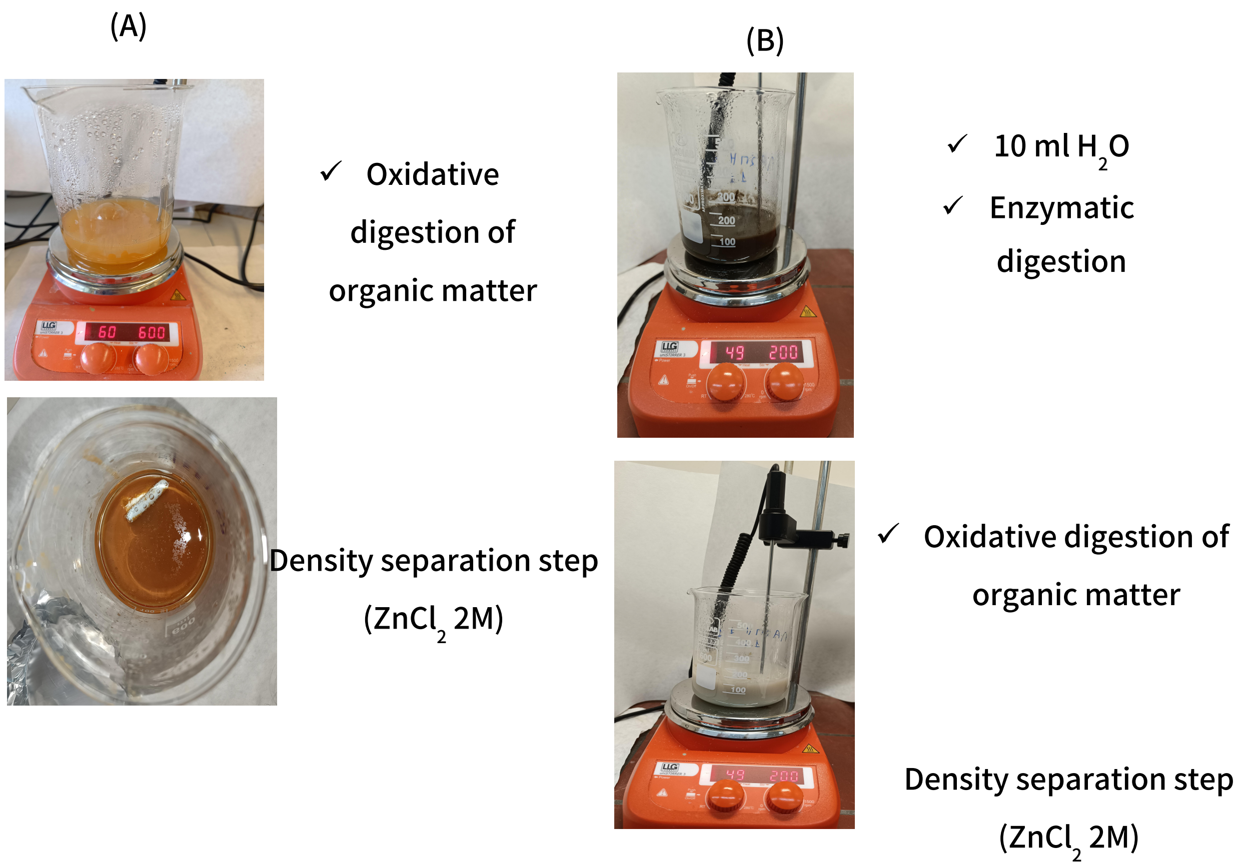
Supplementary Information

Determination of microplastics in municipal wastewater treatment plant effluents and sludge using micro-Raman spectroscopy



Supplementary Figure 1. Appearance of (A) wastewater effluents and (B) sludge samples after removing organic matter.

