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Impact of Soil Matrix on Microplastics Analysis by Py-GC/MS

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Introduction

- The matrix is not just background—it actively participates in pyrolysis chemistry.
- Lignin-rich soils can co-pyrolyze, producing compounds that overlap with common PS or PVC markers, complicating interpretation.
- Matrix variability is substantial, with clear chemical and physical differences between forest soils, agricultural land, river sediments, and landfill cover materials.
- Soil particles act as sinks and sorbents, interacting with microplastics and altering degradation pathways.
- Sample preparation can introduce bias, and in some cases does more harm than good.
- In this poster, we present a method to improve quantitative accuracy in Py-GCMS microplastics analysis by assessing the matrix effect, while also addressing key challenges in the qualitative identification.

Experimental Methods

- Three soil samples were collected from different locations (Figure 1) and homogenized using a mortar/pestle.
- From each sample, 200g were dried in a vial for 3 hours at 40C and 2mg was weighed into a PY cup.

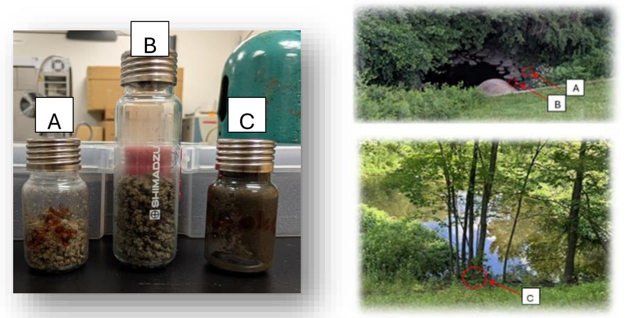


Figure 1. Soil samples and it's respective sampling locations

- Targeted microplastics include PE, PP, PS, ABS, PMMA, PC, PVC, N6, and N66. The percentage distribution of polymers in the MPs-CaCO3 standard, as well as the mass of each analyte in a 4 mg standard within a CaCO3 diluent, is shown in Figure 1.
- These were analyzed using a PY-GCMS instrument, shown in Figure 2.
- A 5-point calibration curve was prepared, in triplicate, by weighing 0.2mg, 0.4mg, 0.8mg, 2.0mg, and 4.0mg from Frontier's Low calibration standard mix of microplastics.
- A matrix-matched calibration curve was generated by spiking sample B with the same concentration as the calibration levels.
- Samples were analyzed, and analytes in the sample were quantified in µg, calculated using the calibration curve of known standard concentration.
- Recovery studies were performed in blank samples to evaluate matrix effect for the targeted analytes. For this, a 2mg sample was weighed in triplicate, and 2mg of the standard mix was combined with 2mg of CaCO3 diluent.

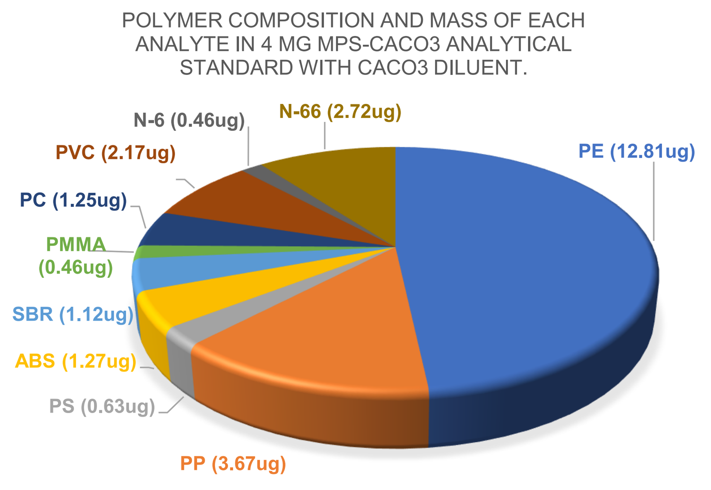


Figure 2. Polymer composition and mass of each analyte in 4 mg analytical standard with CaCO3 diluent

