Analysis of plastics with Py-GC-MS – limitations and challenges

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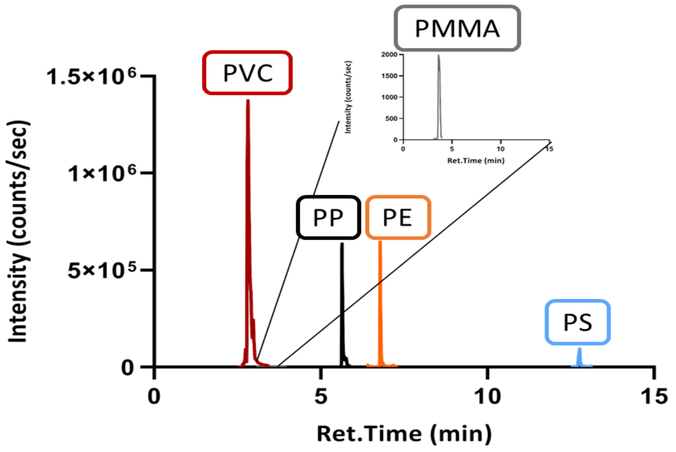
Pyrolysis-Gas Chromatography Mass Spectrometry

Mass based quantification

- Plastic is thermally decomposed at 650°C – breaks down into smaller molecules
- Small molecules are separated and detected with GC-MS
- Results reported as **total mass** of each plastic in a sample
- Is not size limited but does not provide characterisation (morphological) details

Plastic particles/fibres

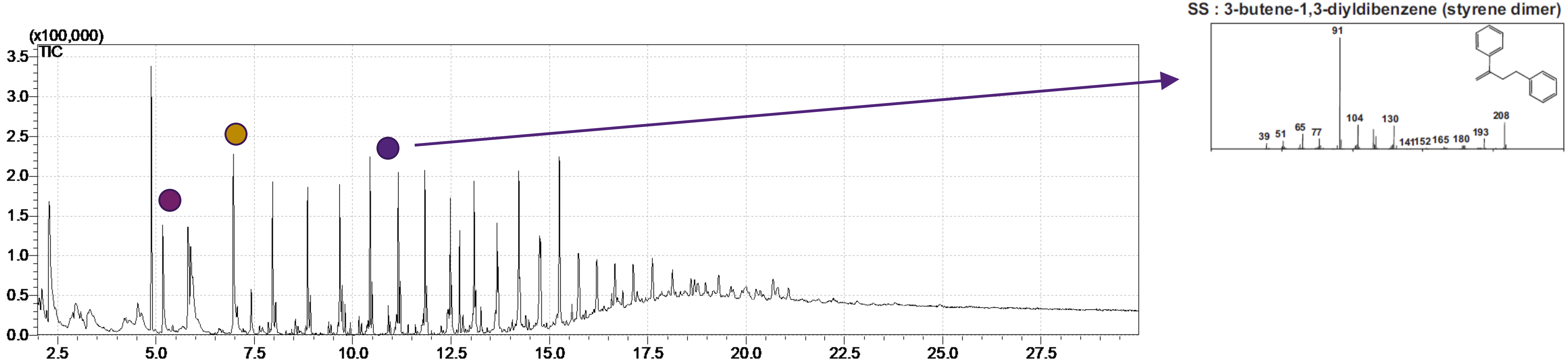


Sample cup

Py-GC-MS Analysis

ID and concentration of different polymers

Quantifying polymers



Plastic indicator compounds and ions

Plastic	Abbr.	Pyrolysis Product	Indicator ions (m/z)	Retention time (min)
Polypropylene	PP	2,4-Dimethyl-1-heptene	70, 83, 126	5.15
Polyethylene	PE	1-Decene (C10)	83, 97, 111, 140	6.97
Polystyrene	PS	3-butene-1,3-diyldibenzene (styrene dimer)	91, 117, 194, 312	16.77
Polyvinyl chloride	PVC	Benzene	78, 74, 52	2.86
Polyethylene terephthalate	PET	Vinyl benzoate	105, 77, 148, 51	8.42
Polycarbonate	PC	Bisphenol A	213, 119, 91, 165, 288	15.41
Poly-(methyl methacrylate)	PMMA	Methyl methacrylate	69, 100, 89	3.41
Styrene Butadiene Rubber	SBR	4-vinylcyclohexene	54, 79, 108	4.42
Natural Rubber	NR	Dipentene	68, 136	6.56

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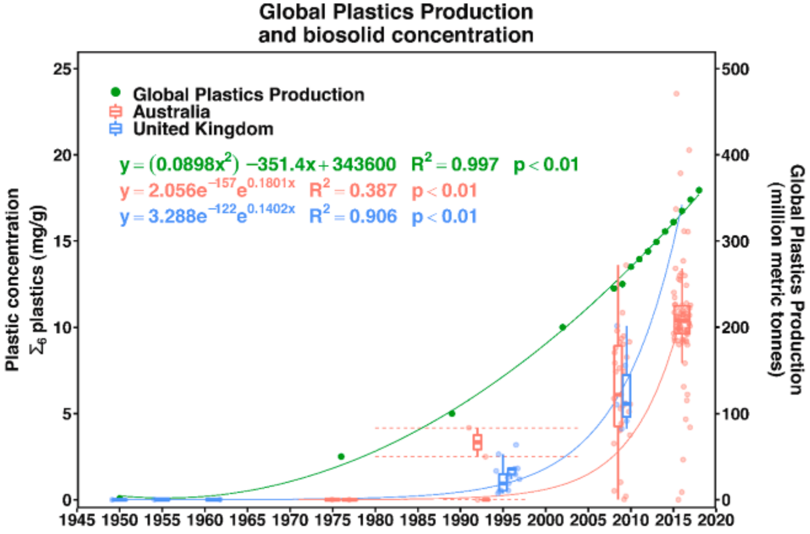
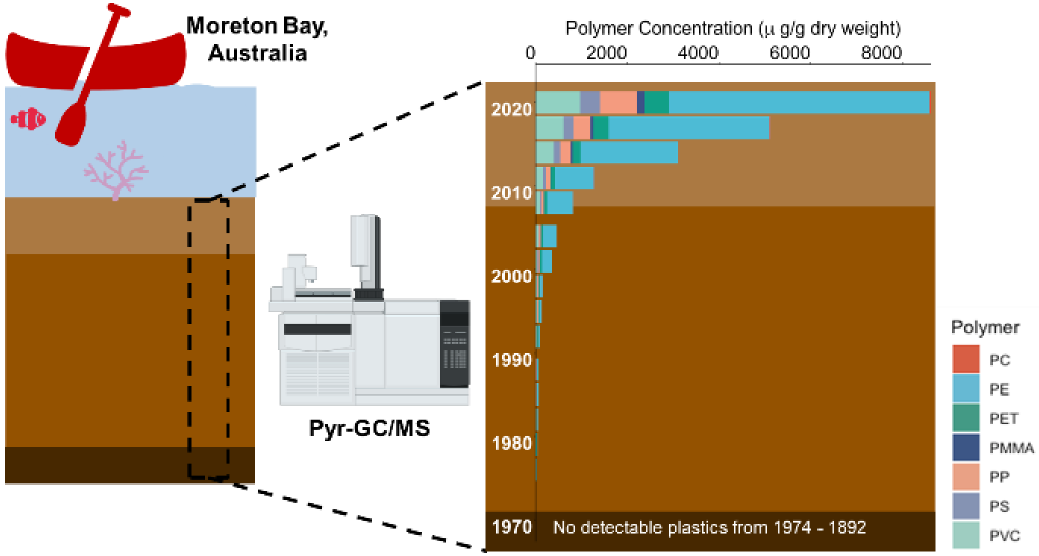
Validated methods for environment samples



