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Assessing Mass-based Fates of Microplastics Throughout the Waste Water Treatment Process Using a Novel TD-GC-MS Methodology

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Mass-based fates of microplastics throughout wastewater treatment processes

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Microplastics in Sewage Treatment Plants

Background

- Sewage treatment plants (STPs) play a vital role in removing microplastics from wastewater.
- They are also significant sources of microplastic pollution in the environment.
- Since STPs are not specifically designed for microplastic removal, understanding the mass-based fate of these particles during treatment is crucial for improving removal efficiency.

Microplastics in Sewage Treatment Plants

Traditional Analysis

- Primarily estimated based on particle number, namely their abundance
- Complications and disparities in the sampling and analysis procedures.
- Microplastic mass could be employed to quantify the fates of microplastics scientifically and accurately throughout the treatment processes.
- More recently, thermal analytical approaches based on the thermal decomposition of polymers have been well-documented for quantifying microplastics
  - Pyrolysis gas chromatography–mass spectrometry (Py–GC/MS)
  - Thermo-extraction desorption coupled with gas chromatography–mass spectroscopy (TED–GC/MS)

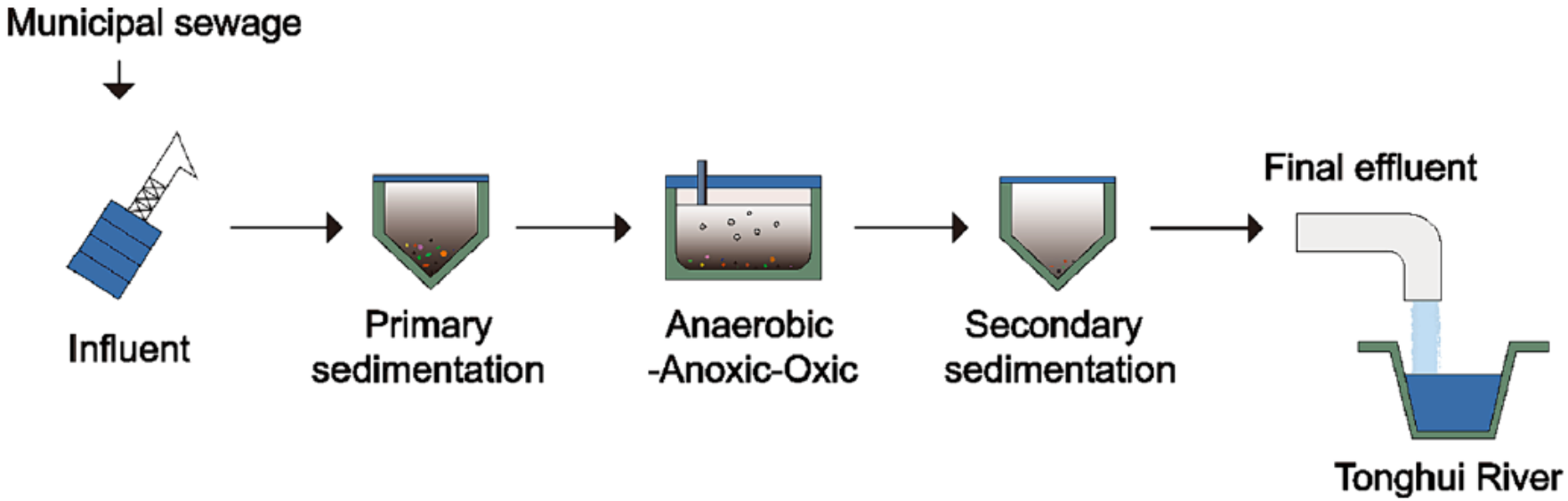
Microplastics in Sewage Treatment Plants

Project overview

- Thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) method was developed to quantify five common microplastics
  - Polyethylene (PE)
  - Polypropylene (PP)
  - Polystyrene (PS)
  - Polyvinyl chloride (PVC)
  - Polyethylene glycol terephthalate (PET)
- Size range of 0.22 µm to 5.00 mm.
- This approach was applied to assess microplastic fate throughout the entire STP treatment process.
- Unlike pyrolysis (Py)-GC/MS analysis the thermal desorption approach utilises an offline pyrolysis step which enables a large sample size; resulting in high levels of reproducibility between samples.

