

Supporting Information for: “Comparative Assessment of Five Analytical Methods for Airborne Microplastics Highlights Importance of Identifying Sub-10 µm Methods”

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airborne OR atmosphere OR atmospheric AND microplastics OR microplastic OR nanoplastic
OR nanoplastics AND TD-PTR-MS

Results = 4

airborne OR atmosphere OR atmospheric AND microplastics OR microplastic OR nanoplastic
OR nanoplastics AND py-gc-ms OR py-gc/ms OR pyrolysis

Results = 17

airborne OR atmosphere OR atmospheric AND microplastics OR microplastic OR nanoplastic
OR nanoplastics AND raman OR μ Raman

Results = 143

airborne OR atmosphere OR atmospheric AND microplastics OR microplastic OR nanoplastic
OR nanoplastics AND FTIR OR μ FTIR

Results = 166

airborne OR atmosphere OR atmospheric AND microplastics OR microplastic OR nanoplastic
OR nanoplastics AND Nile red OR fluorescence microscopy

Results = 11

Methods

Sampling Information

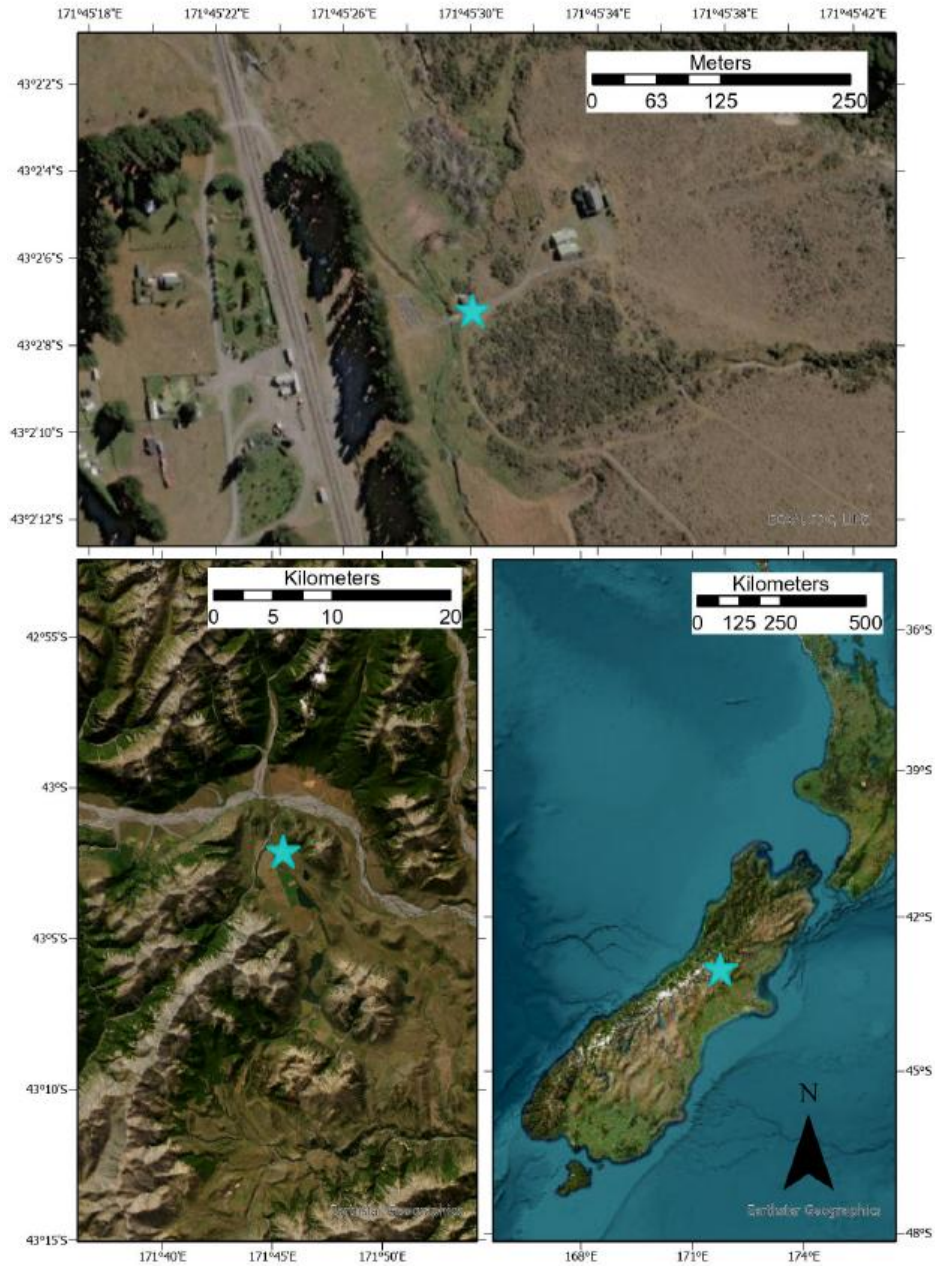


Figure S1. Cass field station sampling site map, blue stars indicate sampling site. Map created in ArcGIS Pro with basemap imagery from Earthstar Geographics, Environment Canterbury, Selwyn District Council, and Land Information New Zealand.