Okoffo et al., 2021, *Water Research,* 201:117367



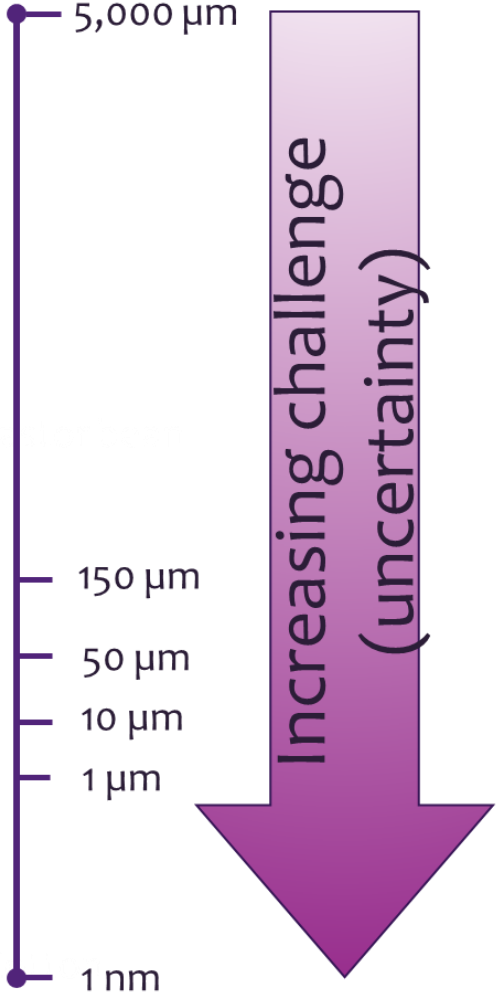
Yenney et al., 2024, *ES&T Water*, 4:4510

Biosolids: Okoffo et al, 2020, *STOTEN*, 715:136924; Okoffo et al, *ES&T*, 2022, 56:13785
Compost: Kaur et al, 2025, *STOTEN*, 973:179153
Road Dust: O'Brien et al, 2021, *J. Haz. Mat*, 15:125811
Soil & Sediment: Okoffo et al, 2024, *STOTEN*, 920:170987

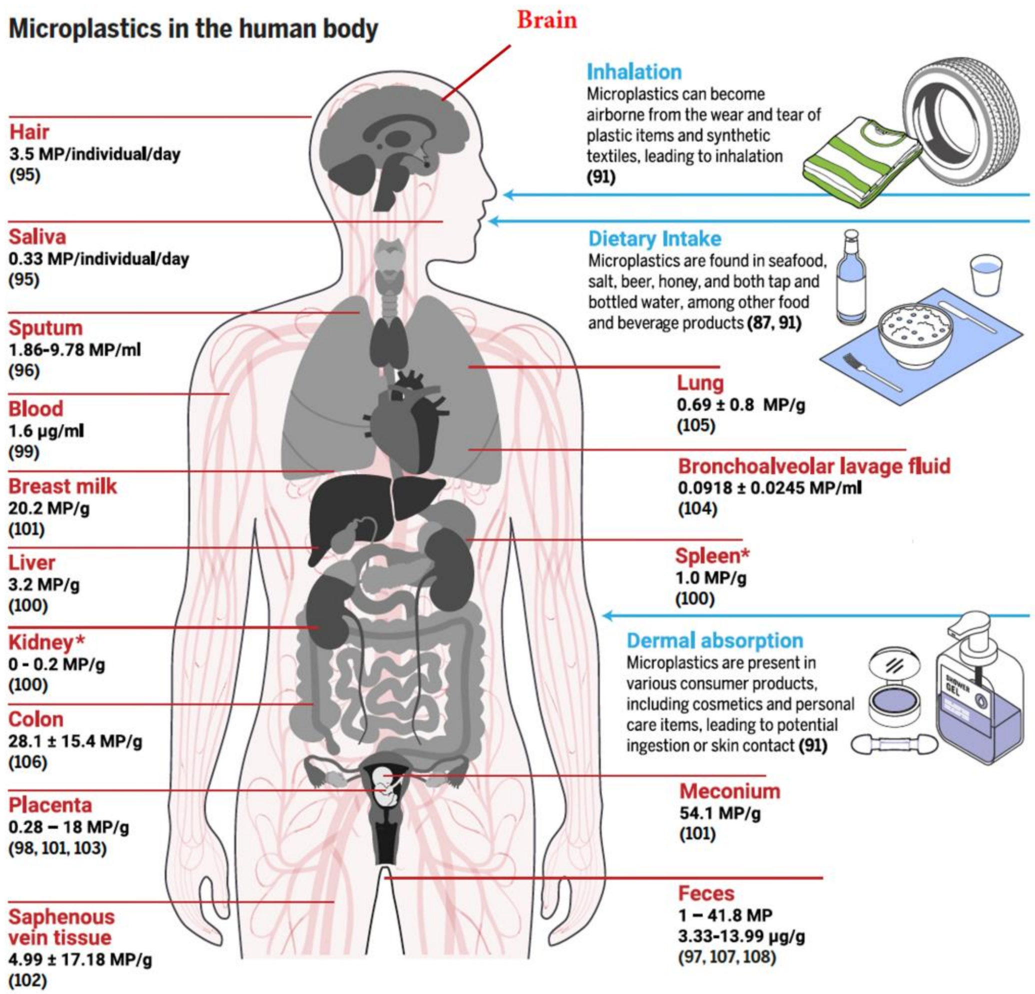
Biological samples – a challenging matrix

Key Challenges

1. MNPs are very small particles
   - the smaller you get the more uncertain the analysis
2. Complex matrices challenge accurate analysis
   - Increased background (hide the plastic signal)
   - Increased chance for matrix interferences
3. Very low concentrations challenge current analytical techniques
   - Are our detection limits enough to detect concentrations we expect in human matrices?



