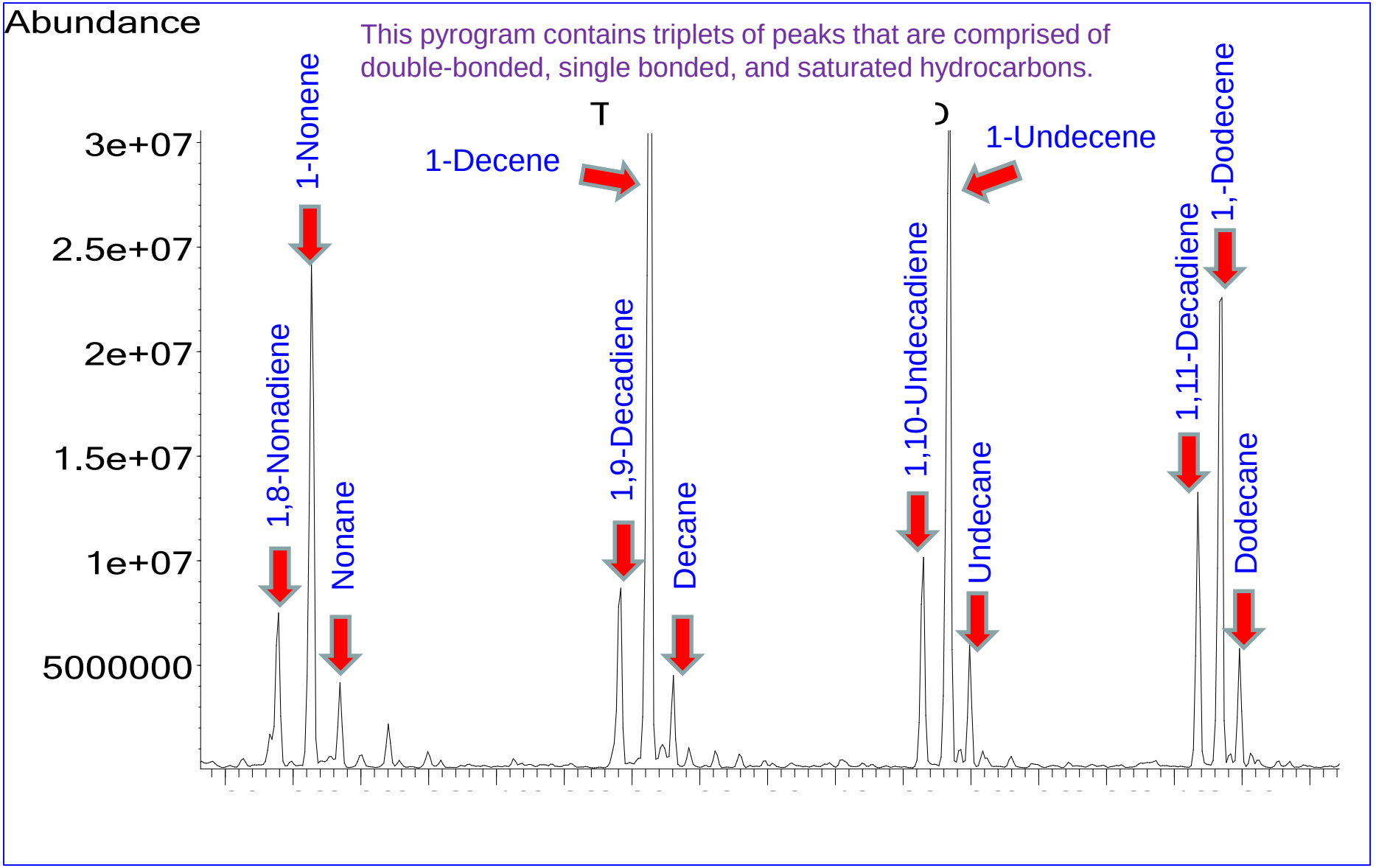
Library Search: Find Best Match for Mass Spectrum in the NIST Library



High-Density Polyethylene (HDPE)



High-Density Polyethylene (HDPE)

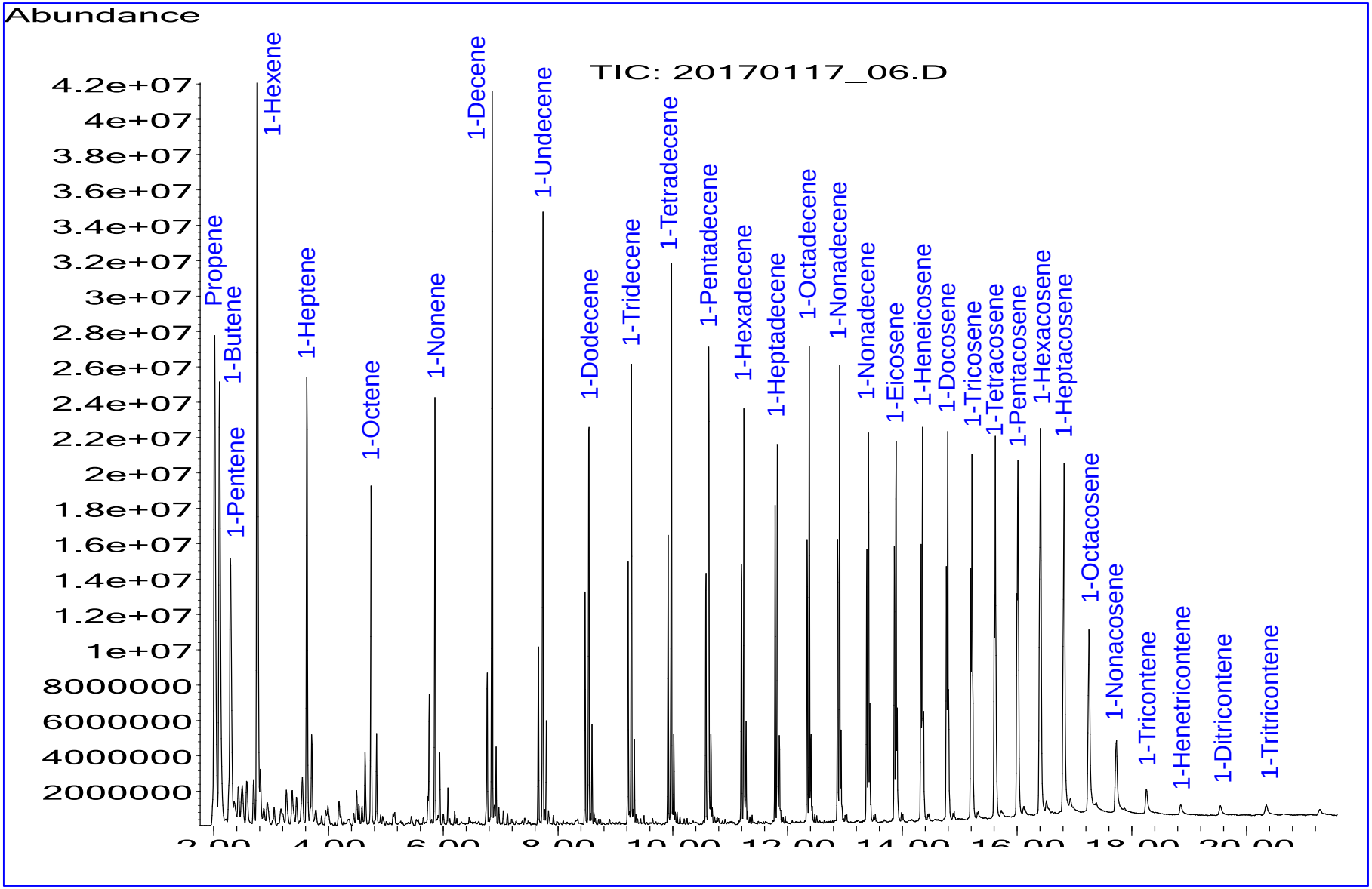


With a little more patience and perseverance

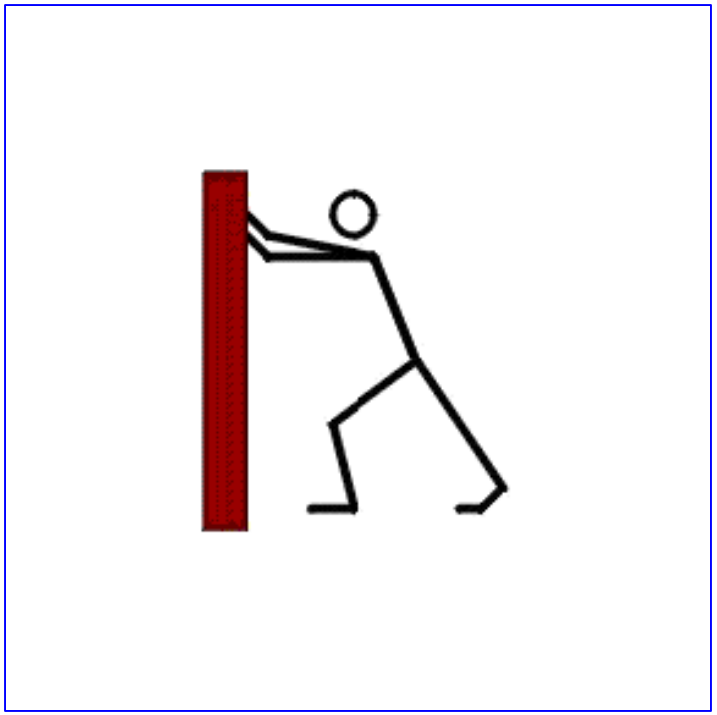
characterize remaining peaks in the entire pyrogram of

High-Density Polyethylene (HDPE)

High-Density Polyethylene (HDPE)

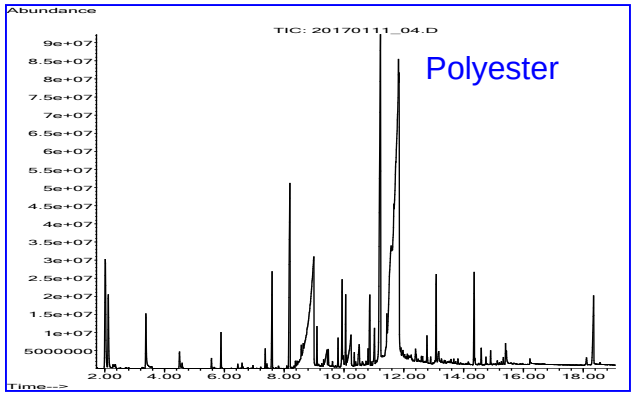


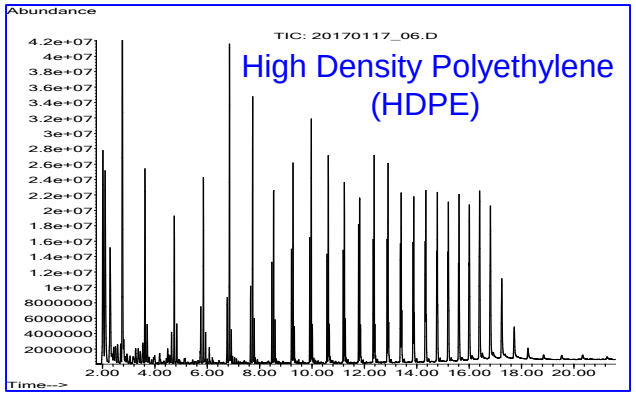
HDPE Pyrogram Fully Characterized!!!

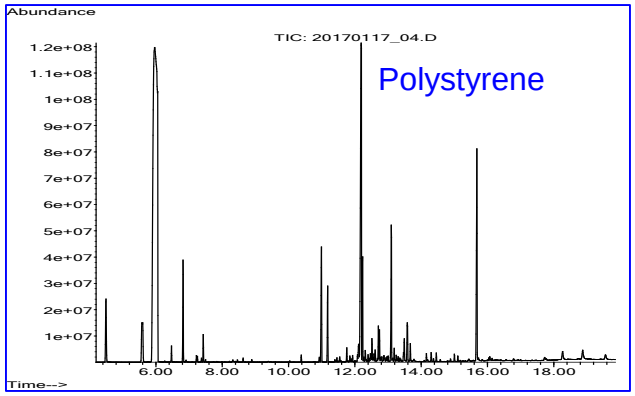


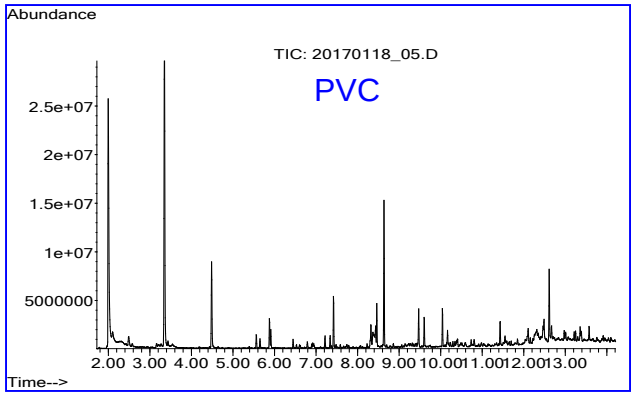
Likewise, pyrolysis GC-MS databases are created for other polymers.

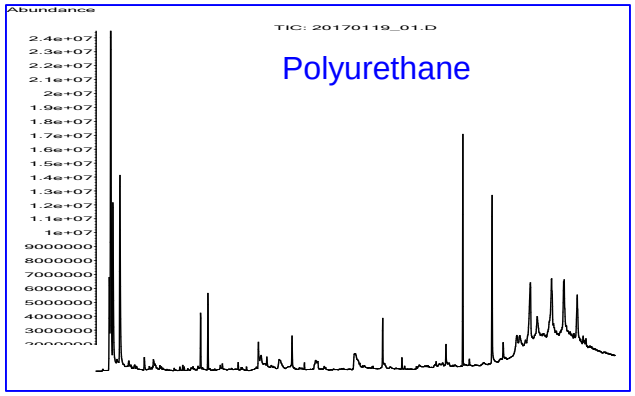
Examples of Pyrolysis GC-MS Pyrograms of Plastic Polymers

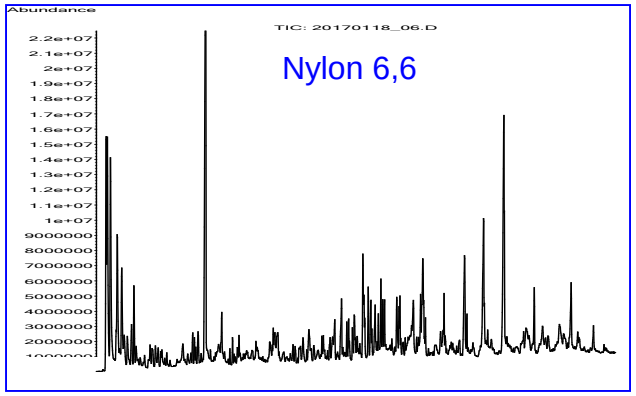












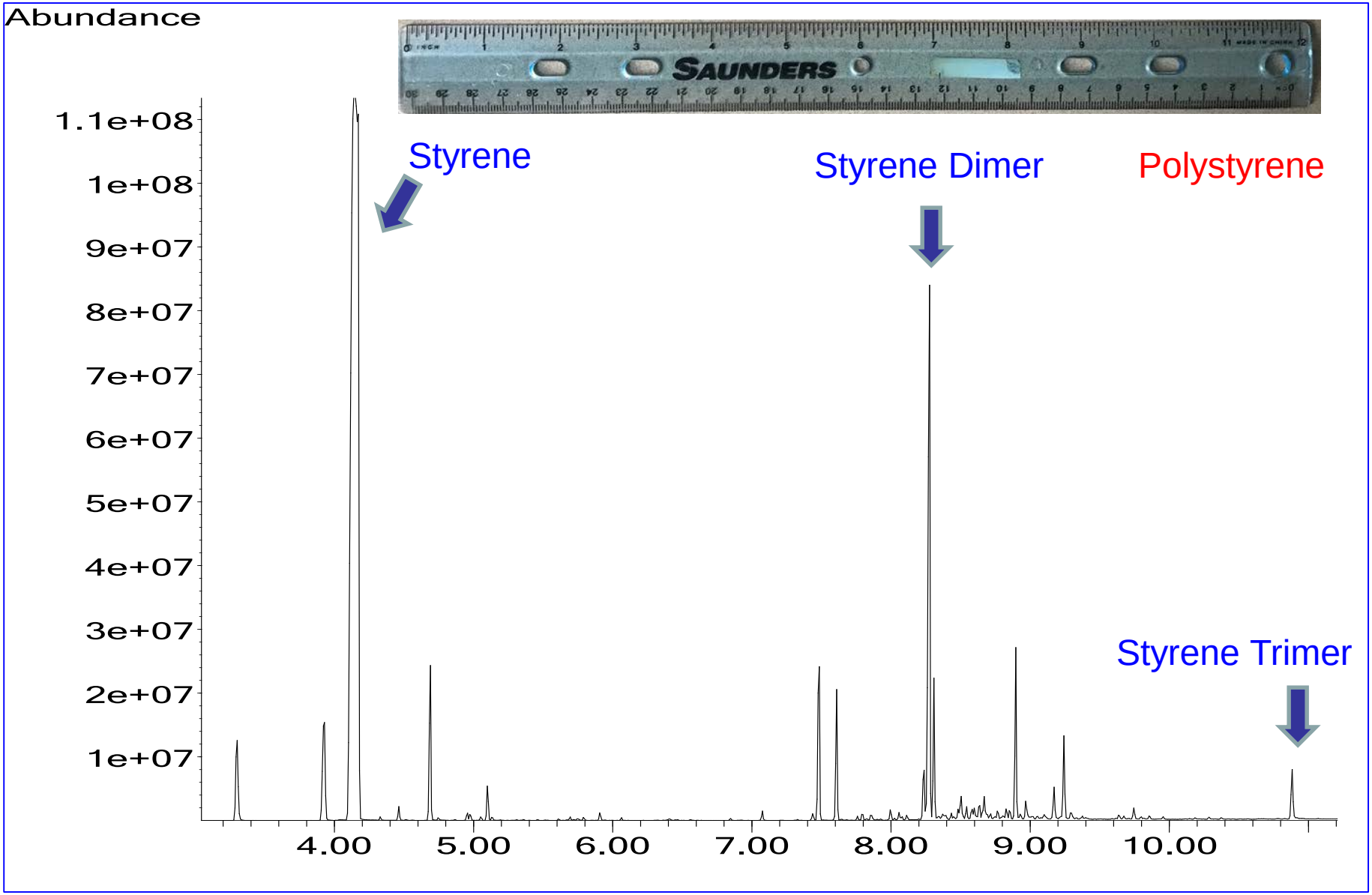
We have to do this work only once to create the library!!!