Sample Collection

- Gaobeidian Sewage Treatment Plant (gSTP)
- Total treatment capacity of 1.0 million m^3/day of domestic wastewater discharging from 2.4 million residents



Sample Collection

- 6-10 L of Wastewater were sampled from each treatment Unit.
- 3 replicate Samples
- Tools and bottles were carefully washed three times with ultrapure water.
- No mechanical pumping of plastic tools were used.
- Samples were mixed thoroughly in original bottles and then passed through a stainless-steel sieve with a pore size of 5 mm to remove any large particles

Influent before treatment system (IN)
Primary sedimentation tank (PST)
Aerated grit chamber (AC), secondary sedimentation tank (SST)
Final effluent (Eff)
After ultrafiltration and Ultraviolet (UV) disinfection treatment

Sample Collection

Samples filtered consecutively through a 500-µm and 20-µm stainless–steel filter membrane

Followed by a 0.22- µm glass fiber membrane to isolate particles with different sizes.

Membranes containing particles were then individually placed into 30 % hydrogen peroxide (H_2O_2), 24 h at 50 ◦C with slow shaking to remove organic matter.

An additional 25 mL of H_2O_2 was added to further remove organic matter until no discernible solid matter remained.

Samples were further filtered through a 0.22- µm glass fiber membrane individually to maximize the particle recovery.

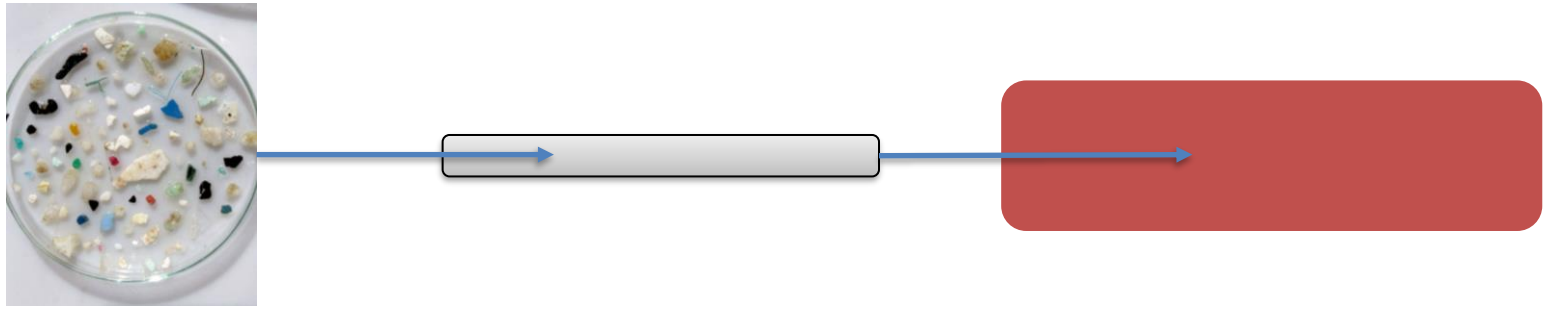
The beakers were cleaned three times with ultrapurified water, and the rinsed water was also filtered through the corresponding filters.

The membranes were rinsed with 60 mL ultra-purified water, 10 mL acetone, and 10 mL methanol to remove possible interference from other substances.