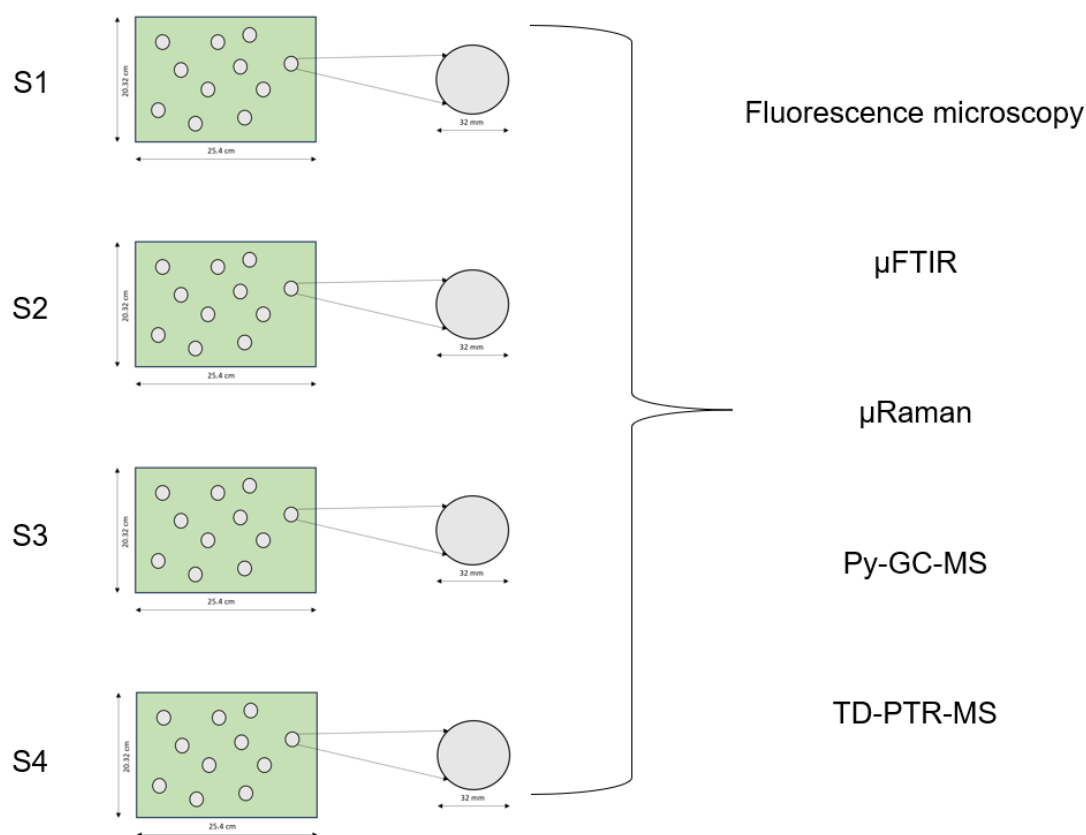


Figure S2. Diagram of sampling for each day: four high volume aerosol filters collected and subdivided per day ($d = 4$) (each subsample 32 mm in diameter).

Quality assurance and quality control

Cleaning of equipment

All glassware was soaked overnight in lab-grade detergent (Decon 90) and scrubbed, triple rinsed with deionized water, triple rinsed with ultrapure water ($18\text{M}\Omega$, $0.2\ \mu\text{m}$), triple rinsed with methanol and triple rinsed with acetone. All solvents used were HPLC grade ($>99.99\%$, Thermo Fisher). All aluminium storage tins were soaked overnight in lab grade detergent (Decon 90) and scrubbed, then triple rinsed with deionized water. Once dried, all tins were triple rinsed with ultra-pure water and methanol. All aluminium storage trays were triple rinsed with ultra-pure water and methanol. All aluminium foil was prebaked in a muffle furnace at $450\ ^\circ\text{C}$ for 4-5 hours.