After creation of the library, the next step is to test the..

- Common Plastic Items
- Weathered Plastics

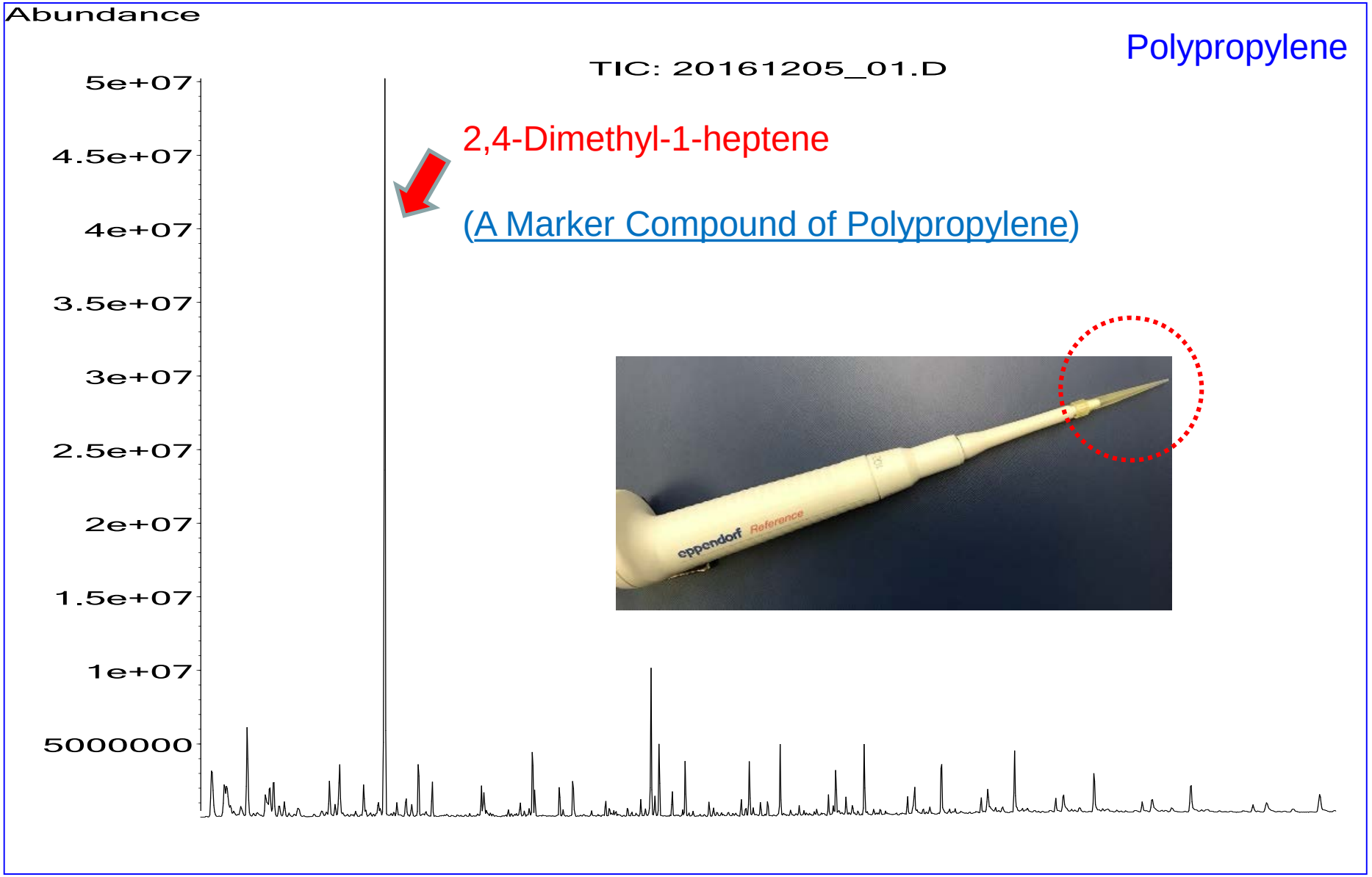
Common Plastic Items

12" Hard Plastic Ruler



Micropipette Tip (100 μl)

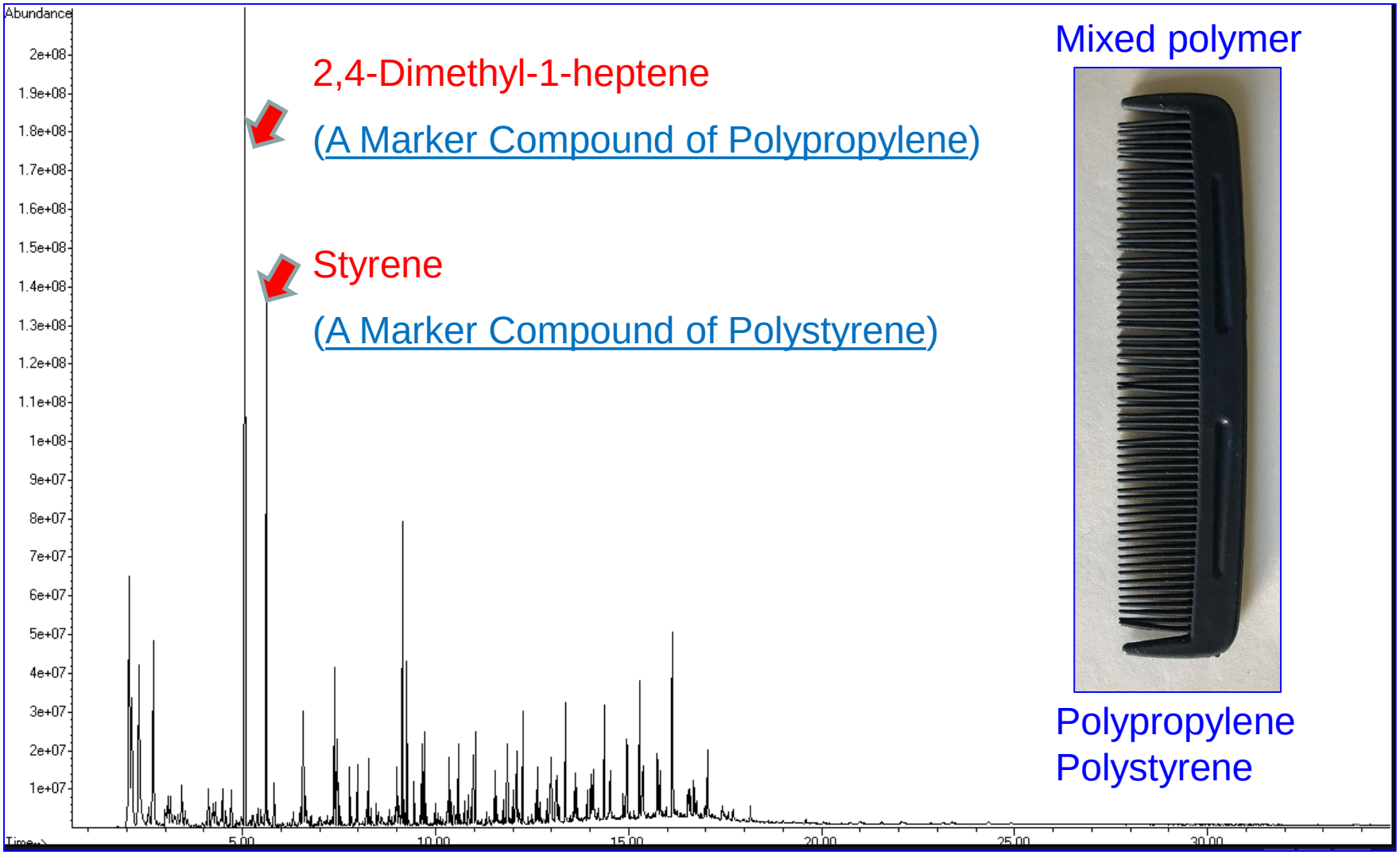
Polypropylene



2,4-Dimethyl-1-heptene

(A Marker Compound of Polypropylene)

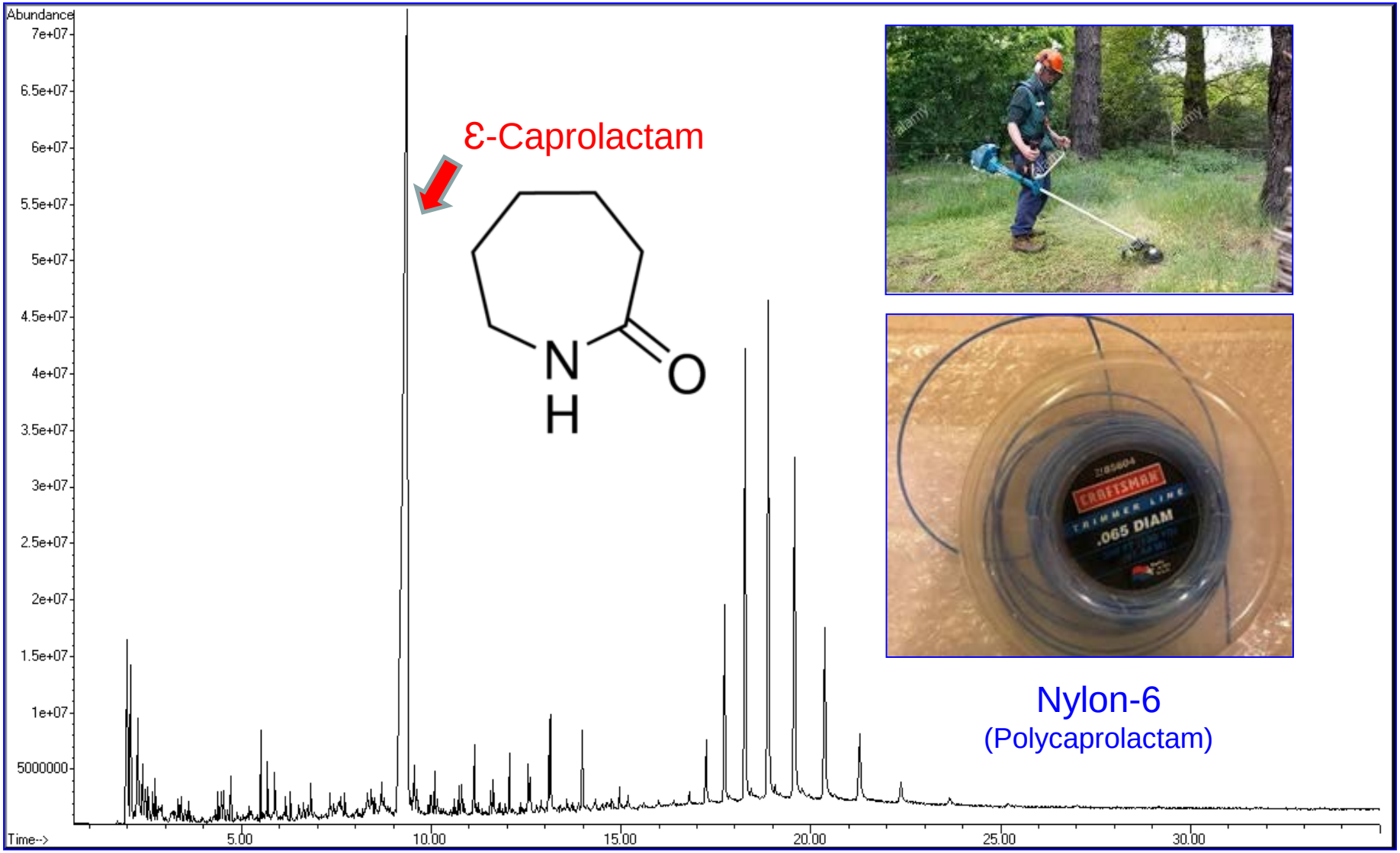
Hair Comb



Mixed polymer

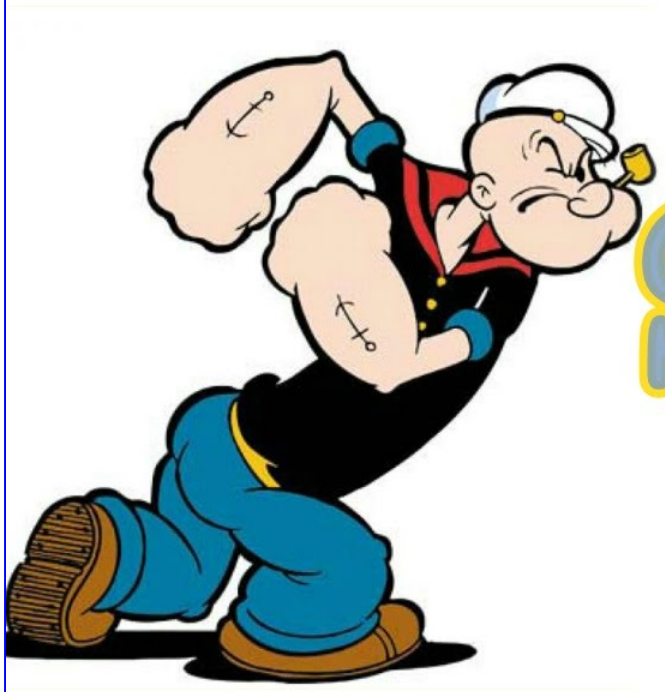
Polypropylene
Polystyrene

Weed Wacker Trimmer Line



Ɛ-Caprolactam

Nylon-6
(Polycaprolactam)