Studies now reporting MNPs in human matrices



Thompson et al., *Science*, 2024, 386:6720

Spectroscopy techniques report a range of sizes:

Sputum: 20 – 500 μm

Breast milk: 20 – >150 μm

Liver, kidney, spleen: 3 – 30 μm

Placenta: 5 – 307 μm

Lung: 9 – 2475 μm

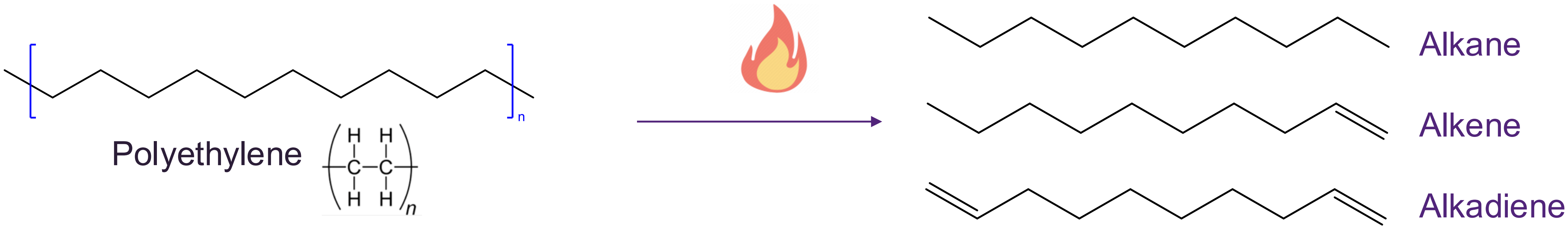
Py-GC-MS now used to report total mass. Common plastics:

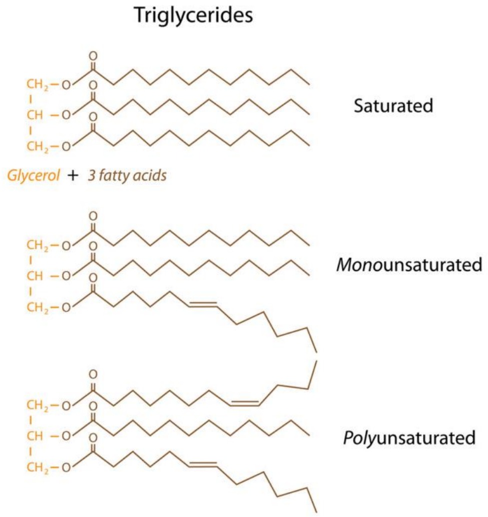
Polyethylene (PE)

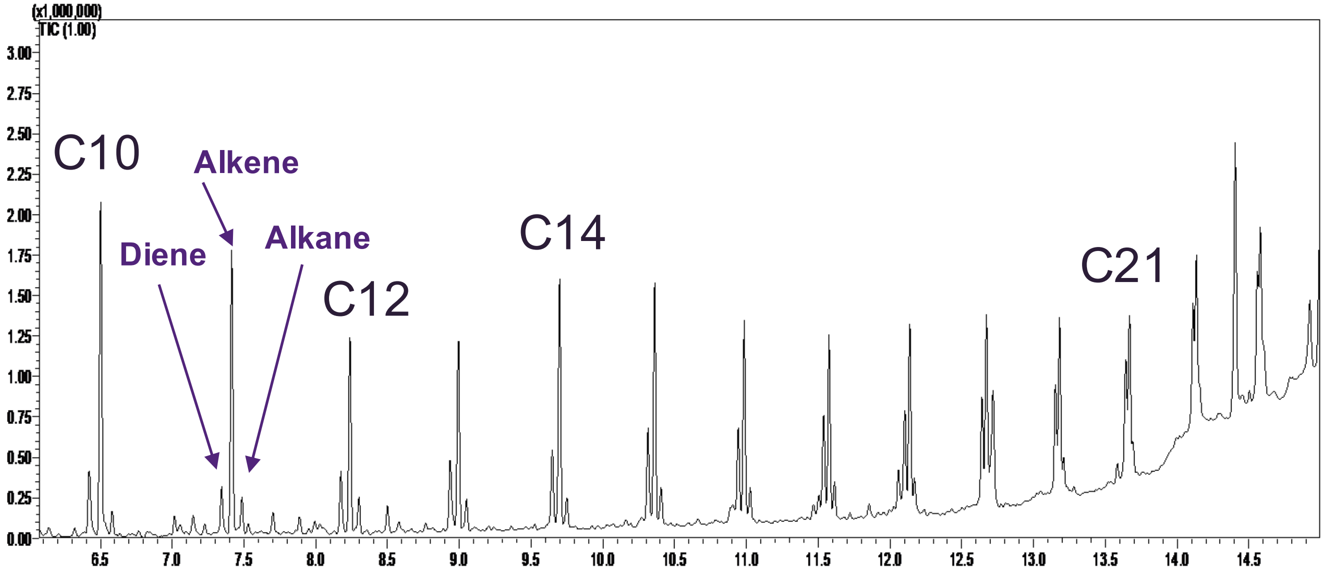
Polyvinyl chloride (PVC)

Nylons

Pyrolysis of Polyethylene

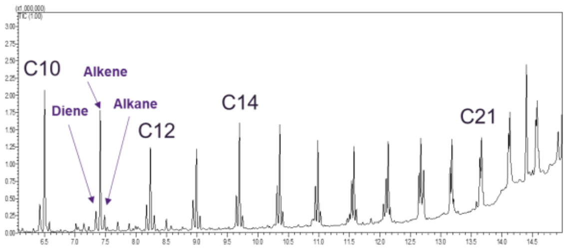






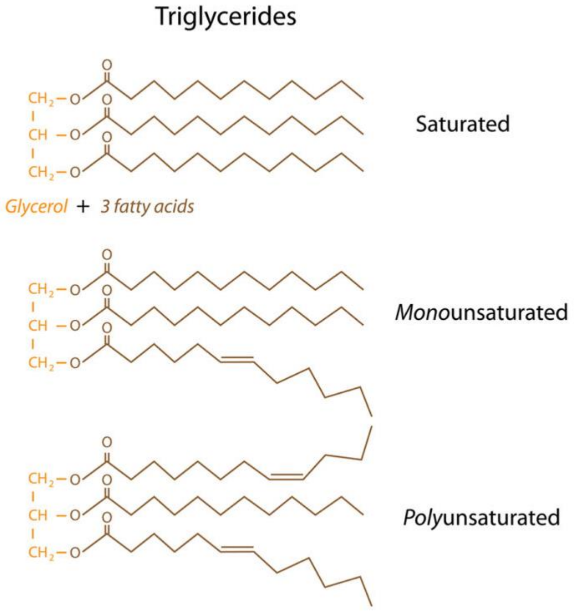
C10 alkene
C12 alkene
C14 alkene
C21 alkadiene

