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How Important is the Matrix when Analyzing Microplastics by PY-GCMS?

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What Are Microplastics and Why Should We Care?

- Not just "plastic confetti"—includes fragments, fibers, spheres, films
- Polymer ≠ plastic product: Additives, degradation products, and weathering change behavior
- Size ≠ impact: Nanoplastics (<1 µm) behave more like chemicals than particles
- We say "microplastics," but we often analyze their thermal fingerprint, not the particle itself

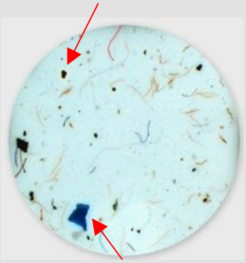
Common Analytical Methods

Spectroscopy
(FTIR, Raman)

Features:
- Non-destructive
- Morphological information
- Quantitative analysis (number of particles/m^2)*

Challenges:
- Poor in complex (dark) matrices, fluorescence interference
- No additives information
- Limitation of sample size

Polyethylene (40 µm x 30 µm)



Polystyrene (200 µm x 100 µm)

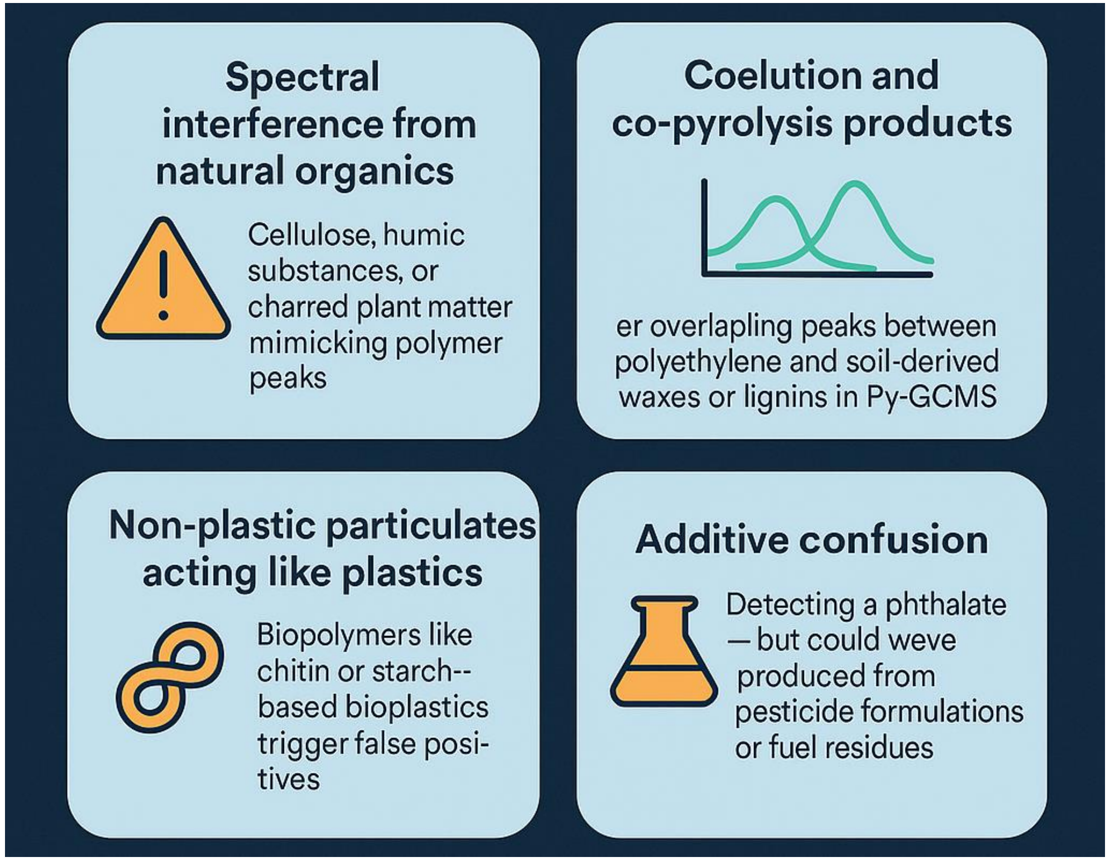
Separation/Thermal
(Py-GC/MS, EGA-MS, TD-GC/MS)

Features:
- Acquisition of additives information
- Acquisition of thermal property information
- Quantitative analysis (amount of sample/m^2)

Challenges:
- Destructive
- No morphological, color, size information

Polymer/Additives
Polymer: PE
Additives 1: Methyl stearate
Additive 2: Tinuvin P

Emerging Challenges in Microplastics



Microplastics – Choose your Matrix

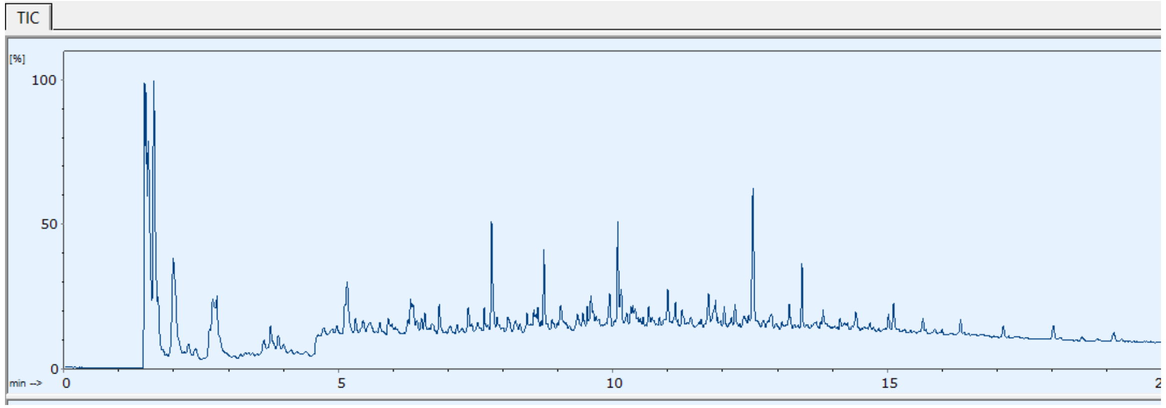
"Microplastics are no longer just an ocean problem."