Membranes were transferred to another clean glass Petri dish and dried

Sample Analysis

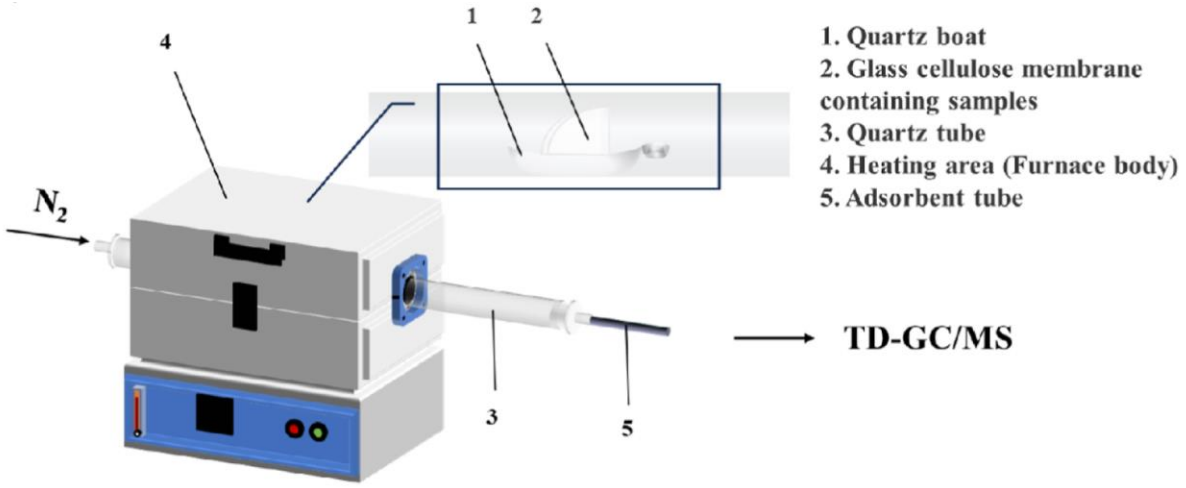
Tube furnace



Sample

Quartz tube

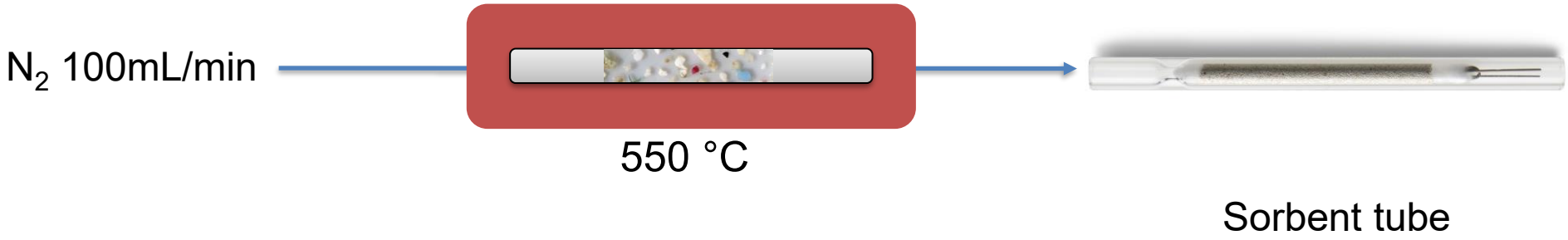
Tube furnace



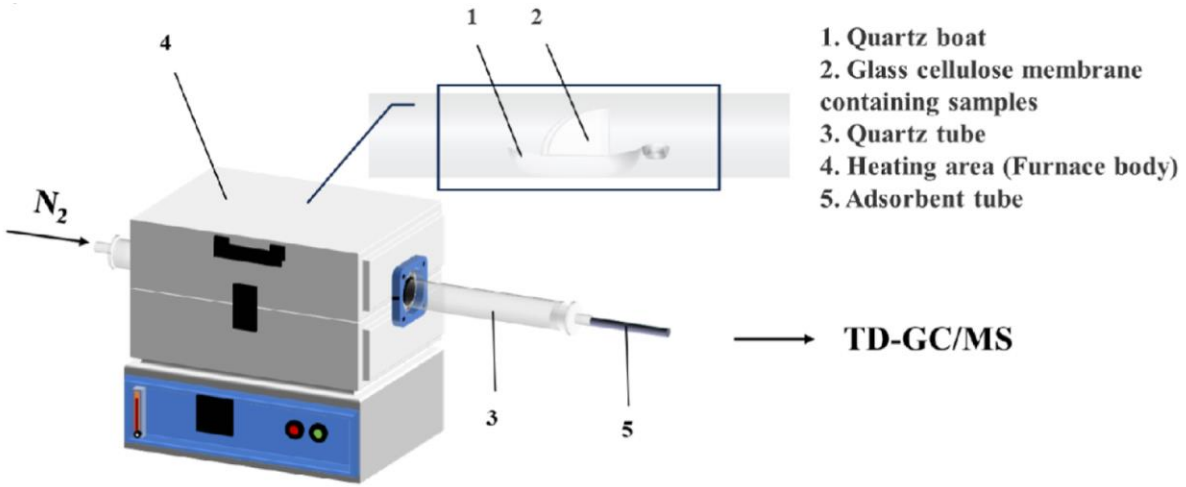
- Whole sample placed into quartz tube compatible with furnace.
- Quartz tube placed inside tube furnace.