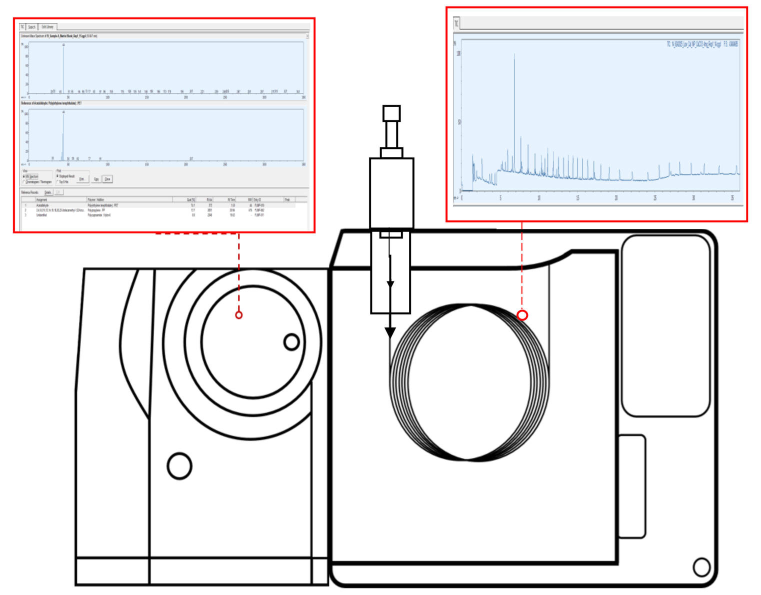


Figure 3. Schematic of PY-GC-MS

Results

Scope A: Improving quantitative accuracy in Py-GCMS microplastics analysis by assessing the matrix effect

- A standard calibration curve with triplicates of each level was generated using the average responses for each microplastic.
- Calibration curves demonstrated linear response (R^2 > 0.9927; Table 1) for all compounds across the concentration ranges evaluated in this study.
- From the three replicates of the lower level of the calibration curve 0.2mg), a short-term repeatability test was conducted, and the percent relative standard deviation (%RSD) of each polymer was calculated. Results are also shown in Table 1.

Microplastic	Marker	R^2	RSD (n=3), 0.2mg
PE	20-Heneicosadiene	0.9980	9.94
PP	2,4-Diemethyl-1-heptene	0.9989	3.10
PS	Styrene trimer	0.9973	6.56
ABS	2-Penyl-4phenylpent-4-enenitrile	0.9982	13.72
PMMA	Methyl Methacrylate	0.9978	20.71
PC	Polycarbonate	0.9927	28.36
PVC	Naphthalene	0.9991	6.03
N6	E-Caprolactam	0.9991	12.08
N66	Cyclopentanone	0.9989	6.36

Table 1. Linear fit calibration and repeatability at 0.2mg for the 9 microplastic standard.

- From Table 1, we can see the markers used for the identification and quantification of each microplastic.
- The three samples were analyzed, and the software was used to identify any of the 9 microplastics.
- Total ion chromatograms for the three samples are shown in Figure 4.
- Sample C showed a higher background compared to the other samples.