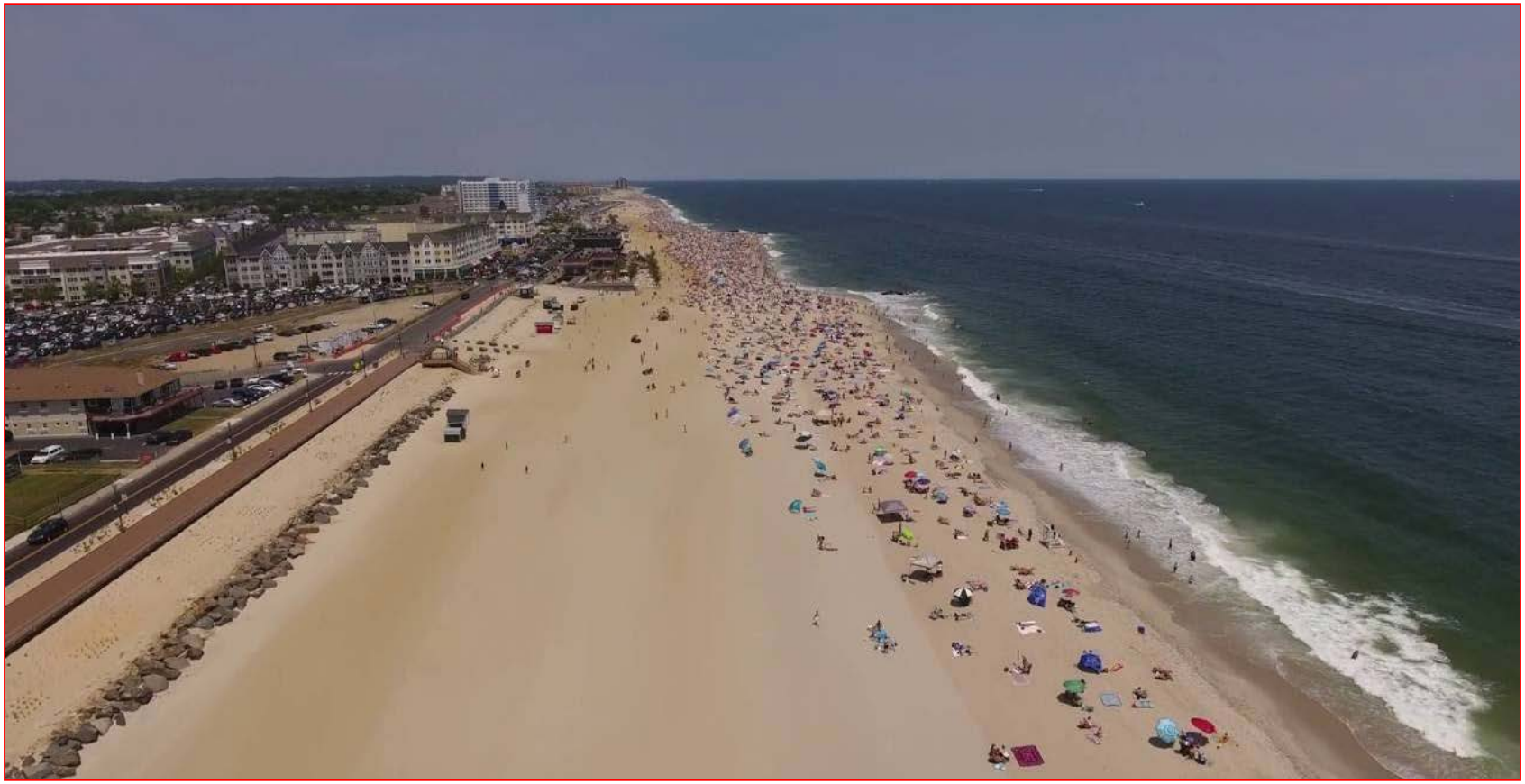


So Far
So Good

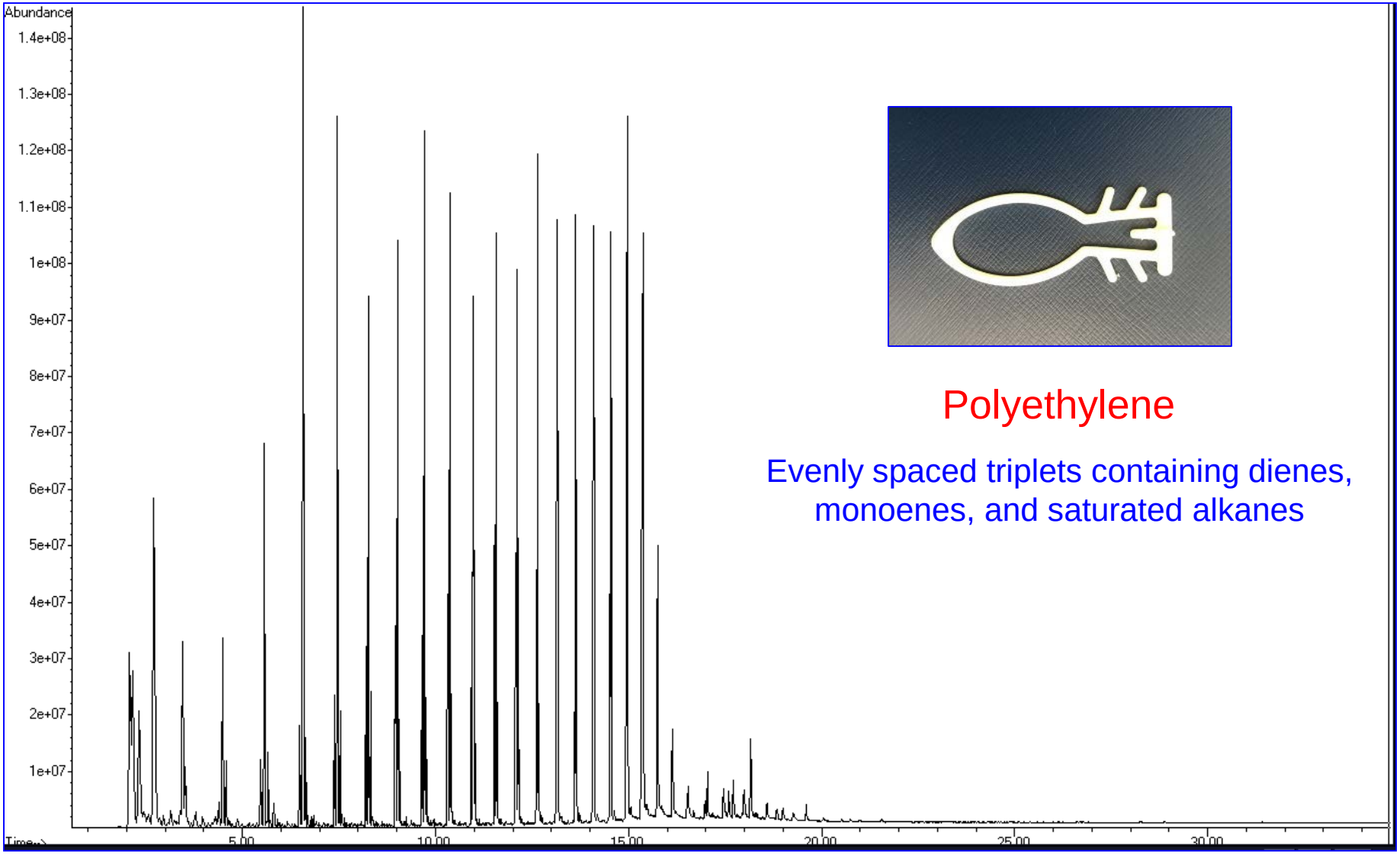
The final step in microplastics method development is to test the real-world, weathered plastic fragments:

- Microplastics on Beach
- Microplastics in River/Estuary
- Microplastics in Ocean

Plastic Fragments from a Beach in Long Branch, New Jersey



Fish shaped beach plastic

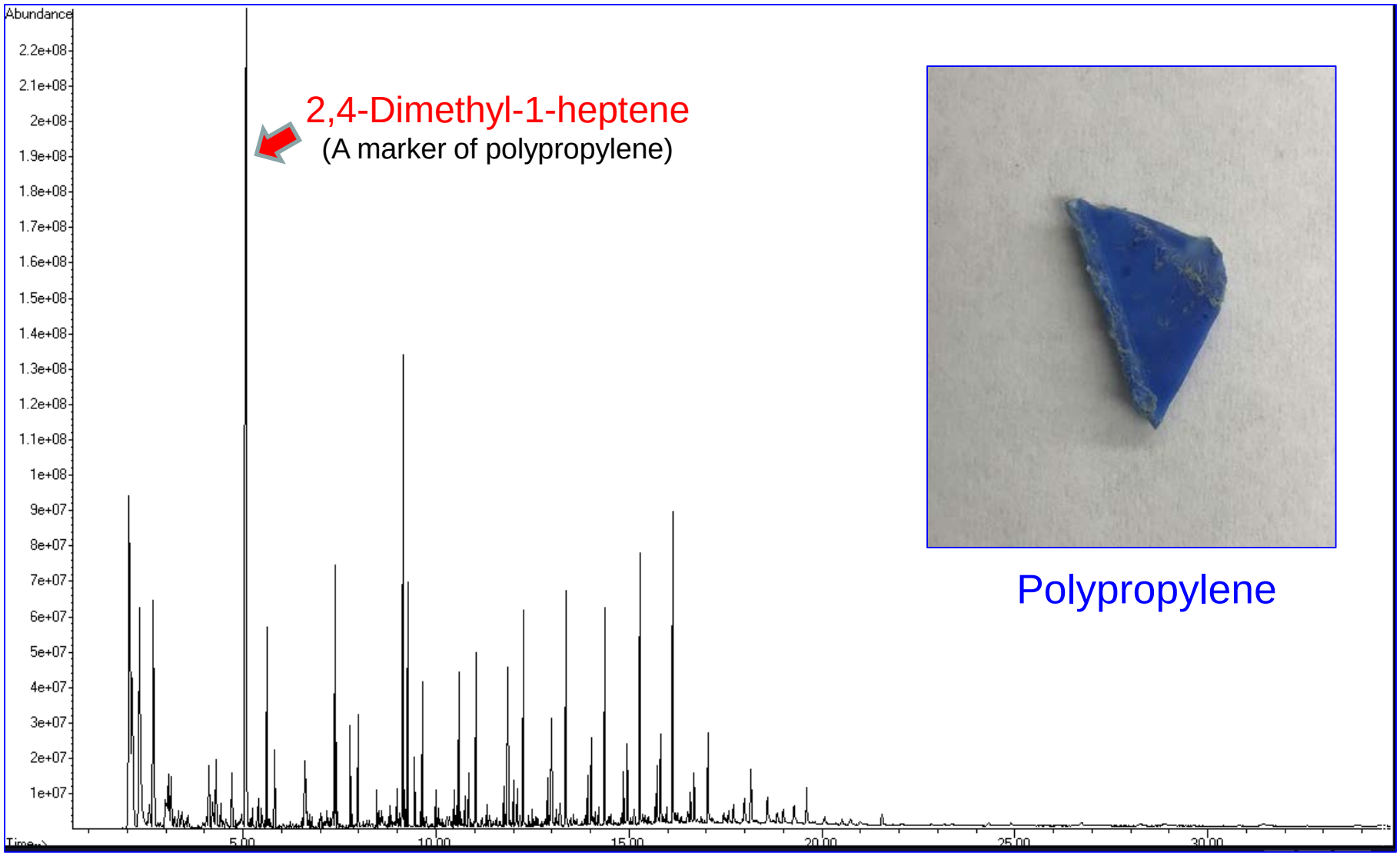


Polyethylene

Evenly spaced triplets containing dienes, monoenes, and saturated alkanes

Found on Long Branch, NJ Beach

Blue Fragment of Plastic

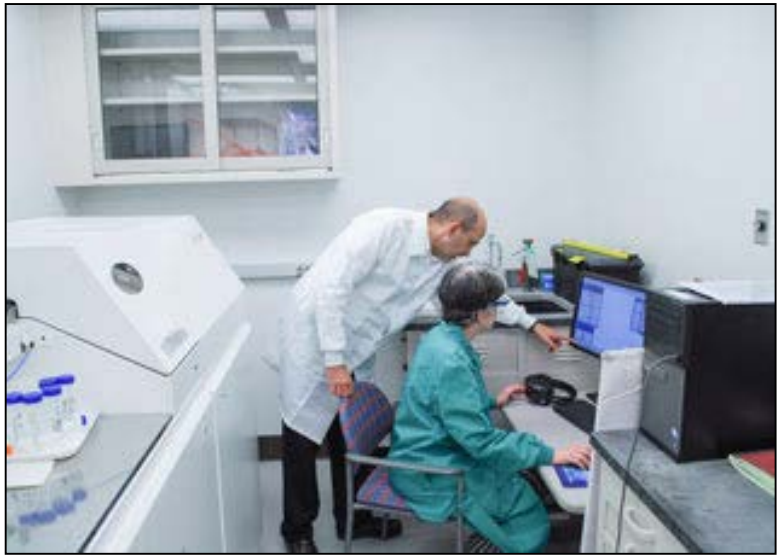


Polypropylene

Found on Long Branch, NJ Beach

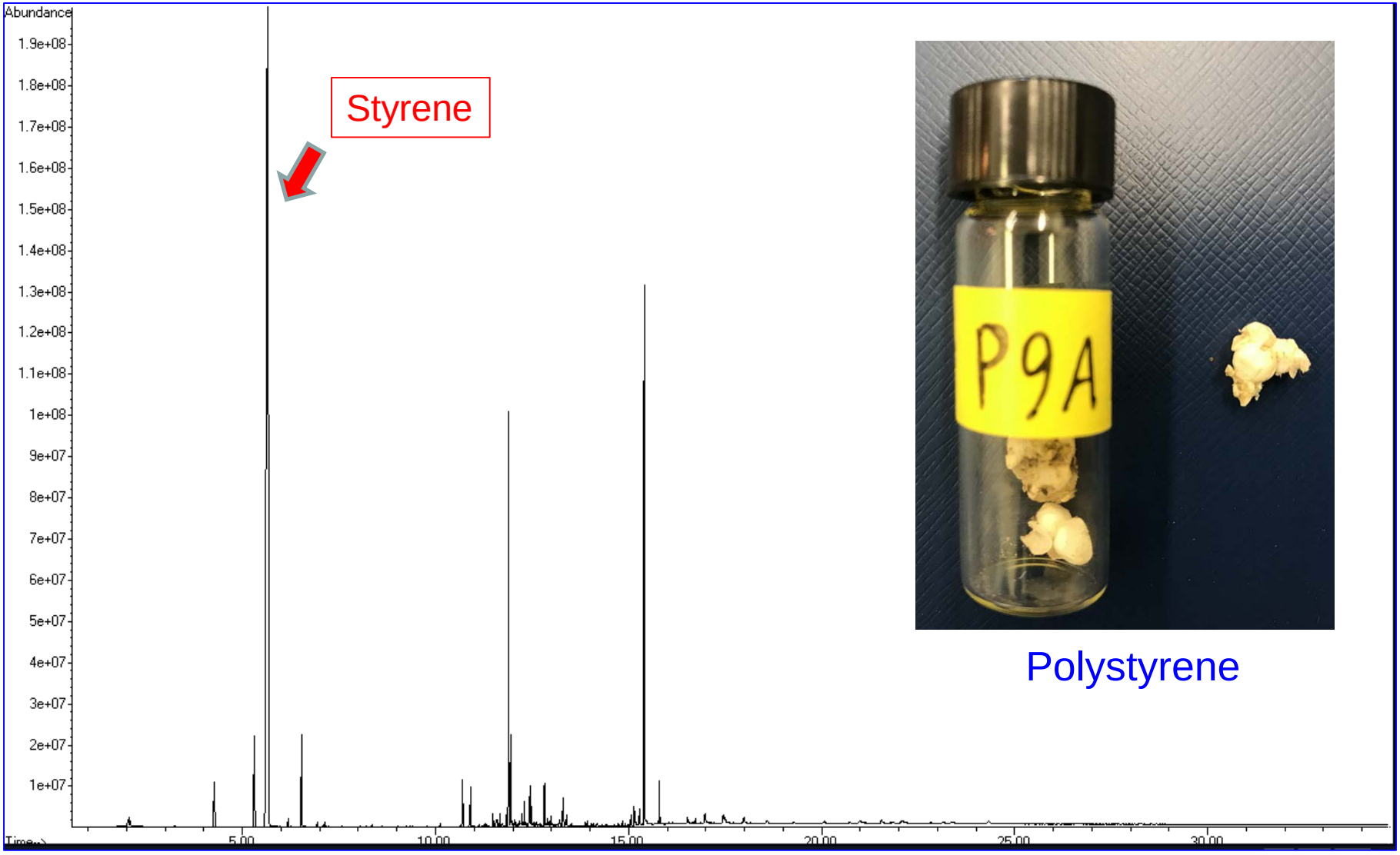
Microplastics from
Passaic River, New Jersey

Dr. Keith Cooper and Dr. Beth Ravit (Rutgers University)



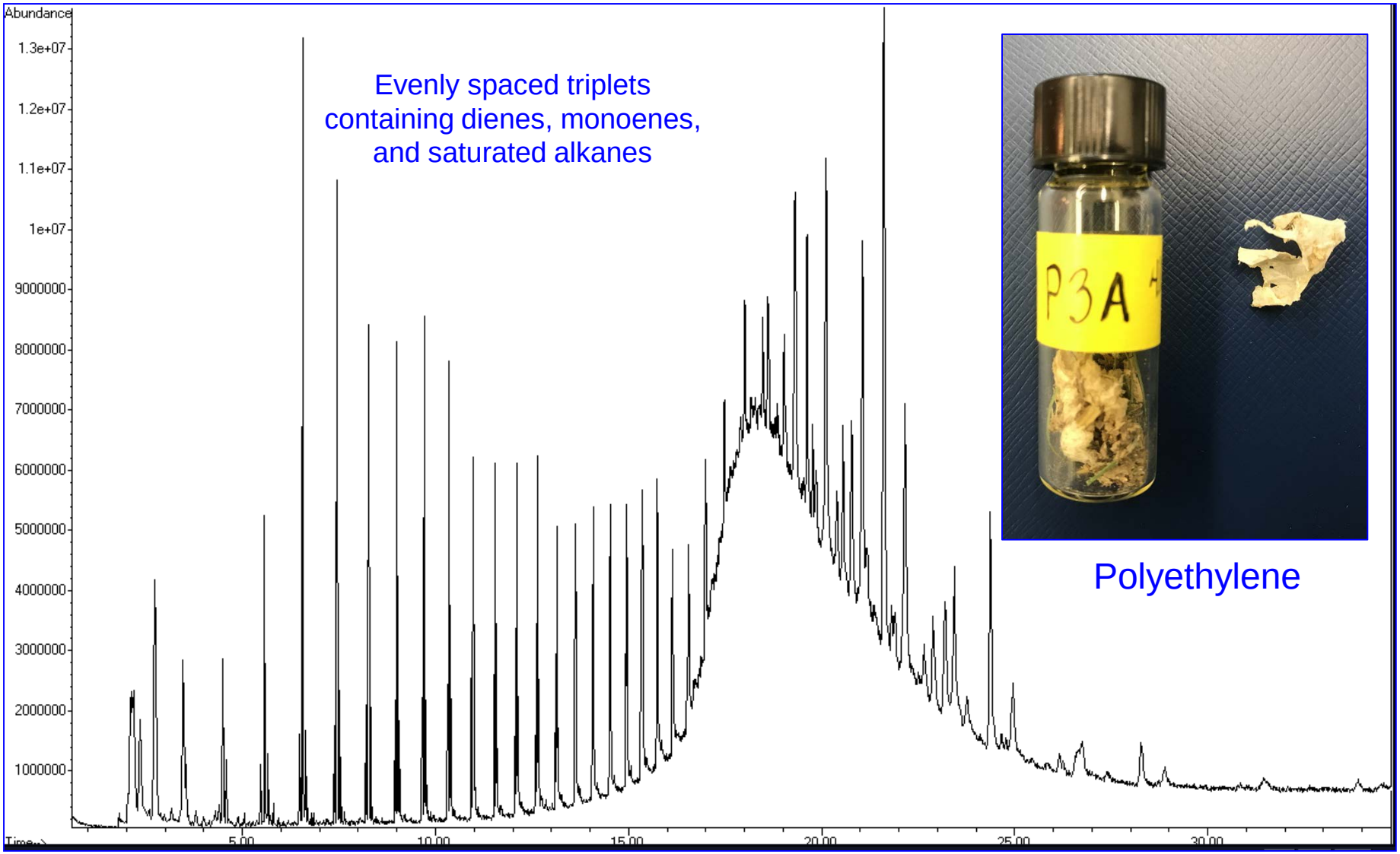
Dr. Brian Buckley (Rutgers University)

