TNI Environmental Measurement Symposium
Garden Grove, California

August 5th, 2024

Challenges and Opportunities to Forensic Approaches in Microplastics

Kelsey Rousteau[1], Scott A. Stout[1], and Jeffery H Hardenstine[1]

[1]*NewFields Environmental Forensics*

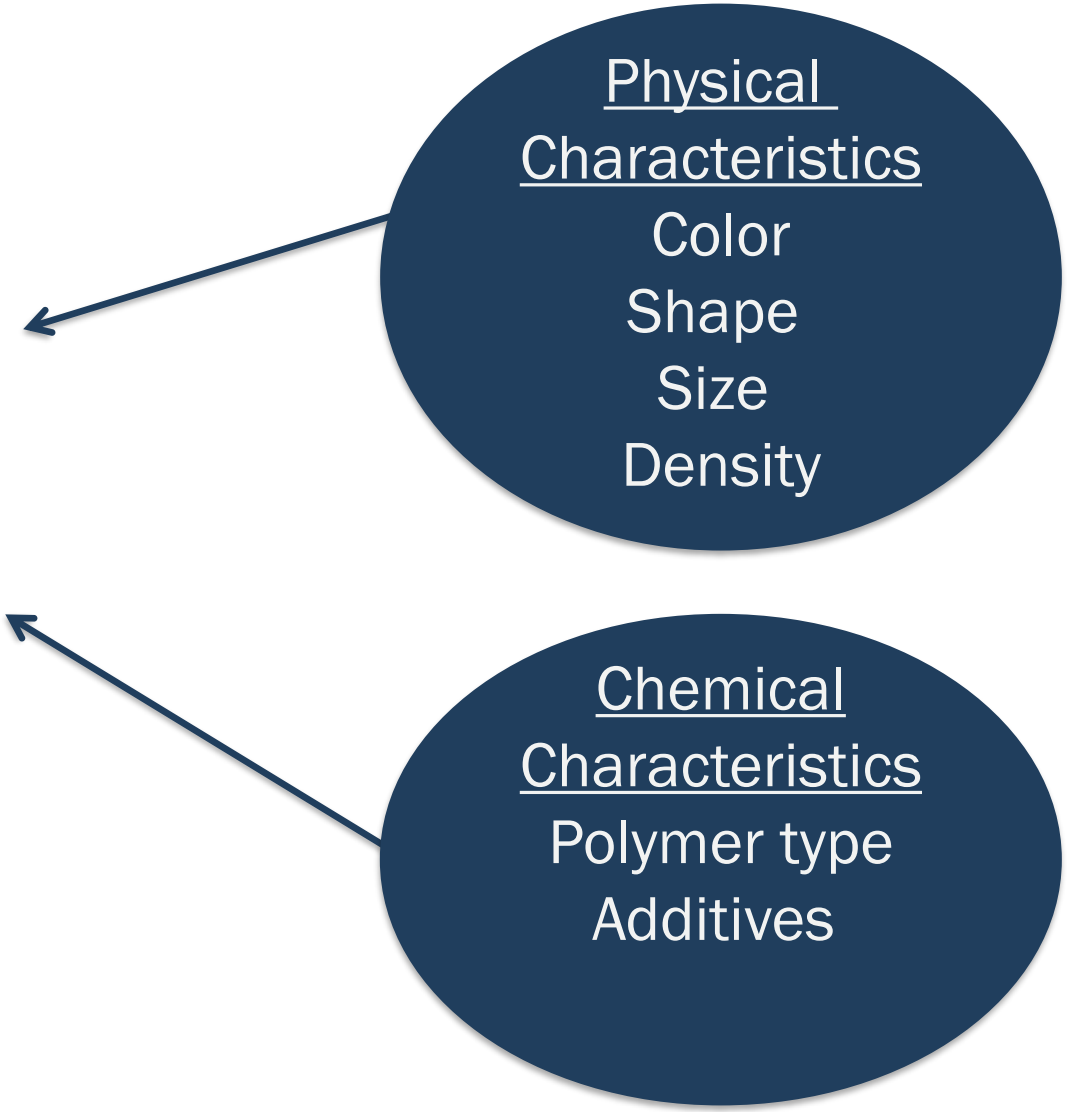
NewFields

How many pieces of plastic do you have on you?

Famara Beach, Lanzarote, Canary Islands, Spain

Forensic Questions

- Age
- Original Material
- Source Location
- Who made it?



The Tiered Approach to Forensics

Photo credit: K Rousteau

- Tiered approach to build up the basics of plastics fingerprinting
- Follow similar approach used historically in developing and applying fingerprinting of other contaminants, e.g., PAHs and PCBs

Tier I: conventional analyses of known and unknown plastics
Tier II: analyses of microplastics and environmental plastic samples
Tier III: exploring pyrolysis/ high resolution analytical methods

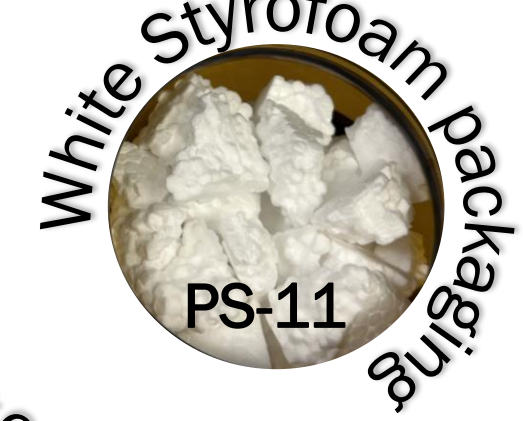
Current Focus (Tier I): What kind of forensic information can be obtained from plastics through conventional, commercially available methods?