Supplementary Table 1. Detailed information for microplastic polymers detected in this study, including monomer, density and hazard score[1]

Polymer	Abbreviation	Monomer	Density	Hazard score
p-acrylic acid	PAA	Acrylic acid		230
p-vinyl chloride	PVC	vinyl chloride		10000

p-butyl-methacrylate	PBMA	butyl-methacrylate	4
p-ethylene	PE	Ethylene	11
p-ethylene oxide	PEO	Ethylene	263
p-propylene	PP	Propylene	1
p-styrene	PS	Styrene	30
p-vinyl-alcohol	PVA	Vinyl acetate	1
Polyamide	PA	Adipic acid	63
p-ethylene terephthalate	PET	terephthalic acid, ethylene glycol	4
ethylene-vinyl-acetate	EVA	Ethylene, vinyl acetate	9
p-vinyl acetate	PVAc	Vinyl acetate	1

Supplementary Table 2. Risk categories range of MPs hazard index (HI) and pollution risk index (PRI) [2,3]

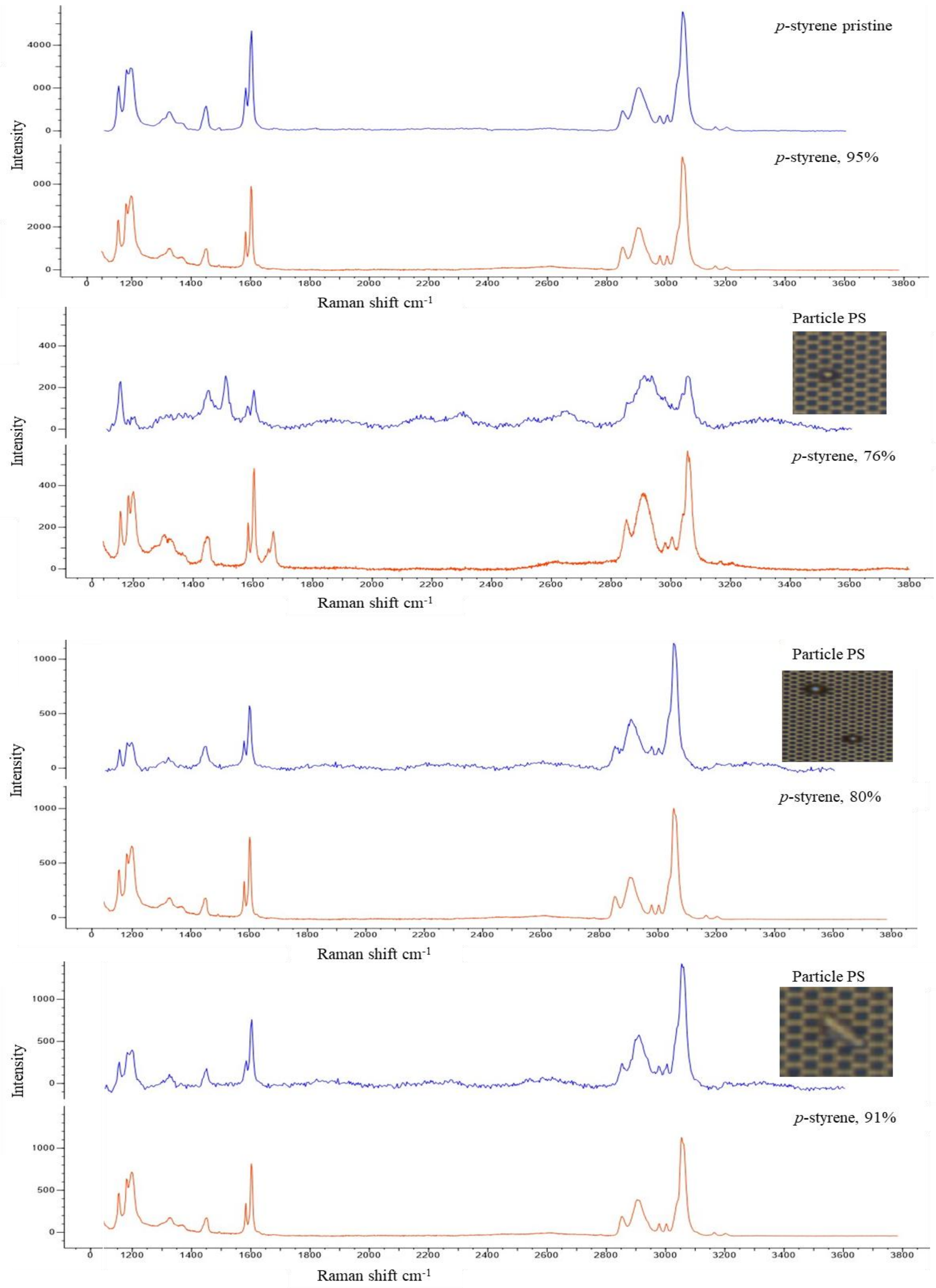
HI	PRI	Risk Category
< 10	< 150	Low
10 – 100	150 – 300	Low Medium
101 – 1000	300 – 600	Medium
1001 – 10,000	600 – 1200	High
> 10,000	> 1200	Very High