Rutgers Field Collection P9A

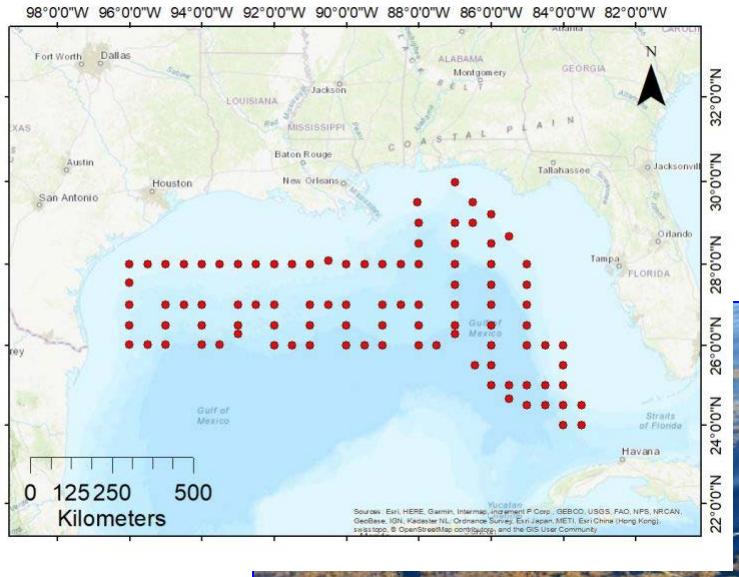


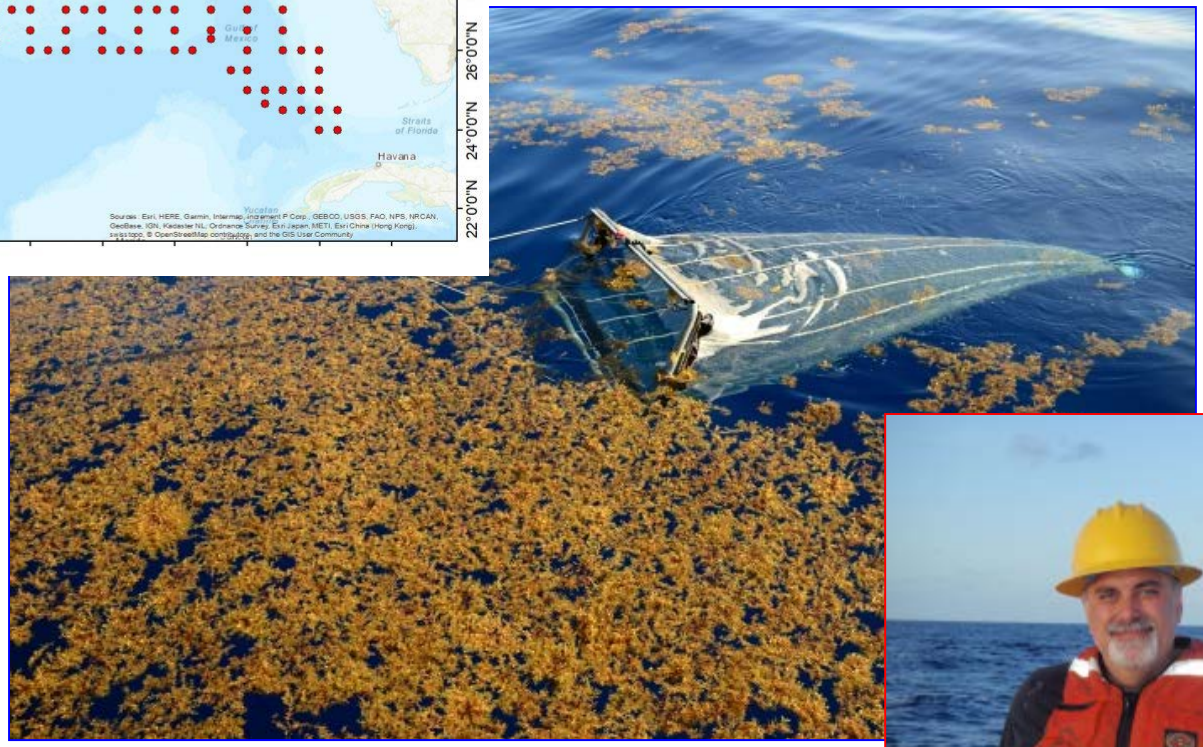
Polystyrene

Rutgers Field Collection P3A



NOAA Restore Cruise
Gulf of Mexico

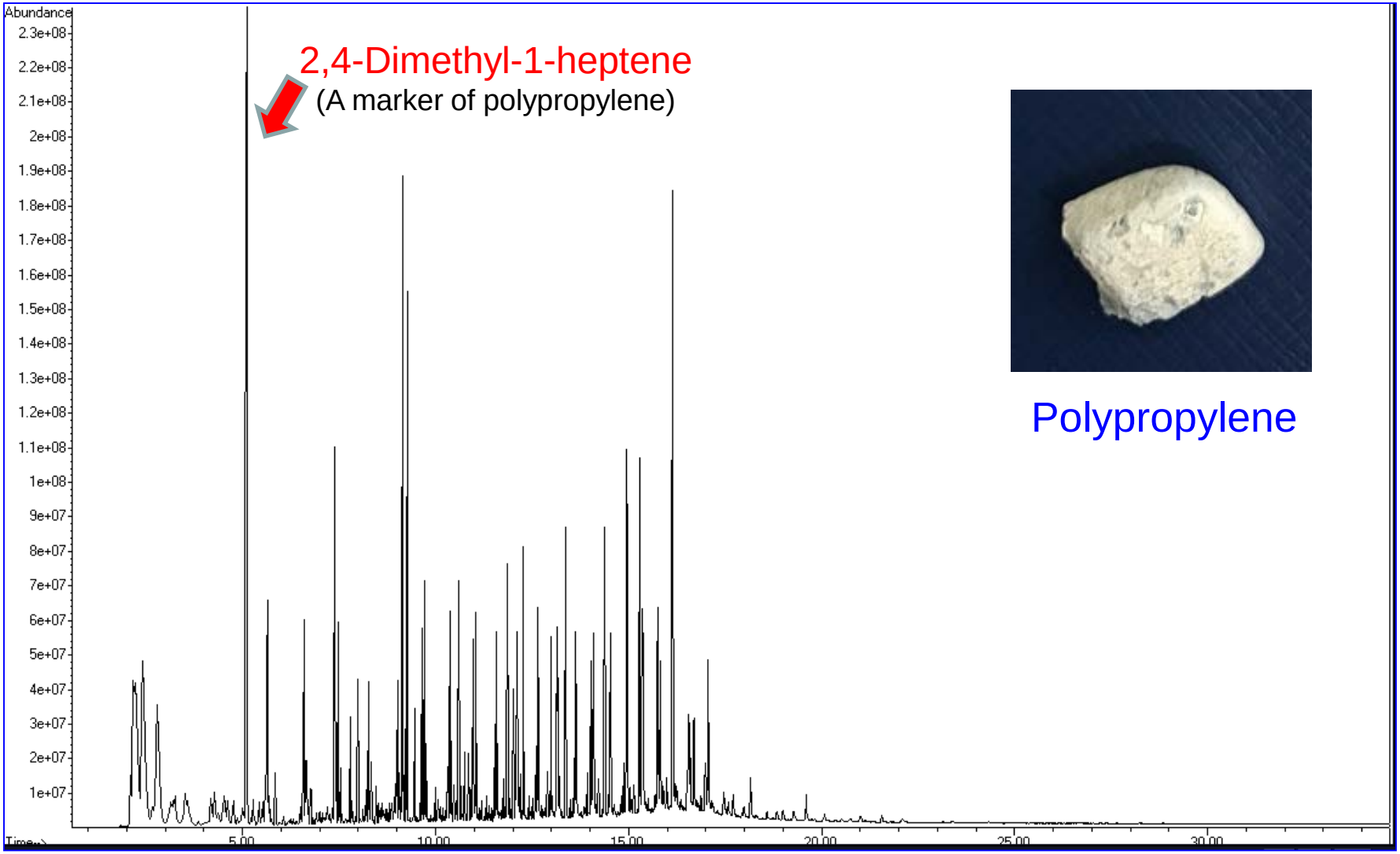




Microplastics in Sargassum Mats

Dr. Frank Hernandez
University of Southern Mississippi

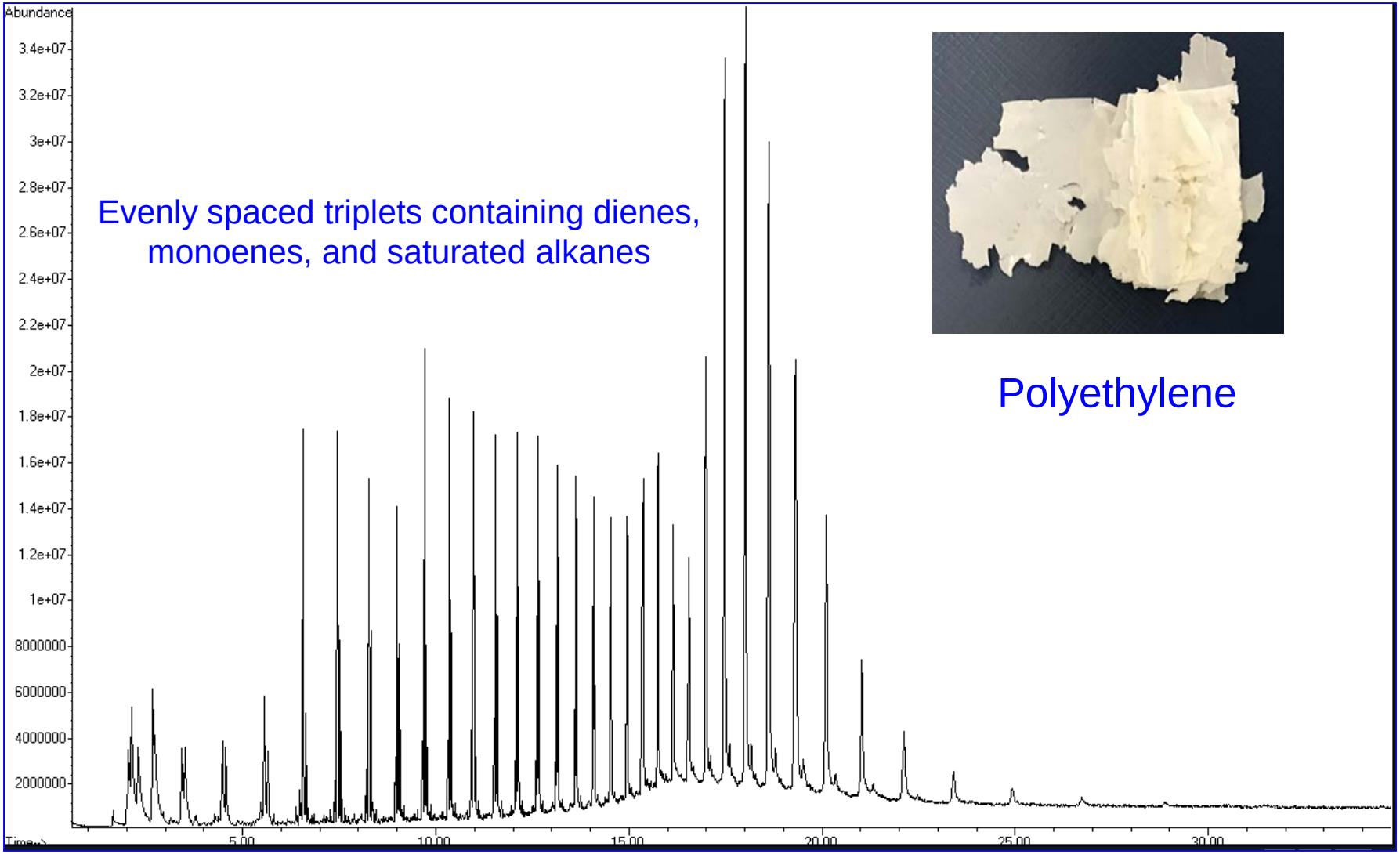
NOAA Restore Cruise PS-17-07 Sample 7



Polypropylene

Gulf of Mexico Surface Water Dip Net

NOAA Restore Cruise PS-17-07 Sample 3



Polyethylene

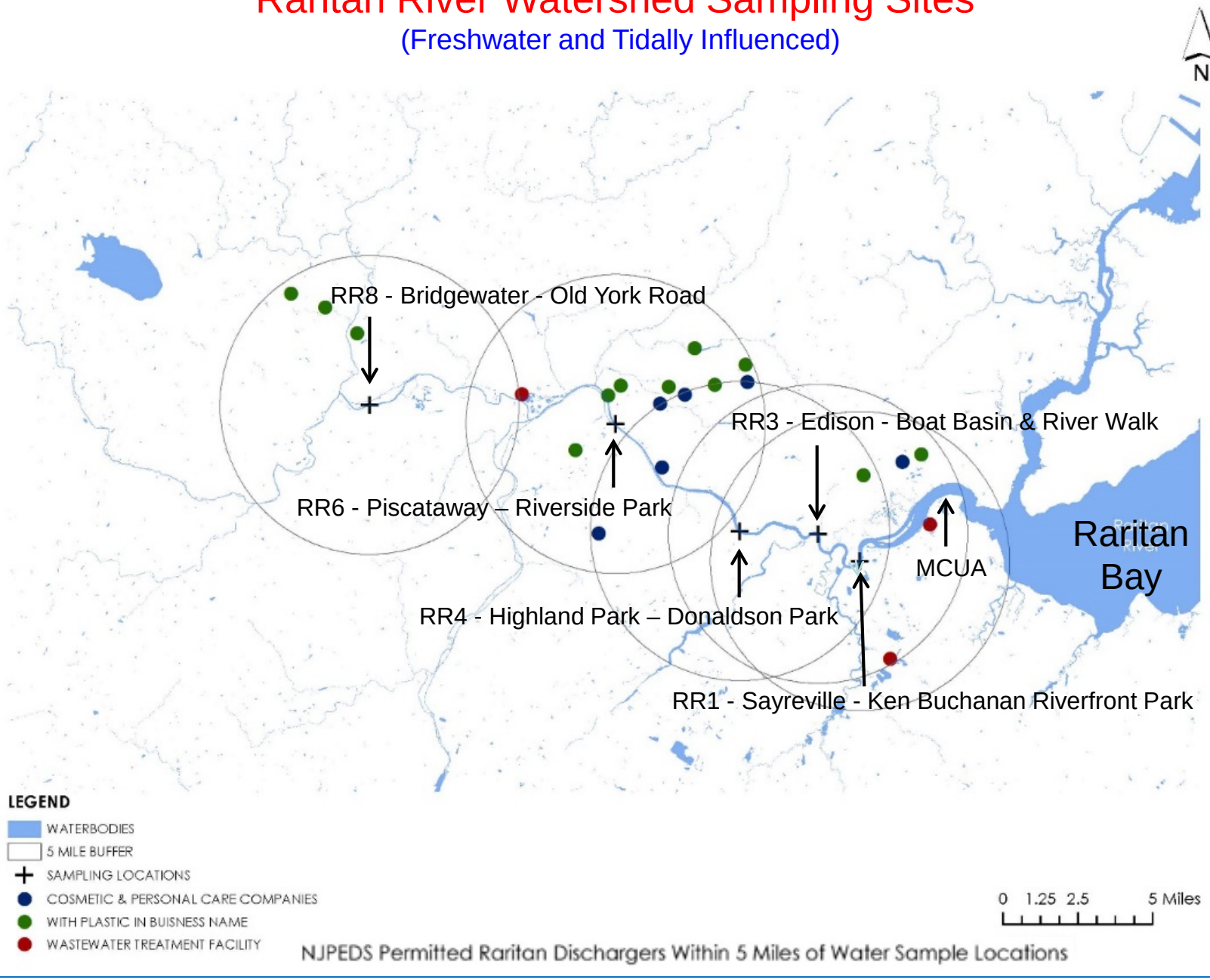
Gulf of Mexico Surface Water Dip Net


Proof of
Concept

NOAA-Rutgers University Collaborative Study

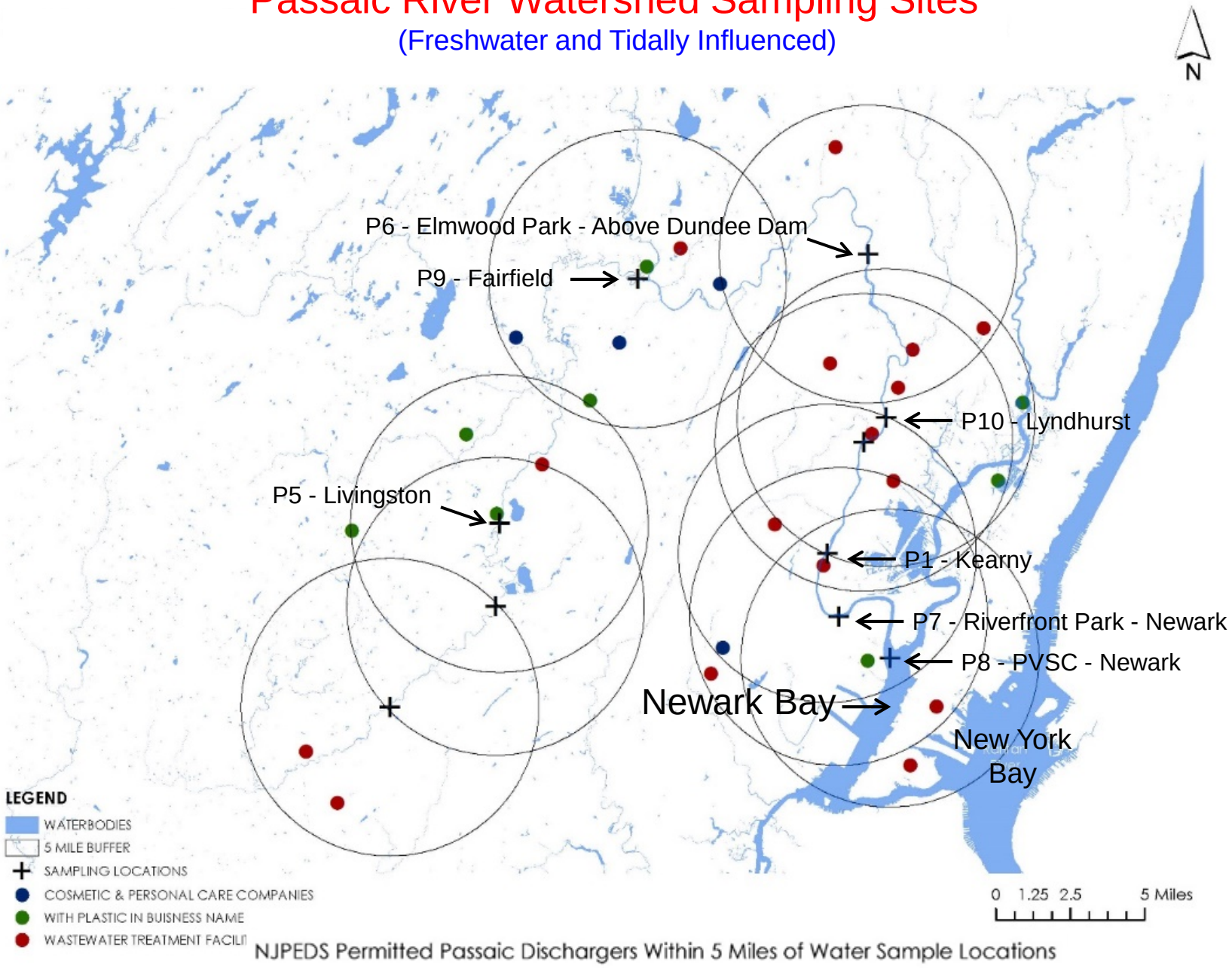
Raritan River Watershed Sampling Sites

(Freshwater and Tidally Influenced)



Passaic River Watershed Sampling Sites

(Freshwater and Tidally Influenced)



Microplastics Sampling

- River Sampling: At each location, and in each river, a 330µ mesh manta trawl net was held in a stationary position at water surface for fifteen minutes.
- Bay Sampling: Bay samples were collected by pulling the manta trawl net with the attached flow meter with a boat.
- Collected sample was filtered to remove the materials larger than 330µ.

Two types of climate-related samples were collected:

- Dry Samples: These samples were collected under dry weather conditions - defined as a period without rain for at least 48 hours.

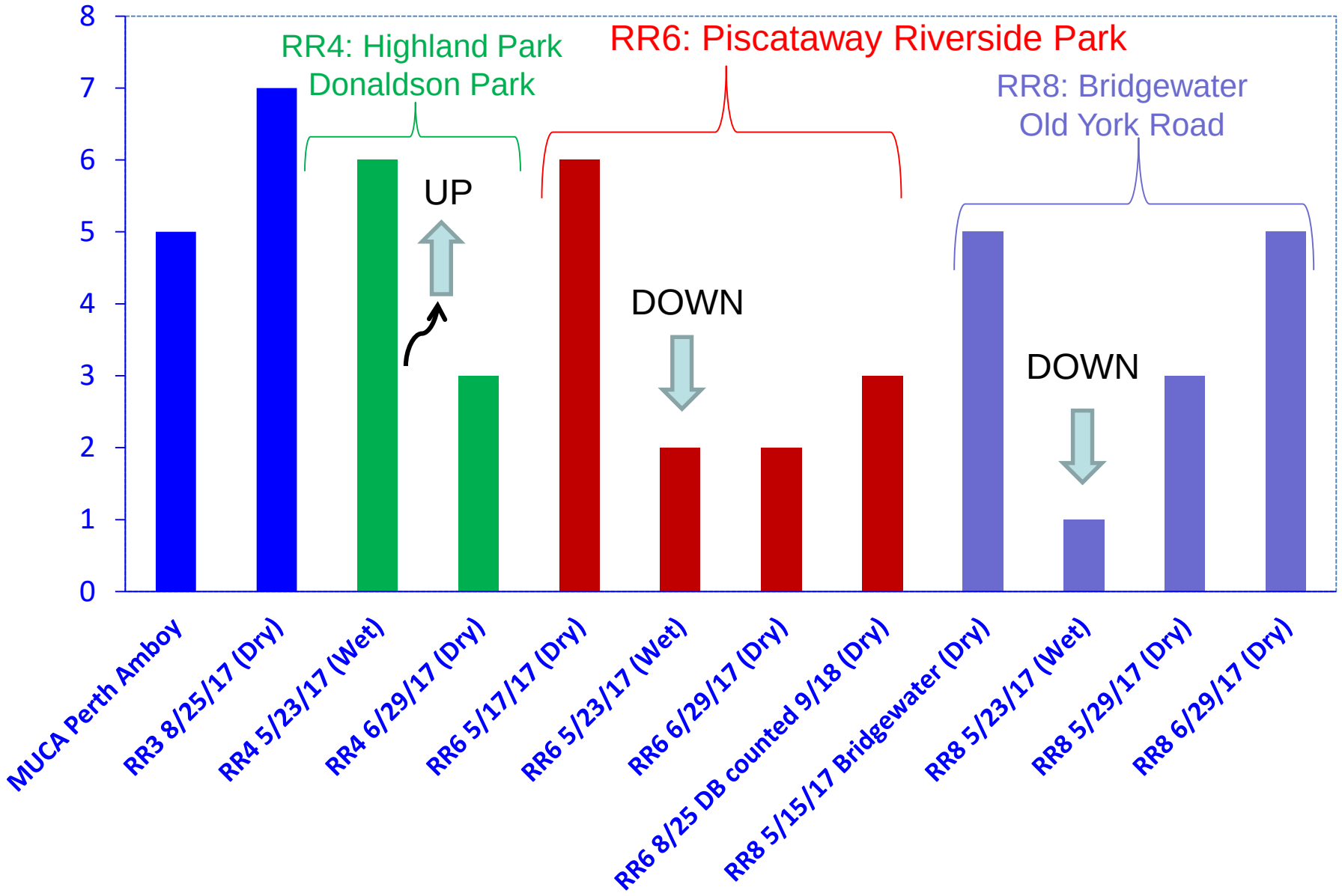
- Wet Samples: These samples were collected under wet weather conditions - defined as a period of 24 hours or less after a rain event of 2.2 cm.

Selection of Sites for the Pyrolysis GC-MS Analyses:

- Microplastics samples were first analyzed for the persistent organic pollutants (POPs) by Dr. Brian Buckley's Laboratory by using headspace solid-phase micro-extraction coupled with gas chromatography/ion-trap mass spectrometry (HS-SPME/GC-ITMS).

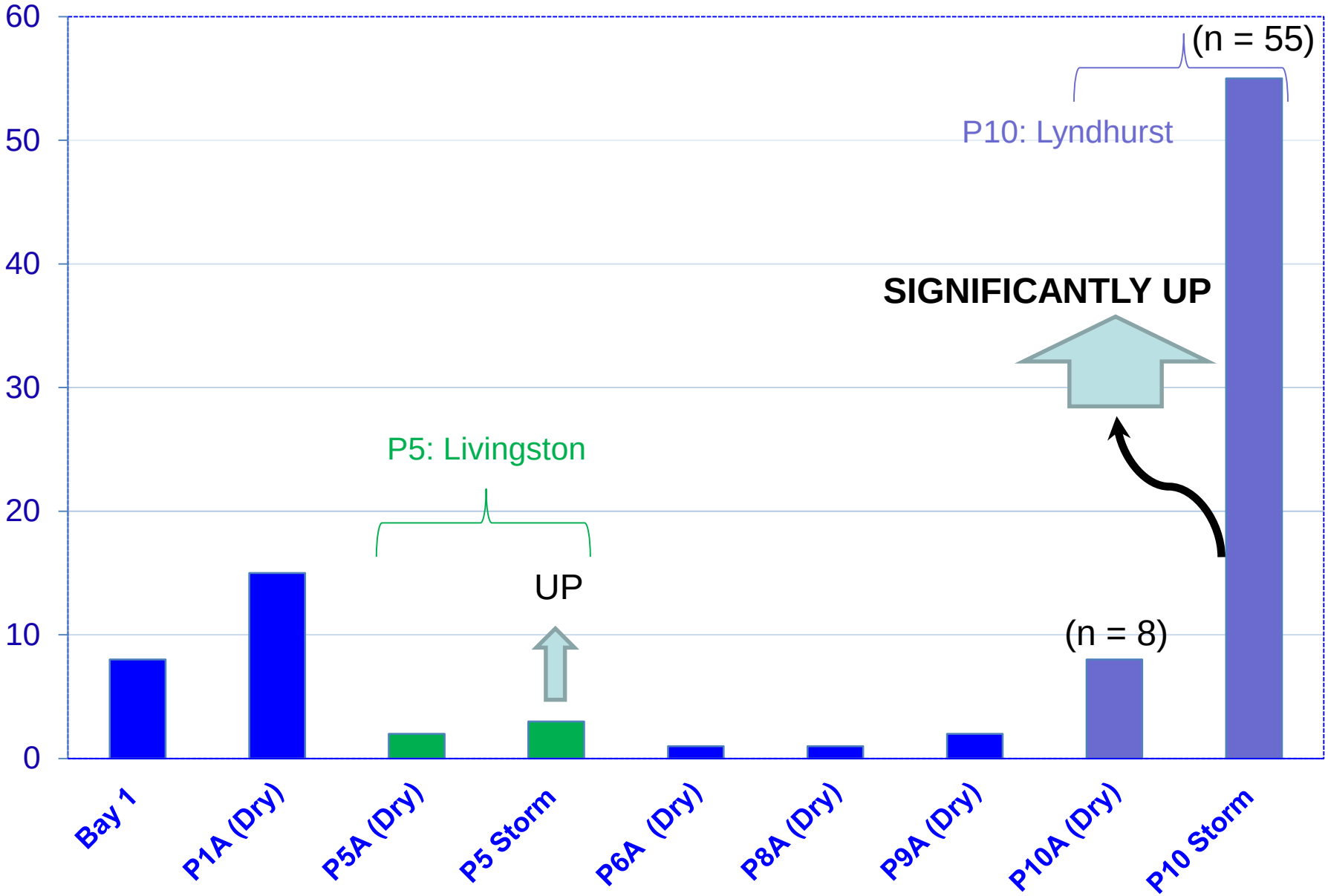
- Pyrolysis GC-MS analyses were then performed on a total of 143 microplastics samples from those locations that showed the elevated levels of adsorbed POPs in the HS-SPME/GC-ITMS analyses.

Number of Microplastics Analyzed for Each Raritan River Location



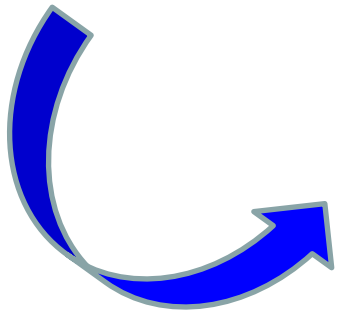
No particular trend was observed in the mobilization of microplastics due to the wet weather.

No. of Microplastics Analyzed for Each Passaic River Location

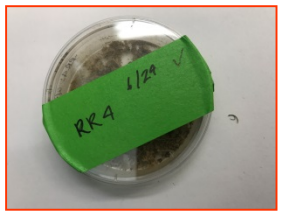


Number of microplastics at Lyndhurst appeared to be highly significantly mobilized due to wet weather.

A few examples of microplastics pyrograms..