Samples

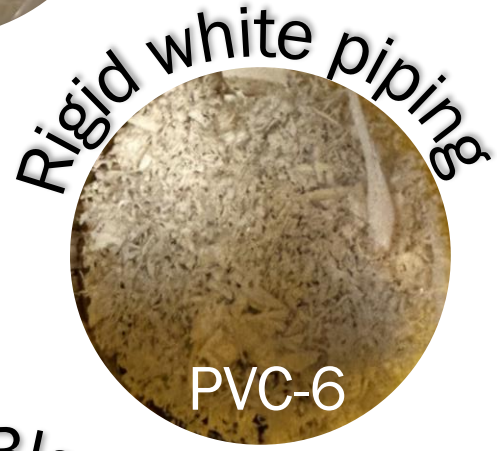

Fleece Blanket
PET-3


Clear shopping bag
HDPE-4


Clear plastic bag
LDPE-8


White Styrofoam packaging
PS-11


Frozen food container
PET-2

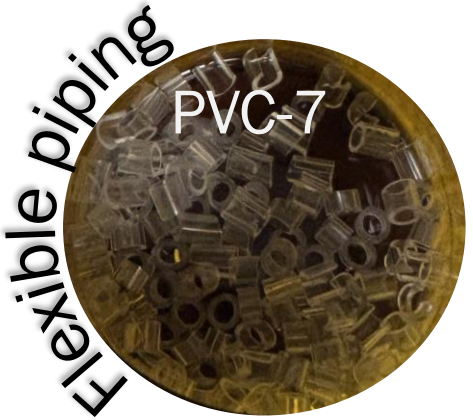

Rigid white piping
PVC-6


Multi-colored printed plastic bag
LDPE-9


Clear Polystyrene cups
PS-12


Clear salad container
PET-1


Black Shopping bag
HDPE-5


Flexible piping
PVC-7


White Nylon Rope
Nylon-13

Methods

- Cut films into strips and hard plastics into 1x1cm squares
- Microscale solvent extraction with DCM
  - Timing: 4 hours; 1 hour; 30 minutes
- Extracts filtered through sodium sulfate funnels
- Gravimetric weight measured to determine yield
- Extracts analyzed by Full Scan GC-MS
  - Prep and analysis by Pace Alpha Labs in Mansfield, MA
- Conventional FTIR analysis
  - McCrone Associates (not shown here)

Microscale Solvent Extractions with DCM

Sample ID	Percent Sample Wt Extracted
PET-1	0.39
PET-2	0.32
PET-3	1.42
HDPE-4	0.42
HDPE-5	0.32
PVC-6	26.02
PVC-7	9.80
LDPE-8	0.73
LDPE-9	1.07
PP-10	0.30
PS-11	55.90
PS-12	10.16
Nylon-13	0.53

Chromatograms and Peak Identification

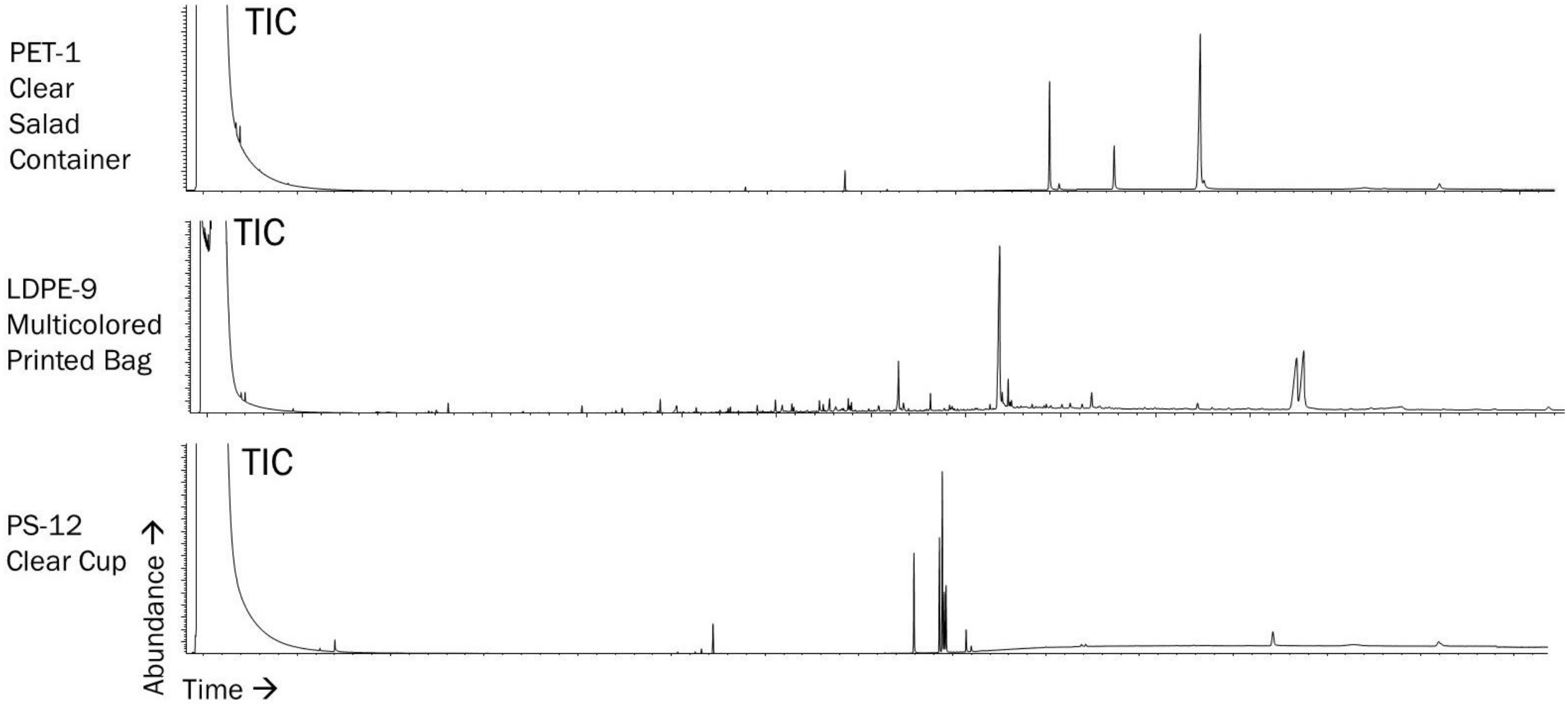
Chromatograms:

- GC resolution carbon range C5 to ~C45
- MS scan range 35 to 450 amu; 70 eV EI
- Also analyzed a North Slope Crude oil as a retention time standard and method (solvent) blank for QC

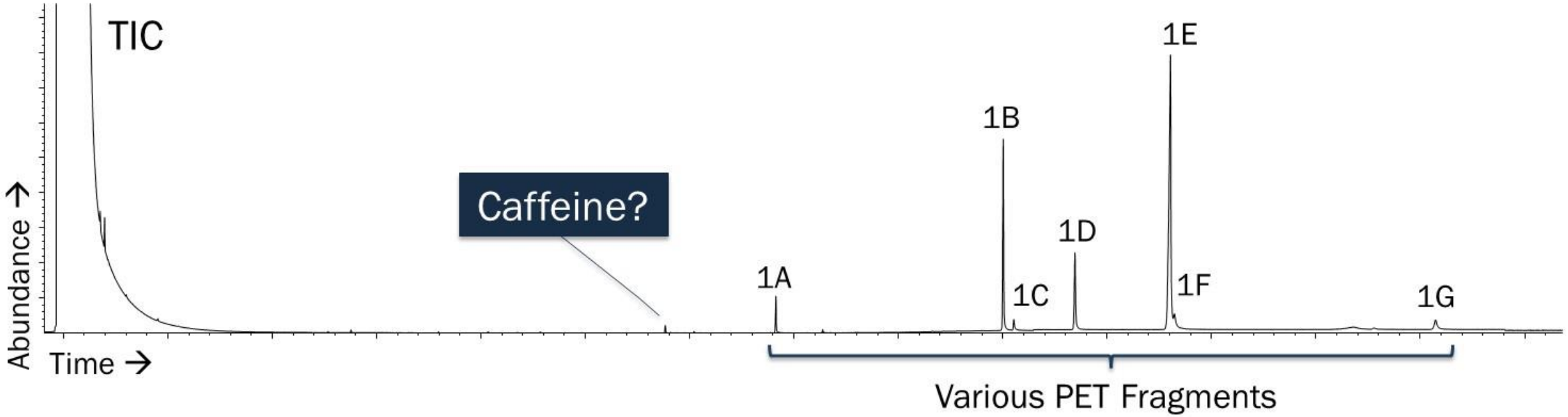
Extractable Compounds Identification:

- NIST library matches >90%
- Tentatively identification via spectral interpretation and comparison of ion fragments to available plastic extractables literature