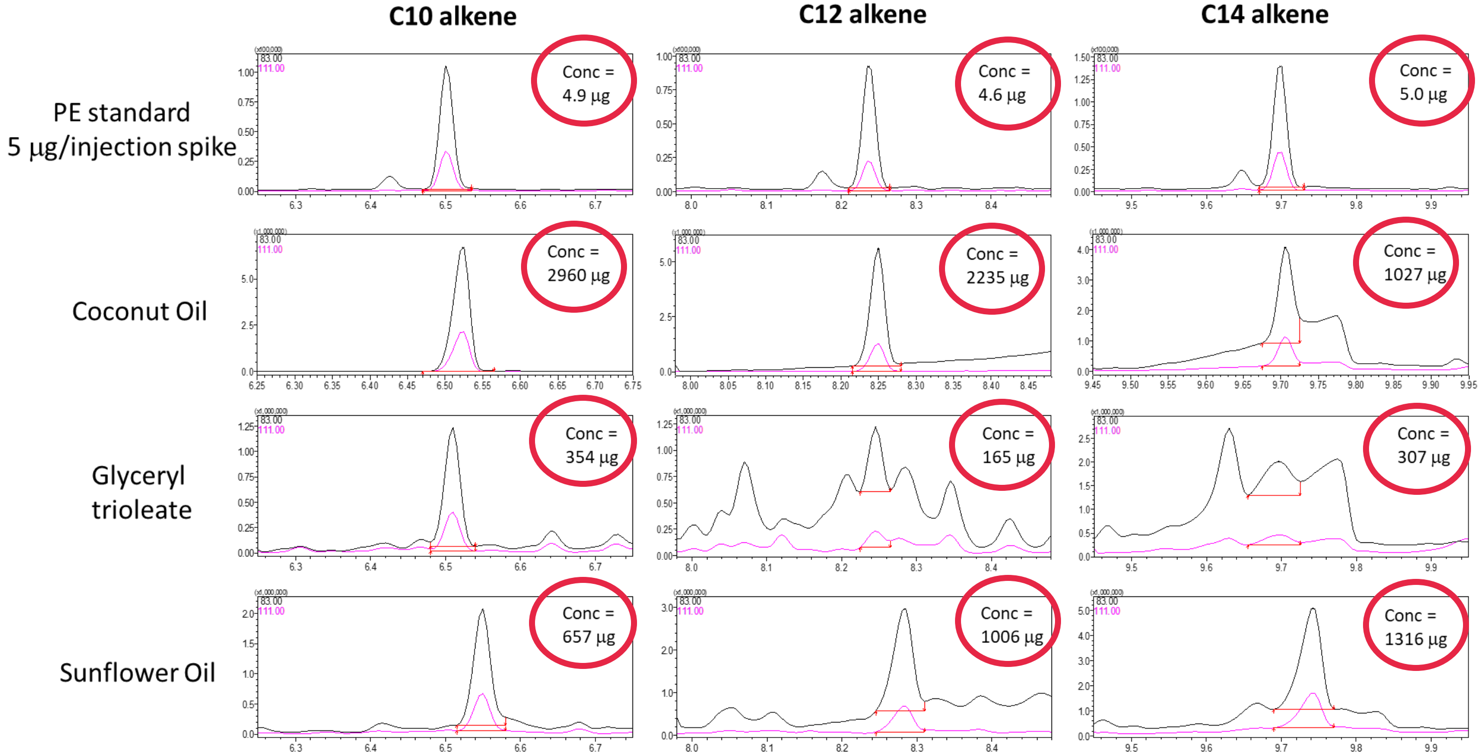
Assess potential matrix interferences



Our Previous study:

- Triacylglycerols (fatty acid type lipids) provide a false positive signal for PE



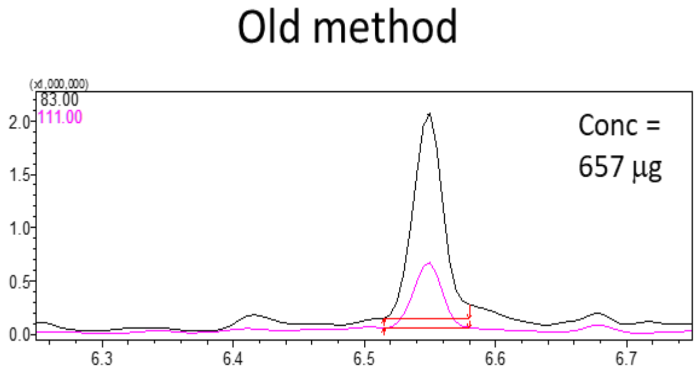


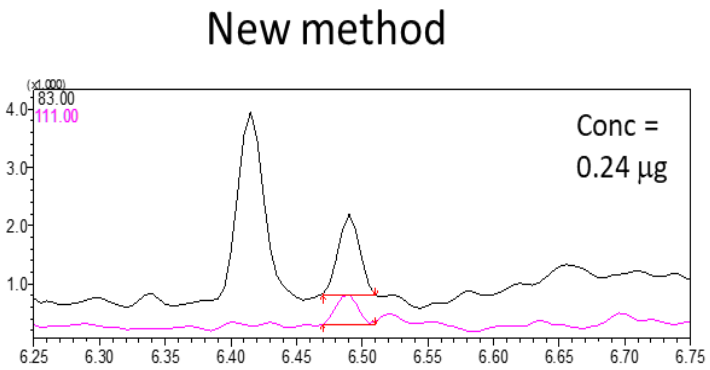
Rauert et al. (2022) *Journal Environmental Exposure Assessment*, 1:13

Removal of matrix interferences

Trials to remove from sample:

- Cannot remove during analysis (thermally decompose at same temperature as PE)
- Cannot remove with solvent extraction
- *Enzyme digestion to break triglycerides into short chain fatty acids and glycerol*
  - Develop protocol with pancreatic enzyme supplement CREON® (lipase, amylase, protease)
  - Softer digestion than acids, bases





Suitability of Py-GC-MS for human matrices

Pyrolysis-GC-MS has ability to provide information on nano-sized plastics

- Important for human exposure and risk assessments
- Potential to cross biological barriers in the body