Sample Analysis

Tube furnace



- Furnace heated to 550 °C at 20 °C/min
- Nitrogen flow (100 mL/min) sweeps the pyrolysis products onto a sorbent tube
- After pyrolysis, the sorbent tube is removed and taken to the thermal desorption system.



What is pre-concentration?

Thermal desorption

Sample collection
Up to **several hundred litres** of vapour is sampled off-line onto a sorbent tube.

Tube desorption
The sorbent tube is heated and the analytes are swept onto a focusing trap in **100–200 mL** of carrier gas.

Trap desorption
The focusing trap is heated rapidly and the analytes are transferred to the GC column in **100–200 µL** of carrier gas.

Volume of gas transferred

SORBENT TUBE

FOCUSING TRAP

GC

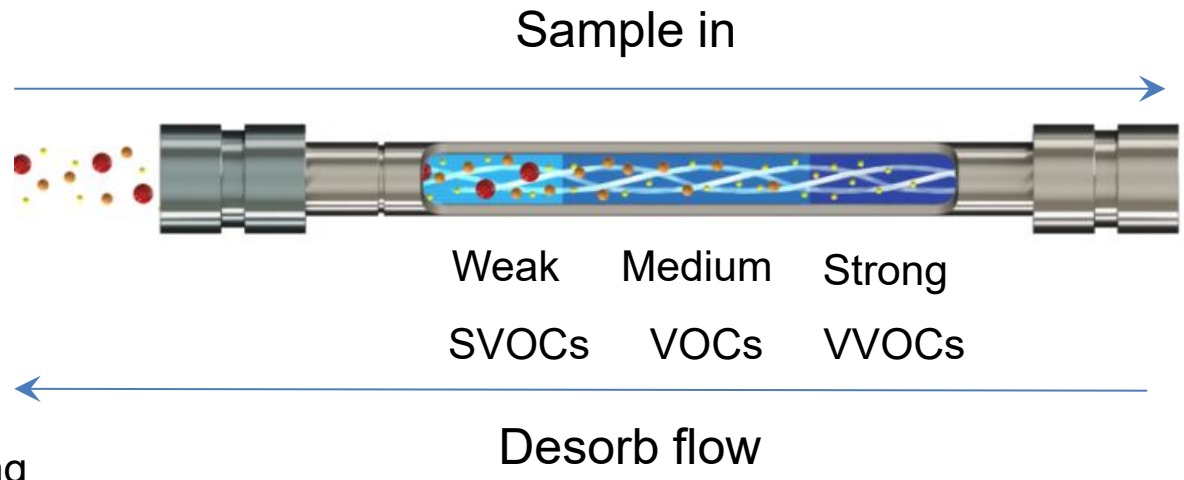
Practical aspects of sampling

Sorbent name	Volatility range
Quartz wool / Silica beads	$C_{30} – C_{44}$
Tenax TA	$C_7 – C_{30}$
Carbograph 2TD	$C_8 – C_{20}$
Carbograph 1TD	$C_{5/6} – C_{14}$
Carbograph 5TD	$C_{3/4} – C_{6/7}$
SulfiCarb	$C_3 – C_8$
Carboxen 1003	$C_2 – C_5$
Carbosieve SIII	$C_2 – C_5$