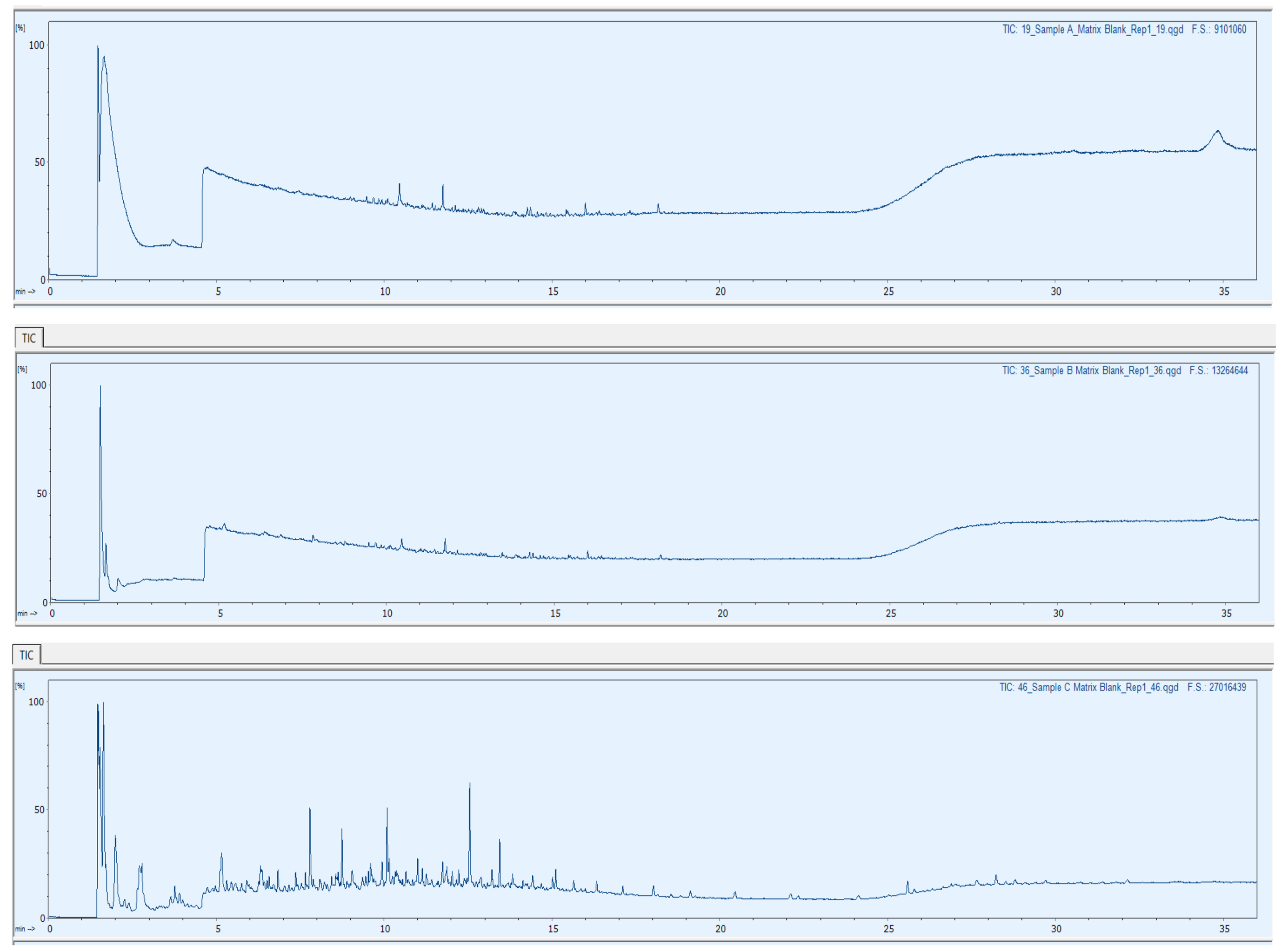


Figure 4. TIC for Sample A (top), Sample B (middle), Sample C (bottom).

- In order to study how the matrix will affect the recovery, a calibration curve was done by spiking Sample B.
- Most of the polymers spiked into Sample B resulted in R^2 > 0.9900, as shown in Table 2.

Microplastic	R^2
PE	0.9905
PP	0.9972
PS	0.8041
ABS	0.9992
SBR	0.9495
PMMA	0.9980
PC	0.9988
PVC	0.9442
N6	0.9979
N66	0.9996

Table 2. Linear fit calibration for Sample B spiked with the polymer's standard.

- Samples were spiked with 2mg of the microplastic standard to evaluate their recovery.
- Recovery percentages were calculated by using both calibration curves; the results of the average of three replicates are shown in Figures 8 and 9.
- When using the standard calibration curve, recovery percentages were unsatisfactory, while we noticed there were some improvements of the recovery percentages when using the calibration curve spiked into the matrix.
- Sample C still showed higher responses, probably due to the higher background.