As the filters were too large to be placed in available furnaces to be pre-baked, they were taken directly from the supplier's box to be placed into the sampler. Baking of filters would otherwise be recommended for any studies to remove potential contamination. All results presented have been blank corrected throughout to account for any contamination caused from this. Field blanks were collected during every sampling period by exposing an identical filter to those placed in the high-volume samplers to the field site for 30 s and handled in the same way as field samples as stated above.

Labrocare fume hood cabinets were first cleaned and wiped down with ethanol and lined with aluminium foil. The fume hood was turned off during sample preparation to limit air movement and contamination from airborne particles. Any solvent rinsing in between sample preparation was completed in another fume hood, which was turned on, but all laboratory equipment being cleaned was kept covered in pre-cleaned aluminium foil. Cotton lab coats were worn when undertaking laboratory work, and in general, in any setting, researchers wore only clothing made of natural fibres (i.e. cotton or merino wool) when handling samples.

Quality assurance and quality control steps applied to individual analytical methods are described below.

Nile red

All samples were imaged under the same settings to ensure the automated ImageJ process was consistent throughout at identifying particles. All field-blank samples underwent identical preparation and staining steps to account for contamination during staining.

Micro-Fourier transform infrared spectroscopy

Calcium fluoride disks were stored in glass petri dishes between sample plating and analysis. Images were taken before and after analysis of the disks to compare for contamination and to provide a reference image of the particles analysed. Tweezers were cleaned with methanol and acetone in between uses. Spiked samples and blanks were made up by adding 10 spiked particles (of a range of polymer types and sizes, with the smallest spike being $\sim 32\text{ }\mu\text{m}$) to two blanks and two sample filters. All spiked particles were successfully retrieved and identified, yielding a 100% spiked recovery rate. As no analysed particles, except for spikes, showed plastic properties in the spectral outputs, no further QA/QC measures were applied.

Micro-Raman spectroscopy

The microplastic laboratory used for Raman analysis has controlled access, functions under a HEPA filtered (clean air) environment and is cleaned prior to any new sample analysis. All researchers wore 100% cotton clothing and lab coats while working with the samples in the positive-pressure fume hood.

Pyrolysis-gas chromatography-mass spectrometry

All solvents used for cleaning steps were HPLC grade and a cotton lab coat was always worn during sample preparation. The instrument was pre-heated before running samples, heating the pyrolysis unit to 800 °C for 5 minutes and the GC to 320 °C for 5 minutes. An empty, clean pyrolysis cup was run in single shot between sample sets as a cleaning step. The auto-shot sampler was cleaned using ethanol, Kimtech wipes and cotton q-tips before and after each use. Internal standard blanks were run for each sample set with just the internal standard to check for contamination during this analysis stage, with no detection of any polymers across all of these. All results were checked following the same quantification steps as samples, with no polymers identified. These were done alongside field blanks, which were used to account for any contamination in the study through blank corrections. All components and mixing balls for the ball mill were stainless steel and were pre-cleaned with solvents and in the oven. Instrument recovery rates were calculated using triplicate spiked blanks from a midpoint weight of the Microplastics Calibration Standard set for MPs analysis using Py-GC/MS from Frontier Laboratories.

Thermal desorption-proton transfer reaction-time of flight-mass spectrometry

Glass vials and stainless-steel screw caps used were all pre-cleaned and heated up to 250 °C for two hours. Teflon caps were used, with PTFE being excluded from analysis. System blanks and field filter blanks were also processed using identical methods to ensure any contamination was accounted for. An overall field blank mean was calculated after ppb calculations. All sample results were checked against the field blank results using a t-test, with all samples returning significant results (p value < 0.05). All sample results were blank-subtracted, and triplicate values were averaged for each sample. To monitor ionisation efficiency and recovery rates, random samples and blank samples were spiked with 200 ng of PS nanoparticles (0.5 µm, analytical standard, Sigma Aldrich) and the polymer was successfully identified in all spiked

samples. An average of 119 ng out of the 300 ng spike was measured, indicating an ionisation efficiency/recovery rate of 40%. The transmission efficiency was calibrated with NPL (UK) gas standards resulting in: m/z 21 = 0.007, m/z 79 = 0.41, m/z 93 = 0.54, m/z 107 = 0.64, m/z 147 = 0.86, m/z 181 = 1.0.