Weak

Strong

Water retention



Sample Analysis – Thermal Desorption GC-MS validation

Tube desorption and inlet split

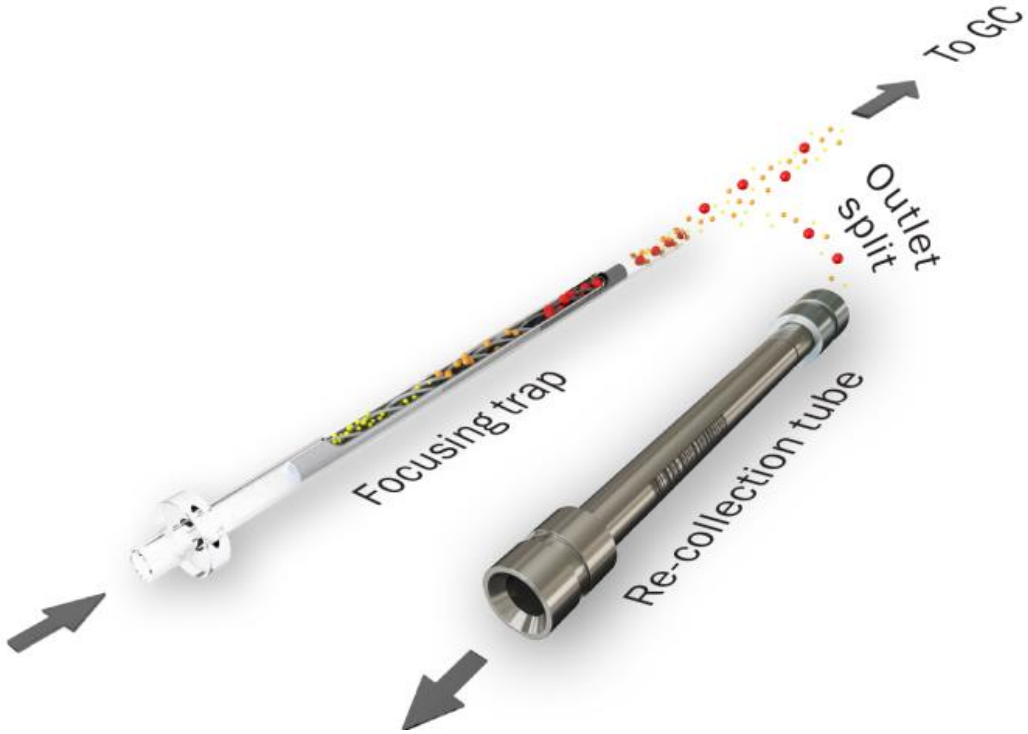
'If any compounds exhibits lower than expected recovery (relative to the split ratio and/or to the recovery of other compounds in the standard) as the sequence proceeds, this indicates poor desorption efficiency for those compounds'.

ISO16000-6/ISO16017

Sample tube heated in flow of carrier gas and analytes swept onto an electrically cooled focusing trap, typically held between ambient and –30° C.

Sample Analysis – Thermal Desorption GC-MS validation

Trap desorption and outlet split



- Validate complete transfer of compounds
- Ensure desorption efficiency
- Method validation
- Analyses trace odorous compounds

Focusing trap rapidly heated (up to 100° C/s) in a reverse flow of carrier gas (‘backflush’ operation), to transfer the analytes to the GC column.

Finding indicative compounds

Testing mixed polymer standards

Indicative compounds chosen for quantitating and qualifying microplastic presence.