Supplementary Table 3. The uses of representative polymers identified as microplastics in wastewater effluents and sludge [4–6]

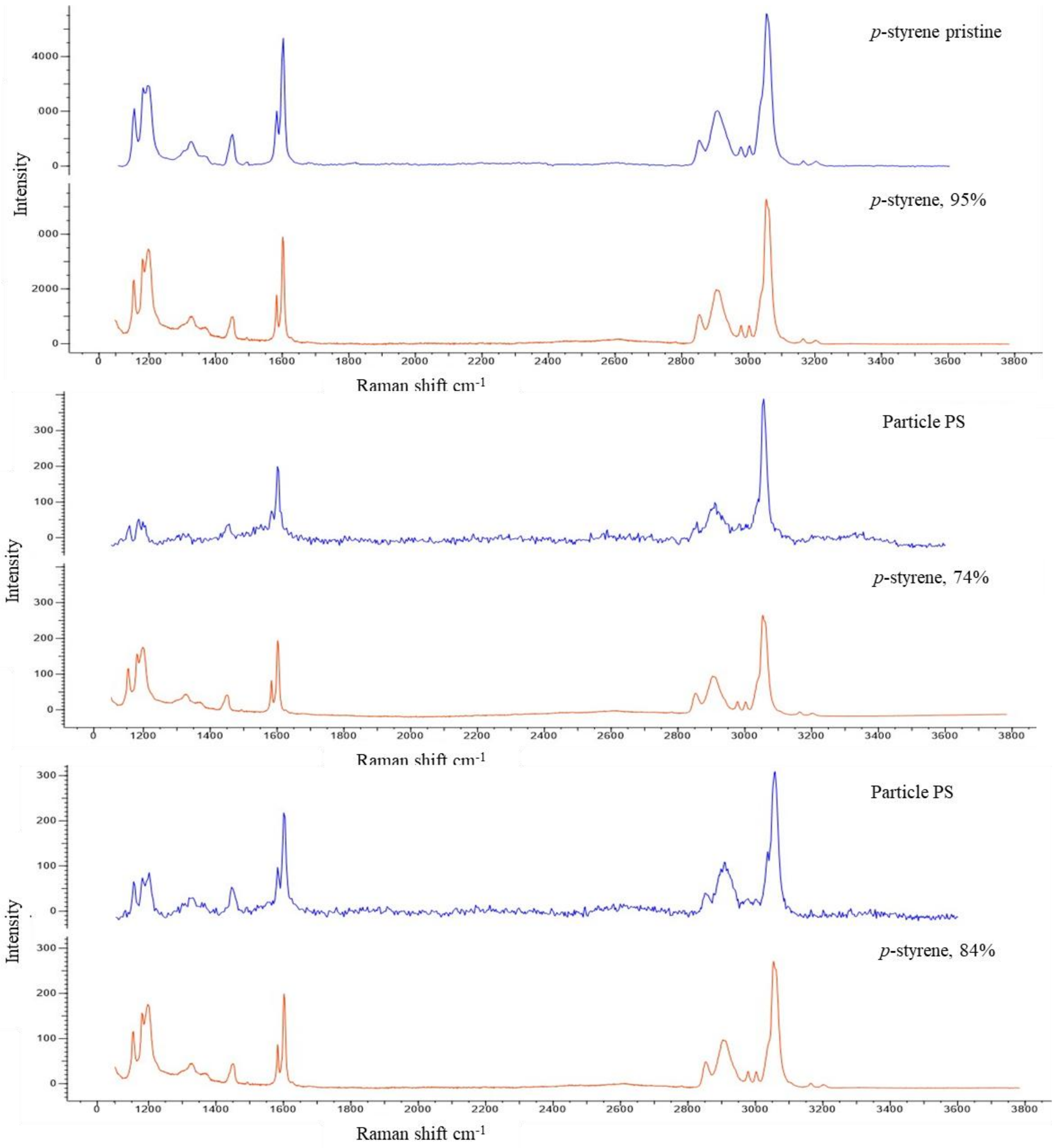
Polymer type (Abbreviation)	Uses
p-ethylene (PE)	Bottles for drinks, plastic bags, packaging film, drainage and irrigation pipes
p-propylene (PP)	Bottle caps, containers for yogurt, take-out meals, drinking straws, and carpet
p-styrene (PS)	Coffee cup lid, plastic fork, protective foam packaging
Polyamide (PA)	Fibres, bristles for toothbrushes, tubing, clothing, fishing line
p-acrylic acid (PAA)	
p-vinyl chloride (PVC)	Shrink wrap, pipes, railing, blood bags, medical tubing, raincoats, automobile seat covers, garden hoses, shoe soles, shower curtains.
p-ethylene terephthalate (PET)	Textile, soft drink bottle, water bottle
p-butyl methacrylate (PBMA)	Perspex, plexiglass, eyeglass lenses, touch screens, etc.