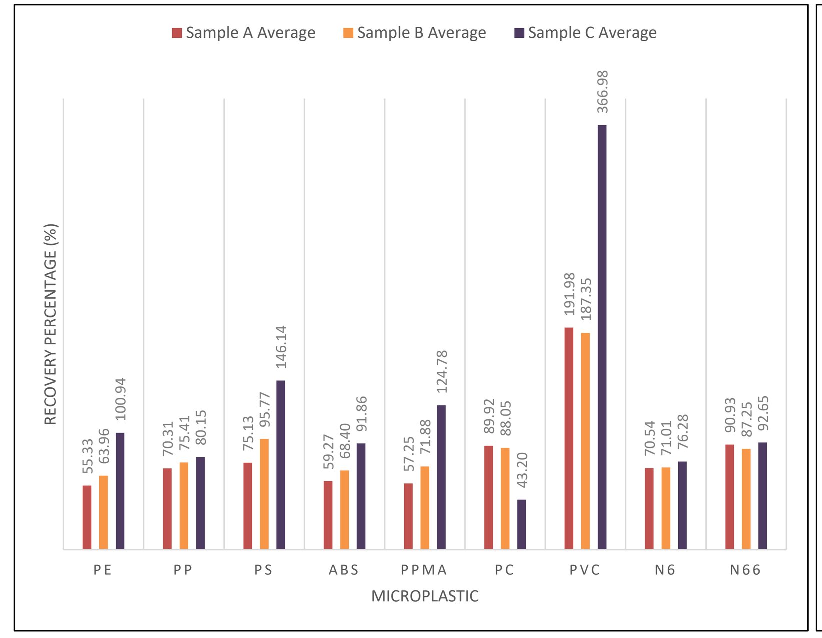


Figure 8. Recovery % for samples spiked at 2mg using the standard calibration curve.

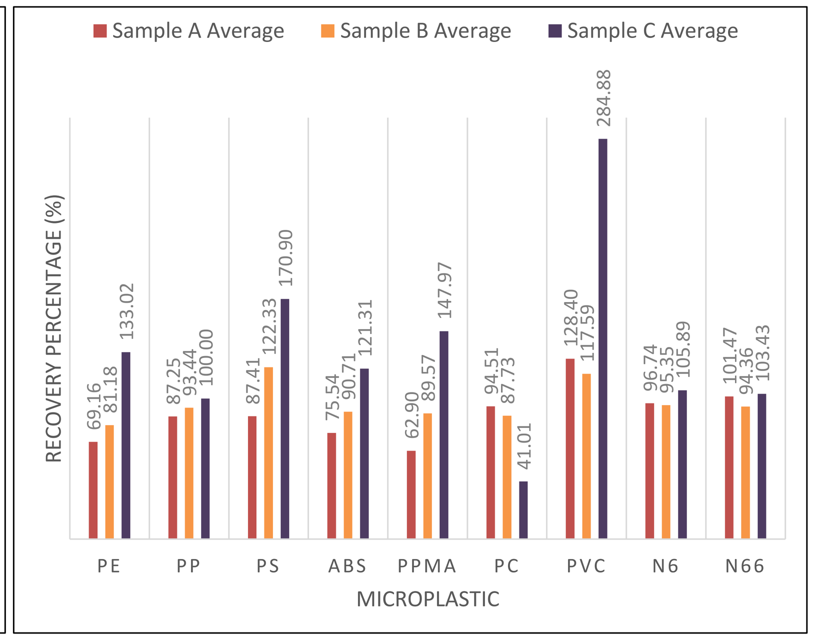
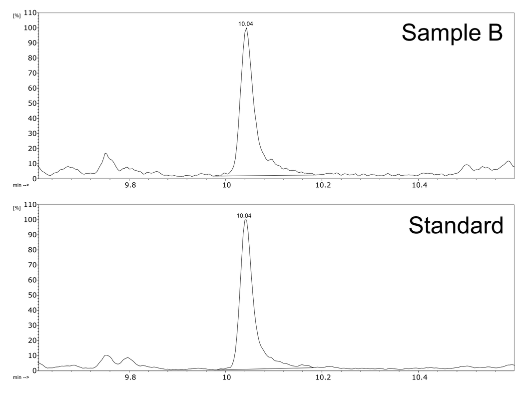


Figure 9. Recovery % for samples spiked at 2mg using the Sample B standard spiked calibration curve.

