Supporting Information

Evidence and mass quantification of atmospheric microplastics in a coastal New Zealand city

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S1. Particle analysis using ImageJ. Fluorescence images were converted to 8-bit, and a thresholding of 30–175 was used to allow for better visualization of fluorescent particles. Following this, the “analyze particles” function was used to measure all the particles on each image and generate the results of the areas and Feret diameters of each particle (Scheider et al., 2012). The particles on each image were outlined and labeled. To avoid background noise from the PCTE filters under the 40x magnification, a particle size threshold was used in the “analyze particles” function to only measure and count the particles that had areas larger than 79 μm^2 (in a perfect circular shape, diameter = 10 μm) (Scheider et al., 2012). However, the particle’s shape was not necessarily a perfect circle, so – after the data was imported to RStudio, a final selection was made using Feret ≥ 10 μm as the final cut-off size reported. As MP fibers do not fluoresce in the same manner as MP fragment particles do, the fibers were measured by length and color in the bright field microscopic images using the “line tool” in ImageJ. These data were also automatically generated for each filter (Klein & Fischer, 2019; Scheider et al., 2012).

Equations.

$$Relative\ response\ factor\ (RRF) = \frac{Slope\ of\ indicator\ ion\ of\ each\ polymer}{Slope\ of\ calibration\ curve\ of\ cholanic\ acid} \qquad (S1)$$

$$MP\ mass = \frac{Peak\ area\ of\ polymer's\ indicator\ ion \times mass\ of\ cholanic\ acid}{Peak\ area\ of\ quantifier\ ion\ of\ cholanic\ acid} \times \frac{1}{RRF} \qquad (S2)$$

S2. Positive Controls. Microplastic standards were subjected to the same filtration, digestion, and analysis procedures as the atmospheric deposition samples. Both polyethylene (size ~500 µm) and polyvinylchloride (size ~100 µm) particles were added to a 2 L glass bottle containing Type I water and then filtered onto a PCTE membrane. The PCTE membrane containing the positive controls was subjected to the same H_2O_2 digestion process as the samples, as described in Section 2.3. The positive controls were then dyed with Nile Red and examined using fluorescence microscopy (Section 2.4). The microplastic standards were recovered, giving confidence to the validity of the sample preparation and analysis methods.

Table S1. Pyrolysis-GC/MS parameters.

Micro furnace pyrolyzer	**EGA/PY-3030D FrontierLabs**
Pyrolysis purge gas	Nitrogen
Pyrolysis temperature	700 °C
Interface temperature	300 °C
Pyrolysis time	12 s
Gas chromatograph	**GC-2010**
Injector temperature	300 ^{o}C
Injector mode	Split 50:1
Column	Frontier Labs GC UA5, 5 % diphenyl – 95 % dimethylpolysiloxane (30 m, 0.25 mm i.d., 0.25 μm)
Carrier gas	Helium
Carrier gas flow rate	1.0 mL min^{-1}
Temperature program	70 °C (2 min hold), increase to 320 ^{o}C at 20 °C min^{-1} (5 min hold)
Mass spectrometer	**GCMS-QP2010S Shimadzu**
Transfer line temperature	300 ^{o}C
Ion Source temperature	230 ^{o}C
Ionization energy	70 eV
Scan range	29-500 *m/z*

Table S2. Indicator ions and retention time and index of standard common consumer plastics determined in this study. The retention index is Kováts Retention Index, which was calculated using pyrolysis production of PE (alkenes).

Polymer	**Pyrolysis product**	***M* *(amu)***	**Indicator ion (*m/z*)**	**Retention Index**	**Retention time (min)**
Polyethylene (PE)	CH_2=CH(CH_2)$_7$CH=CH_2 (C11)	152	83	1400	8.65
	CH_2=CH(CH_2)$_{10}$CH=CH_2 (C14)	194	83	1494	9.28
	CH_2=CH(CH_2)$_{11}$$CH_3$ (C14)	196	83	1594	9.91
	CH_3(CH_2)$_{12}$$CH_3$ (C14)	198	83	1487	9.23
Polystyrene (PS)	3-butene-1,3-diyldibenzene (styrene dimer)	208	91	1756	10.85
	5-hexene-1,3,5-triyltribenzene (styrene trimer)	312	91	2486	14.38
	Styrene	104	104	901	4.20
Polypropylene (PP)	2,4-dimethylhept-1-ene	126	70	839	3.58
	2,4,6,8-tetramethyl-1-undecene	210	69	1310	8.01
Polyvinyl Chloride (PVC)	Benzene	78	78	649	2.27
	Naphthalene	128	128	1202	7.17
	Indene	116	116	1056	5.83
Nylon6	*ε*-caprolactam	113	113	1262	7.64
Polymethyl methacrylate (PMMA)	methyl methacrylate	100	100	708	2.51
Polyethylene terephthalate (PET)	Acetophenone		105	965	4.90
	Vinyl benzoate	148	105	1145	6.67
	Ethan-1,2-diyldibenzoate	270	105	2190	13.04
	Divinyl terephthalate	218	175	1581	9.83
Polycarbonate (PC)	Phenol	94	94	993	5.20
	p-cresol	108	107	1185	6.90
	p-ethylphenol	122	107	1081	6.08
	p-isopropenylphenol	134	134	1307	7.99