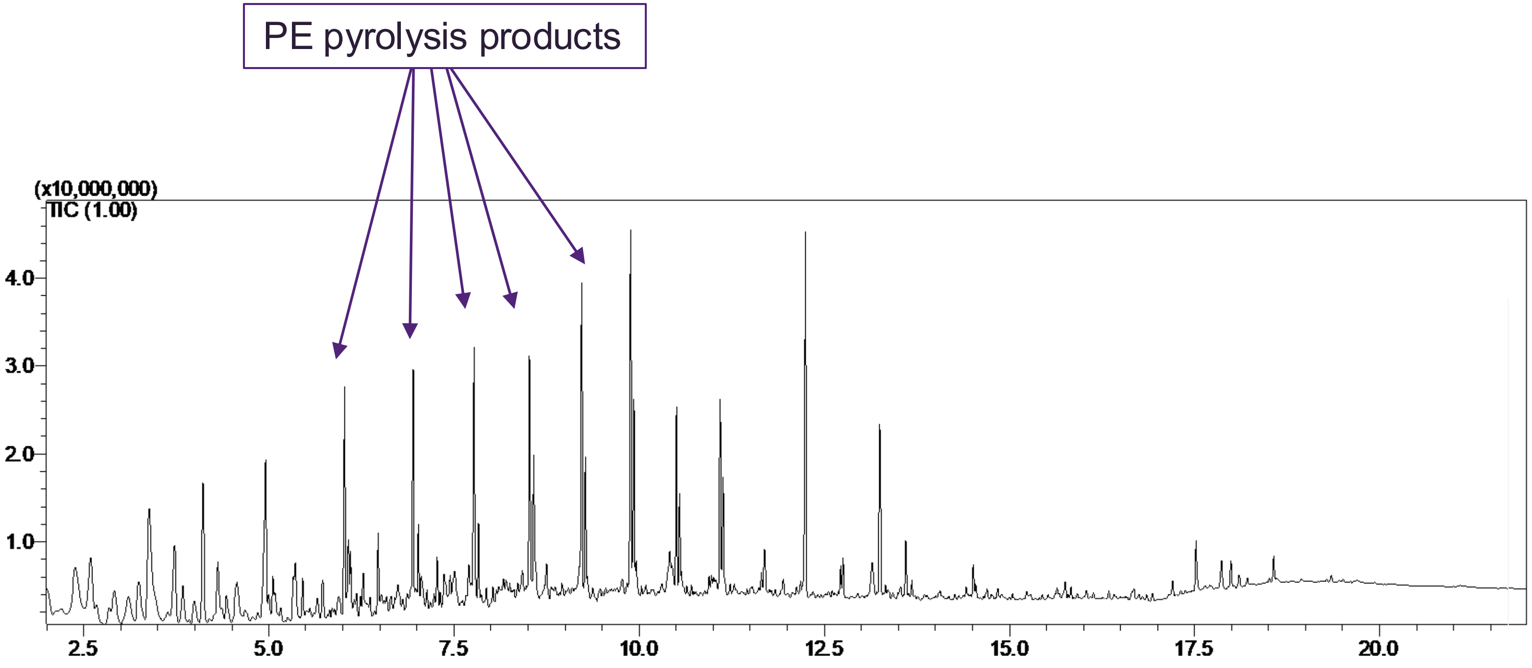
<u>Aim</u>: Asses the use of Py-GC-MS for identification and quantification of polymers in human blood

Rauert et al., 2025, *ES&T,* 59:1984

Blood - Assessing potential interferences

Potential interferences in blood

- Whole blood is only ~0.15% triglycerides
- But we still see a significant PE matrix interferences
  - The PE concentration calculated using different breakdown products is highly variable



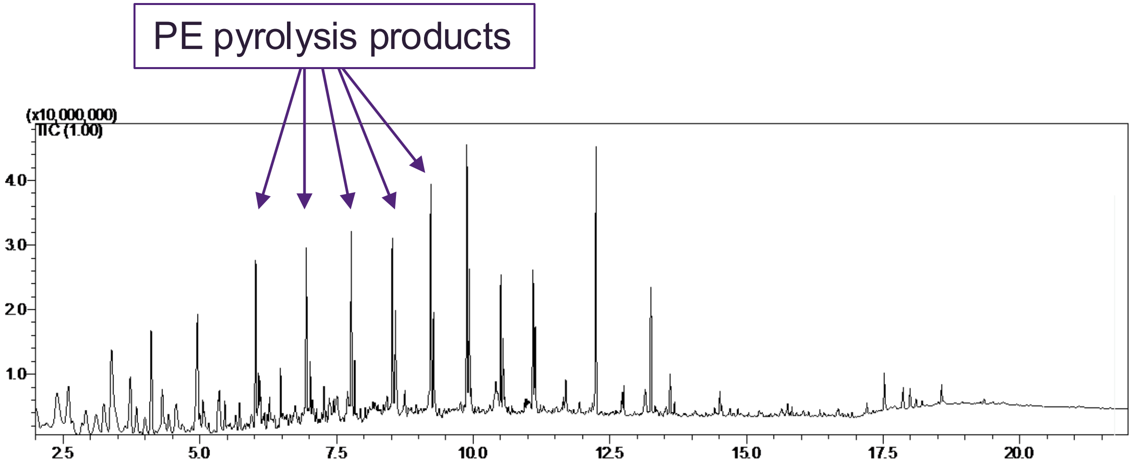
Blood – removal of interferences

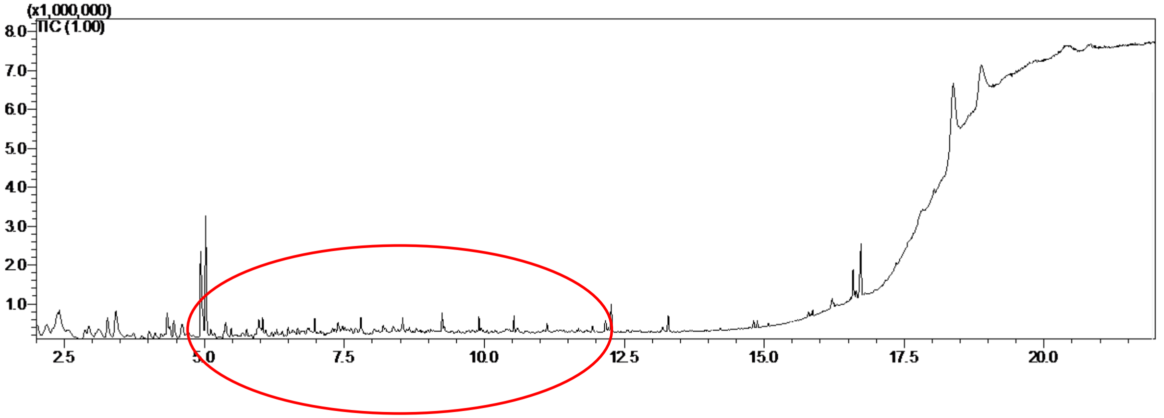
Extraction protocol developed with sequential digestions

1) Enzymatic digestion (lipase, proteinase K, amylase)