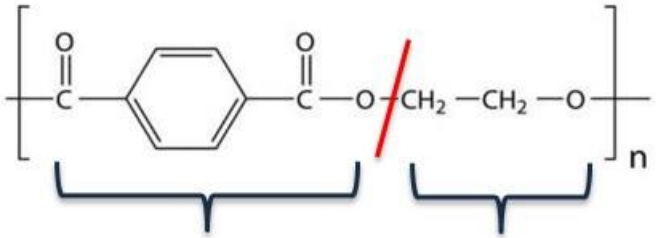
Plastics- Total Ion Chromatograms



PET-1 Clear Salad Container



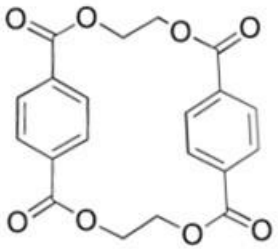
PET Monomer
193 m/z



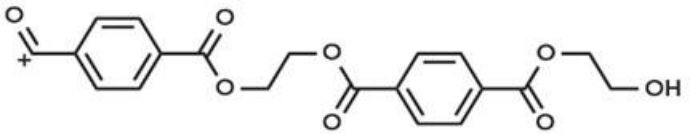
Terephthalate
149 m/z

Ethylene glycol
44 m/z

PET Cyclic Dimer
384 m/z



PET Linear Dimer
385 m/z

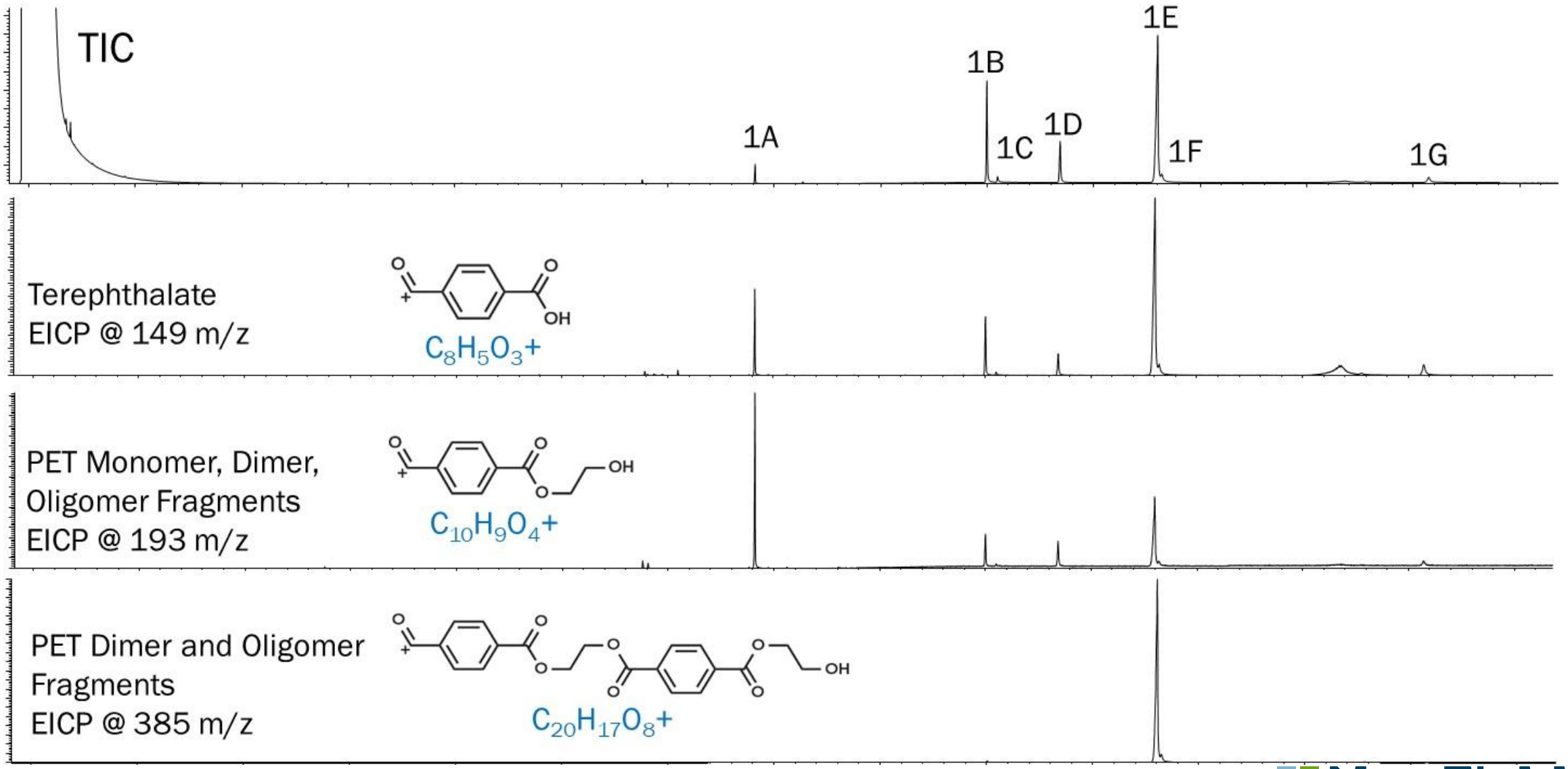


Repeating linear PET monomer

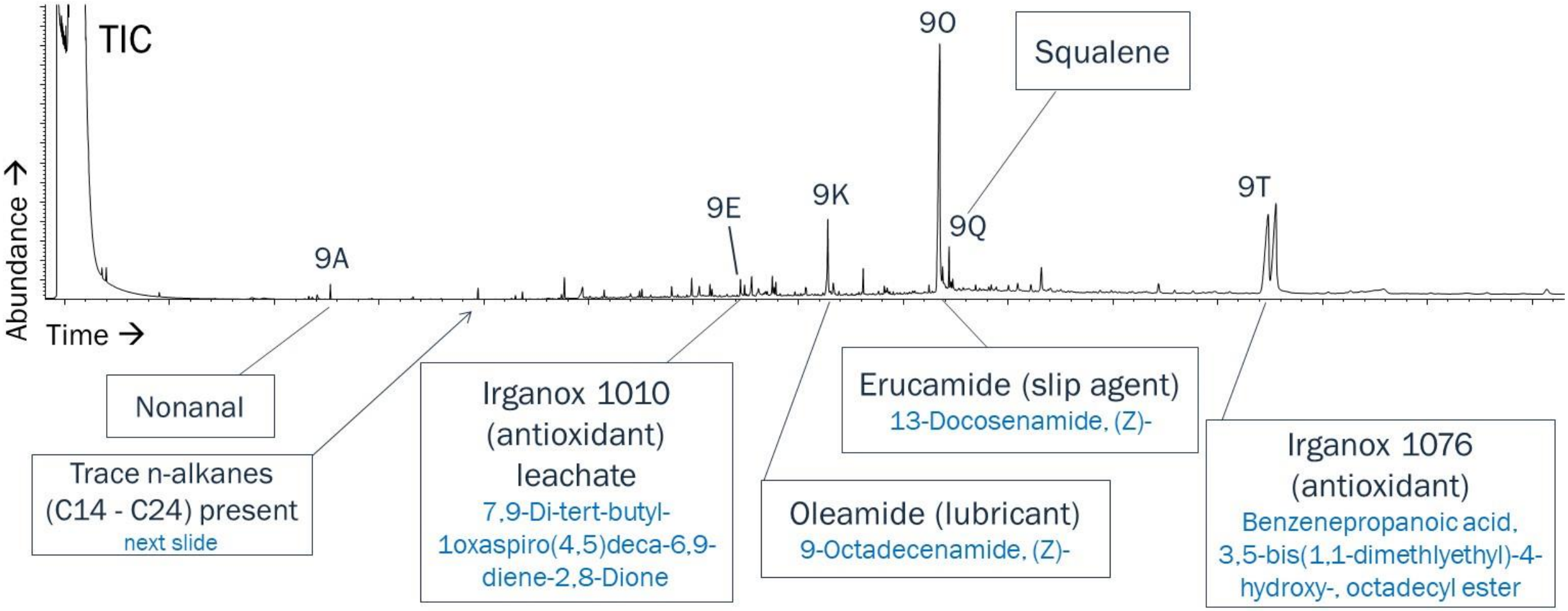
(Sun et al., 2021. Curr. Trends Mass Spectrom 19;1. p 20-24)