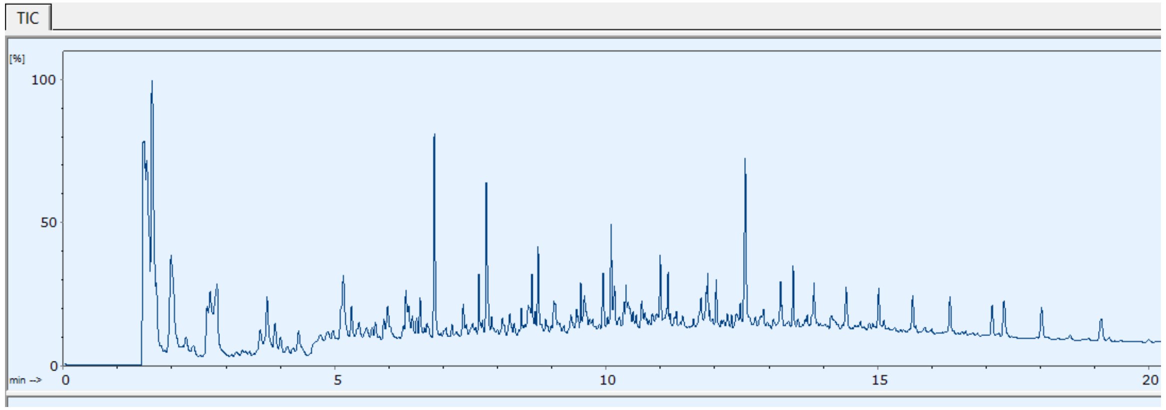
- Found in tap water, bottled water, seafood, honey, table salt, vegetables, and even clouds.
- Detected in human blood, lungs, placenta, and breast milk.
- Present in remote mountain air, Antarctica, and agricultural soils.

"The matrix is everywhere."

- Environmental monitoring shows soil may hold more microplastic mass than oceans.
- Agricultural reuse of biosolids and plastic mulch film is a key contributor.
- Transport through wind and rain is now proven (Brahney et al., 2020).

The Soil Matrix Problem





It's not just background—it's biochemistry

Lignin-rich soils co-pyrolyze into compounds like PS or PET markers

Matrix variability is enormous.

Forest soil ≠ farmland ≠ river sediment ≠ landfill cover

Soil particles act as sinks and sorbents

Some polymers degrade or oxidize differently depending on mineral content

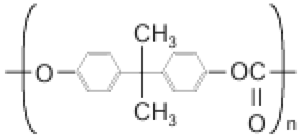
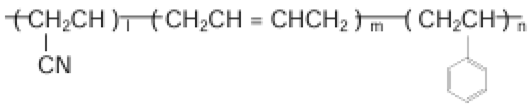
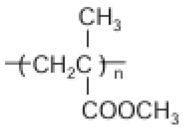
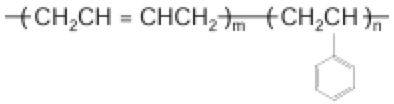
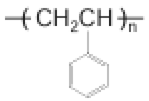
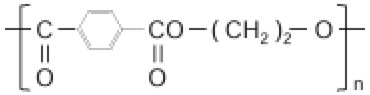
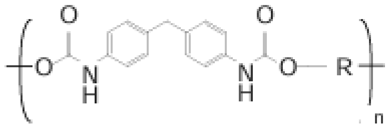
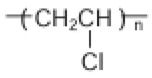
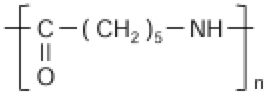
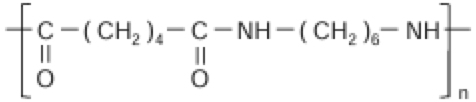
Prep methods often do more harm than good

Density separation doesn't work when soil has similar-density components

MP Calibration Curve – Frontier Low Standard Set

MPCS information (12 polymers)

Diluents : Calcium Carbonate ($CaCO_3$) or Silicon dioxide (SiO_2)

 Polyethylene (PE)	 Polycarbonate (PC)	 Acrylonitrile-butadiene-styrene resin (ABS)
 Polypropylene (PP)	 Poly(methyl methacrylate) (PMMA)	 styrene-butadiene rubber (SBR)
 Polystyrene (PS)	 Polyethylene terephthalate (PET)	 Polyurethane* (PU)
 Polyvinyl chloride (PVC)	 Nylon 6 (N6)	 Nylon 66 (N66)

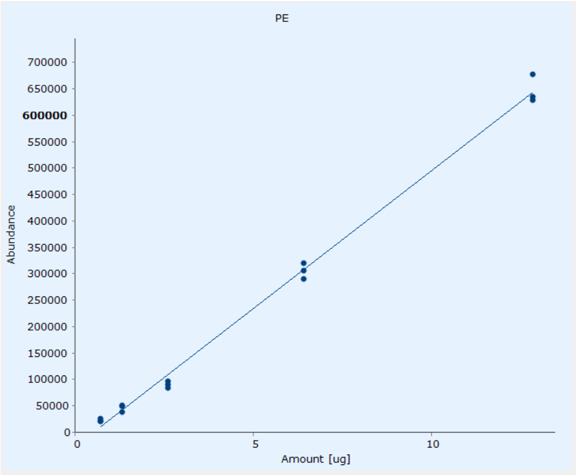
* PU can be analyzed only when $CaCO_3$ diluent is used.

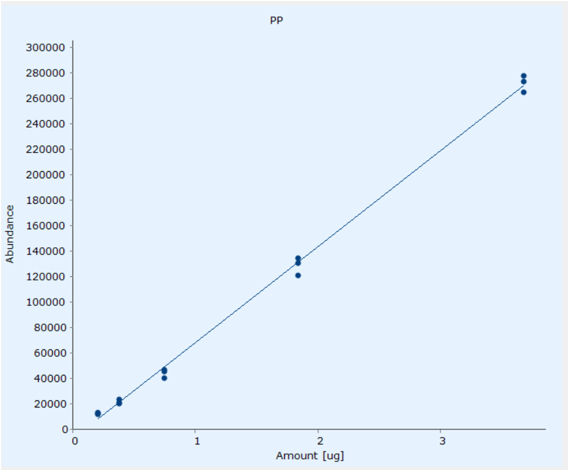
MP Calibration Curve Data

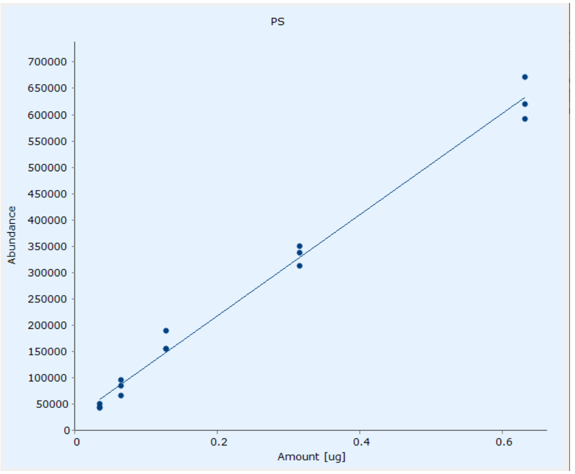
- 5-point curve from 4mg – 0.2mg
- MP ug range ~10x lower than standard kit (shown below)
- 3 x replicates