2) Oxidation of organic material with hydrogen peroxide

3) Sequential filtering to separate micro and nanosized plastics





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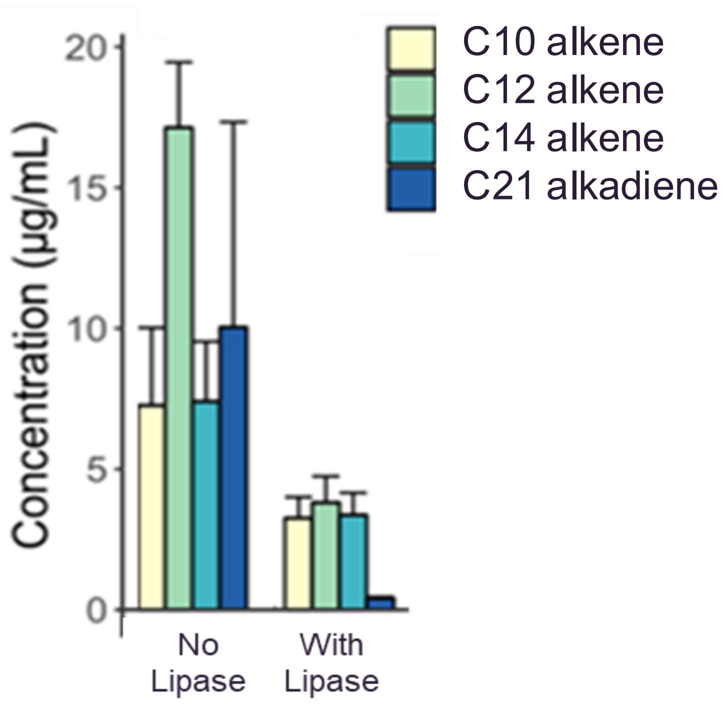
Enzymes significantly reduce the presence of interferences

- *However, trace levels are still present*
  - Concentration ratios suggest they are interferences

Conclusion

- Py-GC-MS not suitable for quantifying PE and PVC in human matrices
- Can be used for other polymers if concentration is high enough

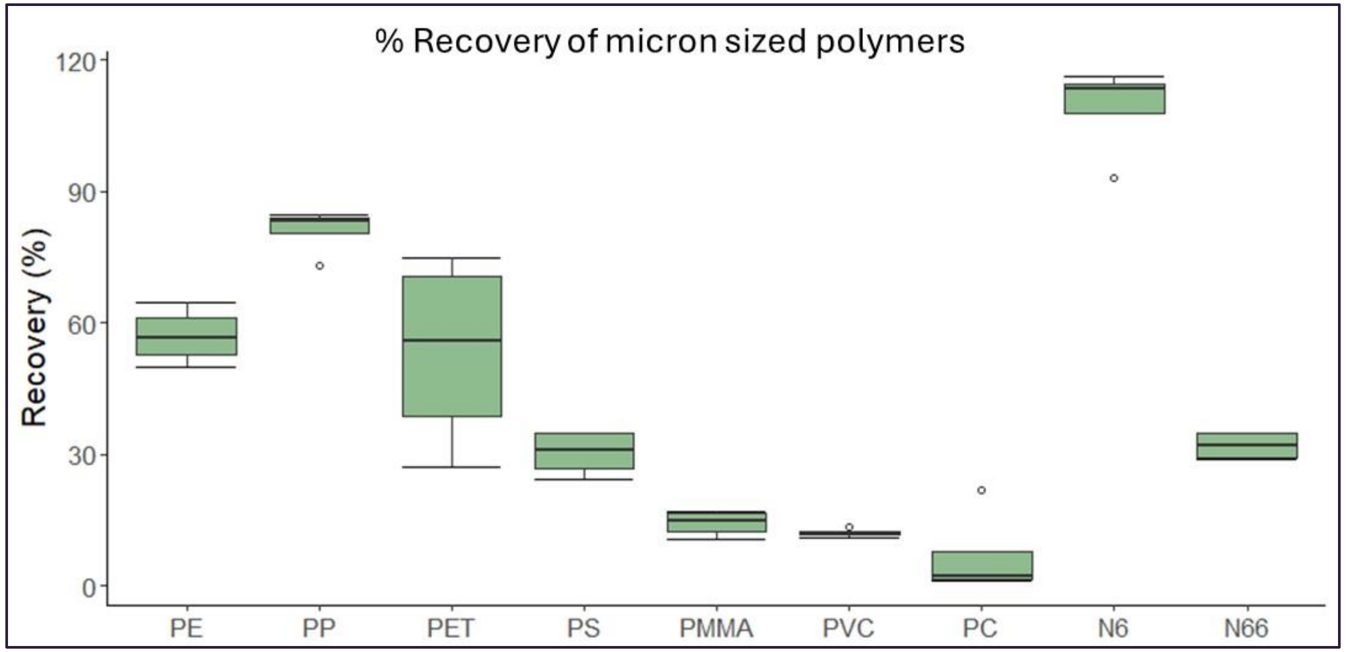
PE pyrolysis products



Method validation - Recovery tests

Commercial standards of nanosized plastics are not available for all polymers

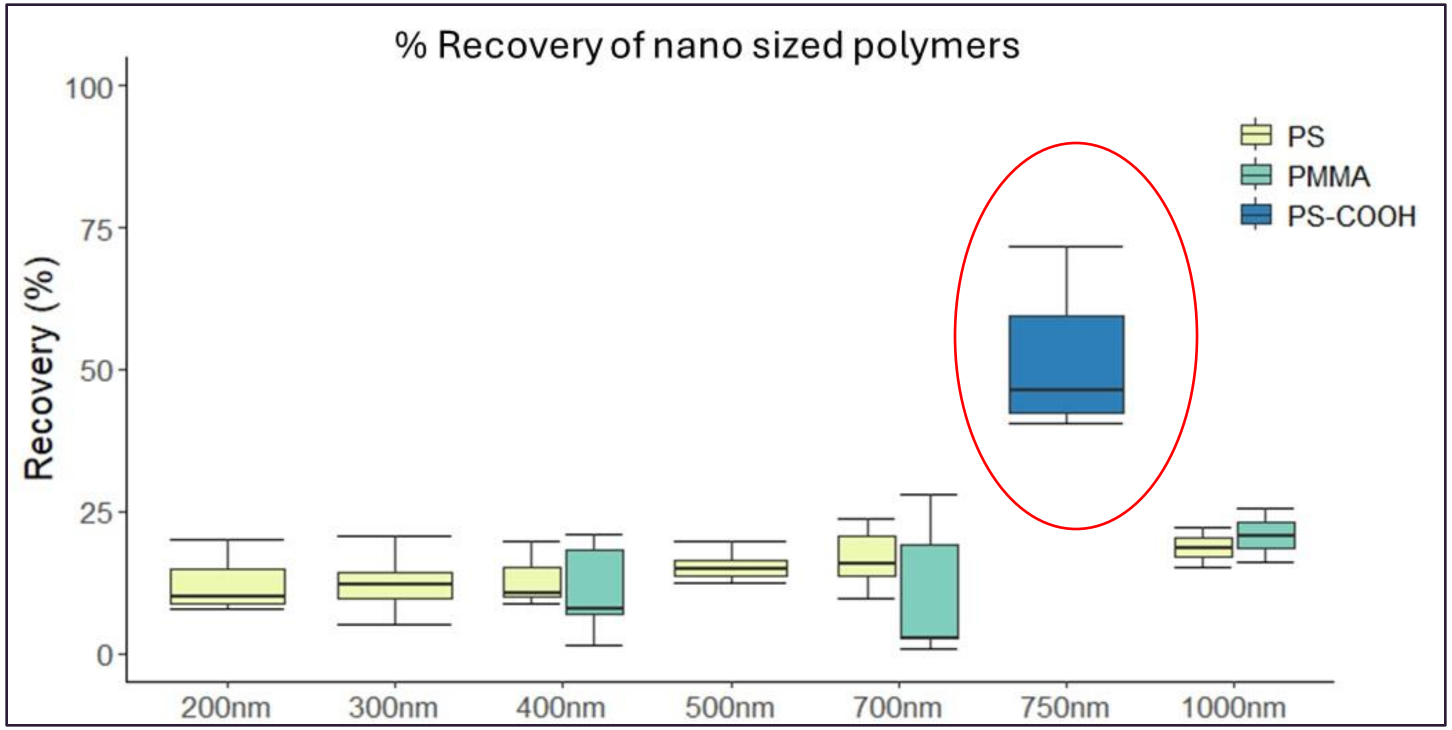
- Initial recovery tests with **micron-sized plastic standards** (<25 μm)
- Recoveries were polymer dependant
  - Only polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and Nylon 6 above 50%