ImageJ Image Processing Macro

```
input = "source directory";
output = "output directory"

setBatchMode(true);
list = getFileList(input);
for (i = 0; i < list.length; i++) {
    action(input, output, list[i]);
}
setBatchMode(false);
function action(input, output, filename) {
    open(input + filename);
    run("Set Scale...", "distance= \"reference\" known=1.0 pixel=1 unit=µm global");
    run("8-bit");
    setThreshold(Apply);
    run("Set Measurements...", "area shape feret's perimeter redirect=None decimal=3");
    run("Analyze Particles...", "size=1-Infinity show=outlines display clear include");
    saveAs("Results", output + filename + "_results.csv");
    run("Enhance Contrast", "saturated=0.35");
    saveAs("Tiff", output + filename + "_processed.tif");
}
```

Micro-Fourier transform infrared spectroscopy analysis – spectral databases

Wiley IR spectral databases used were - *industrial chemicals, pure organic compounds; organosilicons; polymers, Hummel defined basic; Sadtler acrylates and methacrylates; Sadtler fibres and textile chemicals; Sadtler fibres by microscope; Sadtler inorganics; Sadtler polymers and monomers (comprehensive); Sadtler polymers, Hummel; Sadtler standards (organic and polymeric compounds subset); Sigma-Aldrich library of FT-IR spectra; Microplastic Classifications - Wiley.*

Pyrolysis-Gas Chromatography/Mass Spectrometry Specifications

Table S1. Py-GC/MS Instrument Settings and Specifications

Apparatus	Parameters	Settings
Micro-furnace Pyrolyzer (Frontier Labs Double-shot Pyrolyzer, PY-2020 ID)	First-shot furnace temperature programme (thermal desorption)	Ramped from 100 °C at 20 °C /min, up to 300 °C (held for 1 min)
	Second-shot furnace temperature programme (pyrolysis)	650 °C
	Interface temperature	320 °C
	Pyrolysis time	12 s (0.20 min)
	Frontier Labs MJT- 1030E Microjet Cryo- Trap	−190 °C
GC (Agilent Technologies, 7890A GC System)	GC column	J&W DB-5MS GC Column: 60 m length, 0.25 mm diameter, 0.25µm film thickness, 5 inch cage, fused silica (Agilent Technologies)
	Injector temperature	300 °C
	GC column oven temperature program	40 °C (2 min) → (20 °C /min) → 320 °C (hold time 14 mins)
	Injector mode	Split: 5:1 (5 mL/min)
	Carrier gas	Helium, 1.0 mL/min
MS (Agilent Technologies, 5975C, inert EI MS)	MS Source temperature	230 °C
	MS Quadrupole temperature	150 °C
	Electron Ionisation	70 eV
	Scan range	<i>m/z</i> 40-600
	Scan frequency	2.6 Hz

Table S2. Pyrolysis products with quantification ions and specific instrument retention times used for quantification of polymers. Ions in bold were used for quantification, *ions were used for assessing ratios.

Polymer	Monitored pyrolysis products	Indicator ions (<i>m/z</i>)	Molecular ion (<i>m/z</i>)
PE	Alkadienes (C ₂₁) <i>n</i> -alkenes (C _{10,12,14})* <i>n</i> -alkanes (C _{10,12,14})	82 95, 83 85	294
PP	2,4-Dimethylhept-1-ene	70, 83, 111, 126	126
PS	2,4-Diphenyl-1-butene (dimer)	91 , 130, 193, 208	208
PMMA	Methyl Methacrylate	69, 100 , 89	100
PC	Isopropenylphenol	119, 134 , 91	134
PVC	Benzene Naphthalene 1-Methylnaphthalene * 2-Methylnaphthalene*	78 128 142 142	128
Nylon 6	ε-caprolactam	113 , 85, 55	113
Nylon-66	cyclopentanone	84 , 55	84
<i>Deuterated Polystyrene(d₅-PS)</i>	<i>d₅-styrene monomer</i>	54, 82, 107, 109	

**Bolded ion was used for quantification with * ion used to assess for standard ratios.*

TD-PTR-MS Specifications

We used the following operation parameters of PTR-TOF-MS: inlet temperature = 180 °C, drift temperature = 120 °C, drift tube pressure = 2.9 mbar, and drift tube voltage = 480 V, resulting in the approximate reduced electric field (E/N) of 120 Td.