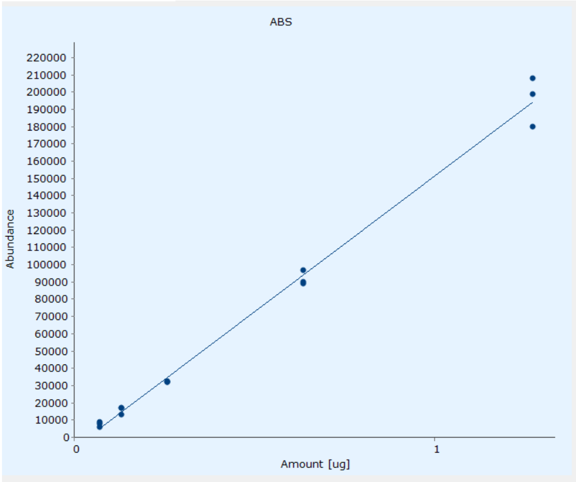
Level	PE	PP	PS	ABS	SRB	PMMA	PC	PVC	PU	PET	N6	N66
0.2mg	0.705	0.202	0.0347	0.0698	0.0616	0.0253	0.0688	0.119	0.177	9.35E-03	0.0237	0.15
0.4mg	1.31	0.376	0.0646	0.13	0.115	0.0471	0.128	0.222	0.329	0.0174	0.0441	0.279
0.8mg	2.59	0.743	0.128	0.257	0.227	0.0932	0.253	0.439	0.65	0.0344	0.0871	0.551
2.0mg	6.41	1.83	0.315	0.635	0.56	0.23	0.625	1.08	1.6	0.085	0.215	1.36
4.0mg	12.8	3.67	0.63	1.27	1.12	0.46	1.25	2.17	3.21	0.17	0.43	2.72

MP Calibration Curve Data



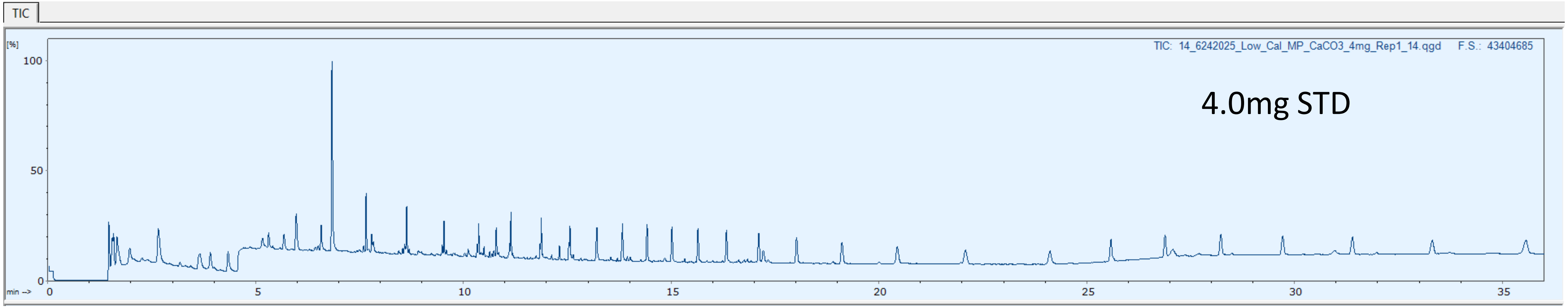


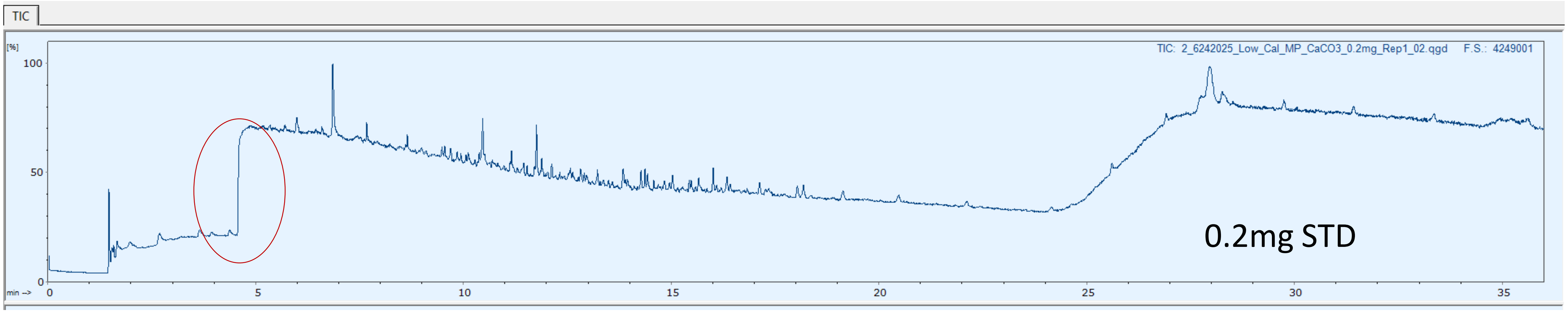




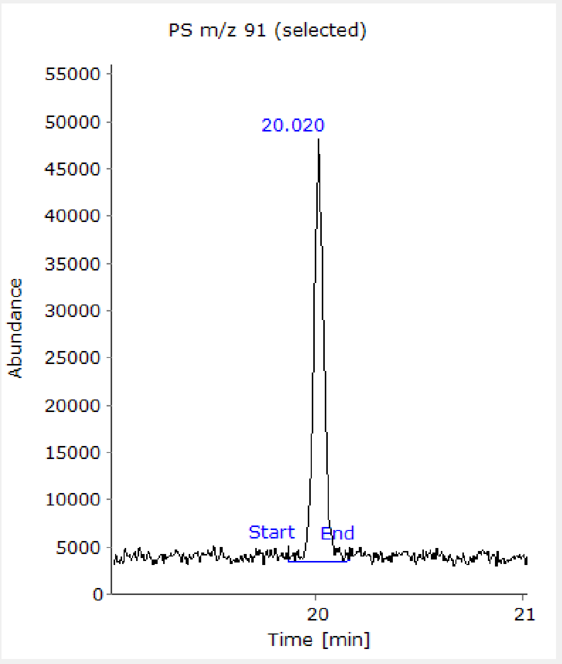
Microplastic	R^2	RSD (n=3), 0.2mg
PE	0.9980	9.94
PP	0.9989	3.10
PS	0.9973	6.56
ABS	0.9982	13.72
SBR	0.9994	8.92
PMMA	0.9978	20.71
PC	0.9927	28.36
PVC	0.9991	6.03
PU	0.9721	28.55
PET	0.7863	47.90
N6	0.9991	12.08
N66	0.9989	6.36