<u>Quantifying compounds shown here:</u>

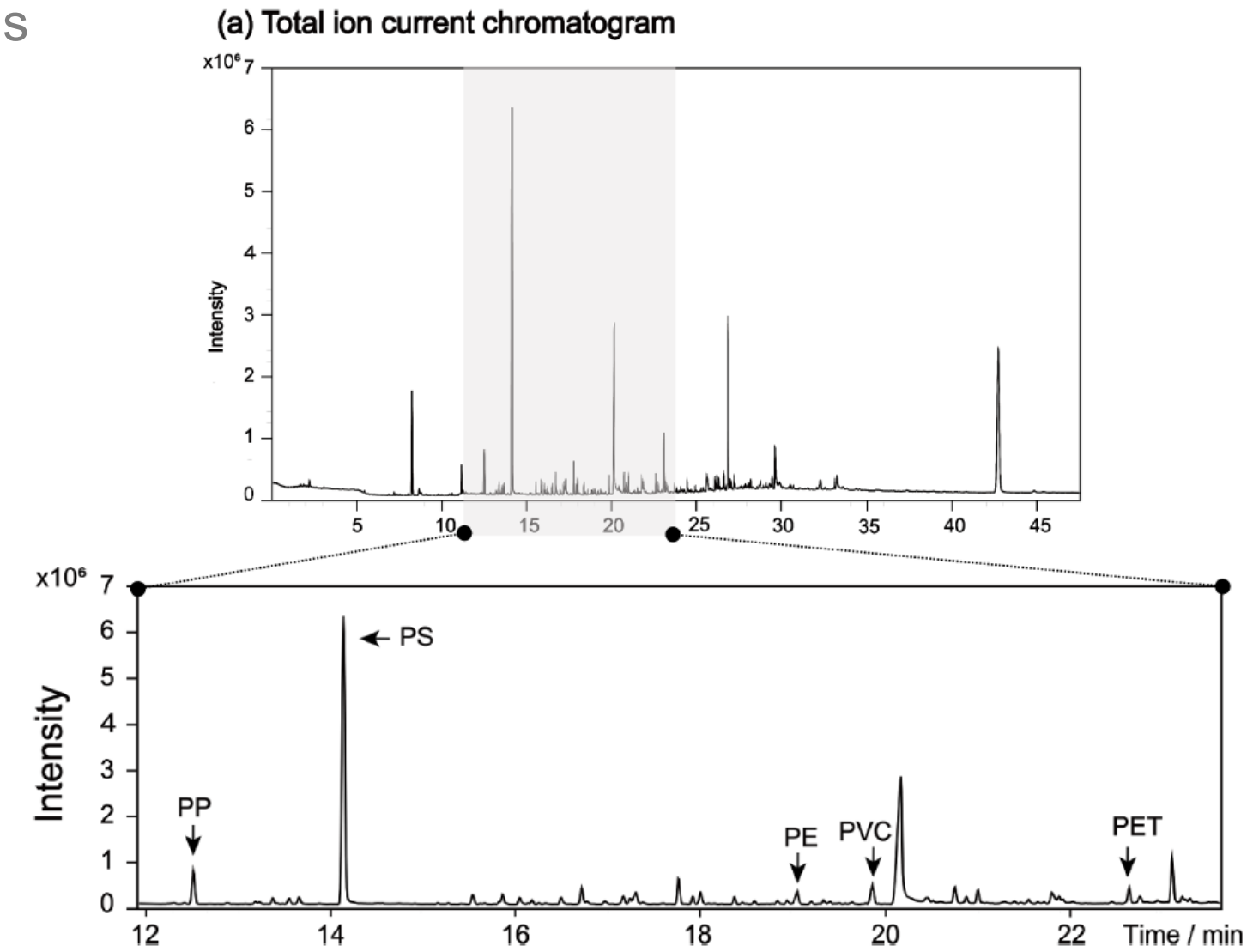
PP – 2,4-Dimethyl-1-heptane

PS – Styrene

PE – 1-Dodecene

PVC – Naphthalene

PET – Diphenyl



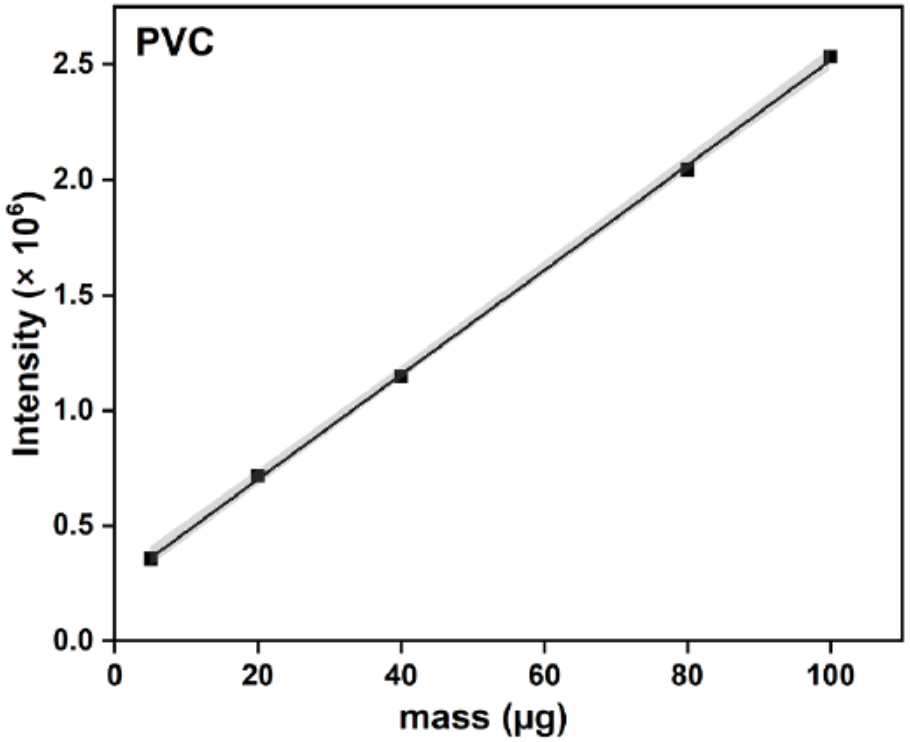
Method performance

5 polymers: PE, PS, PP, PVC, PET

- All testing carried out with the 5 polymers in a single sample
  - 0.22 μm – 5.00 mm in size