Adsorption / Weathering experiments

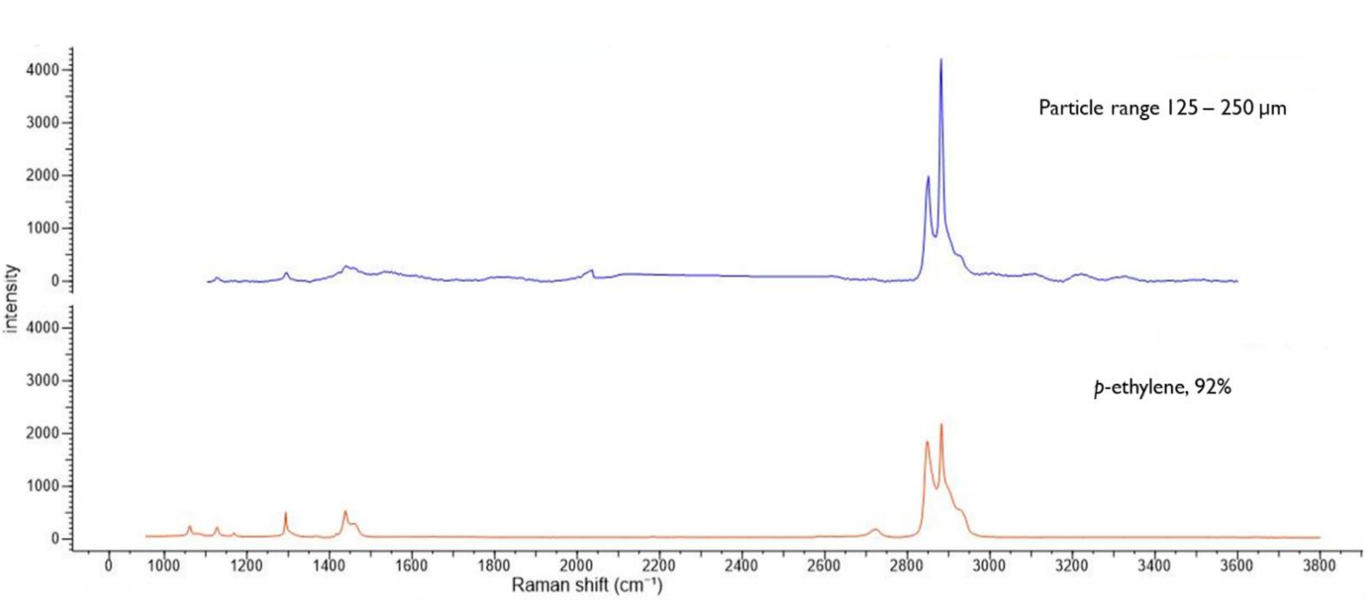
In order to study the effect of adsorbed pollutants or weathering on the Raman spectra of microplastics adsorption and weathering experiments have been additionally carried out using PS as model polymer. Four emerging contaminants (pyriproxyfen, metronidazole, sulfamethoxazole and carbamazepine) have been selected for adsorption onto the microplastics surface. Specifically, analytes solution with a concentration of 5 mg/L and polystyrene suspension of 3000 particles/mL was added to a glass vial and shaken in a shaking incubator at a shaking speed of 500 rpm at 25 ^{o}C for 48h. The suspended solution was then filtered on a silicon membrane filter. The equilibrium concentration of selected organic pollutants in the solution after adsorption was determined using high performance liquid chromatography (Kyoto, Japan) equipped with an SPD-M40 photodiode array detector. Chromatographic separation were performed with a Supelco Discovery C18 column (15 mm × 4.6 mm, 5 μm particle size) (Bellefonte, PA, USA), while a mixture of water with 0.1% formic acid and acetonitrile acted as the mobile phase. The column temperature was set at 40 ^{o}C and the flow rate was 1.0 mL min^{-1} while the injection volume was 20 μL. Calibration curves were used for quantitative analysis. The experiment results indicated that the three pharmaceutical compounds (metronidazole, sulfamethoxazole and carbamazepine) were adsorbed on the PS particles in low percentages from 3.98% to 7.71% while the pesticide pyriproxyfen was adsorbed at 50% on the PS surface. More specifically, pristine PS particles adsorbed 0.2 μg MTZ per gram of PS, 2.3 μg/g of Pyr, 0.1 μg/g of CMZ and 0.4 μg/g of SMX. Afterwards, PS particles separated on silicon filter have been analyzed by micro-Raman spectroscopy and Particle Finder™ software. The recorded PS particles were matched with the KnowItAll™ library database reference with >70% identification (Supplementary Figure 2). Furthermore, the photolytic aging experiment was carried out using an Atlas SUNTEST XLS+ solar simulator (Linsengericht, Germany) which was supplied with a Xe lamp 2.2 kW and special ultraviolet cut-off filters for wavelengths smaller than 290 nm. An aqueous suspension of pristine PS solution (300 particles/mL) was transferred into a pyrex reactor and irradiated for 24 h with an irradiation intensity of 500 W/m^2. Afterwards, the suspension was filtered on a silicon membrane filter. The recorded PS particles were matched also with the KnowItAll™ library database reference with >70% identification (Supplementary Figure 3).