Results

Nile red fluorescence microscopy

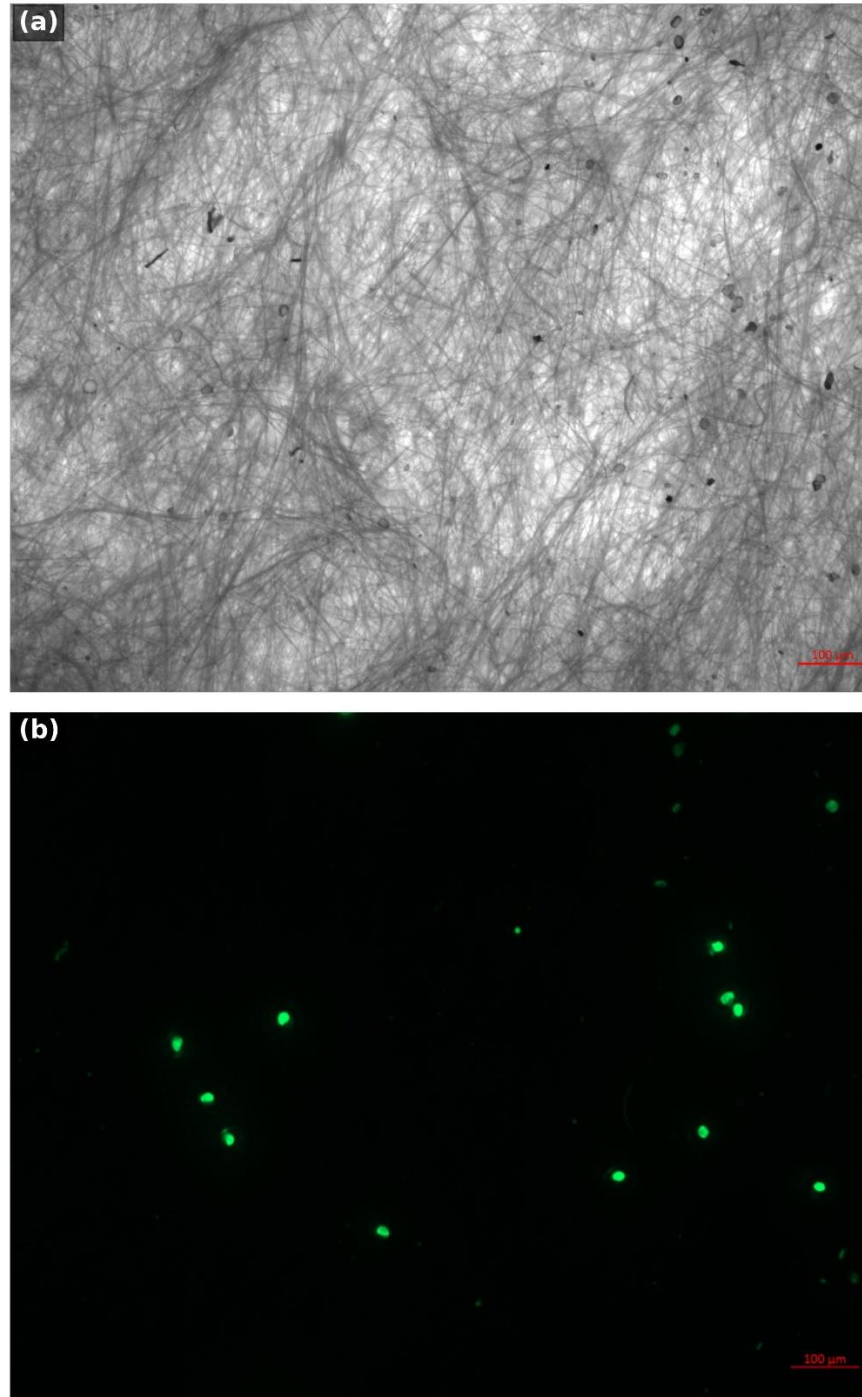


Figure S3. Example of (a) bright field imagery of filter sub-section and corresponding (b) GFP imagery. This specific image is from d1_s1.

Table S3. Summary table for Nile red particle count results. Mean results for each sample in particles m⁻³, mean and standard deviation of replicates for each day and the daily mean and standard deviation. D1 refers to day 1, S1 refers to sampler 1.

Sample	Sample mean (particles m ⁻³)	Replicate mean (particles m ⁻³)	Daily mean (particles m ⁻³)
D1_S1	1493.97	1314.83 (±170.58)	1890.56 (±1051.24)
D1_S2	1351.96		
D1_S3	1083.34		
D1_S4	1330.06		
D2_S1	197.19	699.19 (±403.62)	
D2_S2	1140.83		
D2_S3	588.22		
D2_S4	870.52		
D3_S1	3895.49	2814.14 (±750.52)	
D3_S2	2427.43		
D3_S3	2212.13		
D3_S4	2721.51		
D4_S1	2470.20	2734.07 (±774.51)	
D4_S2	2735.41		
D4_S3	1944.59		
D4_S4	3786.06		

Table S4. Fibres vs fragment particle counts from Nile red fluorescence microscopy

Day	Total Fibres	Total Fragments
1	6	740
2	6	485
3	15	1688
4	30	1682

Raman

Table S5. Summary table for Raman results. Sample mean for all summed polymer types in MP m⁻³, replicate mean ($\pm$ std dev) and daily mean ($\pm$ std dev).