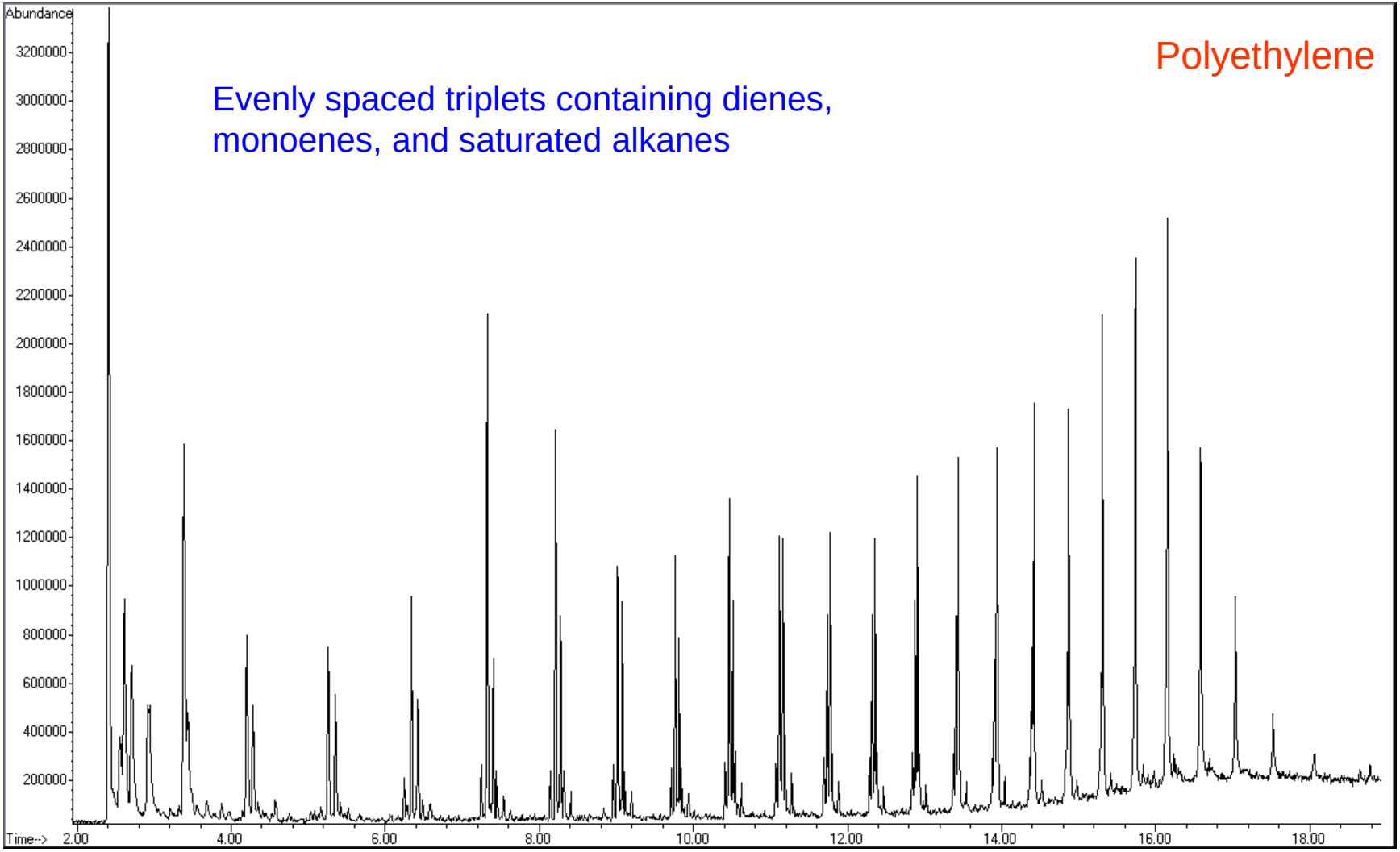


Rutgers Sample RR4 6/29
Tiny greenish blue fragment/fiber



Polyethylene

Evenly spaced triplets containing dienes, monoenes, and saturated alkanes



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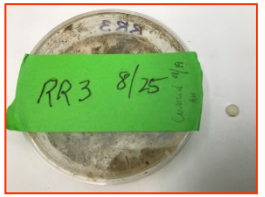
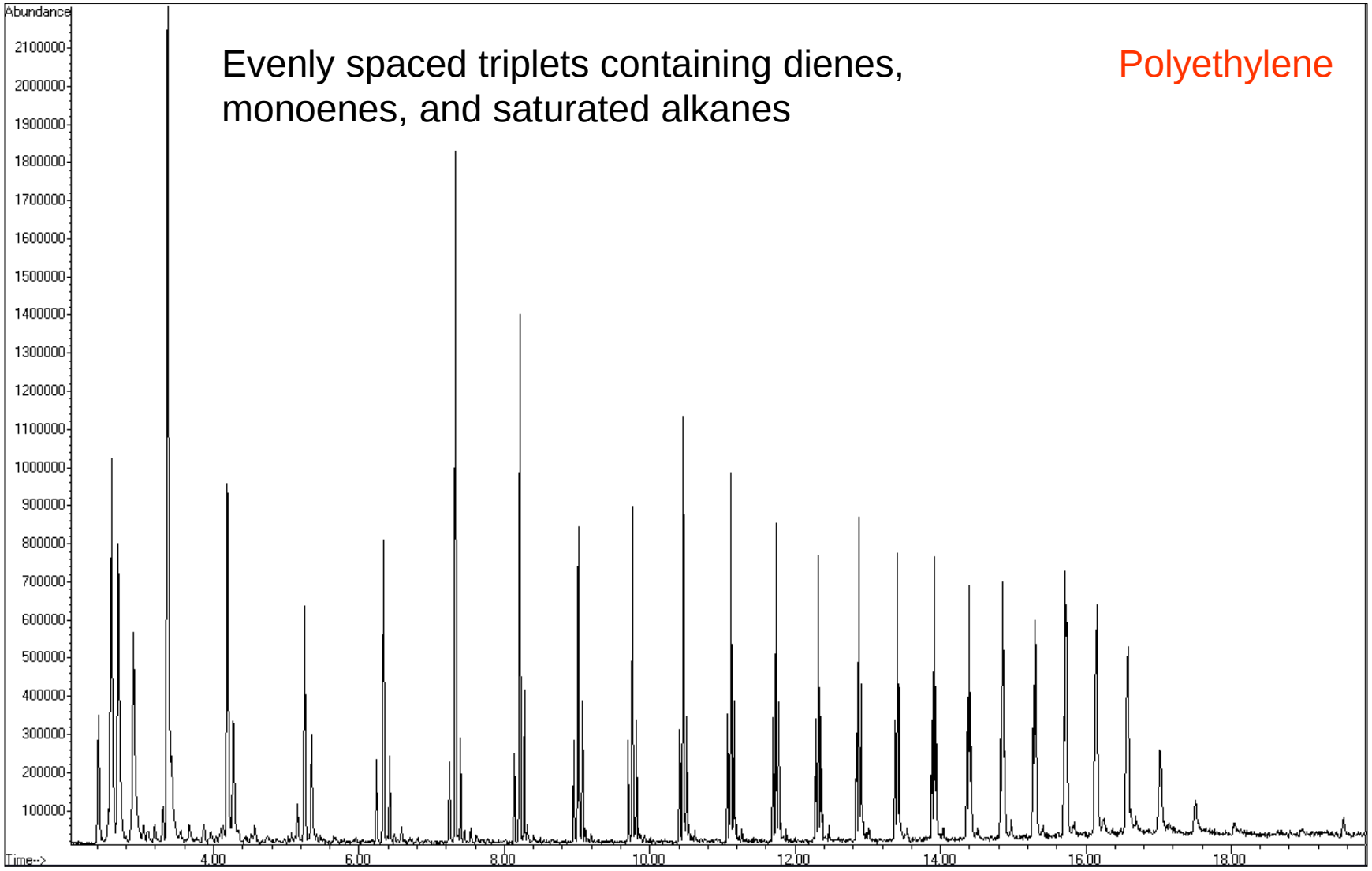
Rutgers Sample RR3 8/25
off-white nurdle



Evenly spaced triplets containing dienes, monoenes, and saturated alkanes

Polyethylene



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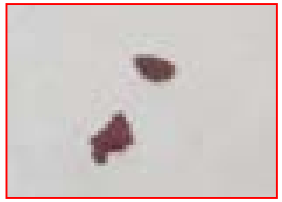
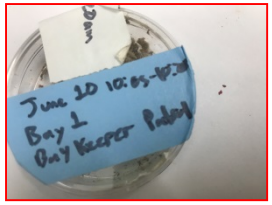


Rutgers Sample June 10 Bay 1 Baykeeper Patrol Boat
Orange brown plastic piece



Polypropylene

2,4-Dimethyl-1-heptene
(A marker compound of polypropylene)

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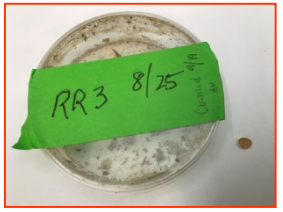
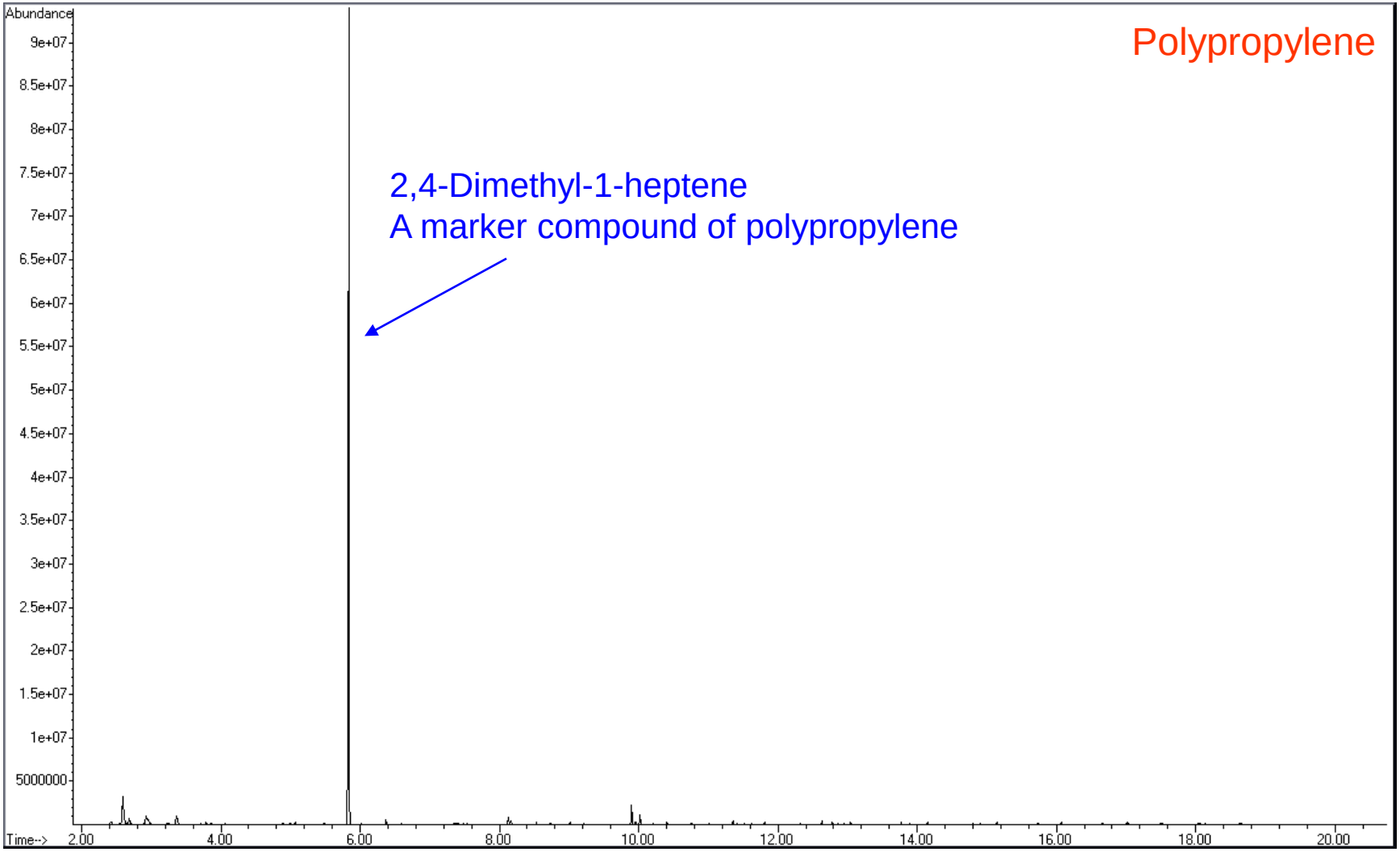
Rutgers Sample RR3 8/25
semi-transparent nurdle



Polypropylene

2,4-Dimethyl-1-heptene
A marker compound of polypropylene



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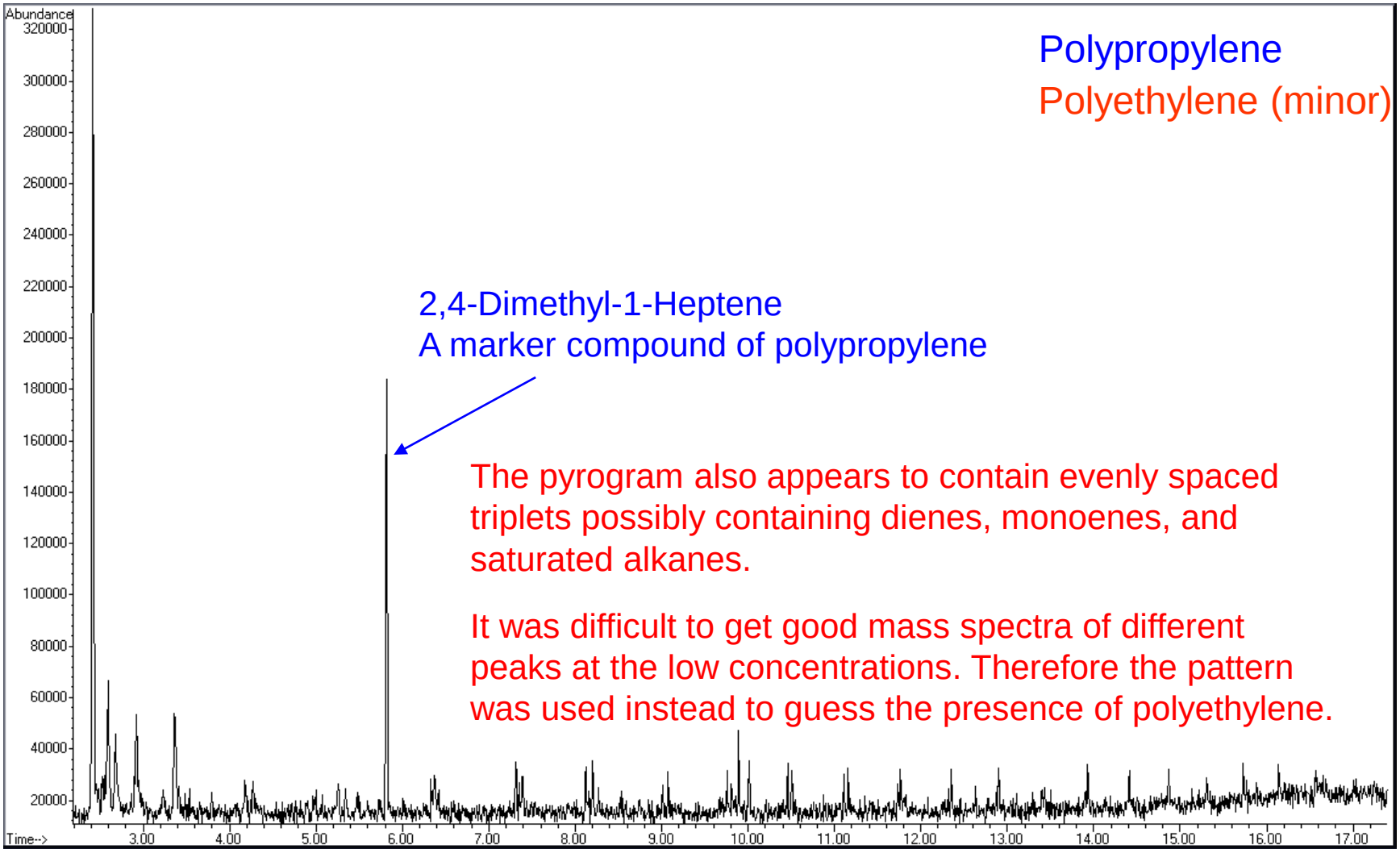
Rutgers Sample P5A
Soft off-white foam fragments



Polypropylene

Polyethylene (minor)

2,4-Dimethyl-1-Heptene
A marker compound of polypropylene

The pyrogram also appears to contain evenly spaced triplets possibly containing dienes, monoenes, and saturated alkanes.

It was difficult to get good mass spectra of different peaks at the low concentrations. Therefore the pattern was used instead to guess the presence of polyethylene.

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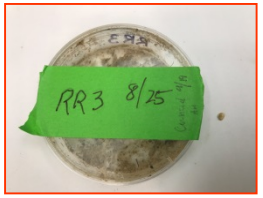
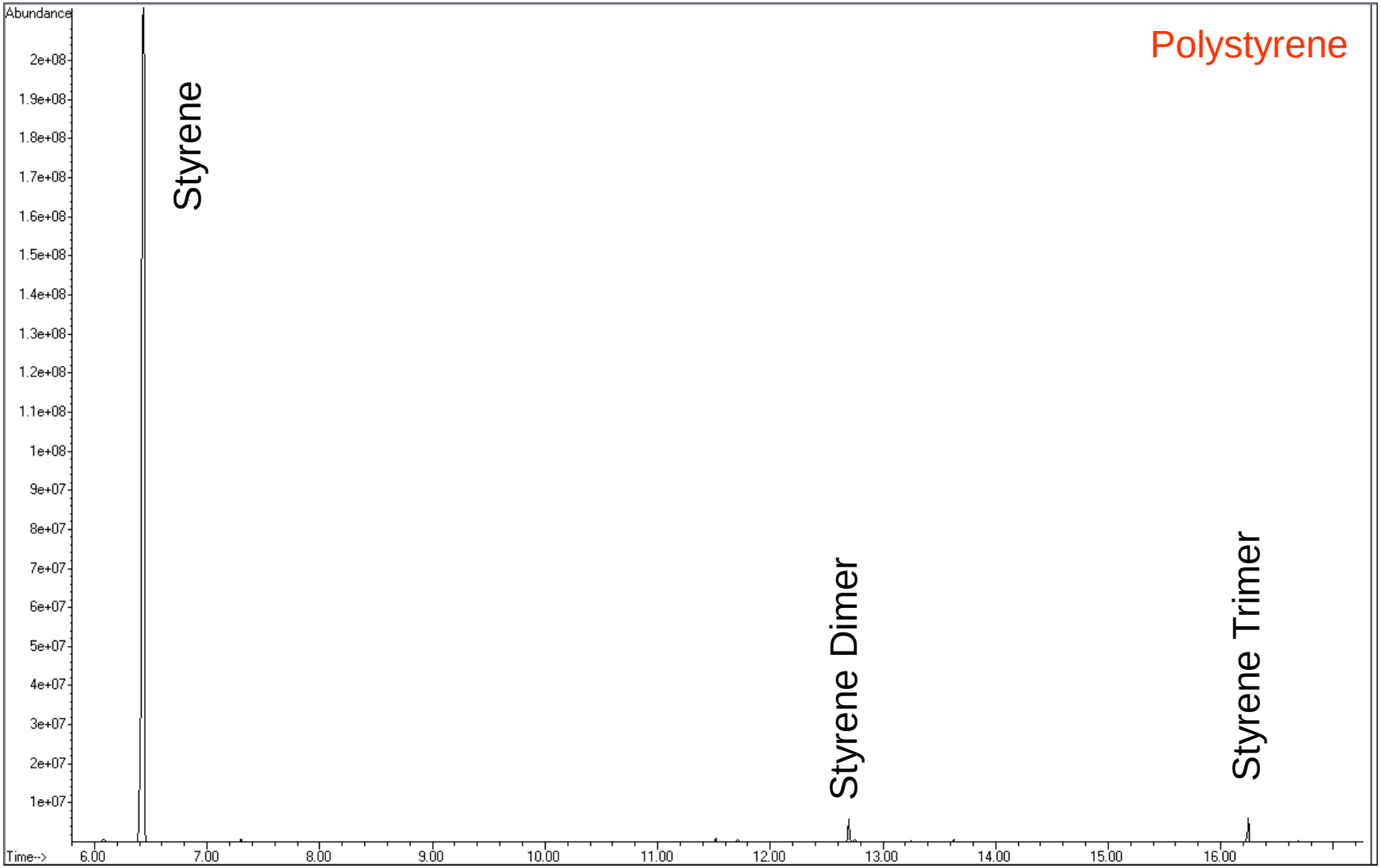
Rutgers Sample RR3 8/25
small round off-white foam