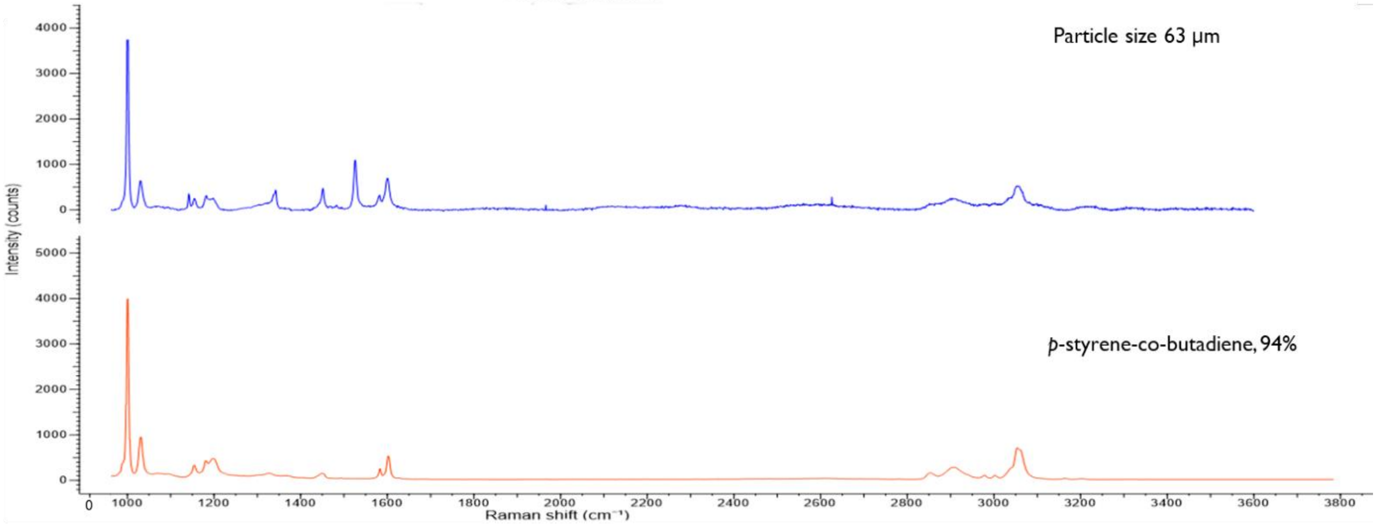


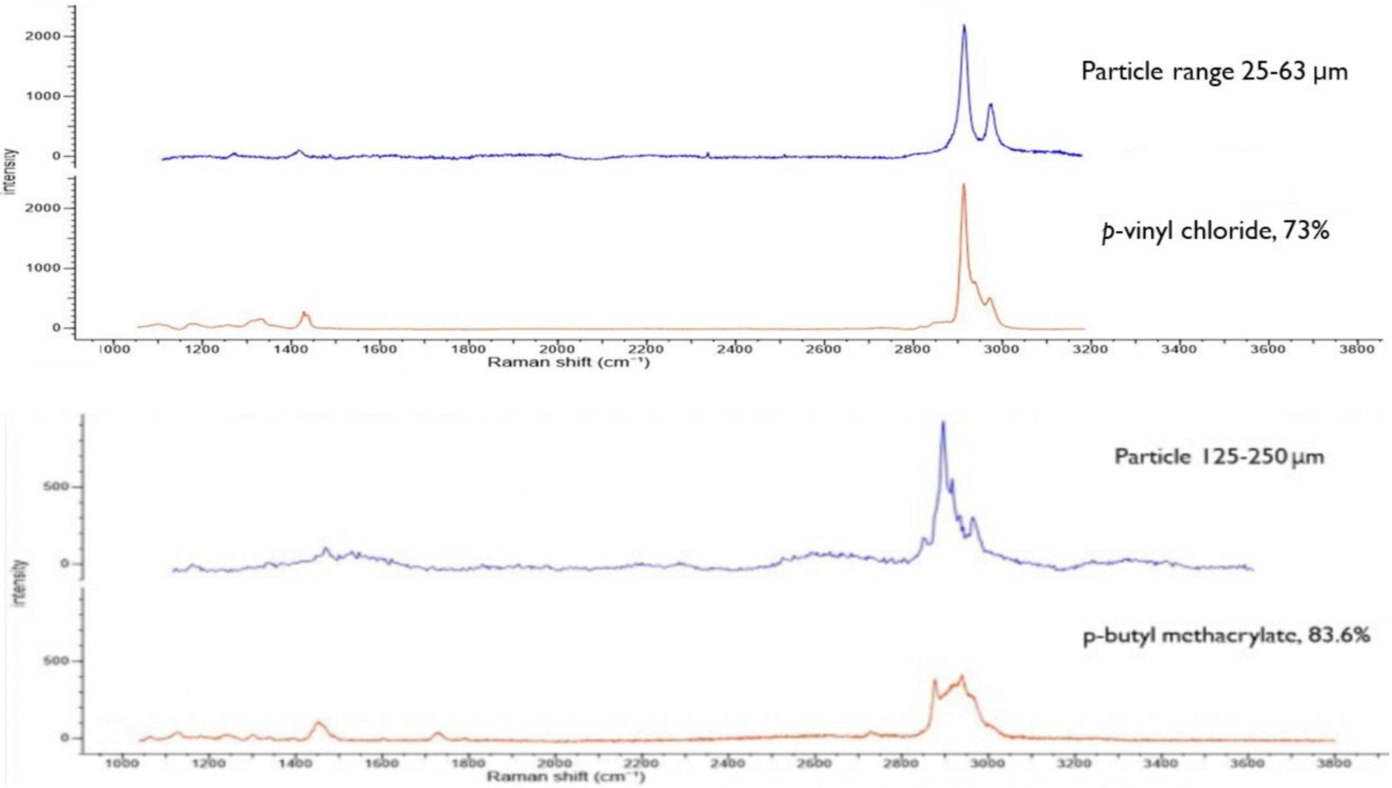
Supplementary Figure 2. Representative examples of Raman spectra for pristine PS and PS particles detected after pollutant adsorption experiment.