Polymers spiked at 3 different concentrations: 20, 40 and 70 ug/L of filtrate.

- Average recovery: 89 – 121 %
- Average relative standard deviation: 10 – 13%
- Calibration: R of > 0.98

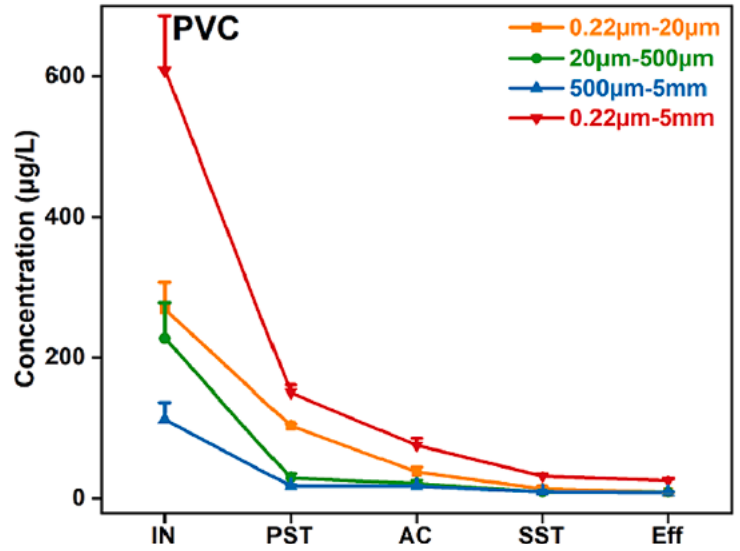


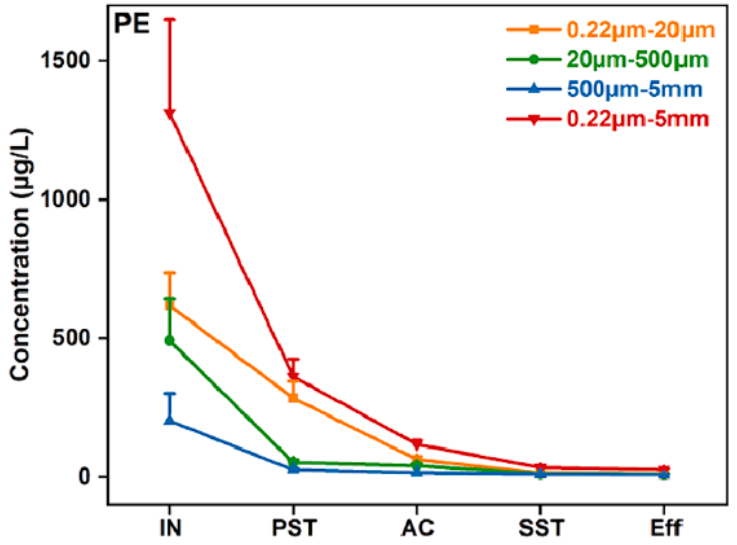
Other techniques such as TED-GC-MS cannot analyze PVC. Tube furnace + TD-GC-MS can reliably quantify PVC.