Scope B: Highlighting key challenges for the qualitative identification in samples



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	

Figure 5. PVC identification on Sample B using F-search MP 2.1 software.

- PVC was detected with more than 90% library match for all three samples. Sample B was used as an example, as shown in Figure 5.
- This could be one of the causes of why the recovery percentages were high for PVC on the samples, as Naphthalene is the marker used for quantitation of this microplastic.

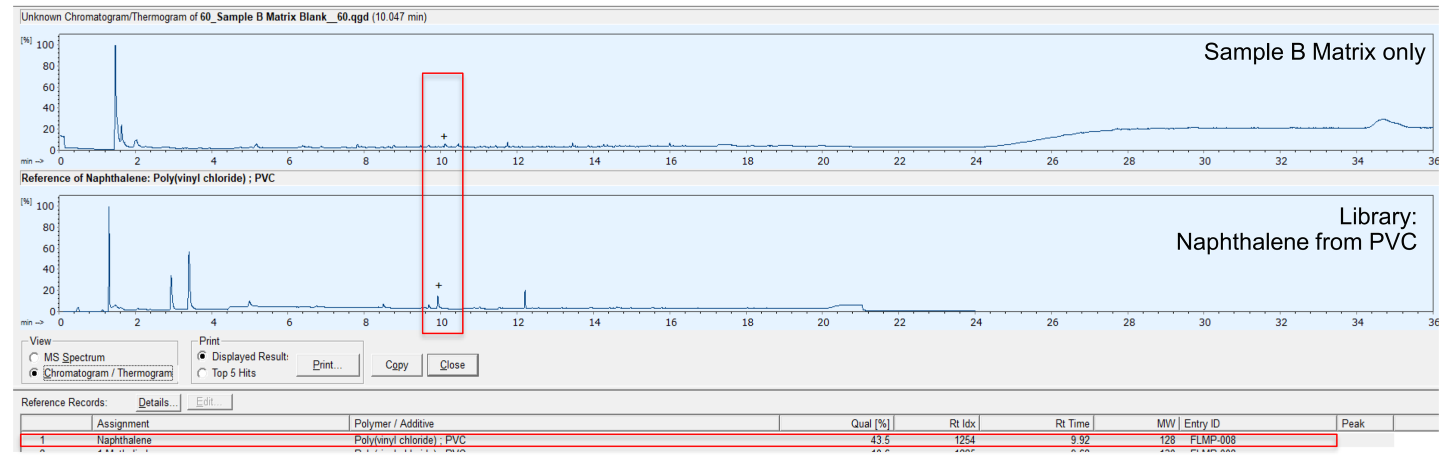


Figure 10. Library search result for the peak at 10.04 min on Sample B.

- When looking at the specific peak at 10.04 min, Naphthalene coming from PVC has a quality percentage of 43.5, meaning that PVC is not present in this sample, and Naphthalene is coming from another source. Shown in Figure 10.
- There are other markers used for PVC, such as hydrogen chloride, benzene, toluene, and styrene.
- These were not found on any of the samples.
- A pure PVC sample was used to compare the identification of these markers, as shown in Figures 11 and 12.