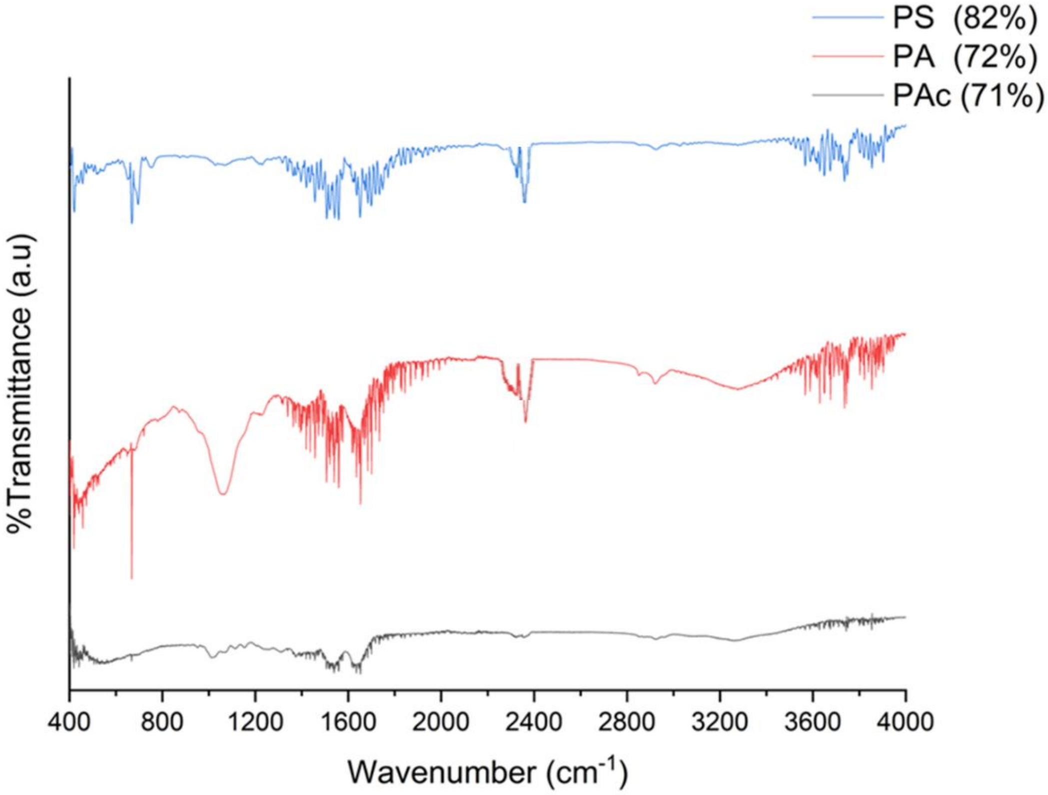
Supplementary Figure 3. Representative examples of Raman spectra for pristine PS and PS particles detected after weathering experiment.


Particle range 125 – 250 µm
p-ethylene, 92%
intensity
Raman shift (cm⁻¹)


Particle size 63 µm
p-styrene-co-butadiene, 94%
Intensity (counts)
Raman shift (cm⁻¹)



Supplementary Figure 4. Representative examples of Raman spectra for microplastics detected in effluents and sludge samples with micro-Raman spectroscopy.



Supplementary Figure 5. Representative ATR-FTIR spectra of microplastics detected in wastewater samples (size range 500 – 1000 and > 1000 μm).

References

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