Sample	Sample mean (MP m ⁻³)	Replicate mean (MP m ⁻³)	Daily mean (MP m ⁻³)
D1_S1	225.55	146.20 (±57.23)	160.63 (±55.81)
D1_S2	90.22		
D1_S3	126.74		
D1_S4	142.28		
D2_S1	230.03	230.94 (±90.52)	
D2_S2	348.41		
D2_S3	217.33		
D2_S4	127.99		
D3_S1	391.43	168.98 (±148.82)	
D3_S2	107.32		
D3_S3	77.88		
D3_S4	99.31		
D4_S1	79.06	96.41 (±20.98)	
D4_S2	78.48		
D4_S3	107.91		
D4_S4	120.19		

Py-GC/MS

Table S6. Py-GC/MS calibration r^2 values, recovery rates, limit of detection and method detection limits for each polymer type. LOD is used when MDL = 0.

Polymer	r^2	Mean Recovery %	LOD (μ g)	MDL (μ g)
PE	0.98	85	0.98	0.98
PP	0.96	106	0.25	0.25
PS	0.86	101	0.06	0.06
PMMA	0.97	105	0.23	0.49
PC	0.97	90	0.34	0.34
PVC	0.97	96	0.31	3.20
N-6	0.97	88	0.37	0.37
N-66	0.98	102	0.18	1.05

Table S7. PE Ratios, checking that results are within a 1:2 range of standards.

sample	CONCENTRATION (ug)				RATIOS		
	PE_C10	PE_C12	PE_C14	PE_C21	PE-C10/C12	PE-C10/14	PE-C10/C21
PE STD	5.82	5.66	5.76	5.27	1.03	1.01	1.11
D1/S1	0.00	0.00	8.13	0.68	-	-	-
D1/S2	10.08	12.72	10.53	0.54	0.79	0.96	18.54*
D1/S3	9.67	11.52	9.96	1.25	0.84	0.97	7.73*
D1/S4	0.00	11.96	9.25	0.00	-	-	-
D2/S1	0.00	0.00	8.43	0.32	-	-	-
D2/S2	10.17	13.40	10.47	1.18	0.76	0.97	8.59*
D2/S3	9.50	12.94	9.77	1.29	0.73	0.97	7.38*
D2/S4	10.02	13.46	10.05	1.95	0.74	1.00	5.15*
D3/S1	0.00	0.00	8.00	0.36	-	-	-
D3/S2	0.00	0.00	8.77	0.00	-	-	-
D3/S3	0.00	0.00	0.00	0.00	-	-	-
D3/S4	0.00	0.00	0.00	0.00	-	-	-
D4/S1	0.00	0.00	12.53	0.94	-	-	-
D4/S2	0.00	0.00	0.00	0.00	-	-	-
D4/S3	<MDL	23.65	16.93	2.08	-	-	-
D4/S4	<MDL	<MDL	<MDL	0.41	-	-	-

* Results excluded after ratio assessment.

Table S8. Polyvinylchloride (PVC) Ratios, checking that results are within a 1:2 range of standards.

sample	CONCENTRATION (ug)			RATIOS	
	naphthalene	2-methylnaphtalene	1-methylnaphtalene	naphthalene/2-methylnaphtalene	naphthalene/1-methylnaphtalene
PE STD	1.91	2.06	1.85	0.93	1.03
D1/S1	3.53	5.98	6.45	0.59	0.55
D1/S2	3.56	7.03	6.26	0.51	0.57
D1/S3	4.49	7.47	8.25	0.60	0.54
D1/S4	4.17	7.43	7.15	0.56	0.58
D2/S1	4.31	7.08	7.43	0.61	0.58
D2/S2	5.41	9.58	9.17	0.56	0.59
D2/S3	5.56	9.35	10.04	0.60	0.55
D2/S4	4.74	7.26	8.29	0.65	0.57
D3/S1	0.00	5.14	4.65	-	-
D3/S2	0.00	5.28	4.87	-	-
D3/S3	0.00	0.00	2.55	-	-
D3/S4	0.00	5.03	4.44	-	-

D4/S1	3.71	11.12	10.65	-	0.35*
D4/S2	3.29	4.79	4.65	0.69	0.71
D4/S3	12.32	13.98	15.75	0.88	0.78
D4/S4	3.80	4.54	4.77	0.84	0.80

* Results excluded after ratio assessment.