Polystyrene



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Rutgers Sample P10 Storm
pale yellow transparent film

Polyethylene terephthalate (PET)

Abundance
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00

Acetaldehyde
Benzene
Acetophenone
Vinyl benzoate
Benzoic acid
Phthalic anhydride
Divinyl terephthalate
4-(Vinyloxycarbonyl) benzoic acid

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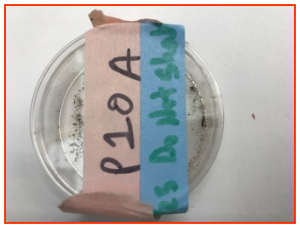
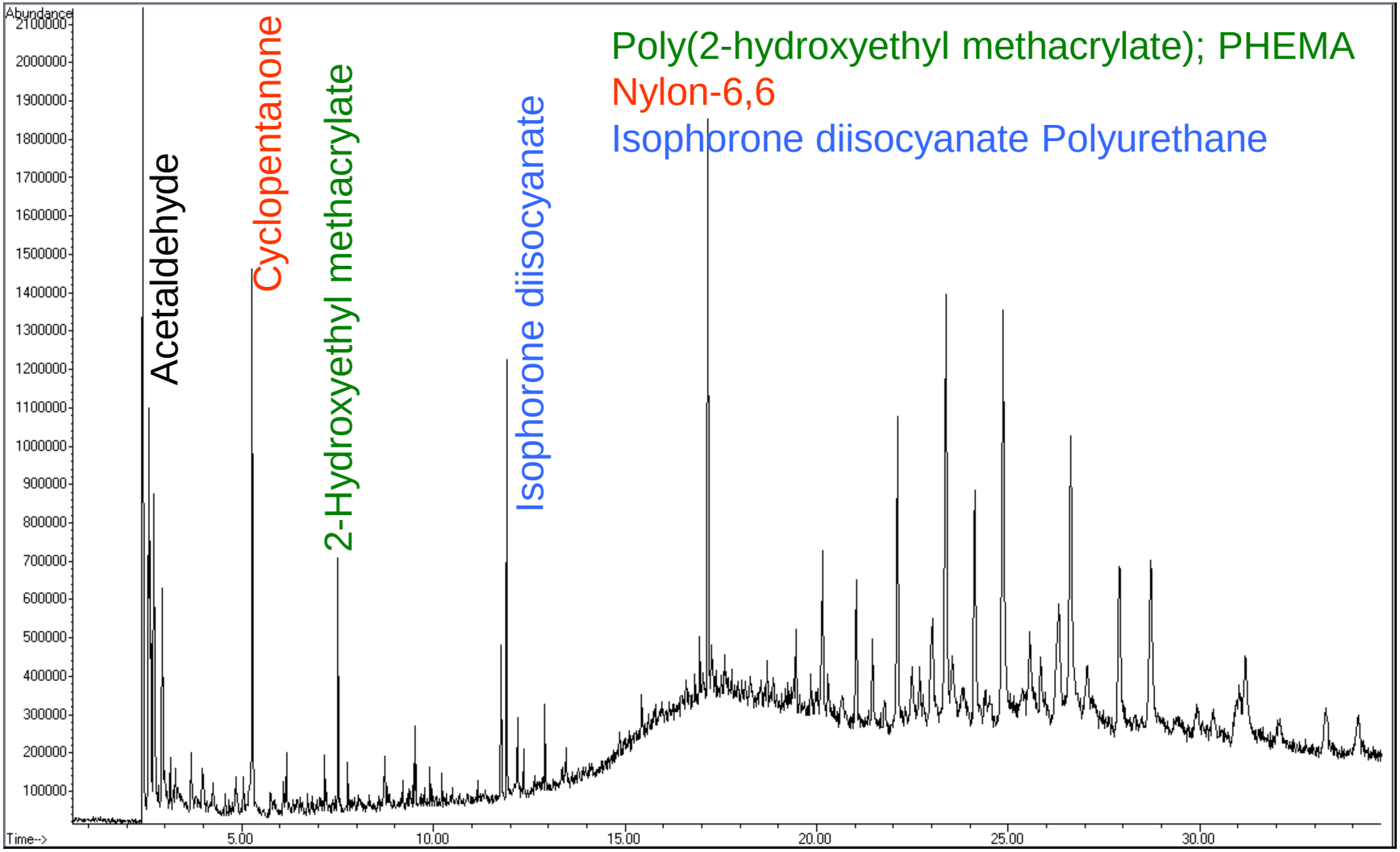
Rutgers Sample P10A
Very tiny red fragment





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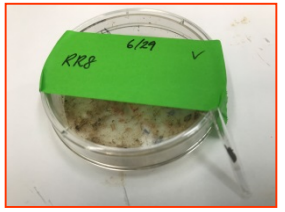
Rutgers Sample RR8 6/29
black thin peel



Polymethyl methacrylate; PMMA
Polybutyl acrylate; PBA

1-Butene
1-Butanol
Methyl methacrylate
n-Butyl acrylate
n-butanal
dibutyl glutarate
dibutyl 2-methylenepentanedioate (dimer)
tributyl hex-5-ene-1,3,5-tricarboxylate (trimer)

Abundance
900000
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
Time-->
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00

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Rutgers Sample RR8 5/15/17 Bridgewater
black peel

Cellulose
(+Polycarbonate?)

Bisphenol-A ?
Furfural
Xylene
2-Methylcyclopentanone
5-methyl furfural
Phenol
2-Methoxyphenol
Cresol
Levoglucosenone
Ethylphenol
4-Vinylphenol
3-methyl- ,2-benzenediol
2-Methoxy-4-vinylphenol
Levoglucosan

Abundance
Time-->

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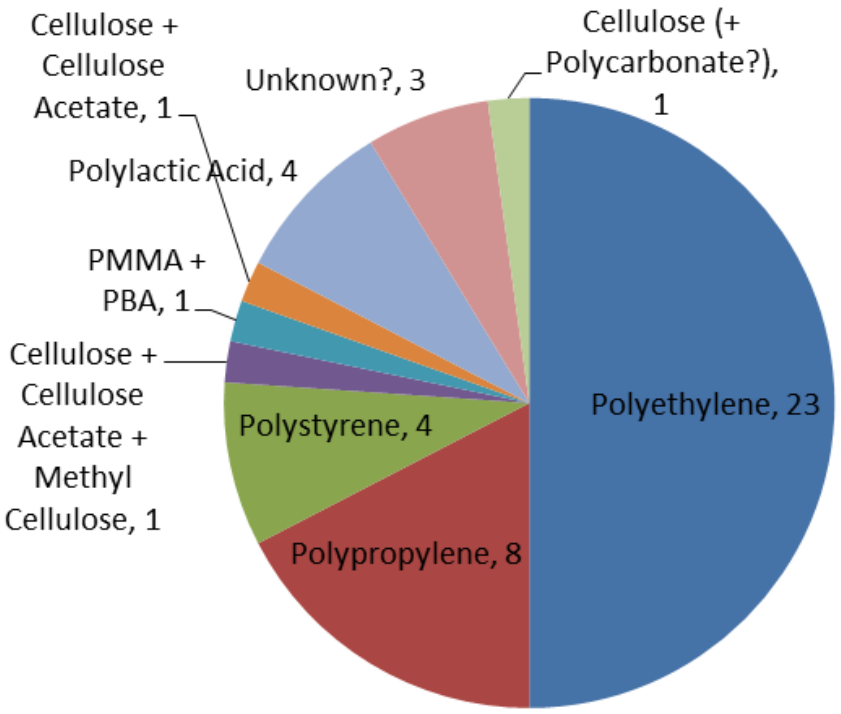
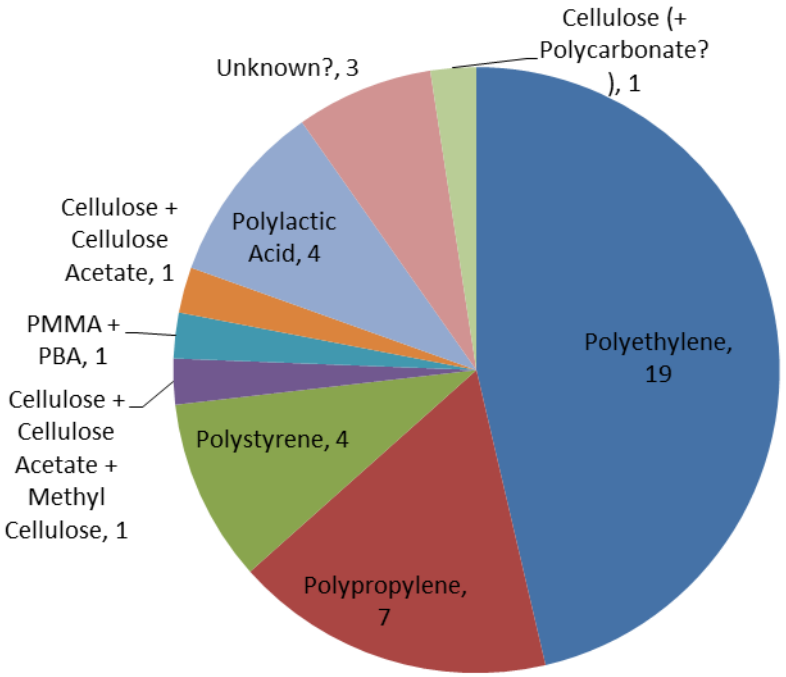
Quantitative Analyses

Microplastics in Raritan River/ MCUA System (n=46)



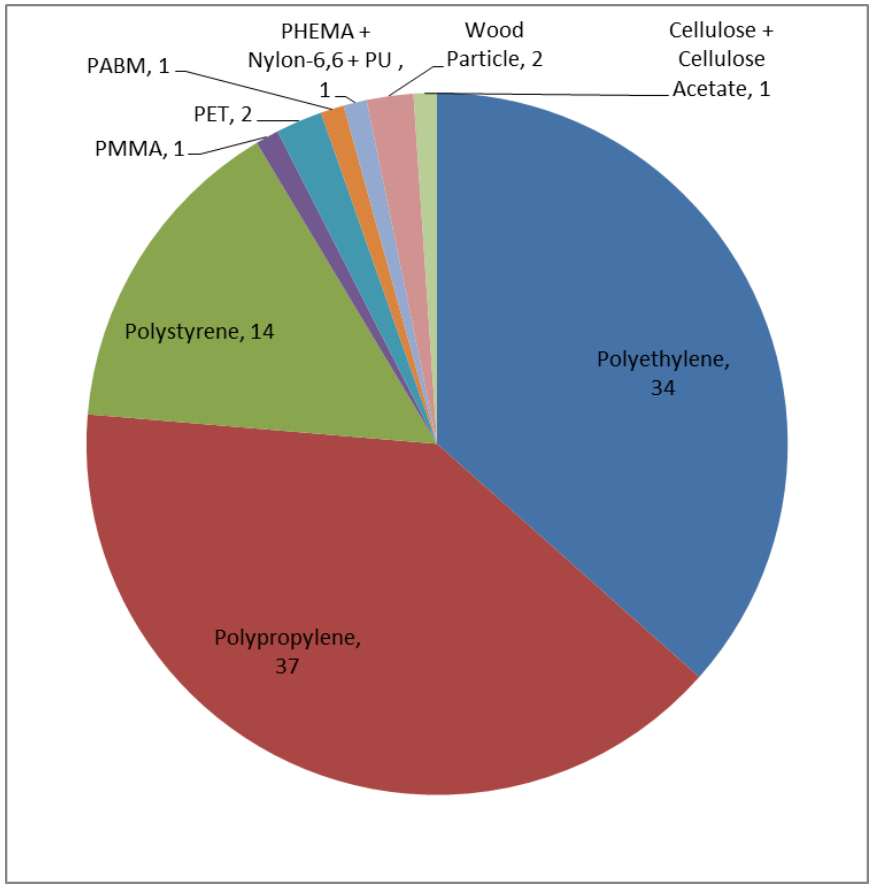
Microplastics in Raritan River/ (n=41)



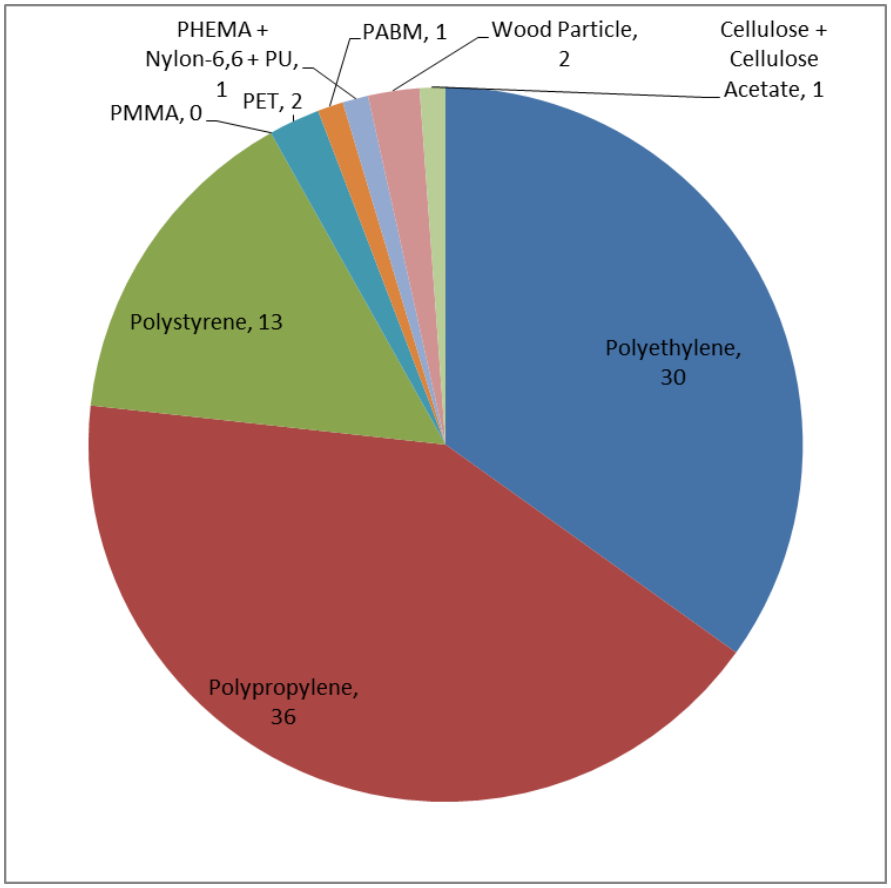
Polyethylene >>> Polypropylene >> Polystyrene

*if multiple pieces of polystyrene foams were encountered, not all were counted or analyzed

Microplastics in Passaic River/ Newark Bay System (n=92)