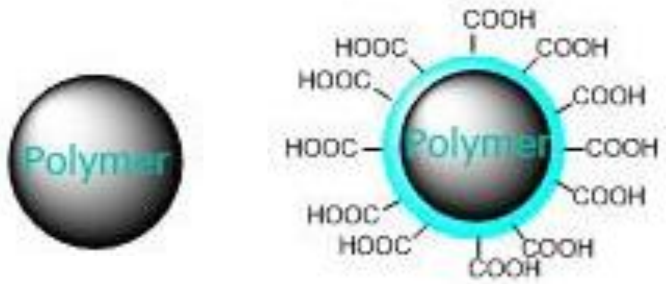


Method validation - Recovery tests

Commercial nanosized standards available for polystyrene (PS) and polymethyl methacrylate (PMMA)

- Spherical virgin plastics (may not be representative of environmental exposure)
- **Surface modification greatly improves recoveries**

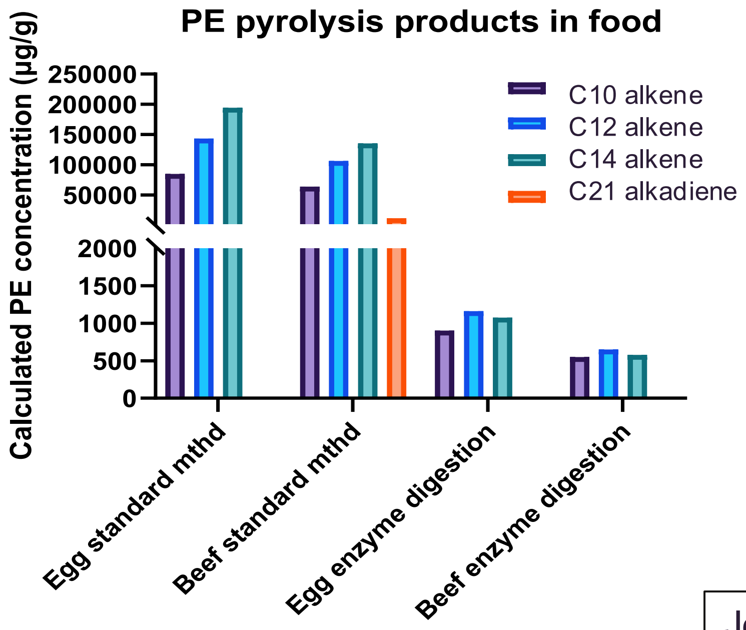




Application to food and beverages

Australian food basket survey – are we really ingesting a credit card a week?

- PP and PMMA detected in food (fruits and vegetables, grains and cereals, fish, dairy)
  - PP = 6300-6900 μg/g
  - PMMA = 1.3-10 μg/g
- Interferences for PE, PVC and PET (methylated product)

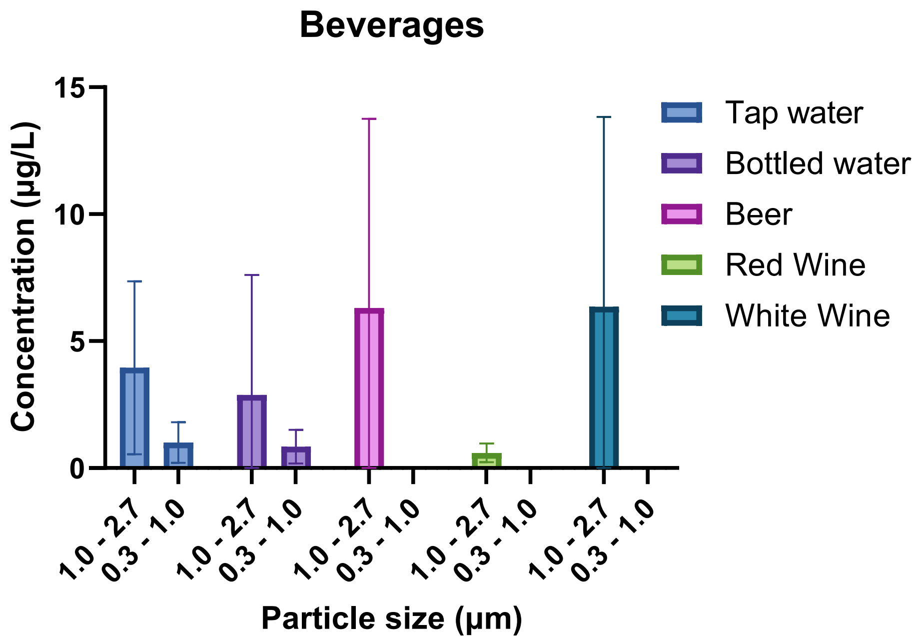


Jeffries et al., 2025, *ACS Food Sci. Technol.*, 5:1536

Application to food and beverages

Higher detection frequency in beverages (lower detection limits)

- Primarily PP (83% of samples, <0.03 – 7.14 µg/L)
- PET (<0.02 – 7.71), PS (0.004 – 11.64), PC (<0.04 – 1.05 µg/L)