NewFields

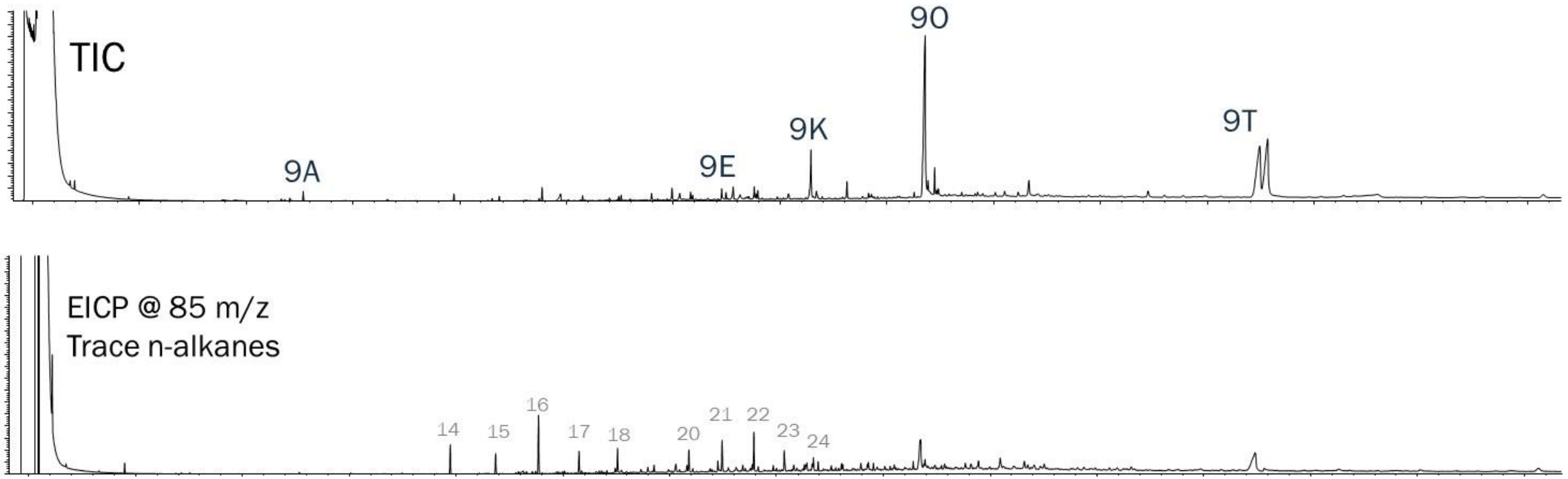
PET-1 Clear Salad Container



LDPE-9 Multicolored Printed Bag



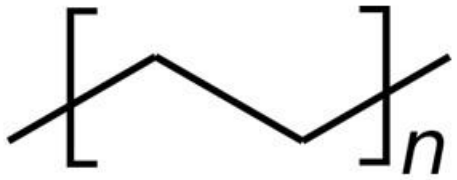
LDPE-9 Multicolored Printed Bag



Potentially from:

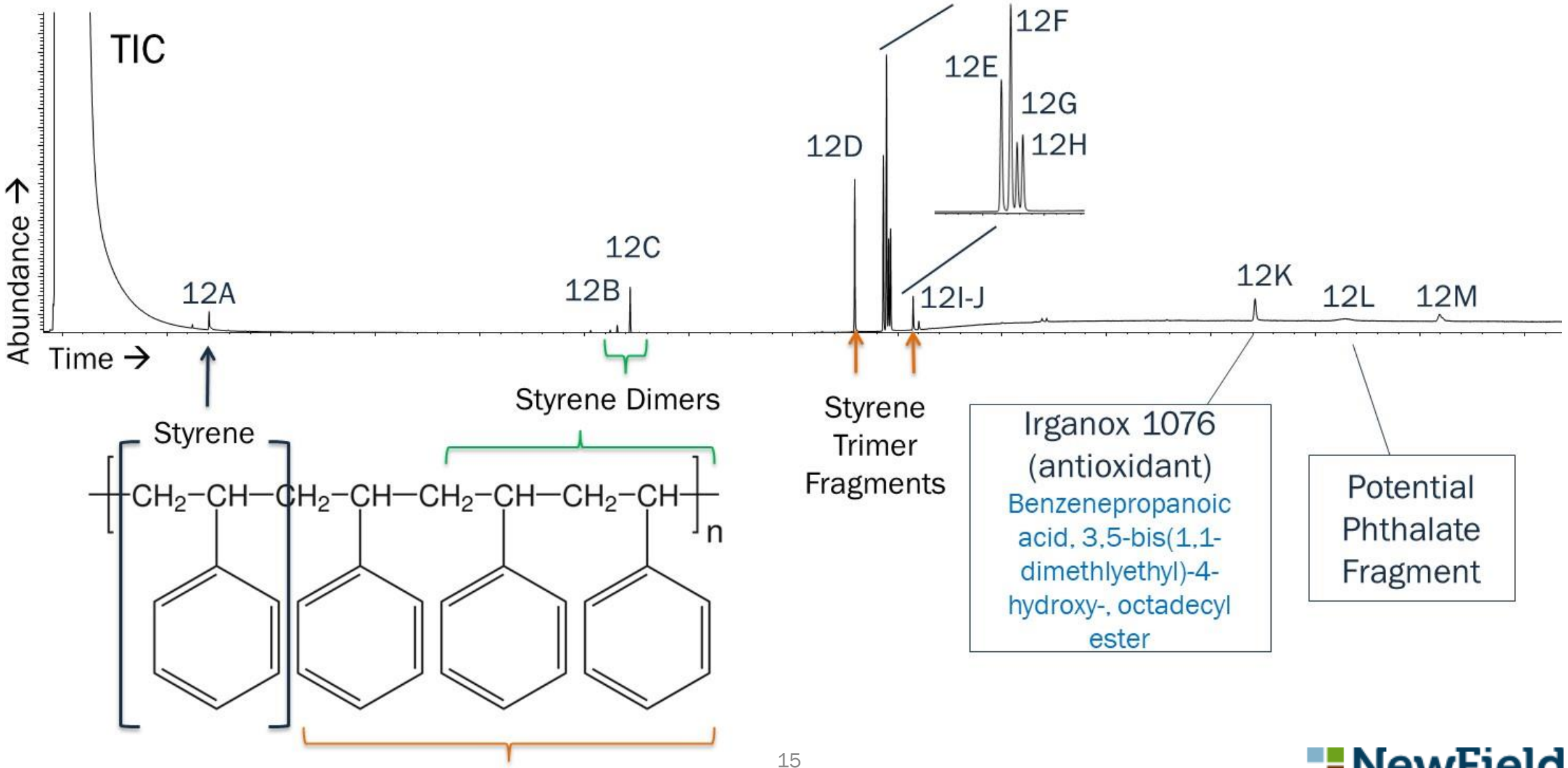
Paraffin-based lubricants or

Polyethylene Fragments

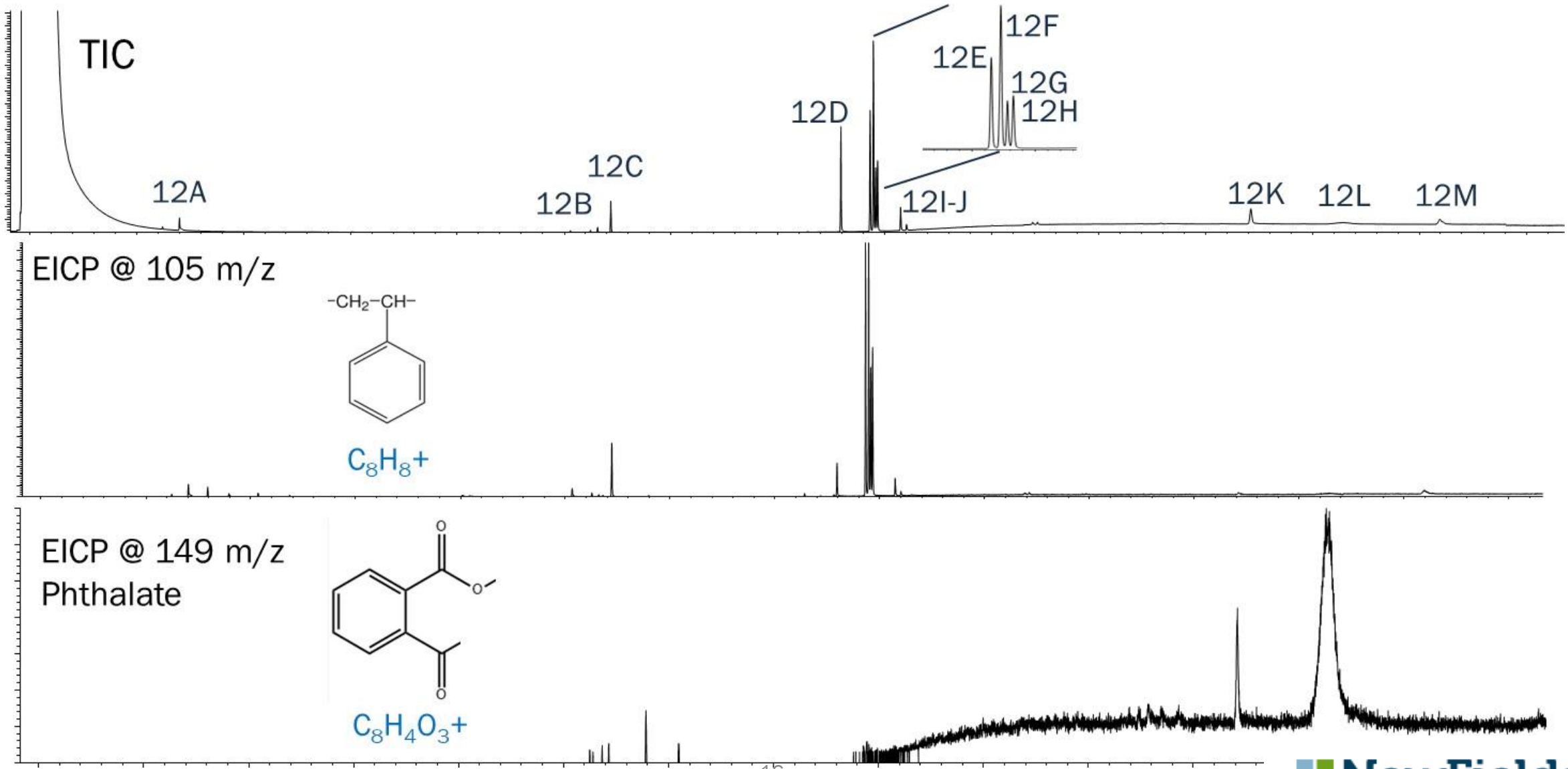


(less likely since not even-carbon dominated and of limited carbon range)