Applying the technique to real samples

Sampling at 5 locations

- The sample locations were before, during and after microplastic remediation.
- Microplastic samples filtered into 4 sizes prior to analysis
- Analysed using the tube furnace method
- All polymers in each sample quantitated simultaneously.
- Clear decrease in microplastic presence as remediation progresses
  - Larger plastics removed quickly
  - Smaller plastics requiring more clean up





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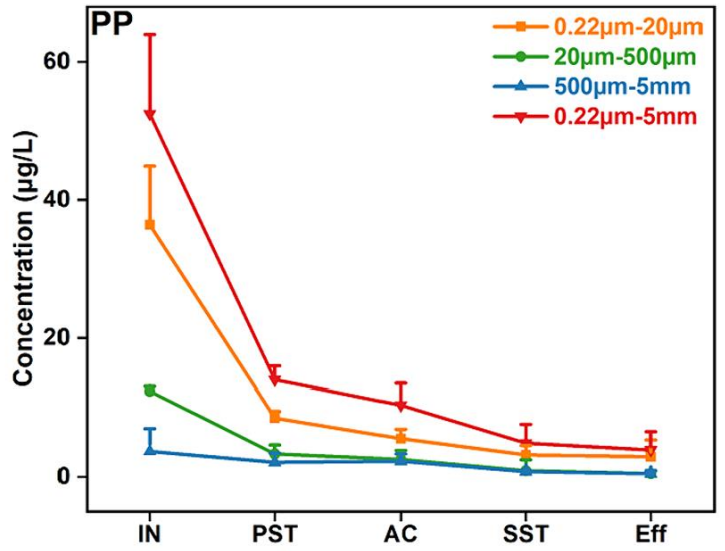

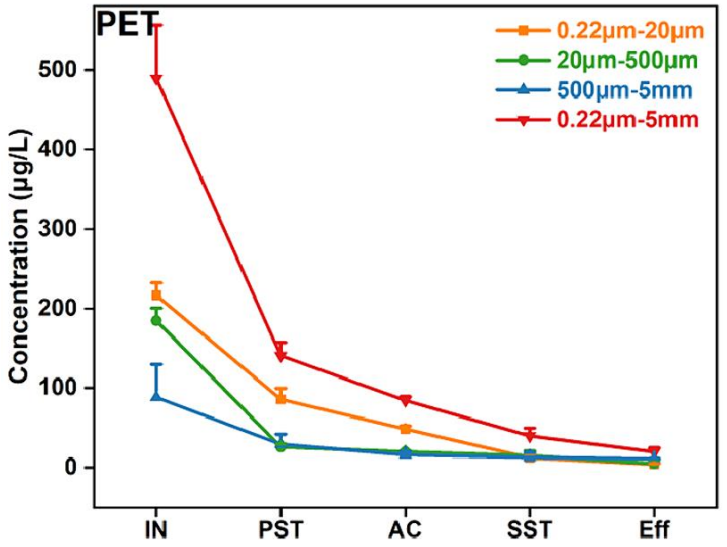

Summary

- TD–GC/MS system for quantifying microplastics, including PE, PS, PP, PVC, and PET, and successfully applied to trace the fates of microplastics within an STP.
- The mass-based outcomes showed that small microplastics (0.22–20 μm) dominated total microplastics (0.22 μm–5.00 mm) both in influent and effluent, higher than those of large microplastics (20 μm–5.00 mm).
- Furthermore, the current tertiary treatment system showed a high microplastic removal with an average of 95.82 % ± 2.02 %.
- First study directly providing the mass-based concentrations of microplastics in the size range of 0.22 μm–5.00 mm within an STP.
- Reduced the uncertainty associated with estimating microplastic mass based on their volume and densities, enabling the comparison of removal efficiencies and emission loads among regional and global studies to update the existing wastewater treatment processes for the future.

Thanks/非常感谢

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