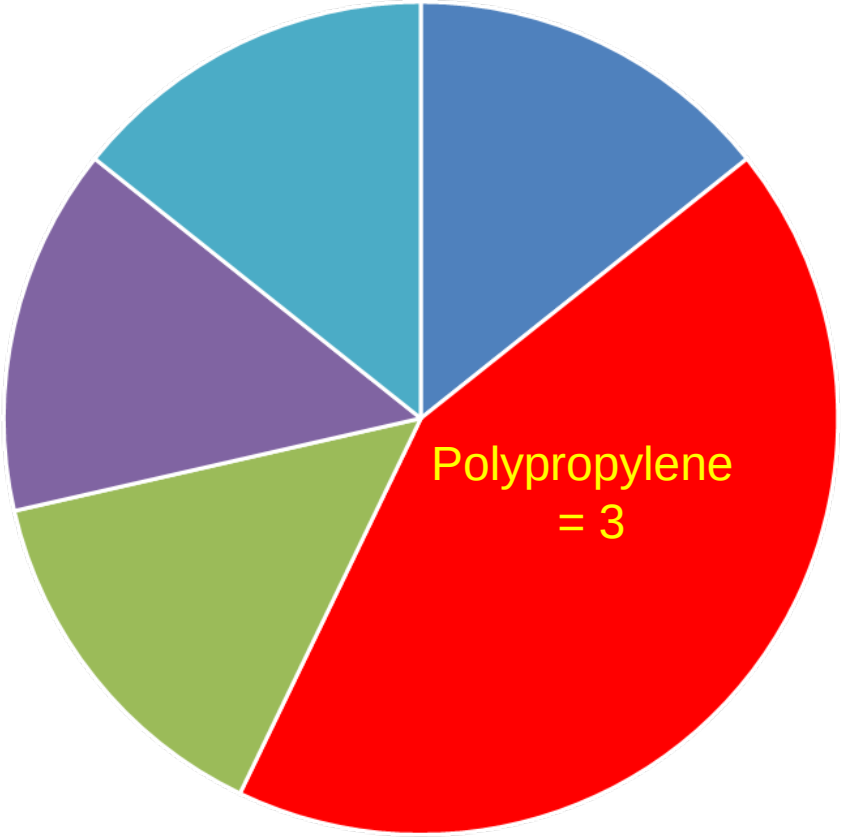
Microplastics in Passaic River (n=85)



Polypropylene ~ Polyethylene >> Polystyrene*

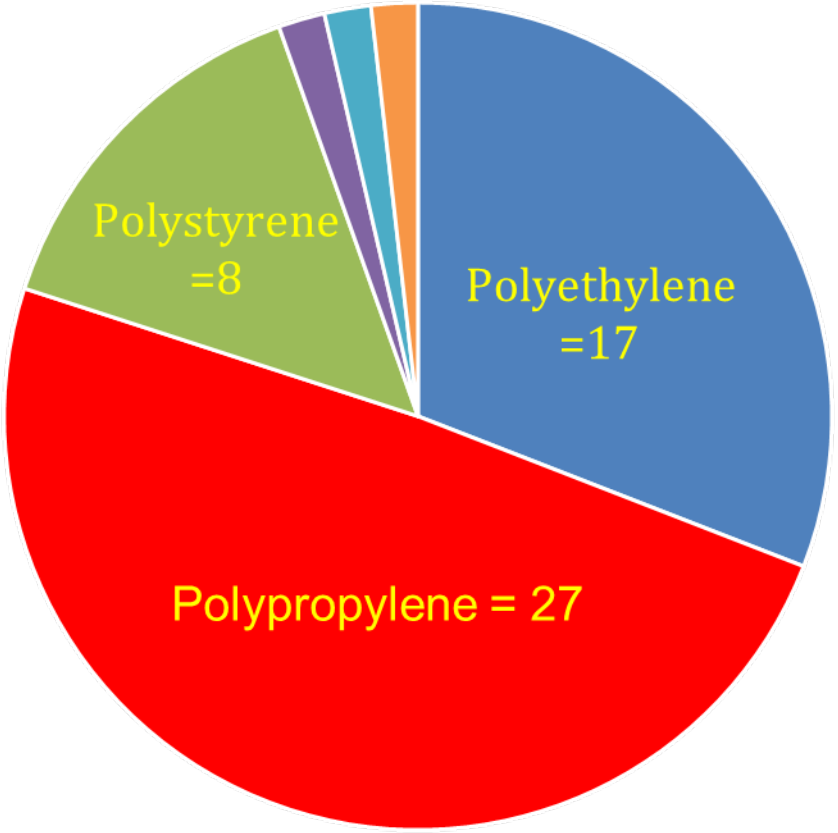
*if multiple pieces of polystyrene foams were encountered, not all were counted or analyzed

Polymers in P10 Dry Microplastics Samples Lyndhurst (n=8)



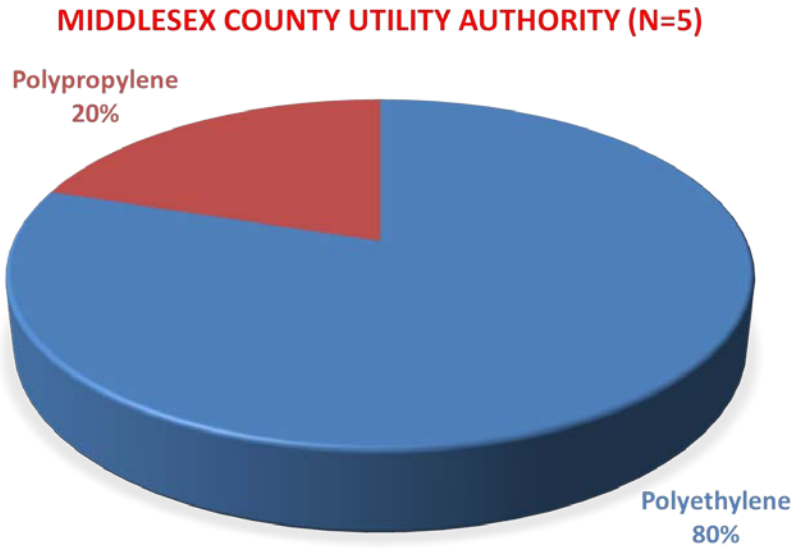
Minor Polymers: One each of Polyethylene; Polystyrene; Wood Fragment; Poly(2-hydroxyethyl methacrylate) (PHEMA) + Nylon-6,6 + Polyurethane of Isophorone diisocyanate; one unidentified polymer (not detected)

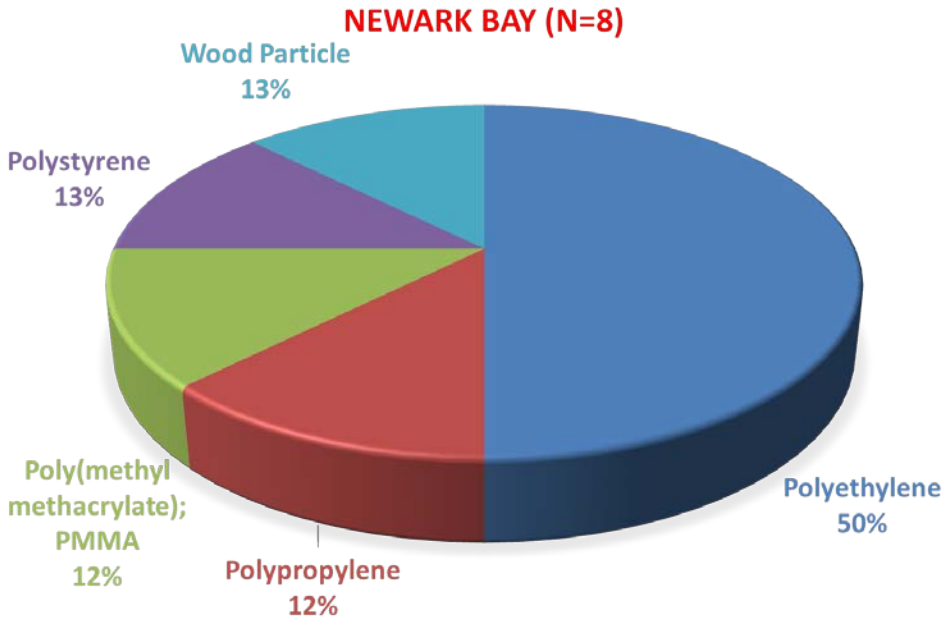
Polymers in P10 Storm Microplastics Samples Lyndhurst (n=55)



Minor Polymers: One each of Polyethylene terephthalate; Polyaminobismaleimide; Cellulose + Cellulose Acetate

During the storm events, polypropylene, polyethylene, and styrene appear to be significantly mobilized from the land-based sources in and around Lyndhurst area.





Polyethylene was prominent polymer in both water bodies.

-- Sinkers and Floaters --

Specific gravity of plastics and different water types, and common applications of plastics found in the marine environment

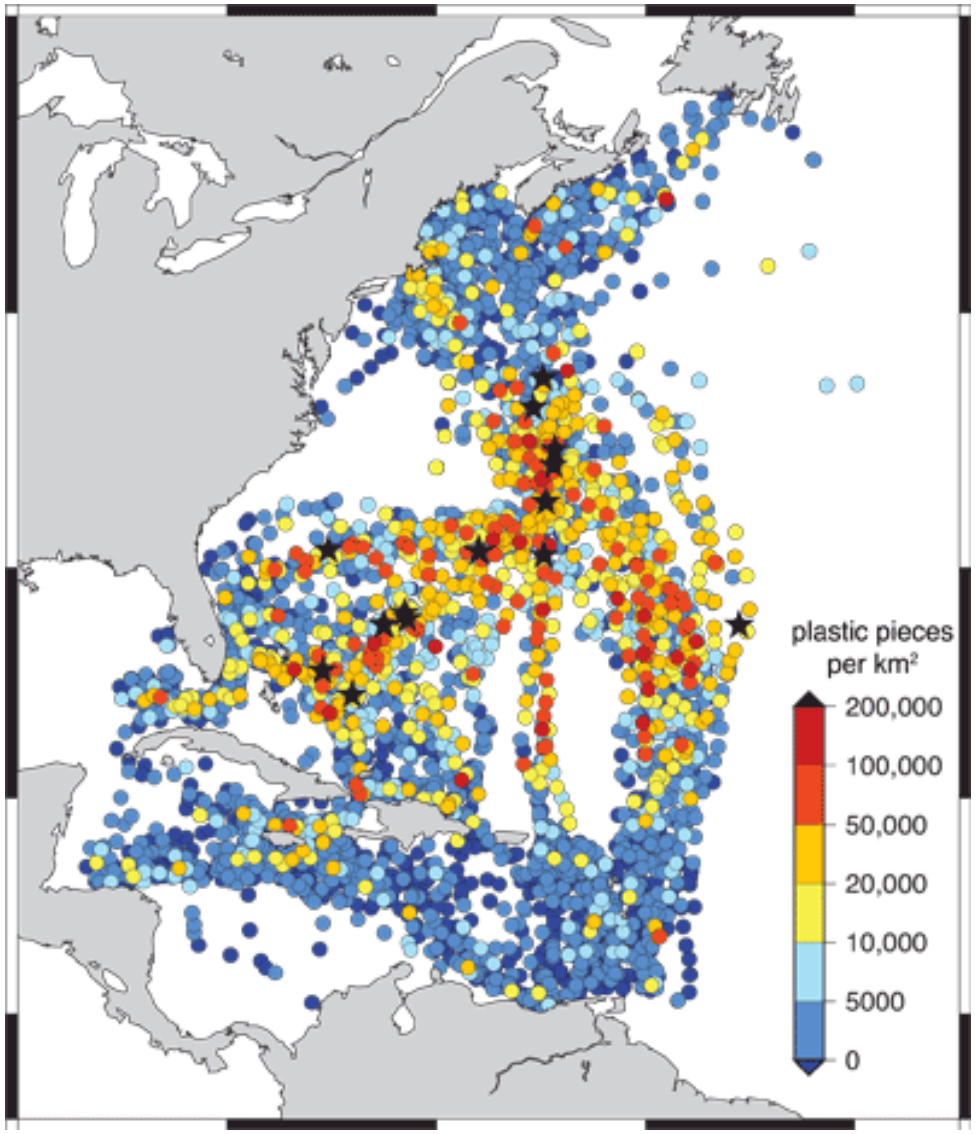
	Plastic type	Common applications	Specific gravity*
Floaters	Polyethylene	Plastic bags, storage containers	0.91–0.95
	Polypropylene	Rope, bottle caps, fishing gears, strapping	0.90–0.92
	Polystyrene (expanded)	Cool boxes, floats, cups	1.01–1.05
Sinkers	Polystyrene	Utensils, containers	1.04–1.09
	Polyvinyl chloride	Film, pipe, containers	1.16–1.30
	Polyamide or Nylon	Fishing nets, rope	1.13–1.15
	Poly(ethylene terephthalate)	Bottles, strapping, textiles	1.34–1.39
	Polyester resin + glass fibre	Textiles, boats	>1.35
	Cellulose Acetate	Cigarette filters	1.22–1.24
	Pure water		1.000
	Sea water		1.027
	Brackish water		1.005-1.012

Source: GESAMP, 2015

* Specific gravity is the ratio of the density of a material to that of pure water at 4°C

- Microplastics collected for this study were surface samples.
- Therefore, the presence of lighter polymers like polyethylene, propylene, and expanded polystyrene was not too surprising.

Distribution of plastic marine debris collected in 6136 surface plankton net tows from 1986-2008 in the western North Atlantic Ocean and Caribbean Sea.



Kara Lavender Law, Skye Moret-Ferguson, Nikolai A. Maximenko, Giora Proskurowski, Emily E. Peacock, Jan Hafner, and Christopher M. Reddy. Plastic Accumulation in the North Atlantic Subtropical Gyre. Science, 2010; DOI: 10.1126/science.1192321

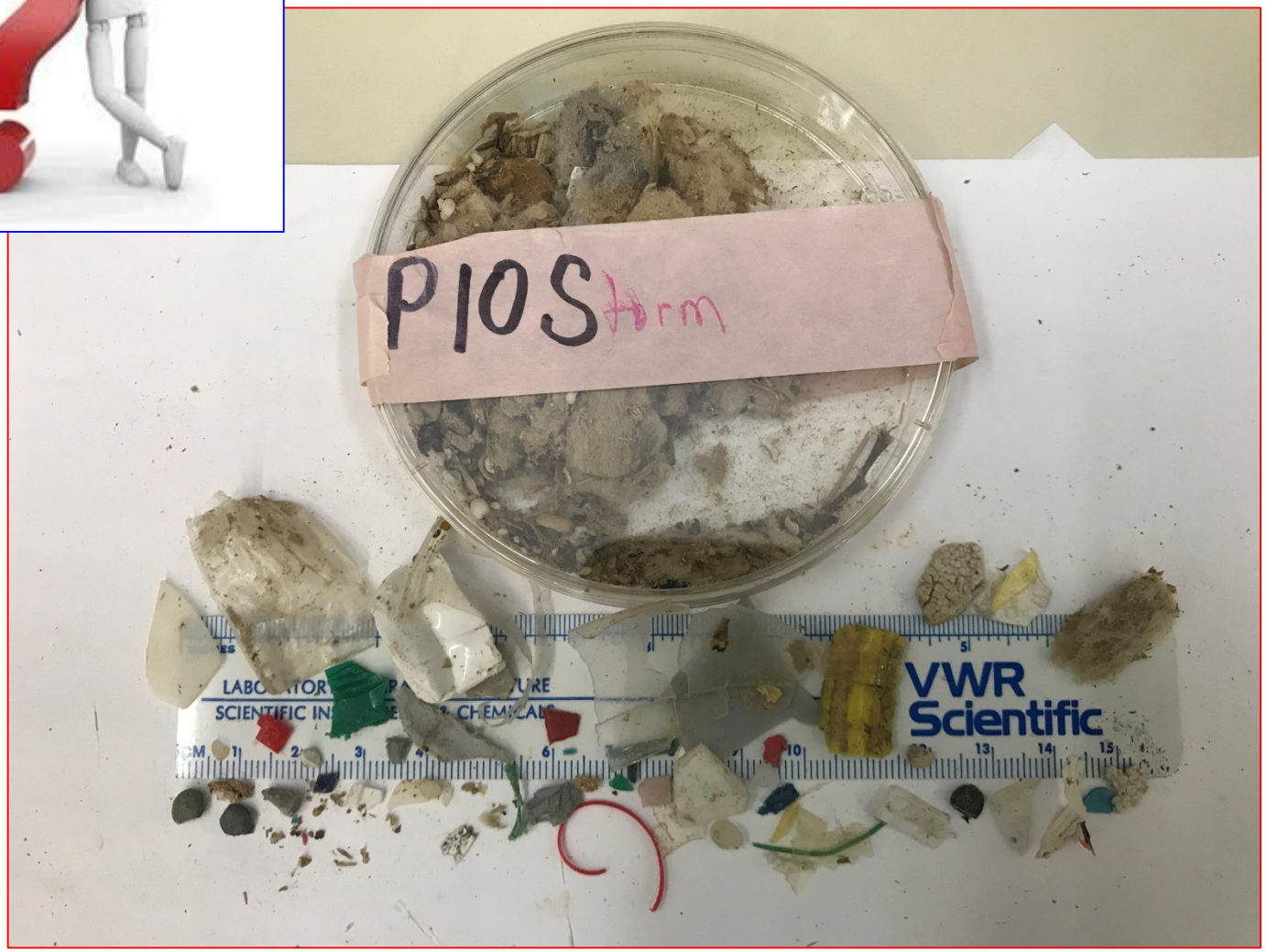
Question: Since these were surface water microplastics samples, it would be interesting and important to know how representative are these microplastics polymers of the respective river ecosystems?

Do they represent:

- Surface water only?
- Entire water column?
- Bottom water?
- Bottom sediments?

Future Research:

- Density-based microplastics polymer distribution, and abundance in the upper, middle and deeper sections of water column.
- Chronology of microplastics deposition in the sediment cores.
- Temporal and seasonal trends in polymer composition - this information could shed light on the diversity of microplastics sources.



Microplastics found in Passaic River at Lyndhurst, NJ after a storm event..