Table S9. Duplicate means for each polymer type in $\mu\text{g m}^{-3}$. All values are above the MDL (blank mean + 3*SD). When MDL was 0 the LOD was used. PE values were quantified using the n-alkadiene assessed against ratios of n-alkenes (ref). PVC values were quantified using naphthalene assessed against ratios of 1,2-methylnaphthalene.

SAMPLES	PE	PVC	PMMA	PS	PC	PP	N-66	N-6	Sum
D1_S1	0.000	1.095	0.251	0.000	0.000	0.000	0.372	0.000	1.718
D1_S2	0.000	1.048	0.179	0.026	0.000	0.000	0.387	0.000	1.640
D1_S3	0.000	0.900	0.164	0.016	0.000	0.000	0.257	0.000	1.337
D1_S4	0.000	0.752	0.000	0.000	0.000	0.000	0.000	0.000	0.752
D2_S1	0.000	1.257	0.268	0.000	0.000	0.000	0.358	0.000	1.883
D2_S2	0.000	1.122	0.135	0.026	0.000	0.000	0.299	0.000	1.582
D2_S3	0.000	1.106	0.157	0.018	0.000	0.000	0.266	0.000	1.547
D2_S4	0.000	0.850	0.000	0.031	0.000	0.000	0.203	0.000	1.084
D3_S1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
D3_S2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
D3_S3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
D3_S4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
D4_S1	0.000	0.000	0.000	0.000	0.000	0.000	0.305	0.000	0.305
D4_S2	0.000	0.671	0.000	0.000	0.000	0.000	0.000	0.000	0.671
D4_S3	0.000	2.419	0.121	0.069	0.000	0.000	0.234	0.000	2.843
D4_S4	0.000	0.674	0.000	0.000	0.000	0.000	0.000	0.000	0.674

Table S10. Summary table for Py-GC/MS results. Sample mean for all summed polymer types in $\mu\text{g m}^{-3}$, replicate mean ($\pm$ std dev) and daily mean ($\pm$ std dev).

Sample	Sample Mean (µg m ⁻³)	Replicate mean (µg m ⁻³)	Daily mean (µg m ⁻³)
D1_S1	1.72	1.36 (±0.44)	1.00 (±0.69)
D1_S2	1.64		
D1_S3	1.34		
D1_S4	0.75		
D2_S1	1.88	1.52 (±0.33)	
D2_S2	1.58		
D2_S3	1.55		

D2_S4	1.08		
D3_S1	0	0	
D3_S2	0		
D3_S3	0		
D3_S4	0		
D4_S1	0.31	1.12 (±1.16)	
D4_S2	0.67		
D4_S3	2.84		
D4_S4	0.67		

TD-PTR-MS

Table S11. Finalised triplicate means from TD-PTR-MS data with standard deviation (all results are blank corrected and calculated to ng m^{-3}). Zeros were removed for all data analysis.

Sample	PE	PET	PP	TWP	Sum
D1_S1	23.19 (± 5.81)	7.08 (± 1.16)	10.60 (± 4.64)	19.91 (± 5.28)	60.78
D1_S2	34.92 (± 1.77)	15.06 (± 5.65)	14.28 (± 2.52)	49.87 (± 30.34)	114.13
D1_S3	32.32 (± 1.49)	10.71 (± 0.97)	13.93 (± 1.55)	23.86 (± 2.04)	80.81
D1_S4	30.19 (± 9.06)	10.58 (± 3.14)	14.06 (± 5.20)	22.72 (± 6.56)	77.55
D2_S1	53.39 (± 14.33)	18.45 (± 6.51)	29.89 (± 6.39)	40.98 (± 14.64)	142.71
D2_S2	52.61 (± 5.45)	18.70 (± 3.56)	27.80 (± 1.49)	40.79 (± 7.41)	139.91
D2_S3	63.35 (± 7.77)	22.78 (± 3.09)	34.24 (± 4.62)	49.22 (± 7.61)	169.59
D2_S4	39.84 (± 5.34)	14.12 (± 1.17)	19.77 (± 3.70)	30.55 (± 2.82)	104.27
D3_S1	42.80 (± 7.83)	11.39 (± 3.55)	27.51 (± 3.42)	26.27 (± 5.08)	107.97
D3_S2	46.21 (± 2.55)	14.36 (± 2.03)	27.05 (± 2.75)	30.63 (± 3.53)	118.26
D3_S3	21.65 (± 4.76)	4.62 (± 1.96)	11.92 (± 2.79)	10.83 (± 4.65)	49.01
D3_S4	28.21 (± 0.45)	5.77 (± 0.41)	17.33 (± 1.83)	13.99 (± 0.70)	65.30
D4_S1	24.06 (± 7.42)	4.06 (± 4.29)	14.79 (± 4.35)	13.52 (± 7.81)	56.43
D4_S2	22.38 (± 3.64)	5.75 (± 1.60)	11.62 (± 2.79)	13.87 (± 3.55)	53.62
D4_S3	25.83 (± 6.07)	6.70 (± 1.53)	14.99 (± 5.39)	17.84 (± 3.49)	65.36
D4_S4	19.66 (± 4.43)	3.99 (± 2.39)	10.95 (± 2.43)	8.99 (± 4.51)	43.60