PS-12 Clear Cup



PS-12 Clear Cup



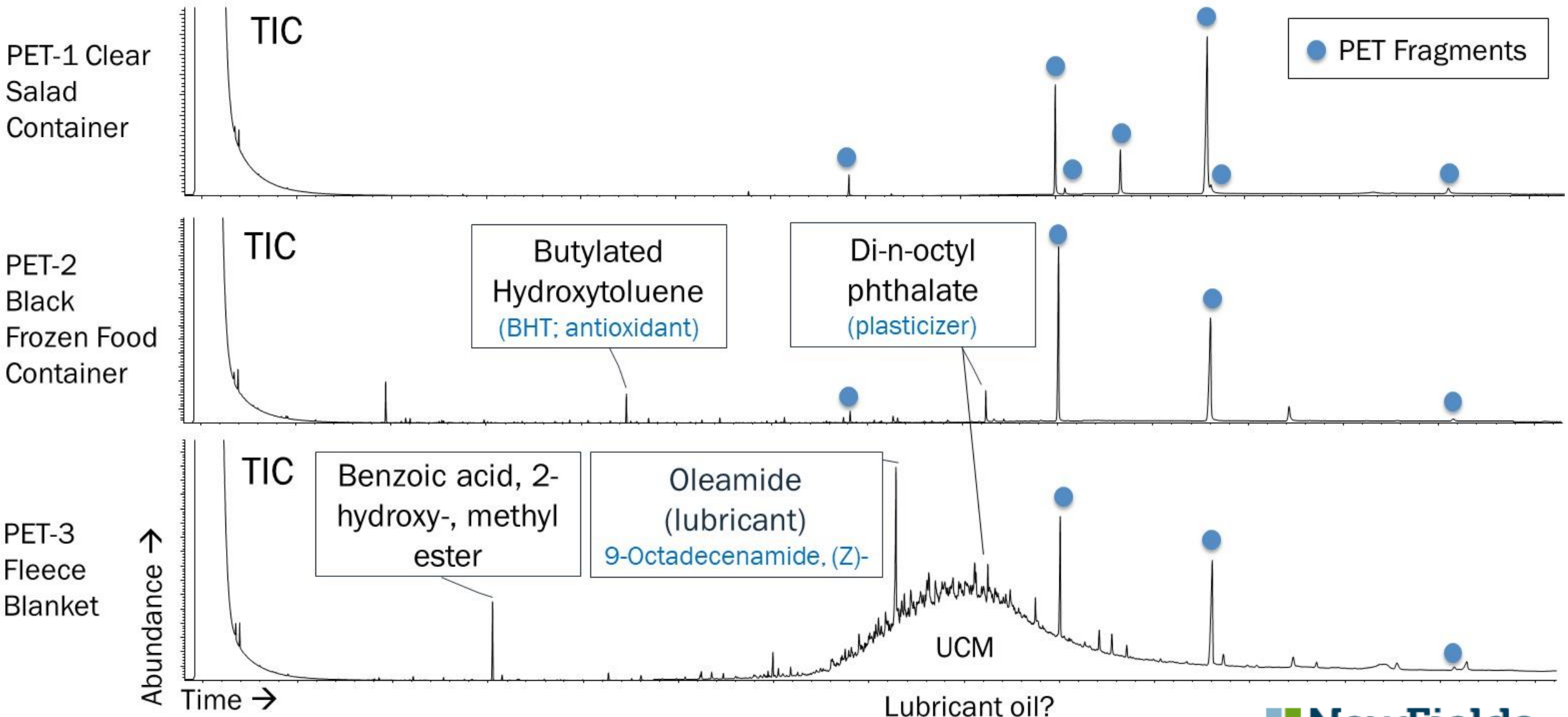
NewFields

Summary of Plastic Extractables Comparison

	PET-1 Salad Container	LDPE-9 Printed Bag	PS-12 Clear Cup
Total Peaks Investigated	8	30	13
Monomer/Oligomer Fragments	7	3	11
Additives	0	21	2
Unknown	0	6	0
Contaminants?	1 – caffeine	0	0
In Common?		2 Antioxidant: Irganox 1076 Plasticizer: Phthalate fragments	

NewFields

Comparing Different PET Products



PET Comparison

	PET-1 Salad Container	PET-2 Black Frozen Food Container	PET-3 Fleece Blanket
Total Peaks Investigated	8	6	16
Monomer/Oligomer Fragments	7	4	3
Additives	0	2	3
Unknown	0	0	10
Contaminants?	1 – caffeine	0	0
In Common?	3 – PET Oligomer Fragments		
	1 – PET Oligomer Fragment		
		1 – Potential Phthalate Plasticizer	