Table S3. The parameters resulting from the polymer calibration curves. The low value provided in the range column can be considered the method limit of quantification for each polymer. RRF = relative response factor compared to cholanic acid (internal standard). Note: due to heterogenous ball milling and solvent solubility issues, a calibration curve for Nylon6 could not be completed. Thus, the RRF used for Nylon6 (12.7) was derived from Klein & Scholz-Böttcher (2017). All Nylon6 data should be considered semi-quantitative.

Polymer	**Quantifier ion *(m/z)***	**Slope**	**R^2**	**RRF**	**Range (ng)**
PVC	78	y=98.4x	0.9900	14.3	53 – 462
PP	70	y=18.3x	0.9927	2.67	46 – 400
PE	83	y=0.956x	0.9479	0.154	740 – 3270
PET	105	y=4.63x	0.9812	0.575	400 – 1470
PC	94	y=30.8x	0.9976	3.67	350 – 1290
PS	91	y=49.4x	0.9540	2.51	77 – 850
PMMA	100	y=156.8x	0.9912	7.95	43 – 474

Table S4. The background signals detected in the Pyr-GC/MS analysis from control samples (n=3).

Quantifier ion	Peak area (mean ± std dev)
m/z 78 from cholanic acid	4990 ± 1405
m/z 83 from quartz filter	577 ± 448
m/z 94 from PCTE filter washing	16868 ± 3193

Table S5. The mass and polymers determined for the individual particles analyzed using Pyr-GC/MS. Note: Nylon6 data should be considered semi-quantitative.

Location	Week	Polymer	Mass (ng)	Notes
Urban	9	Nylon6	10	Transparent particle
Urban	9	PE	190	Transparent particle
		PC	250	
		PET	490	
Urban	9	Nylon6	10	Transparent particle
Residential	2	PC	190	Pink particle
		PET	430	
Residential	2	PC	270	Transparent fragment
		PET	570	
Residential	2	PE	450	Transparent particles
		PC	250	
		PS	110	
		PET	520	
Residential	2	PC	250	Transparent particle
		PET	310	
		PS	80	
Residential	2	PC	40	Transparent fiber
		PET	1970	
		PVC	10	
Residential	3	PE	130	White particle
		PC	210	
		PET	470	
		PS	30	
Residential	3	PE	1880	Transparent fragment
		PC	390	
		PET	120	
Urban	3	PVC	410	Yellowish particle
		PC	560	
		PET	660	
		PS	3440	
Urban	3	PE	780	Transparent particle
		PC	260	
		PET	710	
Urban	3	PE	650	Red fiber
		PC	320	
		PET	470	
Urban	4	PVC	20	Transparent particles
		PE	190	
		PC	340	
		PET	490	
		PS	40	

Urban	4	PE	260	Transparent particle
		PC	420	
		PET	590	
		PS	60	
Urban	5	PC	350	Transparent particle
		PET	590	
Urban	5	PE	190	Transparent particles
		PC	260	
		PET	90	
Urban	5	PC	260	Transparent particles
		PET	470	
		PS	40	
Urban	6	PMMA	40	Yellow particle
Urban	6	PE	450	Transparent particle
Residential	5	PET	140	Transparent particles
		PC	260	
Residential	5	PE	780	Transparent particle
		PC	310	
		PET	430	
Residential	5	PE	390	Multiple particles
		PC	250	
		PET	660	
		PS	100	
Residential	5	PE	650	Transparent fibres
		PC	260	
		PET	730	
Residential	7	PE	450	Transparent particle
		PC	320	
		PET	330	
Urban	8	PE	36170	Red particle
Urban	8	Nylon6	50	Fibres
Urban	8	PE	650	Transparent fragment
Urban	8	PMMA	560	Red fiber
Urban	8	PVC	180	Red fiber and transparent particle
		Nylon6	80	
Urban	8	Nylon6	80	Multiple fragments, black and clear
		PP	200	
Urban	8	PVC	160	Fibers
		Nylon6	110	

Table S6. The Pearson correlation coefficients between MP deposition rates and meteorological factors. The asterisks (*) denote a P value < 0.05.