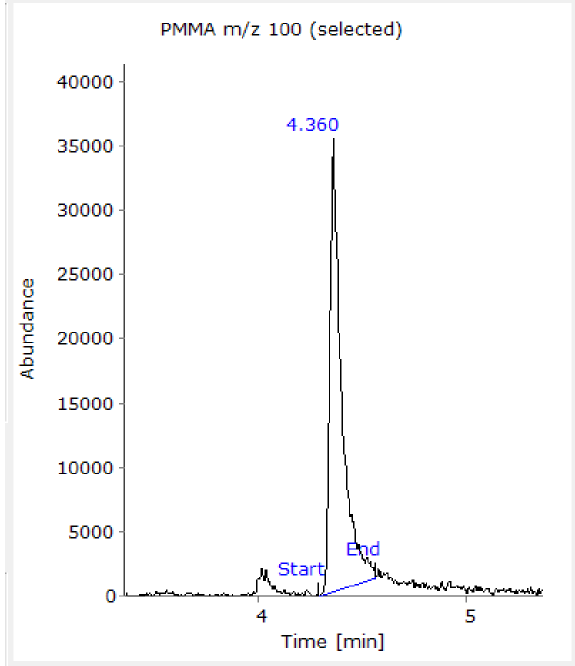
MP Calibration Curve Data

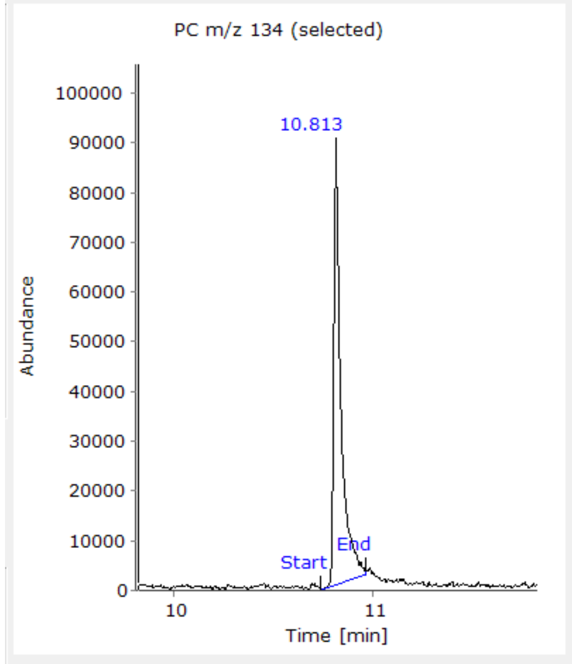


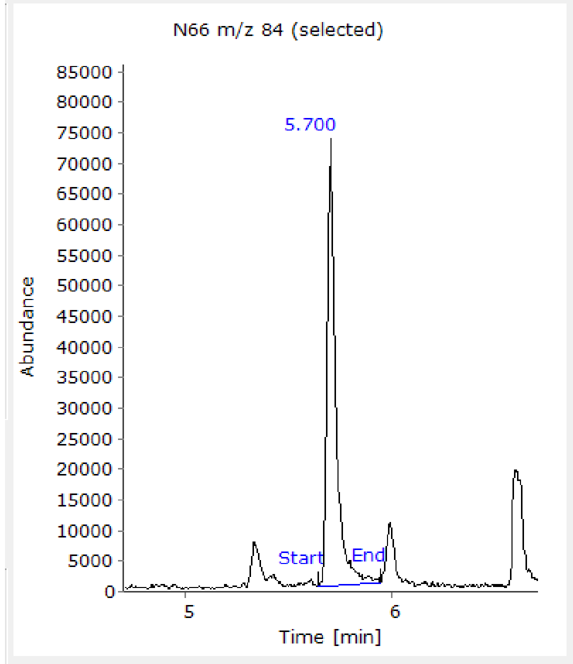


MP Calibration Curve Data - MCs



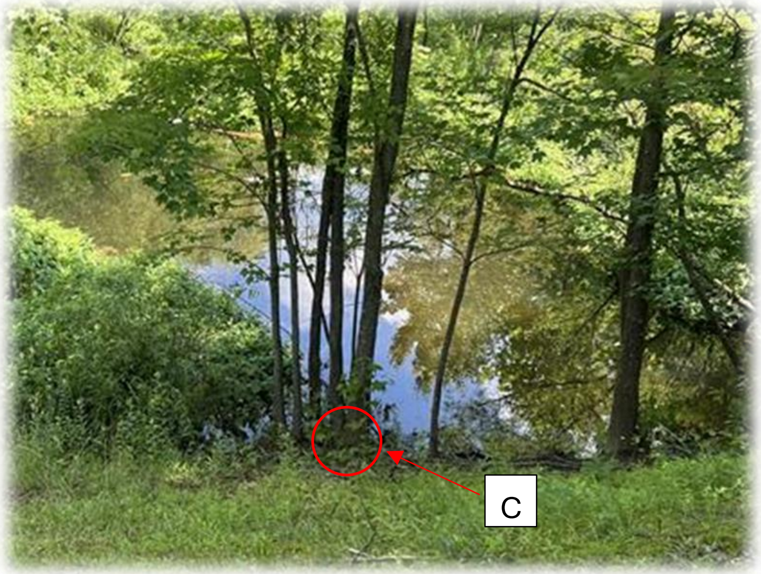




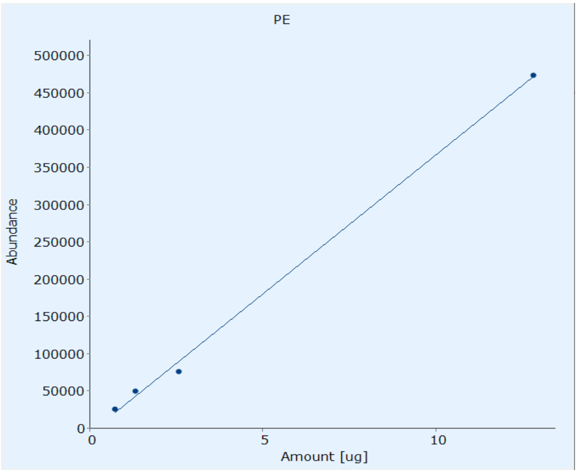


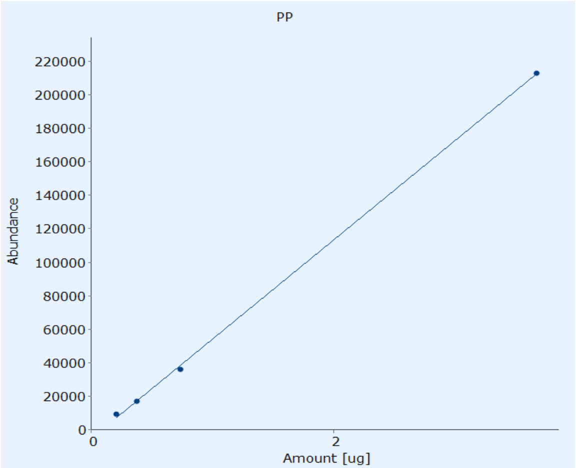
It’s Not Dirt, It’s Data – Sample Preparation Matters

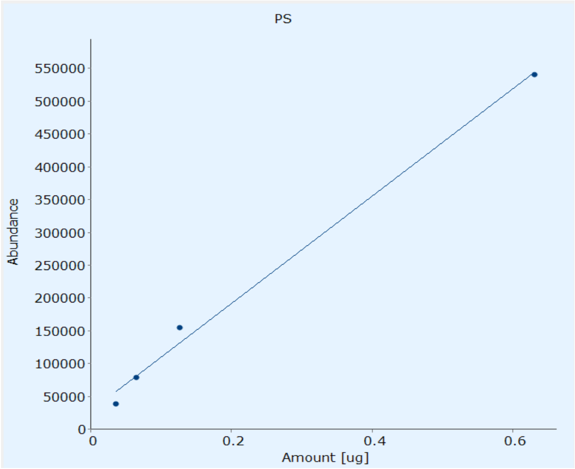
- **Rudimentary Sample Prep**
  - 3 samples from “unknown” location were collected
  - Sample was then homogenized via mortar/pestle
  - ~200g of sample was dried in vial for 3hrs @40C
  - 2mg of sample was weighed into PY cup