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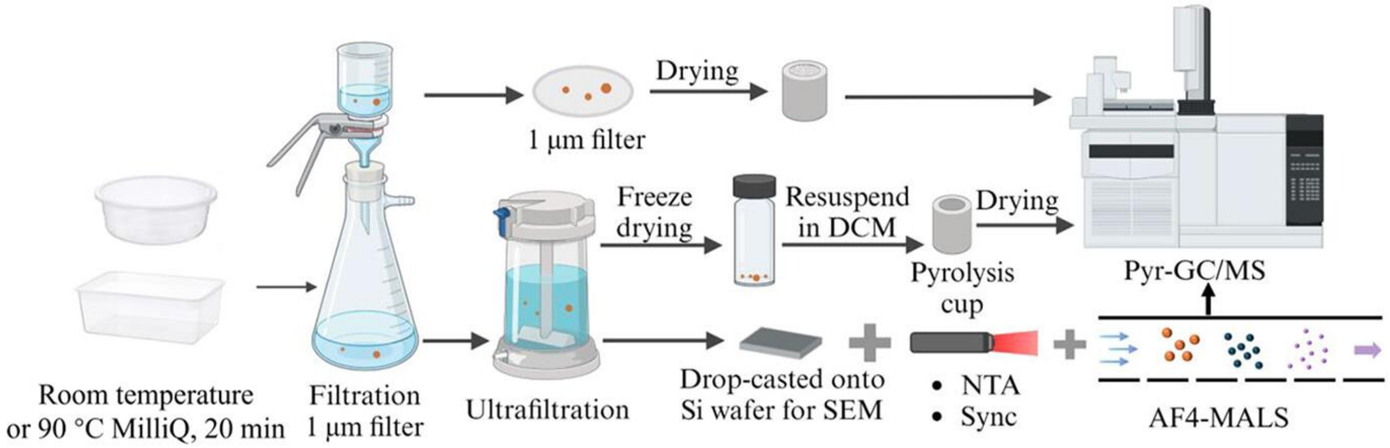
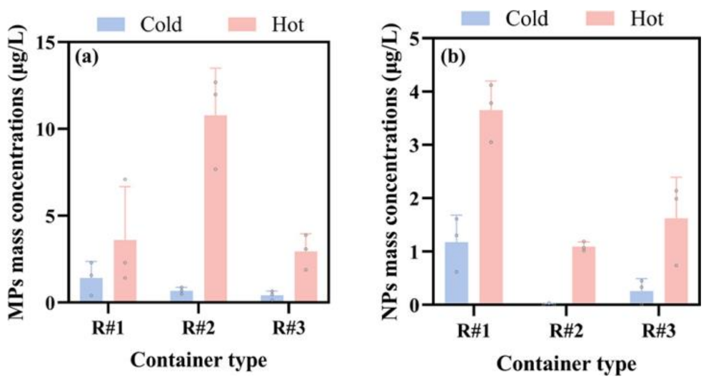
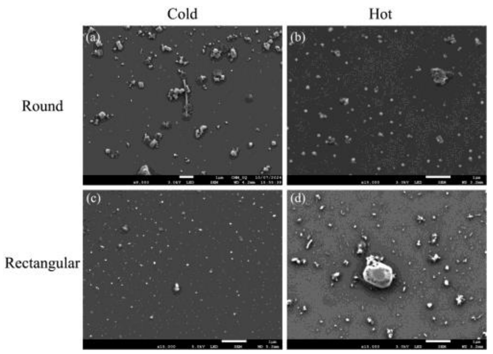
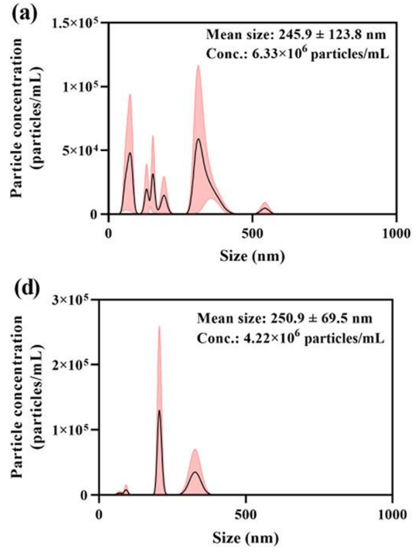
Confidence in reporting nanoplastics

Developing protocols using complimentary analysis techniques









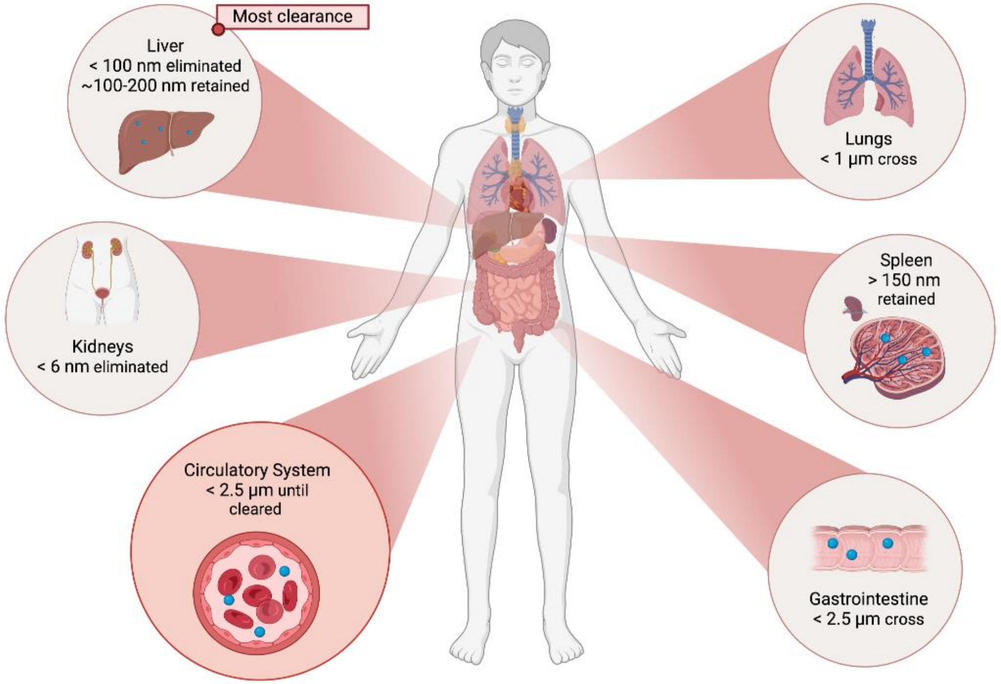
Shi et al., 2025, *J. Agric. Food Chem.* DOI: 10.1021/acs.jafc.5c11270

Interferences – final thoughts

Both mass spectrometry and spectroscopy methods have limitations and can suffer from matrix interferences

- For Pyrolysis-GC-MS:
  - Choose appropriate pyrolysis products (markers)
  - Monitor a range of markers to check for interferences
  - Consider different sample clean up strategies to remove interferences prior to analysis

- For all microplastic studies:
  - Consider background contamination control procedures
  - Consider biological plausibility of data being reported
  - Important to understand the matrix and develop appropriate quality control measures



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Thank you

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