Table S12. Summary table for TD-PTR-MS results. Sample mean for all summed polymer types in MP m⁻³, replicate mean (±std dev) and daily mean (±std dev).

Sample	Sample mean (ng m ⁻³)	Replicate mean (ng m ⁻³)	Daily mean (ng m ⁻³)
D1_S1	60.78	83.82 (±22.34)	90.58 (±35.23)
D1_S2	114.13		
D1_S3	80.81		
D1_S4	77.55		
D2_S1	142.71	139.12 (±26.81)	
D2_S2	139.91		
D2_S3	169.59		
D2_S4	104.27		
D3_S1	107.97	85.14 (±33.25)	
D3_S2	118.26		
D3_S3	49.01		
D3_S4	65.30		
D4_S1	56.43	54.75 (±8.96)	
D4_S2	53.62		
D4_S3	65.36		
D4_S4	43.60		

Overview

Table S13. Summary table of all sample results by all analysis types

Sample	Nile red (particles m ⁻³)	Raman (MP m ⁻³)	Py-GC/MS (µg m ⁻³)	TD-PTR-MS (ng m ⁻³)
D1_S1	1493.97	225.55	1.72	60.78
D1_S2	1351.96	90.22	1.64	114.13
D1_S3	1083.34	126.74	1.34	80.81
D1_S4	1330.06	142.28	0.75	77.55
D2_S1	197.19	230.03	1.88	142.71
D2_S2	1140.83	348.41	1.58	139.91
D2_S3	588.22	217.33	1.55	169.59
D2_S4	870.52	127.99	1.08	104.27
D3_S1	3895.49	391.43	0.00	107.97
D3_S2	2427.43	107.32	0.00	118.26
D3_S3	2212.13	77.88	0.00	49.01

D3_S4	2721.51	99.31	0.00	65.30
D4_S1	2470.20	79.06	0.31	56.43
D4_S2	2735.41	78.48	0.67	53.62
D4_S3	1944.59	107.91	2.84	65.36
D4_S4	3786.06	120.19	0.67	43.60
Mean	1890.56	160.63	1.00	90.58
Median	1719.28	123.47	0.92	79.18
IQR	1406.57	122.35	1.37	55.47
Min	197.19	77.88	0.00	43.60
Max	3895.49	391.43	2.84	169.59

Table S14. Polymers identified via each analysis method

Method	Polymers identified	Polymers analysed for but not identified*
Nile red	Cannot identify polymer types	
μFTIR	No plastic identified	
Raman	PE, PEW, PET, PP, PS, PVC, PU, ABS, PC, PVA, Nylon, PAN, CE, PMMA, PSU, Rubber, PLA, SBR and SAN	
Py-GC/MS	PVC, PMMA, Nylon-66, PS	PP, PC, Nylon 6, PE
TD-PTR-MS	PE, TWP, PP, PET	PVC, PS

*for mass-based methods

Table S15. Coefficient of variation for all analysis methods for each day

Method	D1	D2	D3	D4
Nile red	13%	58%	27%	28%
Py-GC/MS	32%	22%	n/a	103%
Raman	39%	39%	88%	22%
TD-PTR-MS	27%	19%	39%	16%

Table S16. Spearman rank correlation coefficients (ρ) and p-values for pairwise comparisons between analytical methods across all samples ($n = 16$).

	Nile red (MP m ⁻³)	Raman (MP m ⁻³)	Py-GC/MS (μg m ⁻³)	TD-PTR-MS (ng m ⁻³)
Nile red (MP m ⁻³)	—	-0.397 (p = 0.128)	-0.661 (p = 0.005)**	-0.635 (p = 0.008)**
Raman (MP m ⁻³)		—	0.394 (p = 0.131)	0.585 (p = 0.017)*
Py-GC/MS (μg m ⁻³)			—	0.356 (p = 0.177)
TD-PTR-MS (ng m ⁻³)				—

* $p < 0.05$, ** $p < 0.01$.