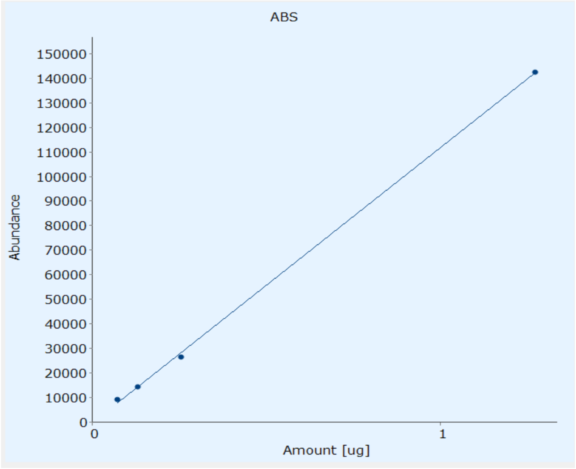


Success Stories in Soil



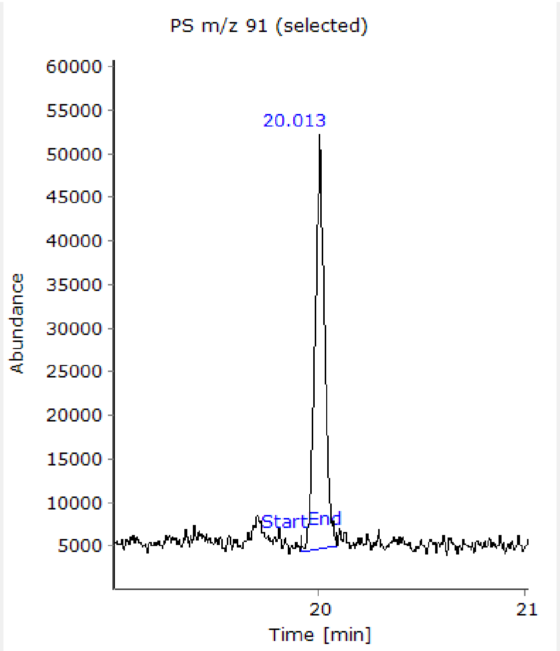


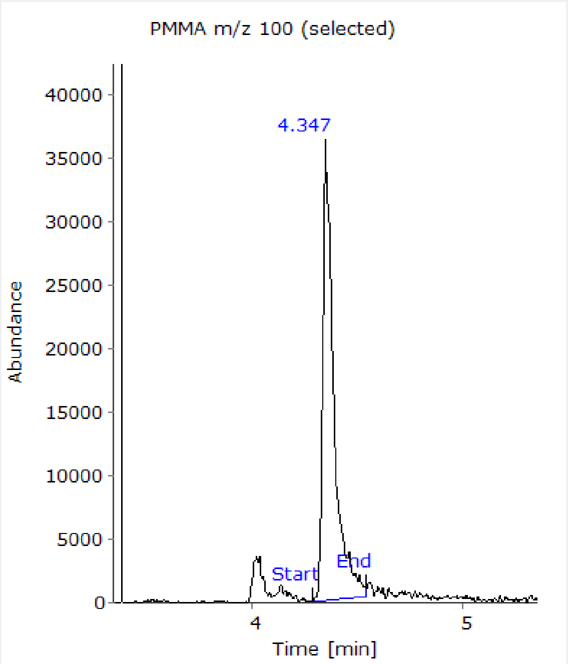


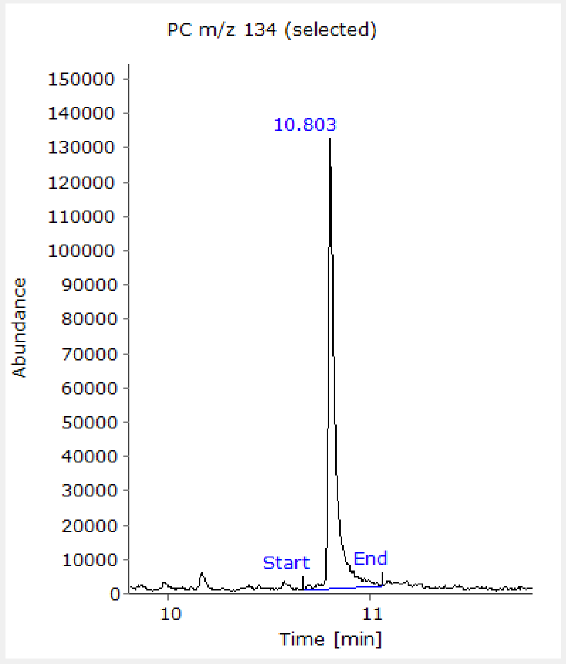


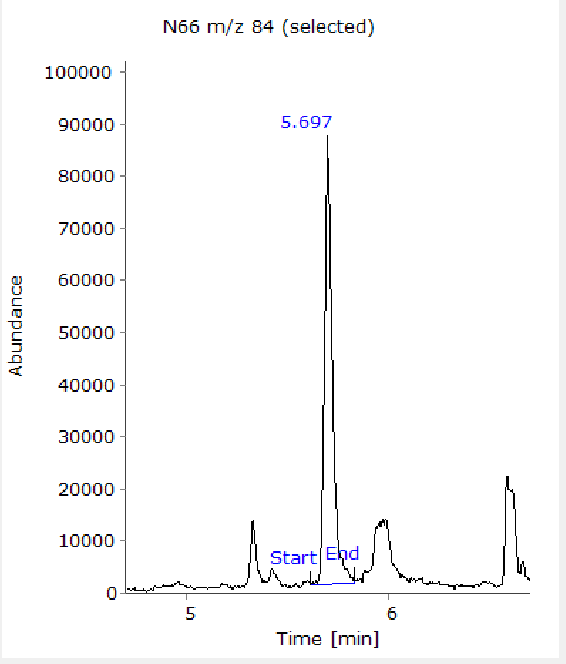
Microplastic	R^2
PE	0.9981
PP	0.9996
PS	0.9946
ABS	0.9995
SBR	0.9994
PMMA	0.9502
PC	0.9997
PVC	0.9812
PU	0.9976
PET	0.0213
N6	0.9995
N66	0.9995

Success Stories in Soil – MCs







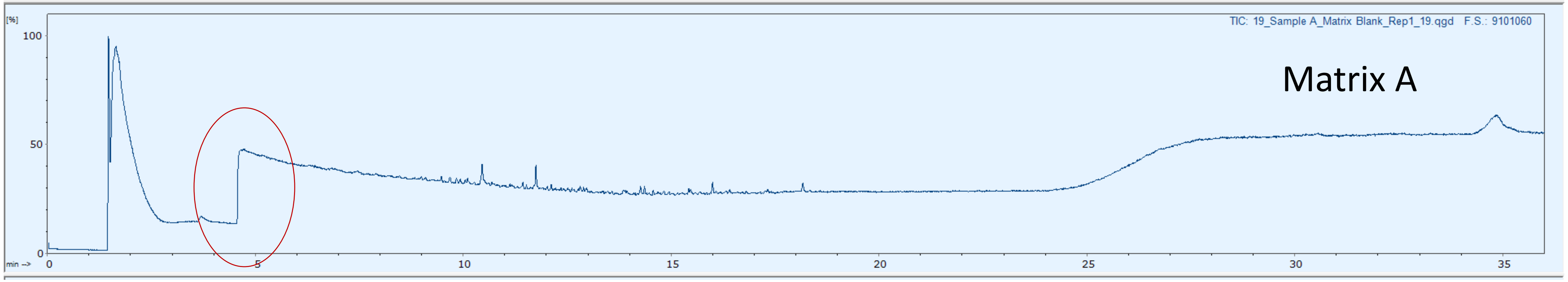


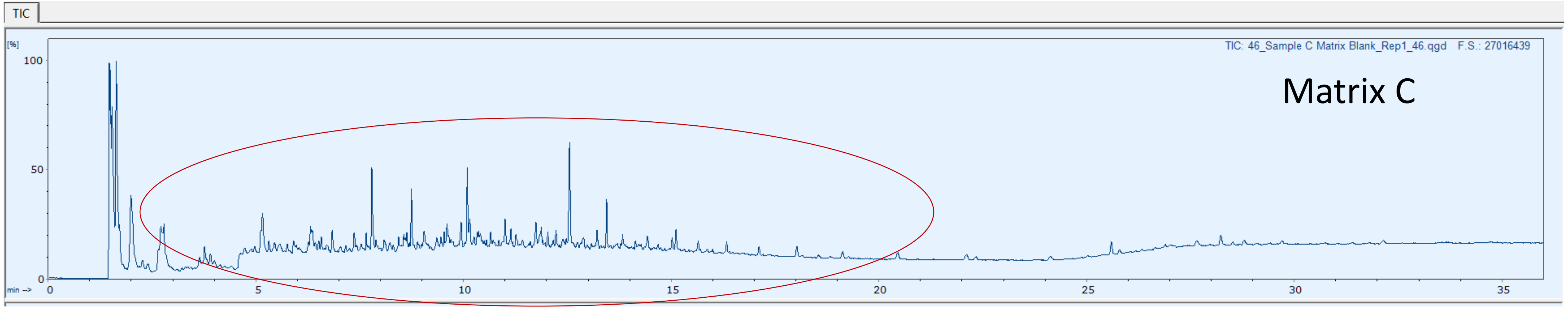
Success Stories in Soil – Recoveries

Polymer	Sample A					
	Matrix Blank			Matrix + Spike 2mg		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Quantity PE (ug)	-	-	-	4.91	4.36	4.03
Recovery PE	-	-	-	76.60	68.02	62.87
Quantity PP (ug)	-	-	-	1.66	1.62	1.51
Recovery PP	-	-	-	90.71	88.52	82.51
Quantity PS (ug)	-	-	0.102	0.318	0.262	0.246
Recovery PS	-	-	-	100.95	83.17	78.10
Quantity ABS (ug)	-	-	-	0.507	0.5	0.432
Recovery ABS	-	-	-	79.84	78.74	68.03
Quantity SRB (ug)	-	-	-	0.472	0.644	0.452
Recovery SRB	-	-	-	84.29	115.00	80.71
Quantity PMMA (ug)	-	-	-	0.157	0.168	0.109
Recovery PMMA	-	-	-	68.26	73.04	47.39
Quantity PC (ug)	-	-	-	0.637	0.596	0.539
Recovery PC	-	-	-	101.92	95.36	86.24
Quantity PVC (ug)	0.133	0.0456	0.102	1.27	1.52	1.37
Recovery PVC	-	-	-	117.59	140.74	126.85
Quantity N6 (ug)	-	-	-	0.201	0.219	0.204
Recovery N6	-	-	-	93.49	101.86	94.88
Quantity N66 (ug)	-	-	-	1.38	1.47	1.29
Recovery N66	-	-	-	101.47	108.09	94.85