NewFields

Potential Markers for other Plastics Analyzed

	PET -1	PET -2	PET -3	HDPE -4	HDPE -5	PVC -6	PVC -7	LDPE -8	LDPE -9	PP-10	PS-11	PS-12	Nylon-13
Tin, dichlorodimethyl-						X	X						
2-Ethylhexyl mercaptoacetate (EHMA)						X	X						
Unknown Siloxanes										X			
Squalene					X			X	X				X
Irganox 1076		X					X	X	X			X	
9-Octadecenamide, (Z)			X	X	X			X	X		X		X
Unknown plasticizers (phthalate)		X	X	X	X		X	X	X	X		X	X

NewFields

Summary of Fingerprinting Plastics

Tier I: Analysis by DCM extractables by GC-MS

- Products (n=13) studied have unique GC/MS TICs (“fingerprints”)
  - between different polymers and different products of the same polymer
- Successful ID of polymer type based on monomer/oligomer fragments
  - confirmed with conventional FTIR spectroscopy
- Tentatively identify additives/ breakdown products that could be used as markers for different plastics
  - e.g., organotins and EHMA (heat stabilizers) unique to multiple found in PVC products

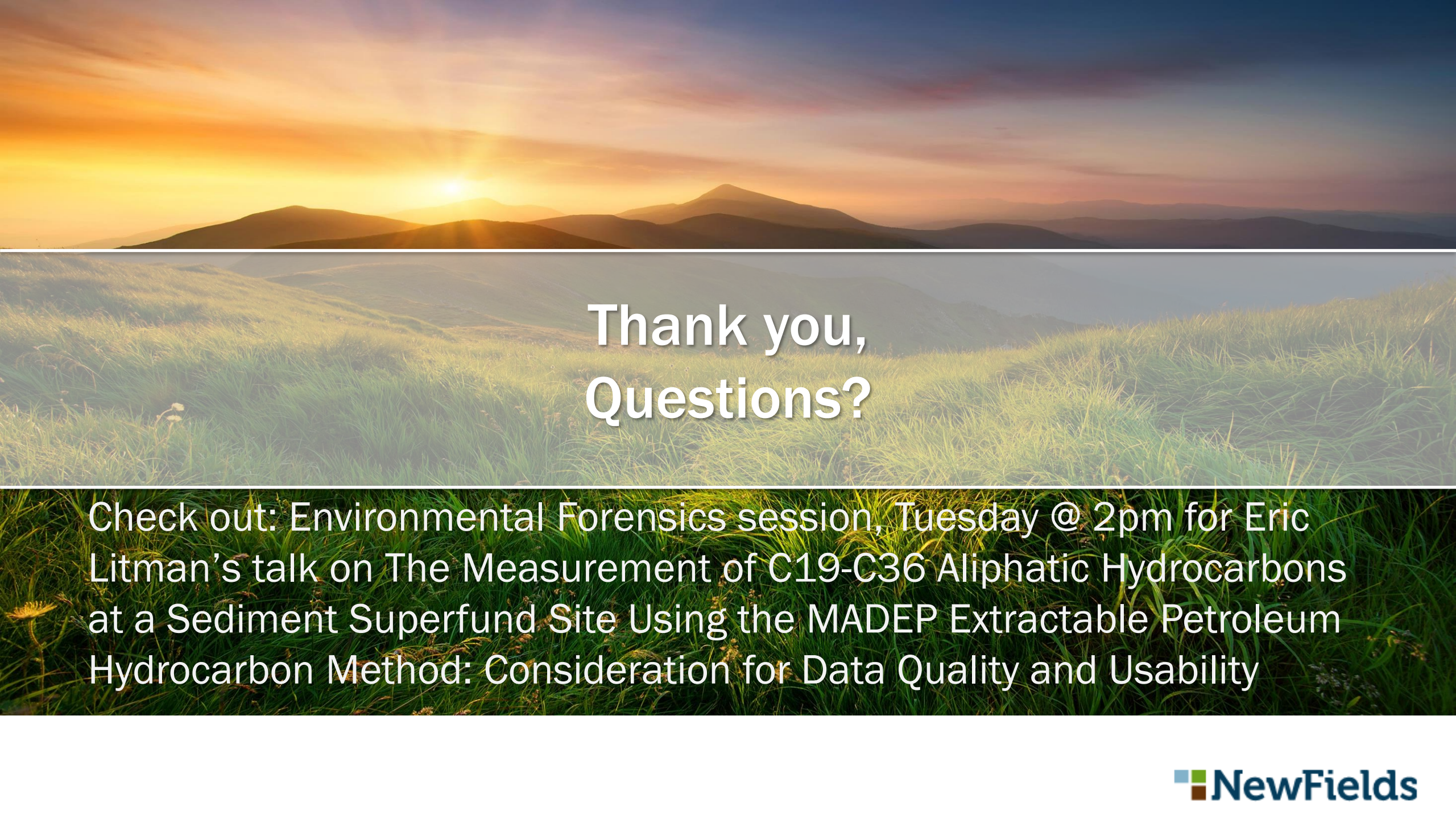
Next Steps

Tier I: (1) Develop library for extractables in plastics (identified and unidentified) and pattern recognition and (2) Explore increasing sensitivity through GC/MS-SIM analysis targeting polymer fragments and additives.

Tier II: Analyze additional plastics

- different size ranges and environmental exposure
- assessment of plastic extractables in sediment/water

Tier III: Pyrolysis or High-Resolution methods for further evaluation of plastic components



Thank you,
Questions?

Check out: Environmental Forensics session, Tuesday @ 2pm for Eric Litman's talk on The Measurement of C19-C36 Aliphatic Hydrocarbons at a Sediment Superfund Site Using the MADEP Extractable Petroleum Hydrocarbon Method: Consideration for Data Quality and Usability

NewFields