Sampling Site	**MP deposition rate**	**Total weekly rainfall *R***	**Average weekly rainfall *R***	**Rain days per week *R***	**Average wind speed *R***	**Wind events per week (speed>10m/s) *R***
Commercial rooftop	By number	0.15	0.20	-0.08	0.51	0.49
	By mass	0.53	0.64	0.23	0.82*	0.78*
Domestic garden	By number	0.41	0.47	0.15	0.55	0.54
	By mass	0.14	0.24	0.47	0.47	0.48

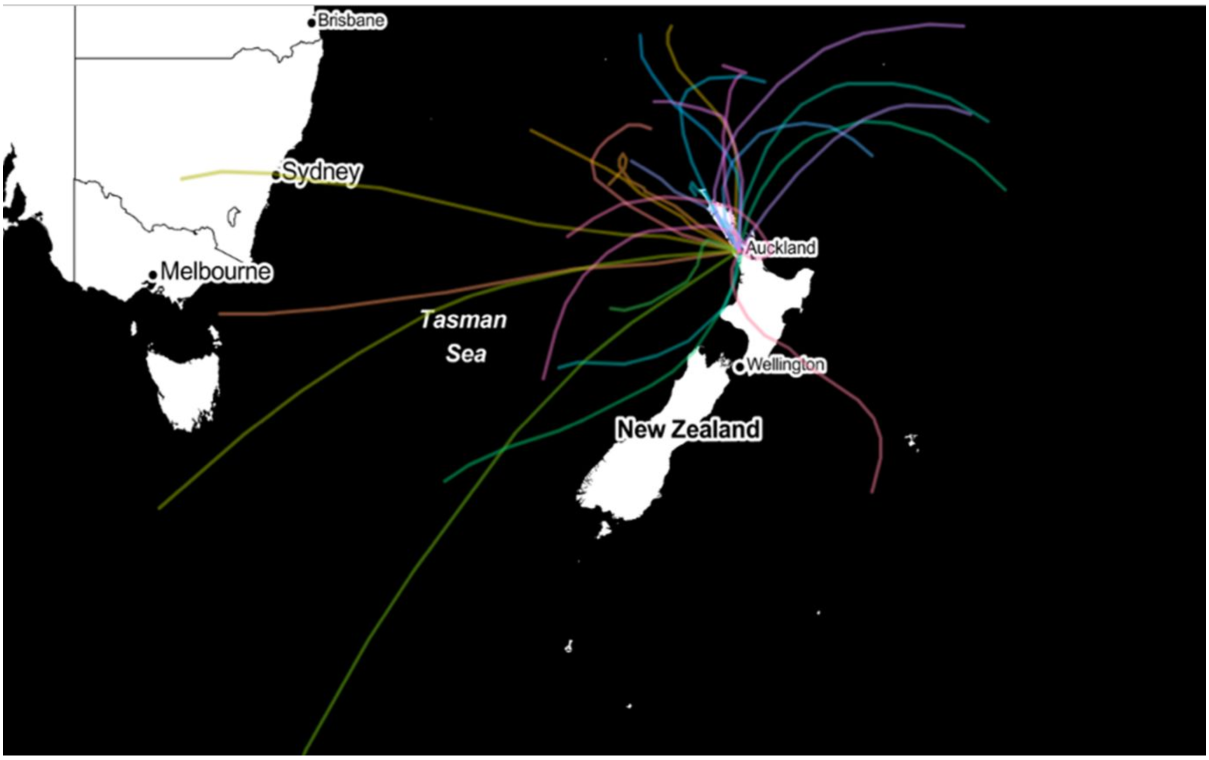

Figure S1. The 48 h air parcel back trajectories at 100 m calculated using the HYSPLIT model available from NOAA for rain events recorded in Auckland over the sampling period. Map tiles by Stamen Design, under CC BY 3.0. Data by OpenStreetMap, under ODbL.