Polymer	Sample B					
	Matrix Blank			Matrix + Spike 2mg		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Quantity PE (ug)	-	-	-	4.9	5.74	4.97
Recovery PE	-	-	-	76.44	89.55	77.54
Quantity PP (ug)	-	-	-	1.65	1.94	1.54
Recovery PP	-	-	-	90.16	106.01	84.15
Quantity PS (ug)	-	-	0.0173	0.418	0.36	0.378
Recovery PS	-	-	-	132.70	114.29	120.00
Quantity ABS (ug)	-	-	-	0.551	0.622	0.555
Recovery ABS	-	-	-	86.77	97.95	87.40
Quantity SRB (ug)	-	-	-	0.422	0.61	0.401
Recovery SRB	-	-	-	75.36	108.93	71.61
Quantity PMMA (ug	-	-	-	0.214	0.238	0.166
Recovery PMMA	-	-	-	93.04	103.48	72.17
Quantity PC (ug)	-	-	-	0.551	0.607	0.487
Recovery PC	-	-	-	88.16	97.12	77.92
Quantity PVC (ug)	0.246	0.195	0.349	1.05	1.17	1.59
Recovery PVC	-	-	-	97.22	108.33	147.22
Quantity N6 (ug)	-	-	-	0.186	0.213	0.216
Recovery N6	-	-	-	86.51	99.07	100.47
Quantity N66 (ug)	0.112	0.121	0.118	1.26	1.31	1.28
Recovery N66	-	-	-	92.65	96.32	94.12

The Matrix Strikes Back

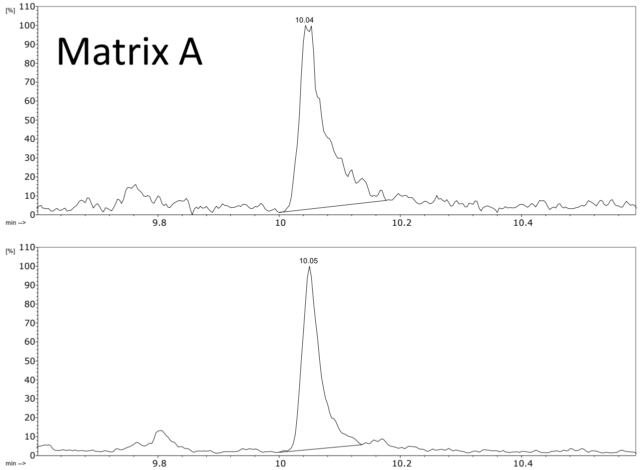




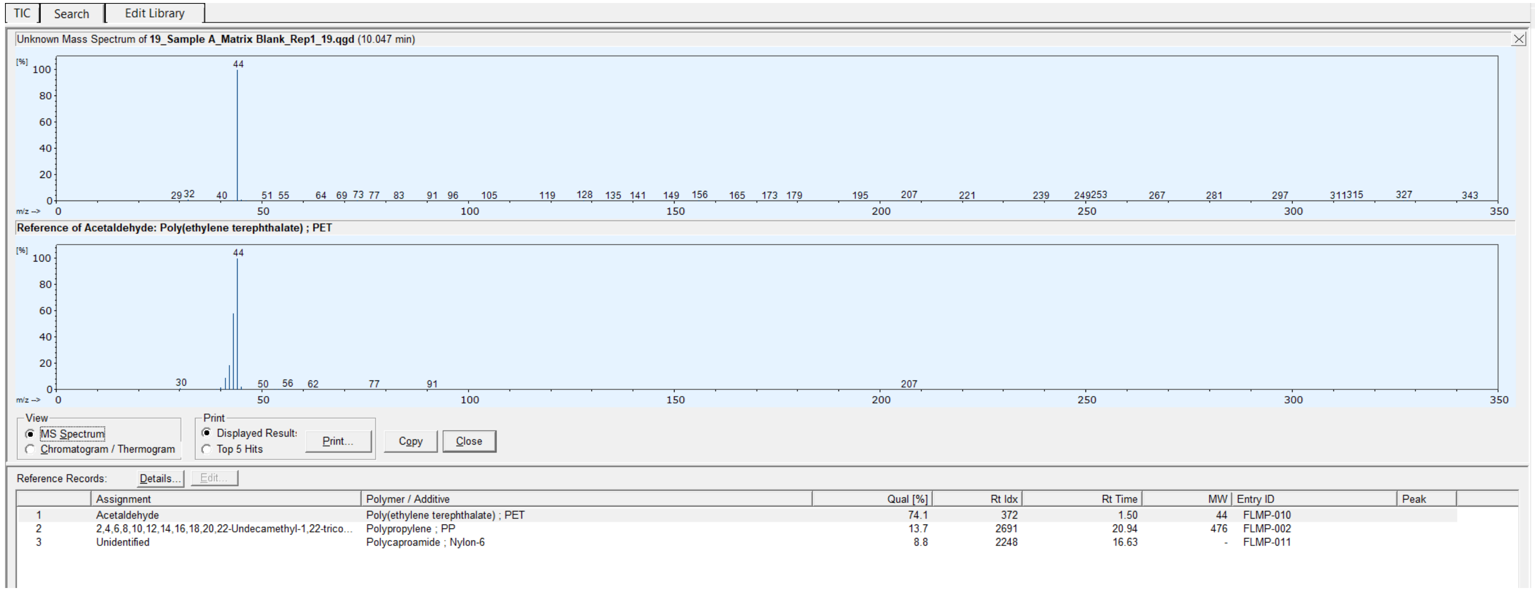
- **Matrix "blank" – much higher background**
- **Mystery Peaks?**