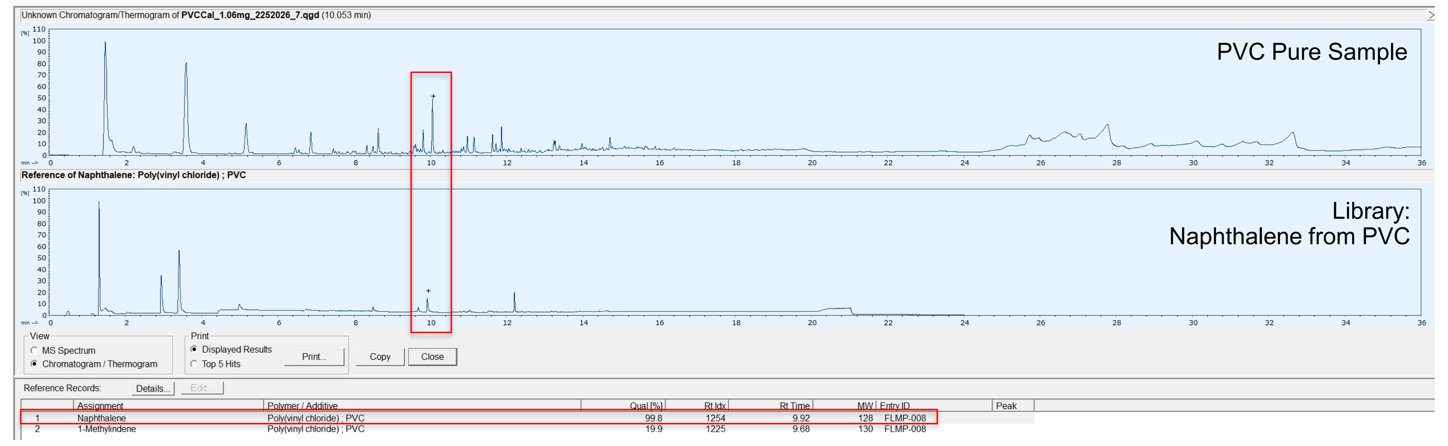


Figure 11. Library search result for the peak at 10.04 min on Pure PVC sample.

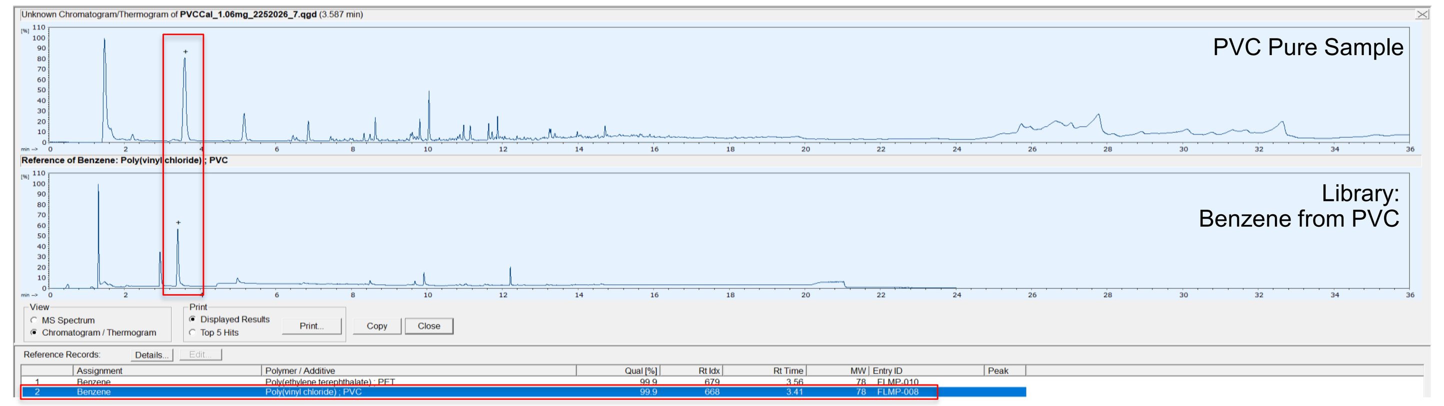


Figure 12. Library search result for the peak at 3.58 min on Pure PVC sample.

Conclusions

- Future work will focus on improving microplastic identification by using multiple markers to reduce false positives, while advancing polymer identification tools and spectral libraries to better handle high-background matrix interferences.
- Sample preparation is an important factor, and it needs to be considered and studied for different sample types, including environmental and clinical samples.