The Matrix Strikes Back – A Blank

- **Match for PVC ~96%**
- **Individual peak search returned zero match**

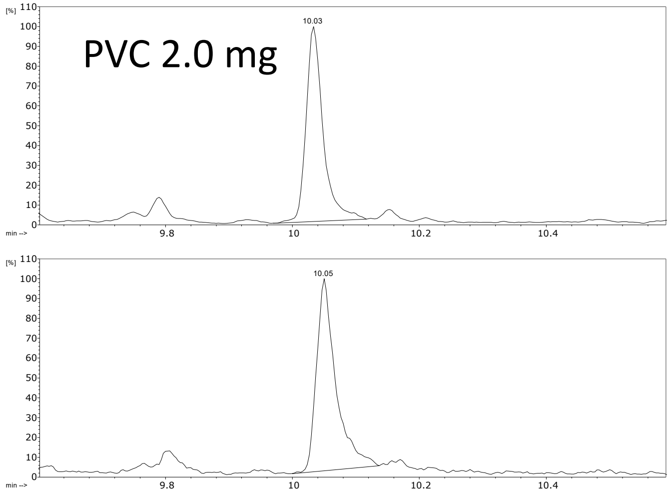


Polymer	Prob. [%]	Qnty [ug]	Ratio [%]	Area	RT [min]	LO
PE	66.9	0.525	37.6	1813	15.72	
PU	64.1	0.342	24.5	1024	17.27	
PVC	94.9	0.133	9.54	38595	10.04	
PP	56.6	0.0996	7.13	517	6.47	
N66	76.6	0.0948	6.79	3743	5.73	
PC	36.3	0.0918	6.58	837	10.63	
ABS	94.1	0.0392	2.80	728	17.18	
SBR	41.1	0.0298	2.14	1856	11.54	
PMMA	49.6	0.0149	1.07	215	4.90	
N6	88.3	0.0139	0.994	552	10.70	
PET	97.3	0.0123	0.879	4723	13.53	
PS	89.8	---	---	5920	19.72	
			(100)			

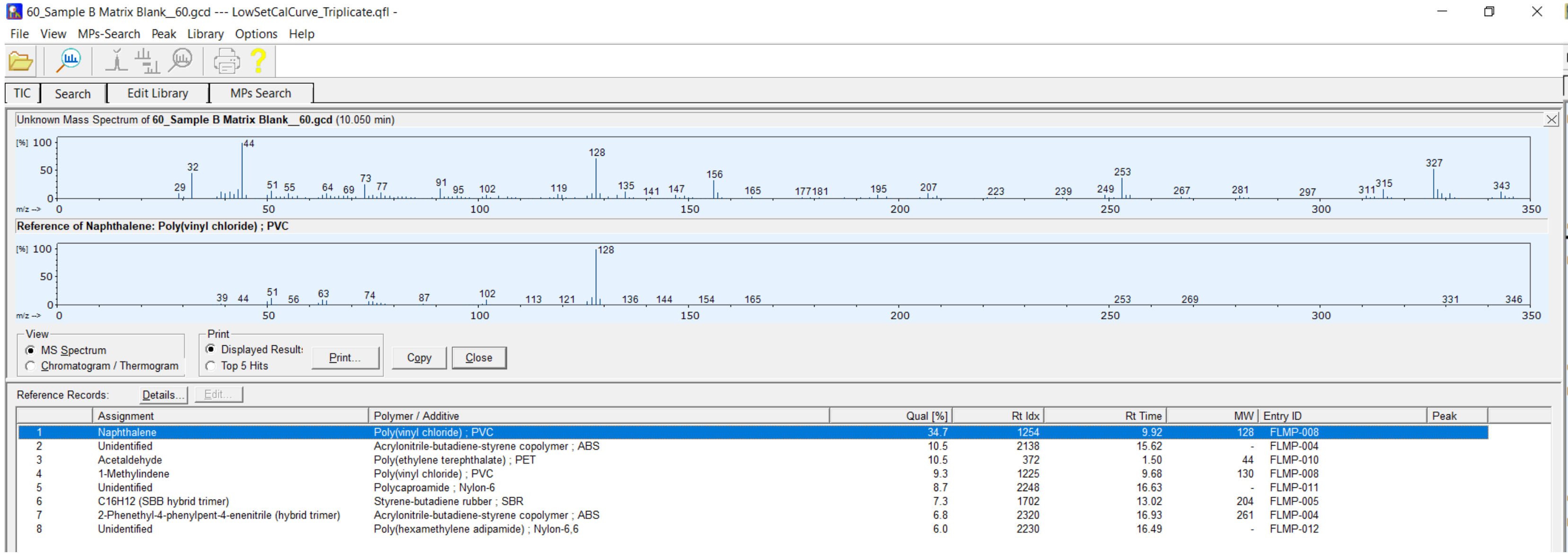


The Matrix Strikes Back – A Spiked

- Match for PVC ~90%
- Individual peak search returned lower quality match



Polymer	Prob. [%]	Qnty [ug]	Ratio [%]	Area	RT [min]	LOQ
PE	96.5	0.533	28.0	2246	15.65	
PVC	90.2	0.398	20.9	115401	10.04	
PU	65.6	0.342	17.9	1221	17.92	
SBR	60.4	0.177	9.27	15144	10.99	
PP	86.2	0.131	6.85	2869	6.08	
N66	88.2	0.109	5.72	10880	5.71	
PC	61.7	0.0952	4.99	7315	10.74	
PET	52.0	0.0514	2.69	8440	13.72	
ABS	89.0	0.0373	1.95	430	17.98	
N6	66.7	0.0176	0.922	2743	11.00	
PMMA	74.7	0.0162	0.848	2782	4.14	
PS	87.3	---	---	4443	20.19	
			(100)			



Lessons Learned

- **PU and PET detection is inconsistent in soil.**
  - PET pyrolyzates (like benzoic acid) easily suppressed by organics.
  - PU fragments often overlap with soil-derived amines
- **PVC: Identification pitfalls**
- **Sample prep matters... but “quick and dirty” isn’t always wrong.**
  - Surprisingly, basic drying and sieving + thermal desorption got us decent trends.
  - Full digestion/filtration would improve quantitation and recoveries

Polymer	Sample B					
	Matrix Blank			Matrix + Spike 2mg		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Quantity PU (ug)	-	-	-	1.16	0.799	1.44
Recovery PU	-	-	-	72.50	49.94	90.00
Quantity PET (ug)	-	-	-	0.344	0.244	0.344
Recovery PET	-	-	-	404.71	287.06	404.7059

The Road Ahead

- **Continue the work and expand on sample preparation**
  - Develop protocols that account for diverse soil types.
- **Spiked reference soils with multiple polymers (including aged/weathered plastics) are rare or nonexistent**
  - Ideal materials that represent environmental microplastics — not pristine lab-grade beads
- **Software for polymer ID is still developing in high-background matrices.**
  - Real-world interferences (like PVC false positives) must inform future libraries.

Thank you for your attention.